MATERIALS FOR MEETING WITH GORDON WAGGETT

MAY 9, 2007

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May 9, 2007

Gordon G. Waggett, Esq.
Gordon G. Waggett, P.C.
550 Westcott Street
Suite 350
Houston, TX 77007-5099

Re: Meeting of May 9

Dear Gordon:

For our meeting today, I am providing you with a notebook entitled "Materials for Meeting With Gordon Waggett – May 9, 2007." This notebook will provide you relevant information in rebuttal to the claims of Ru-Ling Meng. With respect to her various declarations, I will simply note that any reasonable person would doubt the credibility of Meng in view of her reversal of sworn testimony regarding the disclosure by Dr. Chu to Meng in a mid-December 1986 call of Y and Lu as replacements for La. Secondly, I provide you with a group of exhibits which describe the state-of-the-art in the formulation and synthesizing of samples or pellets used in superconductivity labs throughout the world for many years prior to the events of November 1986-March 1987 which are in dispute here.

Thirdly, I provide you with the newly discovered calendar of Dr. Chu, which casts even greater doubt upon Ru-Ling Meng's recent statements. The references by Chu to Y and Lu in his handwriting in mid-December fully support a telephone conversation in that time period in which Chu instructed Meng of his next inventive activities—the substitution of Y for La. Further, with respect to Meng's allegations that it was she who conceived that Lu should be used as a substitute for La in the meeting among Pei Hor, Meng, Li Gao, Dr. Wu and others in late December or early January, Chu's calendar demonstrates her claim is incorrect, if not untruthful.

We will discuss these materials with you in detail during the meeting.

Very truly yours,

Lester L. Hewitt

EXHIBITS FOR USE AT MAY 9, 2007 MEETING WITH G. WAGGETT

TAB	DATE	DESCRIPTION
1	1989/06/07	Declaration (of Ru-Ling Meng) Under 37 C.F.R. § 1.639 (no exhs used)
2	1990/12/04	Declaration of Ru-Ling Meng (w/exhs A-C)
3	1993/02/22	Declaration of Ru-Ling Meng (w/exhs A-N)
4	2006/03/06	Affidavit of Ru-Ling Meng (w/exhs 1-5)
5	2006/05/25	Affidavit of Ru-Ling Meng (no exhs used)
6	2006/10/26	G. Waggett letter to Akin Gump stating R. Meng's position (w/R. Meng CV)
7	2006/10/26	G. Waggett PowerPoint
8	1982	Mattens, Aarts, Moleman, Rachman, Boer, *Chemical Pressure Effects in Sc-Substituted YbCuAl,* Valence Instabilities, pp. 211-214
9	1983	Raaen, Parks, *Mixed Valence in* $CeNi_5$*; Effects of Dilution and Chemical Pressure,* Solid State Communications, Vol. 48, No. 2, pp. 199-202
10	1986	Millon, Gerardin, Bonazebi, Brice, Evrard, *Effet d'une pression chimique locale sur la structure crystalline de* $CaFe_2O_4$*, Revue de Chimie minerale, t.* 23, pp. 782-788
11	1975/02/10	Sleight, Gillson & Bierstedt; *High-Temperature Superconductivity in the* $BaPb_{1-x}Bi_xO_3$ *System,* SOLID STATE COMMUNICATIONS, 17: 27-28
12	1975/10/31	Chu & Huang; *Hydrostatic Pressure Effect on* T_c *of* $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$, SOLID STATE COMMUNICATIONS, 18: 977-979
13	1973/05/25	Longo & Raccah; *The Structure of* La_2CuO_4 *and* $LaSrVO_4$, JOURNAL OF SOLID STATE CHEMISTRY, 6: 526-531

TAB	**DATE**	**DESCRIPTION**
14	1976/03/11	Johnston; *Superconducting and Normal State Properties of* $Li_{1+x}Ti_{2-x}O_4$ *Spinel Compounds. I. Preparation, Crystallography, Superconducting Properties, Electrical Resistivity, Dielectric Behavior, and Magnetic Susceptibility*, JOURNAL OF LOW TEMPERATURE PHYSICS, <illegible>, pp. 145-175
15	1980/05/29	Er-Rakho, Michel, Provost & Raveau; *A Series of Oxygen-Defect Perovskites Containing* Cu^{II} *and* Cu^{III}*: The Oxides* $La_{3-x}Ln_xBa_3[Cu^{II}_{5-2y}Cu^{III}_{1\_2y}]O_{14+y}$, JOURNAL OF SOLID STATE CHEMISTRY, 37: 151-156
16	1982/11/02	USPN 4,357,426 (Murata et al.)
17	1983/11/14	Lin, Shao, Wu, Hor, Jin & Chu; *Observation of a reentrant superconducting resistive transition in granular* $BaPb_{0.75}Bi_{0.25}O_3$ *superconductor*, THE AMERICAN PHYSICAL SOCIETY, 29: 1493-1496
18	1984/11/13	USPN 4,482,644 (Beyerlein et al.)
19	1985/03/05	USPN 4,503,166 (Beyerlein et al.)
20	December 1986-March 1987	Personal Calendar of Ching-Wu (Paul) Chu, Ph.D.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Qadri et al.	§	
	§	Interference No. 101,981
v.	§	
	§	Examiner-in-Chief: Ronald H. Smith
Chu	§	
	§	
v.	§	
	§	
Beyers et al.	§	
	§	
v.	§	
	§	
Batlogg et al.	§	

DuPont

DECLARATION UNDER 37 C.F.R. § 1.639

I, RULING MENG, declare as follows:

1. I received a B.A. degree in Material Science from the Mining and Metallurgy College in Hunan, China in 1958.

2. Since receiving my degree, I have worked as an instructor at the Mining and Metallurgy College, Hunan, China (1958-59); a Research Assistant, Metallurgy and Material Science Division, Institute of Mining and Metallurgy, Academy of Science (1959-73); and a Research Associate, Institute of Physics, Chinese Academy of Science (1973-84) during which time I also held visiting positions as a Research Associate, Department of Physics at University of Houston, Texas (1979-81), University of Konstanz, West Germany (1981-82), and University of Houston, Texas (1984-86).

3. Currently I am a Senior Research Scientist, and Lab Manager of the Experimental Solid State Physics Lab of the Department of Physics, University of Houston, Texas

and of the Texas Center for Superconductivity; positions I have held since 1987.

4. Since 1974 to date, I have authored or been co-author on over 50 publications in the scientific literature most of which have related to the study of superconductivity in intermetallic, oxide and other compounds.

5. I have read and am familiar with the contents of United States Application Serial No. 32,041 filed March 26, 1987 by C.W. Chu (hereafter the "Chu application).

6. I was asked to repeat Example XIII of the Chu Application. In following Example XIII, the following work was performed by me, or by a technician under my direct supervision and control as follows: 0.1 grams of La_2O_3, 0.243 grams of $BaCO_3$ and 0.1465 grams of CuO were thoroughly mixed by mortar-pestle until a fine powder of uniform grey color, was obtained. The powder was pressed into several pellets of about 1/16 inch thickness and about 3/16 inch diameter by applying 250 psi pressure using a standard laboratory press. The pellets were placed in an alumina boat and the boat was placed in a tube furnace, the tube was open to air, and the furnace was heated to 950°C and held at that temperature for about 8 hours. Thereafter the boat containing the pellets was placed in another tube furnace with one end of the tube connected to a vacuum pump through a valve capable of regulating the level of vacuum drawn to 2000 μ. The other end of the tube was communicated to an oxygen cylinder through a regulator providing for a regulated flow of oxygen. This arrangement allowed the tube containing the

boat with the pellets to be provided with an oxygen atmosphere regulated to a pressure of 2000 μ to provide a reduced-oxygen atmosphere (~2000μ). The furnace temperature was brought up to 850°C from room temperature in about two hours. The sample pellets in the boat were then heated at 850°C for an additional 30 minutes under the reduced-oxygen atmosphere (2000 μ) after which time power to the tube furnace was turned off. Oxygen continued to pass through the tube furnace at 2000 μ of pressure until the boat containing the pellet samples returned to room temperature and the boat with sample pellets was then removed from the furnace. One pellet was ground, and an X-ray powder diffraction study was performed. Another pellet was used for a magnetic flux exclusion experiment. I concluded from the X-ray powder pattern that the material contained greater than 90% $LaBa_2Cu_3O_{6+X}$ (X a value that provided orthorhombic crystal symmetry), and a minor amount of $BaCuO_2$. Magnetic flux (Meisnner effect) exclusion results showed an onset of superconductivity at about 84 K. The sample was measured resistively to have a Tc_0 (onset) of 92 K and a Tc_1 (zero resistance) of 77 K.

7. In early 1987 an $EuBa_2Cu_3O_{7-\delta}$ sample was made in accordance with the procedure of Example XIV of the Chu application, with the exception that a sintering temperature of 925°C was employed rather than 950°C. After 20 minutes at a sintering temperature of 925°C, power to the tube furnace was turned off. Oxygen continued to pass through the tube furnace at 2000 μ of pressure until the boat containing the pellet samples

returned to room temperature. Room temperature of the boat with pellets was obtained in approximately 180 minutes after the tube furnace power was turned off. Measurements made on this material established that it had an oxygen content of 6.840 ($EuBa_2Cu_3O_{6.84}$), X-ray lattice parameters of "a" = 3.860Å, "b" = 3.904Å, "c" = 11.727Å, a Tc_0 of 96.5 K, a Tc_1 of 91.5 K and it exhibited a Meissner-effect of 23%.

8. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Chu Application or any patent issued thereon.

EXECUTED this 7 day of June, 1989.

RULING MENG

CERTIFICATE OF SERVICE

I hereby certify that a copy of the foregoing Declaration Under 37 C.F.R. § 1.639 has been mailed, first class mail, postage pre-paid this 7th day of June, 1989 to:

A. David Spevack
Office of Associate Counsel (Patents)
Code 1208.2
Naval Research Lab
Washington, D.C. 20375-5000

Joseph G. Walsh
IBM Corporation
Intellectual Property Law
5600 Cottle Road (951/029)
San Jose, CA 95193

John P. McDonnell
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974-2070

Charles M. Cox

CERTIFICATE UNDER 37 CFR 1.8(a)

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Box Interference, Commissioner of Patents and Trademarks, Washington, D. C. 20231, on June 7, 1989.

Charles M. Cox
James B. Gambrell
Registration No. 17,920
Charles M. Cox
Registration No. 29,057

Date: June 7, 1989

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

WU et al.	§	
	§	Interference No. 102,447
	§	
v.	§	
	§	Examiner-in-Chief:
CHU	§	Ronald H. Smith

DECLARATION OF RU-LING MENG

Box Interference
Commissioner of Patents
  and Trademarks
Washington, D.C. 20231

Attention: Ronald H. Smith
Examiner in Chief

Dear Sir

I, RU-LING MENG, do hereby declare and state that:

1. I am currently a Senior Research Scientist, and Lab Manager of the Experimental Solid State Physics Lab of the Department of Physics, University of Houston, Texas and of the Texas Center for Superconductivity; a position I have held since 1987. Prior to that, during the period 1984 to 1986, I held the position of Research Associate, Department of Physics at the University of Houston, Texas, working under the supervision of Dr. C.W. Chu.

2. During a telephone call in about mid-December 1986, C.W. Chu described to me his belief that substitution of Y for La in a composition La-Ba-Cu-O would produce a composition of Y-Ba-Cu-O which superconducts at a T_c temperature greater than that of a La-Ba-Cu-O composition.

3. During a discussion which occurred in the office of Pei

Hor in late December 1986, after Christmas and before January 4, 1987, which was attended by myself, Pei Hor and Li Gao of the University of Houston, and by M.K. Wu of the University of Alabama, the concept of substitution of Y for La in a composition of La-Ba-Cu-O to produce a composition of Y-Ba-Cu-O which superconducts at a T_c temperature greater than that of a La-Ba-Cu-O composition was described to M.K. Wu.

4. Before January 17, 1987, I identified in my notebook several substituted compositions for production and examination. Among the compositions so identified is one of the formula $Y_{1.2}Ba_{0.8}CuO_y$ as shown on Exhibit A attached hereto which is in my handwriting and made by me on a date prior to January 17, 1987. The date entered on Exhibit A has been masked out of the attached copy.

5. Further, on January 29, 1987, I identified further compositions for production and testing in accordance with Dr. Chu's direction to make compositions involving substitution for variously the La or Ba of a La-Ba-Cu-O composition by other small radii atomic elements as shown in Exhibit B attached hereto which was made by me and is in my handwriting. The amounts of reagents required for the production of compositions as shown in Exhibit B are shown in Exhibit C attached hereto, which is in my handwriting and made by me during January 29-30, 1987. Among the compositions considered for production are several formulations of Y-Ba-Cu-O, one of which is specifically of the formula $Y_{1.2}Ba_{0.8}Cu_1O_y$.

6. In accordance with my prior calculations as recorded in

Exhibit C, I began to prepare compositions of Y-Ba-Cu-O one of which, designated as YB-102, was of the formula $Y_{1.2}Ba_{0.8}Cu_1O_y$ as described in Exhibit C.

7. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Chu Application or any patent issued thereon.

EXECUTED this 4th day of December, 1990.

RULING MENG

[redacted]

YS-2

(甲) $(Y_{0.85}\ Sr_{0.15})_2\ CuO_4$

(乙) $Y_{\overset{0.925}{\cancel{0.85}}\ \cancel{1.67}}\ Sr_{\cancel{0.33}\ 0.075}\ CuO_4$

SY-3

$(Y_{0.6}\ Ba_{0.4})_2\ CuO_4$

[illegible] SB-2 $(Y_{0.85}\ Ba_{0.15})_2\ CuO_4$

SB-3 $(Y_{\cancel{1.67}\ 0.925}\ Ba_{\cancel{0.33}\ 0.075})_2\ CuO_4$

[I] $(Y_{0.85}\ Sr_{0.15})_2\ CuO_4$

YS-2	Y	Sr	Cu	O
	47.25	12.88	19.87	0.20

Y_2O_3 1000

$SrCO_3$: 361.59

CuO : 414.52

(II) $Y_{0.925}\ Sr_{0.075}\ CuO_4$

YS-3

29. Jan 1986

① $(Y_{0.8}Ba_{0.2})_2CuO_4$

② $(Y_{0.6}Ba_{0.4})_2CuO_4$

③ $(Y_{0.4}Ba_{0.6})_2CuO_4$

④ $(Y_{0.2}Ba_{0.8})_2CuO_4$

✓ ⑤ $(Lu_{0.8}Ba_{0.2})_2CuO_4$

⑥ $(Lu_{0.6}Ba_{0.4})_2CuO_4$

⑦ $(Lu_{0.4}Ba_{0.6})_2CuO_4$

⑧ $(Lu_{0.2}Ba_{0.8})_2CuO_4$

⑨ $Sc_{0.8}Ba_{0.2}$

⑪ $Sc_{0.6}Ba_{0.4}$

⑫ $Sc_{0.4}Ba_{0.2}$

⑬ $Sc_{0.2}Ba_{0.8}$

⑭ $Y_{0.8}Pb_{0.2}$

⑮ $Y_{0.6}Pb_{0.4}$

⑯ $Y_{0.4}Pb_{0.6}$

⑰ $Y_{0.2}Pb_{0.8}$

⑱ $(Lu_{0.8}Pb_{0.2})_2CuO_4$

⑲ $(Lu_{0.6}Pb_{0.4})_2CuO_4$

⑳ $(Lu_{0.4}Pb_{0.6})_2CuO_4$

㉑ $(Lu_{0.2}Pb_{0.8})_2CuO_4$

㉒ $Sc_{0.8}Pb_{0.2}$

㉓ $Sc_{0.6}Pb_{0.4}$

㉔ $Sc_{0.4}Pb_{0.6}$

㉕ $Sc_{0.2}Pb_{0.8}$

㉖ $(Y_{0.3}Ba_{0.7})_2CuO_4$

H 50

29—30 Jan. 1987

① $[La_{0.9}(Y_{0.155}Ba_{0.845})_{0.1}]_2CuO_4$ ✓

② $[La_{0.9}(Y_{0.26}Ba_{0.74})_{0.1}]_2CuO_4$

③ $[La_{0.9}(Y_{0.378}Ba_{0.622})_{0.1}]_2CuO_4$

④ $[La_{0.85}(Y_{0.155}Ba_{0.845})_{0.15}]_2CuO_4$

Y_2O_3

① [illegible] 0.031

[illegible]

⑤ $[La_{0.95}(Y_{0.155}Ba_{0.845})_{0.05}]_2CuO_4$

Y_2O_3 78.74 ①

LYb-1 $[La_{0.9}(Yb_{0.155}Ba_{0.845})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
61.96020	0.683	5.752	15.745	15.859

La_2O_3 : 1000mg

Y_2O_3 : 11.937mg

$BaCO_3$: 113.782mg

CuO : 271.256mg

② LYB-2 $[La_{0.9}(Y^{b}_{0.26}Ba_{0.74})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
62.117	1.149	5.050	15.785	15.900

La_2O_3 :	2000 mg	1000 mg
Y_2O_3 :	40.062 mg	20.031 mg
$BaCO_3$:	199.199 mg	99.600 mg
CuO :	542.515 mg	271.258 mg

③ LYB-3 $[La_{0.9}(Y_{0.378}Ba_{0.622})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
62.294	1.675	4.257	15.830	15.945

La_2O_3 :	1000 mg	2000 mg
Y_2O_3 :	29.118 mg	58.236 mg
$BaCO_3$:	83.721 mg	167.442 mg
CuO :	271.258 mg	542.516 mg

④ LYB-4 $[La_{0.85}(Y_{0.155}Ba_{0.845})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
60.604	0.707	5.957	16.307	16.425

La_2O_3 :	2000 mg	1000 mg
Y_2O_3 :	25.266 mg	12.633 mg
$BaCO_3$:	240.843 mg	120.422 mg
CuO :	574.448 mg	287.224 mg

⑤ LYB-5 $[La_{0.95}(Y_{0.155}Ba_{0.845})_{0.05}]_2CuO_4$

La	Y	Ba	Cu	O
65.256	0.341	2.869	15.710	15.824

La_2O_3 :	1000 mg	2000 mg
Y_2O_3 :	5.659 mg	11.318 mg
$BaCO_3$:	53.863 mg	107.725 mg
CuO :	256.983 mg	513.965 mg

Lu_2O_3

Lu : 87.935

⑥ LLB-1 $[La_{0.9}(Lu_{0.149}Ba_{0.851})_{0.1}]_2CuO_4$

La	Lu	Ba	Cu	O
61.560	1.284	5.755	15.644	15.757

La_2O_3 :	2000 mg	1000 mg
Lu_2O_3 :	40.448 mg	20.224 mg
$BaCO_3$:	229.062 mg	114.531 mg
CuO :	542.534 mg	271.267 mg

⑦ LLB-2 $[La_{0.95}(Lu_{0.149}Ba_{0.851})_{0.05}]_2CuO_4$

La	Lu	Ba	Cu	O
65.045	0.643	2.880	15.659	15.773

La_2O_3 : 2000 mg

Lu_2O_3 : 19.171 mg

$BaCO_3$: 108.489 mg

CuO : 513.959 mg

⑧ $[La_{0.95} Y_{0.05}]_2 CuO_4$

La	Y	Cu	O
65.923	2.221	15.871	15.986

La_2O_3 : 1000 mg

Y_2O_3 : 36.484 mg

CuO : 256.989 mg

⑨ $[La_{0.99} Ba_{0.01}]_2 CuO_4$

La	Ba	Cu	O
67.856	0.678	15.676	15.790

La_2O_3 :	1000 mg	2000 mg
$BaCO_3$:	12.241 mg	24.482 mg
CuO :	246.601 mg	493.202 mg

Sinter 7 hours 1100 °C.

LuB-102 $(Lu_{0.6}Ba_{0.4})_2CuO_4$

Lu	Ba	Cu	O
46.932	24.559	14.203	14.306

Lu_2O_3 :	1000 mg	300 mg
$BaCO_3$:	661.202 mg	198.361 mg
CuO :	333.141 mg	99.942 mg

✓ LuB-103 $(Lu_{0.4}Ba_{0.6})_2CuO_4$

Lu	Ba	Cu	O
32.378	38.121	14.697	14.804

Lu_2O_3 :	1000 mg	300 mg
$BaCO_3$:	1487.670 mg	443.601 mg
CuO :	499.684 mg	149.905 mg

✓ LuB-104 $(Lu_{0.2}Ba_{0.8})_2CuO_4$

Lu	Ba	Cu	O
16.773	52.662	15.227	15.338

Lu_2O_3 : 300 mg

$BaCO_3$: 1190.146 mg

CuO : 299.807 mg

✓ YB-101 $(Y_{0.8}Ba_{0.2})_2CuO_4$

Y	Ba	Cu	O
43.806	16.918	19.567	19.709

Y_2O_3 :	300 mg	1.00
$BaCO_3$:	131.09 mg	43.696
CuO :	132.088 mg	44.029

✓YB-102 $(Y_{0.6}Ba_{0.4})_2CuO_4$

Y	Ba	Cu	O
31.005	31.930	18.466	18.599

Y_2O_3 : 300mg
$BaCO_3$: 349.555 mg (243.267.
CuO : 176.122mg

BaO = 99.88

BaO=243.56 mg

YB-1.

Y_2O_3 1000 mg
$BaCO_3$: 194.185
CuO: 391.381

✓YB-103: $(Y_{0.4}Ba_{0.6})_2CuO_4$

Y	Ba	Cu	O
19.568	45.343	17.481	17.608

Y_2O_3 : 300.00 mg
$BaCO_3$: 786.525 mg
CuO : 264.176 mg

✓YB-104: $(Y_{0.2}Ba_{0.8})_2CuO_4$

Y	Ba	Cu	O
9.289	57.397	16.597	16.717

Y_2O_3 : 300.00 mg
$BaCO_3$: 2097.342 mg
CuO : 1528.365 mg

✓YP-101 $(Y_{0.8}Pb_{0.2})_2CuO_4$

Y	Pb	Cu	O
40.335	23.500	18.017	18.148

Y_2O_3 : 300.00 mg
PbO_2 : 158.888 mg
CuO : 132.091 mg

YB-105 : $(Y_{0.3}Ba_{0.7})_2CuO_4$

Y	Ba	Cu	O
14.295	51.527	17.028	17.151

Y_2O_3 : 300mg 100

$BaCO_3$: 1223.488mg 407.829

CuO : 352.252mg 117.417

$Yb_{1.2}Ba_{0.8}CuO_4$
1.1 0.9
1.3 0.7

YbB-102 $Yb_{1.2}Ba_{0.8}CuO_4$

Yb	Ba	Cu	O
46.656	24.687	14.277	14.380

Yb_2O_3 : 300 mg

$BaCO_3$: 200.305 mg

CuO : 100.922mg

YbB-101 $Yb_{1.1}Ba_{0.9}CuO_4$

Yb	Ba	Cu	O
43.114	27.997	14.392	14.496

Yb_2O_3 : 300mg

$BaCO_3$: 245.824 mg

CuO : 110.093 mg

YbB - 10~~4~~7 $Yb_{1.3}Ba_{0.7}CuO_4$

Yb	Ba	Cu	O
50.142	21.429	14.163	14.266

Yb_2O_3 : 300 mg

$BaCO_3$: 161.782 mg

CuO : 93.156 mg

YB - 105 $(Y_{0.5}Ba_{0.5})_2CuO_4 = Y_1Ba_1CuO_4$

Y	Ba	Cu	O
25.129	38.821	17.959	18.090

YB - 106 $(Y_{0.7}Ba_{0.3})_2CuO_4$

$Y_{1.4}$ | $Ba_{0.6}$ | CuO_4

~~25.827~~

~~37.220~~

Y	Ba	Cu	O
37.220	24.641	19.001	19.138

✓ LuB-101 $(Lu_{0.8}Ba_{0.2})_2CuO_4$

Lu	Ba	Cu	O
60.540	11.880	13.741	13.840

Lu_2O_3:	1000 mg	300 mg
$BaCO_3$:	247.951 mg	74.385 mg
CuO:	249.870 mg	74.961 mg

✓ YP-102 $(Y_{0.6}Pb_{0.4})_2CuO_4$

Y	Pb	Cu	O
26.673	41.440	15.886	16.001

Y_2O_3: 300 mg

PbO_2 423.695 mg

CuO: 176.123 mg

✓ YP-103 $(Y_{0.4}Pb_{0.6})_2CuO_4$

Y	Pb	Cu	O
15.901	55.585	14.205	14.308

Y_2O_3: 300 mg

PbO_2: 953.319 mg

CuO: 264.174 mg

✓ YP-104 $(Y_{0.2}Pb_{0.8})_2CuO_4$

Y	Pb	Cu	O
7.190	67.024	12.847	12.940

Y_2O_3: 300 mg

PbO_2: 2542.181 mg

CuO: 528.780 mg

LuP-101 $(Lu_{0.8}Pb_{0.2})_2CuO_4$

Lu	Pb	Cu	O
57.090	16.901	12.958	13.051

Lu_2O_3 : 300 mg

PbO_2 : 90.162 mg

CuO : 74.958 mg

LuP-102 $(Lu_{0.6}Pb_{0.4})_2CuO_4$

Lu	Pb	Cu	O
41.721	32.936	12.626	12.717

Lu_2O_3 : 300 mg

PbO_2 : 240.428 mg

CuO : 99.942 mg

LuP-103 $(Lu_{0.4}Pb_{0.6})_2CuO_4$

Lu	Pb	Cu	O
27.120	48.170	12.311	12.400

Lu_2O_3 : 300 mg

PbO_2 : 540.949 mg

CuO : 149.914 mg

LuP-104 $(Lu_{0.2}Pb_{0.8})_2CuO_4$

Lu	Pb	Cu	O
13.229	62.662	12.011	12.098

Lu_2O_3 : 300 mg

PbO_2 : 1442.603 mg

CuO !! 299.840 mg

CMC:JBG:Lee

*EXS A-C to Meng Declar

The stamp of the Patent Office, placed hereon, acknowledges receipt of:

Applicant: Party Chu

Our Ref.: 79252/1

Interference ~~Serial~~ No.: 102,447

Date Mailed: 12/4/90

Date Due: 12/4/90

Documents Enclosed: Party Chu's Opposition To Wu et al's 1) Motion for Judgment, Chu Claims 17-27 are Unpatentable, Improper Inventorship and 2) Motion for Judgment, Chu Claims 17,19,20,22,23,25 and 26 Are Unpatentable Under 35USC 112 - 37CFR 1.633; Decls of Ru-Ling Meng*, Pei-Heng Hor, C.W. Chu & EXS A-J.

America the Beautiful USA 15

PRAVEL, GAMBRELL, HEWITT,
KIMBALL AND KRIEGER
1177 WEST LOOP SOUTH 10th FLOOR
HOUSTON, TEXAS 77027

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CMC:JBG:Lee

*EXs A-C to Meng Declar

The stamp of the Patent Office, placed hereon, acknowledges receipt of:

FYI

Applicant: Party Chu

Our Ref.: 79252/1

Interference ~~Serial~~ No.: 102,447

Date Mailed: 12/4/90

Date Due: 12/4/90

DEC 6 1990
RECEIVED IN
BOX INTERFERENCE

Documents Enclosed: Party Chu's Opposition To Lee et al's 1) Motion for Judgment, Chu Claims 17-27 are Unpatentable, Improper Inventorship and 2) Motion for Judgment, Chu Claims 17, 19, 20, 22, 23, 25 and 26 Are Unpatentable Under 35USC 102 - 37CFR 1.633; Decls of Ru-Ling Meng*, Pei-Heng Hor, C.W. Chu & EXS A-J.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

WU et al.	§	Interference No. 102,447
	§	
v.	§	Examiner-in-Chief:
	§	Ronald H. Smith
CHU	§	

DECLARATION OF RULING MENG

Box Interference
Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Attention: Ronald H. Smith
Examiner-in-Chief

Dear Sir:

I, RULING MENG, do hereby declare and state that:

1. I received a B.A. degree in Material Science from the Mining and Metallurgy College in Hunan, China in 1958. Since receiving my degree, I have worked as an instructor at the Mining and Metallurgy College, Hunan, China (1958-59); a Research Assistant, Metallurgy and Material Science Division, Institute of Mining and Metallurgy, Chinese Academy of Science (1959-73); and a Research Associate, Institute of Physics, Chinese Academy of Science (1973-84) during which time I also held visiting positions as a Research Associate, Department of Physics at University of Houston, Texas (1979-81), University of Konstanz, West Germany (1981-82), and University of Houston, Texas (1984-86). I am currently a Senior Research Scientist, and Lab Manager of the Experimental Solid State Physics Lab of the Department of Physics, University of Houston, Texas and of the Texas Center for Superconductivity; a position I have held since 1987. Prior to

that, during the period 1984 to 1986, I held the position of Research Associate, Department of Physics at the University of Houston, Texas, working at the direction and under the supervision of Dr. C.W. (Paul) Chu.

2. I first began to make and examine compositions composed of rare earth metal-alkaline earth metal-copper-oxygen for superconducting properties in November 1986. Dr. C.W. (Paul) Chu under whose directions and supervision I worked directed me to make compositions of La-Ba-Cu-O to a nominal formula as described in Bednorz & Muller, Z. Phys. B.-Condensed Matter, 64, pp 189 - 193 (1986) and then test such compositions for the existence of the properties of a superconducting material -- namely, the exhibition at or below a certain critical temperature (T_{c1}) of zero electrical resistance and a diamagnetic property.

3. During November 1986 I prepared several samples of La-Ba-Cu-O compositions to a nominal formula of $La_{4.25}Ba_{0.75}Cu_5O_{5(3-y)}$, as disclosed by the Bednorz & Muller article. Each sample thereof was prepared under various firing conditions, as recorded in my handwriting in Exhibit A at or about the time each such sample was prepared, and thereafter tested by me, or tested by others under my direction and supervision, to measure the sample's electrical resistance at various temperatures from that of about ambient and progressing to the boiling point of liquid helium which is about 4°K. Further, samples which exhibited the attainment of zero electrical resistance at or below a certain critical temperature were measured for the exhibition of a diamagnetic effect by me, or

by others working under the direction and supervision of Dr. Chu and myself.

4. My work with the La-Ba-Cu-O compositions, as described in paragraphs 2-3 above confirmed that a composition described by Bednorz & Muller as one of nominal formula $La_{4.24}Ba_{0.75}Cu_5O_{5(3-y)}$ did, in fact, possessed superconducting properties even though I produced my replicas, as directed by Dr. Chu, by a solid state reaction technique rather than by a precipitation technique as described by Bednorz & Muller.

5. During the remainder of November of 1986, and bridging into December of 1986, as directed by Dr. Chu, I, or others working under the direction and supervision of Dr. Chu and myself, began at least two activities; one being to subject the La-Ba-Cu-O compositions produced to a Bednorz & Muller nominal composition of $La_{4.25}Ba_{0.75}Cu_5O_{5(3-y)}$ which we had confirmed to be superconductors to application of extreme pressure while testing how such pressure affected the T_{c1} property of such composition; the second activity being to produce La-Ba-Cu-O composition to nominal formulas different than that described for a La-Ba-Cu-O composition by the Bednorz & Muller article and to test such different nominal formulations of La-Ba-Cu-O for exhibition of superconducting properties. Among the first samples of La-Ba-Cu-O of a differing nominal composition which I prepared in accordance with Dr. Chu's instructions were La-Ba-Cu-O samples of the following nominal formulas, designed by my identification designation ("J"):

J-1 $(La_{0.4}Ba_{0.6})_2CuO_4$

J-2	$(La_{0.6}Ba_{0.4})_2CuO_4$
J-3	$(La_{0.7}Ba_{0.3})_2CuO_4$
J-4	$(La_{0.8}Ba_{0.2})_2CuO_4$
J-5	$(La_{0.85}Ba_{0.15})_2CuO_4$
J-6	$(La_{0.9}Ba_{0.1})_2CuO_4$

These samples are recorded in my handwriting in my notebook, together with my calculations of the amounts of reagents needed for their production as shown in Exhibit B.

6. From the results of the work which I performed according to Dr. Chu's instructions on La-Ba-Cu-O compositions as described in paragraphs 2-5 above, it was determined that (1) certain La-Ba-Cu-O compositions were superconductors, (2) that compositions of La-Ba-Cu-O of nominal formulations different than that described by Bednorz & Muller for a superconducting La-Ba-Cu-O composition were superconductors; (3) that under extreme pressure application such superconducting compositions of La-Ba-Cu-O exhibited zero electrical resistance at a critical temperature, T_{c1}, which was unexpectedly higher than that at which the sample composition exhibited zero electrical resistance when subjected only to ambient (atmospheric) pressure. These results were reported to Dr. Chu at or about the time the results were obtained.

7. Following the reports to Dr. Chu of the observation of the results measured in La-Ba-Cu-O systems, as described in paragraphs 3-6 above, while Dr. Chu was out of town in about mid-December 1986 tending to other duties, Dr. Chu called me to describe his ideas for making various elemental substitutions in a

La-Ba-Cu-O superconductor system to increase the T_{c1} temperature at which a so substituted composition would exhibit zero electrical resistance without the need for application of great pressure to such substituted compositions.

8. Of the substituted compositions described to me by Dr. Chu during that December 1986 telephone conversation, Dr. Chu described his idea of substitution for Ba as the alkaline earth metal element in a La-Ba-Cu-O system by Sr and Ca.

9. Further, during the mid-December 1986 telephone conversation with Dr. Chu, as described in paragraph 8 above, Dr. Chu also informed me of his idea of superconducting rare earth metal-alkaline earth metal-copper-oxygen compositions which in comparison to one of La-Ba-Cu-O would exhibit zero electrical resistance at a greater temperature (T_{c1}) without application of pressure. Dr. Chu described his idea for compositions wherein the rare earth element of La was substituted for by non-magnetic rare earth and similar elements, including Y or Lu. During this telephone call Dr. Chu described to me his belief that substitution for La in a La-Ba-Cu-O composition would produce a superconductor which superconducts at a T_{c1} temperature greater than that of a La-Ba-Cu-O composition.

10. As related in paragraph 9 above, among other things, Dr. Chu instructed me by that telephone call to next prepare, among other substituted compositions, Y-Ba-Cu-O compositions in accordance with the same program by which I had earlier prepared and tested different nominal formulations of La-Ba-Cu-O for

superconductive properties.

11. During the latter part of December, after Christmas, W.K. Wu and his research graduate student, James Ashburn, arrived at the laboratories of the University of Houston campus at which I worked to have samples, which I understand Dr. Chu had suggested to them (Wu/Ashburn) to prepare, tested for exhibition of superconductive properties. Based on information and belief which I derived from Dr. Chu and independently from M.K. Wu and Ashburn during their attendance at the University of Houston campus, I understood that the sample brought by Wu/Ashburn to be tested were compositions of La-Sr-Cu-O. I further understood that Wu/Ashburn had already tested these compositions for electrical resistance versus temperature and determined that, absent the application of great pressure thereto, such La-Sr-Cu-O samples exhibited a T_{c1} greater than that of a La-Ba-Cu-O of similar nominal composition without the application of pressure.

12. As described in paragraph 11 above, at our labs at University of Houston, while Wu/Ashburn were in attendance, in the supervision of our group at Dr. Chu's directions I, with the assistance of others in our group, tested the Wu/Ashburn made samples of La-Sr-Cu-O for (1) zero electrical resistance at specific temperatures, (2) for diamagnetism, and (3) for T_{c1} under application to such materials of great pressures. These results were reported to Dr. Chu. The results of this testing were encouraging of a belief that a La-Sr-Cu-O composition possessed a higher T_{c1} than do compositions of La-Ba-Cu-O. However, because the

test results were stated by Dr. Chu to be too poor to support a publication, he directed me to prepare higher quality La-Sr-Cu-O samples for evaluation.

13. Dr. Chu's instruction to me to prepare higher quality samples of La-Sr-Cu-O consequently delayed the time at which I could begin preparation of samples of Y-Ba-Cu-O which had been assigned to me. During a discussion which occurred after Christmas in late December 1986, which was attended by myself, M.K. Wu, and others, the concept of substitution of Y for La in a composition of La-Ba-Cu-O to produce a composition of Y-Ba-Cu-O which superconducts at a T_c temperature greater than that of a La-Ba-Cu-O composition was described to M.K. Wu.

14. During the period of December 1986 after Christmas and continuing through January 28, 1987 while I continued to make and study approximately 47 different samples of La-Ba-Cu-O, I also prepared and evaluated thirty-eight different samples of La-Sr-Cu-O compositions. My sample code for a La-Sr-Cu-O sample was "SL" followed by a number or numbers by which I could identify from my records the nominal formulation and sintering conditions of the sample. In the period December 23, 1986 through January 1, 1987 I prepared and evaluated six samples, SL1-SL6 (Exhibit C). Between January 2-18, 1987 I prepared and evaluated twelve additional samples, SL7-SL17 (Exhibits C and D) and between January 18-28, 1987 I prepared twenty additional samples, SL18-SL31 (Exhibit E).

15. As my work with the La-Sr-Cu-O system was progressing, I began to turn my attention to the making of Y-Ba-Cu-O compositions

which I would begin upon conclusion of my work with La-Sr-Cu-O compositions.

16. The formulas of Y-Ba-Cu-O which I first listed for production, as shown by Exhibit F, are "214" nominal formulations wherein the rare earth to alkaline earth metal ratio, Y to Ba, which together comprise the "2" element begins with a slightly greater amount of rare earth metal --y-- (6:4, like the La to Ba ratio in the "J-2" sample of paragraph 5).

17. On January 15, 1987, I identified in my notebook several substituted compositions for production and examination. Among the compositions so identified is one of the formula $(Y_{0.6}Ba_{0.4})_2CuO_4$ (which may also be written as $Y_{1.2}Ba_{0.8}CuO_4$) as shown in Exhibit F attached hereto which is in my handwriting and made by me on January 15, 1987.

18. By January 28, 1987 I had substantially completed my assignment to prepare and investigate higher quality samples of La-Sr-Cu-O and on January 29, 1987 I again returned by attention to the project which Dr. Chu had previously assigned to me, namely the making of rare earth metal-alkaline earth metal-copper oxides in which, compared to a La-Ba-Cu-O system, La is replaced with Y or Lu. To this purpose, with respect to a Y-Ba-Cu-O system, on January 29, 1987 I proceeded to list samples of Y-Ba-Cu-O for production in accordance with a convention I followed when I first made samples of La-Ba-cu-O which differed from the nominal formula of Bednorz & Muller, as discussed in paragraph 5. I listed in my notebook (Exhibit G) the following samples for production, which I

later identified by a "YB" designation, as follows:

YB-101 $(Y_{0.8}Ba_{0.2})_2CuO_4$
YB-102 $(Y_{0.6}Ba_{0.4})_2CuO_4$
YB-103 $(Y_{0.4}Ba_{0.6})_2CuO_4$
YB-105 $(Y_{0.3}Ba_{0.7})_2CuO_4$
YB-104 $(Y_{0.2}Ba_{0.8})_2CuO_4$

In addition to the above Y-Ba-Cu-O composition I further identified twenty other compositions involving various types of substitutions, including four compositions of Lu-Ba-Cu-O.

19. Further, on January 29, 1987, I identified further compositions for production and testing in accordance with Dr. Chu's direction to make compositions involving substitution variously for the La or Ba of a La-Ba-cu-O composition by other smaller radii atomic elements as shown in Exhibit G attached hereto which was made by me and is in my handwriting. The amounts of reagents required for the production of the Y-Ba-Cu-O compositions as shown in Exhibit G are shown in Exhibit H attached hereto, which is in my handwriting and made by me during January 29-30 1987. Among the Y-Ba-Cu-O compositions considered for production, one is specifically of the formula $Y_{1.2}Ba_{0.8}Cu_1O_4$, which is YB-102 (page H65 of Exhibit H).

20. In accordance with my prior calculations as recorded in Exhibit H, I began to prepare compositions of Y-Ba-Cu-O, one of which, designated as YB-102, was of the formula $Y_{1.2}Ba_{0.8}Cu_1O_4$ as described in Exhibit H. I prepared the Y-Ba-Cu-O compositions by weighing out the required amounts of Y_2O_3, $BaCO_3$ and CuO powder

reagents, mixing the powdered reagents by grinding them in a mortar with a pestle until the powder mass was homogeneously mixed. Thereafter the homogeneous powdered mass was subjected to pressure in a die to convert it to pellet form, multiple pellets were made, and each pellet was sintered at 1000°C, the various pellets being sintered for different lengths of time.

21. Y-Ba-Cu-O compositions of nominal formula $(Y_{0.6}Ba_{0.4})_2CuO_4$, which may also be written as $Y_{1.2}Ba_{0.8}CuO_4$, were prepared under various firing conditions and were tested for electrical resistance versus temperature (R/T) on February 1, 1987 (Exhibit I; which is a measurement of electrical resistance as a function of temperature). The results of this R/T testing are listed in my Stenographic Notebook (Exhibit J). One of two samples sintered for twenty minutes exhibited zero electrical resistance at 89°K (T_{c1}) with a beginning onset temperature (T_{co}) at 94°K. The second sample exhibited zero electrical resistance of 90.1°K with an onset temperature of 94°K.

22. Beginning February 2 and continuing through February 3, 1987 Samples of $Y_{1.2}Ba_{0.8}CuO_4$ were subjected to various pressures (3 klb, 6 klb, 9 klb, 12 klb, 15 klbs and 2 klb) and tested for electrical resistance versus temperature (Exhibit K).

23. The $Y_{1.2}Ba_{0.8}CuO_4$ samples described in paragraph 21 were subjected to powder x-ray diffraction analysis on February 2 and 4, 1987. From the x-ray diffraction analysis it was determined that neither of the multiple phases comprising the sample had a crystalline structure like that of K_2NiF_4. The x-ray spectrum is

Exhibit L.

24. On February 5, 1987 the $Y_{1.2}Ba_{0.8}CuO_4$ samples described in paragraph 21 were tested for diamagnetism at temperatures from 140K to 4.2K and were found at 4.2K to exhibit at least about 24% of the diamagnetic signal of a lead sample of similar dimensions as shown by Exhibit M.

25. The $Y_{1.2}Ba_{0.8}CuO_4$ samples described in paragraph 21 were tested on February 6, 1987 for resistivity over a temperature range of about 100K to 30K while subject to various magnetic field strengths and the zero resistivity state at a magnetic field strength of 5.7T was found to remain as high as 40°K, as shown in Exhibit N.

26. From the data acquired on the $Y_{1.2}Ba_{0.8}CuO_y$ samples as described in paragraphs 21-26 above, the upper critical field $H_{c2}(T)$ was determined on February 6, 1987.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Chu Application or any patent issued thereon.

EXECUTED this 22th day of Feb., 1993.

Ruling Meng

1 bar = 750.06 Torr (mm)

0.2×10^{-4} bar = 0.015 Torr = 15 m Torr

0.2×10^{-4} bar = $0.2 \times 10^{-4} \times 760$ mm = $152 \times 10^{-4} \times 10^{3} \mu = 15 \mu$

(I). $Ba_{0.75}La_{4.25}Cu_5O_{5(3-y)}$

$BaLa_5Cu_5O_5$

A: $BaCO_3 + CuO + La_2O_3 \xrightarrow[15\mu O_2]{900°} 4$ hrs $\xrightarrow[15\mu O_2]{900°C} 8$ hrs

$\xrightarrow[15\mu O_2]{925°C} 26$ hrs.

2×10^{-4} a.

(II). $Ba_{0.75}La_{4.25}Cu_5O_{5(3-y)}$

$BaLa_5Cu_5O_5$

$BaCO_3 + CuO + La_2O_3 \xrightarrow[15\mu]{900°C} 4$ hrs $\xrightarrow[15\mu]{900°C} 4$ hrs

$\xrightarrow[15\mu]{925°C} 26$ hrs

(III). $(La\,Ba)_2CuO_4$

① $BaCO_3 + CuO + La_2O_3 \xrightarrow[15\mu O_2]{900°C} 4$ hrs

$\xrightarrow[15\mu O_2]{900°C} 8$ hrs $\xrightarrow[15\mu O_2]{925°C} 26$ hrs.

② $BaCO_3 + CuO + La_2O_3 \xrightarrow[Air]{900} 4$ hs

$\xrightarrow[Air]{900} 8$ hr $\xrightarrow[Air]{925} 24$ hr $\xrightarrow[2000\mu O_2]{400} 5$ h

$\xrightarrow[2000\mu]{900}$ 8 5 h

CHU EXHIBIT A
WU ET AL V. CHU
INTERFERENCE NO. 102,447

background vacuum 3.5×10^{-4}

Ba-La-Cu-O

17 NOV. 1986

Time	To	Tc mV	O_2 pressure		Time	Tc	mV	O_2
8:00					11:15		37.4/5	15
8:20	200		130		11:30		37.3	15.5
8:30	—	13.6	200		11:40		37.3	15.5
8:36	350	14.3	110		12:10 pm		37.3	15.5
8:37	377	15.4	200					
8:39	384	15.7	190					
8:40		15.8	180					
8:43	440	18.0	180					
8:44	440	18.0	175	18 Nov	86	Tc	mV	
8:46	482	19.8	160	12:30 am			0	15
8:49	526	21.7	150	12:39			5.7	30
8:50		22.0	140	12:52			10	25
8:53		24.4	100	12:56		336	13.7	180
8:55	624	25.8	85		1:27	442	18.1	30
8:58	668	27.8	115		1:30		22.4	30
8:59		28.0	110		1:45		23.2	30
9:02	228	30.3	240		1:46	614	25.5	50
9:04		30.5	220		1:48		26.8	75
9:05		30.7	200		2:07		29.1	50
9:10	764	31.7	250		2:09	753	31.3	55
9:10	775	32.2	300		2:11		33.3	70
9:14		32.7	280					
9:15	796	33.1	280		2:12	830	34.5	80
9:15		33.5	300		2:15		36.1	60
9:18	830	34.5	310		2:16		37.2	50
9:19		34.7	300		2:25		37.4	35
9:20	855	35.5	300		2:52		37.4	30
9:22		36.7	340		2:58		37.3	16
9:23		37.1	340		3:14		37.3	15.5
9:24	900	37.3	320		3:19		37.3	
9:27	"	37.4	250		3:27		37.3	15
9:34	"	37.2	170		3:50		37.3	15.5
9:40	"	37.3	140		4:30		37.3	15
9:54	"	37.3	80		5:00		37.3	15.5
10:10	"	37.3	25		5:15		37.3	13
10:20		37.3	14		5:20		37.4	15
10:25	"	37.3	15		5:31		37.3	16
10:50	"	37.3	15		5:57		37.3	15
10:58		37.3	15		6:15		37.3	15
					[illegible]		[illegible]	[illegible]

H 483

20

23 NOV. C-6 1

	mv	
6:05 pm	3	20
6:10	7.4	30
6:18	11.8	20
7:44		
7:44	20.4	15
7:53	26.7	14.5
7:59	29.9	15
8:22	37.3	15
8:26	38.2	15.5
9:06	38.3	16
10:05	38.3	15
12:15	38.3	15
1:30 24NOV	38.4	15.5
9:57 am	38.4	15.5
10:20	38.4	15
12:42	38.4	15.5
4:40	38.4	15
5:27	38.4	15
7:33	38.4	15
10:20	38.4	15

#8 $BaLa_4Cu_5O_{5(3-y)}$, $NaSiO_3$ 25 NOV 86

ø	mv	O_2
10:00 am	5.8	15
10:23	10.8	15
~~16:8~~		
10:38	16.8	15
10:44	26.5	15
1:24	35.5	15
2:00	38.4	15
4:11	38.4	15
5:27	38.4	15
7:24	38.4	15
9:19	38.4	15
10:38	38.4	15
11:30 p.m	38.4	15
9:50 a.m, 26 NOV	38.4	16
11:39	38.4	15
1:40	38.4	15
4:20	38.4	15

#9 4 0 Dec 1986

	mv	
1:00	24.5	16
1:15	31.5	20
1:16	32.5	35
1:45 p.m	38.2	15
3:15	38.3	15
4:43	38.3	15
5:00	38.3	15
10:00 5 DEC	38.2	15
8:00 pm	38.2	15

3.0 hrs.

Sample NO. 5
$BaLa_4Cu_5O_{5(3-y)}$
binder material: O'Glue
Paper glue

Sample NO. 6
$Ba_{0.75}La_{4.25}Cu_5O_{5(3-y)}$
binder materials: O'Glue
Paper glue

NO. 7
$Ba_{0.75}La_{4.25}Cu_5O_{5(3-y)}$
binder materials.
$NaSiO_3$

1st Nov Dec

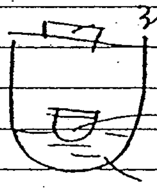
CaO melting point °C 1326 °C
La_2O_3
~~Ca~~ $BaCO_3$

$ErRh_4B_4$

① weight 1:8
12 mm / 60 mm crucible.
The height of the melt was about 4 cm

heat 1350 °C at a rate of 40 °C/h.
soak at 10 h.
cool to 1080 °C 1°/h

below 1080 °C the furnace was cooled naturally to room temperature.



pt 坩埚 KCl + 原 materials.

$KClO_3$ ([illegible])

② BpB

20-30 °C/h, 1000, (17—20 hrs)
2-3 °C/h

③. 1000 °C lower. MgO – 2800 °C
only use 1250 °C

1

2 ~~Nov.~~ Dec. 1986

Molten Salt (Flux) – Growth $BaLa_4Cu_5O_5$

(1) Flux: KCl
(2) material: $BaLa_4Cu_5O_{5(3-y)}$
(3) Growth proceed:

ⓐ $BaLa_4Cu_5O_5 + KCl \xrightarrow{\Delta}$ 900°c at a rate of 30°/

ⓑ Soak at 900°c for 12 h

ⓒ cooled at a rate of 2°c/h from 900–600°c

ⓓ Below 600°c the furnace was cooled naturally to room temperature.

4 Dec 1986.

$La_2O_3 + 2BaCO_3 + CuO \rightarrow (Ba\,La)_2\,CuO_4$

⑦ $+ 2CO_2 + O_2$

$1.7\,La_2O_3 + \overset{0.3}{\cancel{2}}BaCO_3 + CuO \rightarrow Ba_{0.3}La_{1.7}CuO_4$
(5.1) 0.9

$+ \underline{0.3\,CO} + O_2$

⑧ $1.7La_2O_3 + 0.3BaCO_3 + 2CuO \rightarrow (Ba_{0.3}La_{1.7})_2\overset{+2}{}CuO_4$
7 16

$\rightarrow O$ [illegible] + [illegible]

2 Dec 1986

3:00 pm $BaLa_4Cu_5O_5(3-y)$

<1>. 25°C — 900 30 h

(4 Dec. 9 p.m.)

<2>. 900 — 900 12 h

4/ 9.pm — 5/ 9.am

③ 900 — 750 75 h 8. 11 a.m

④ 750 — 600 75 h 11 11:a.m

⑤ 600 — 54 — 5h

✓ Stop. 8 Dec 4 p.m
after 4:00 pm use water to wash.

Single crystal

10 Dec 1986.

① 25°c — 1000°c ~~30 h~~ 32.5 h

② 1000 — 1000 ~~24 - 36 h~~

⑤ ~~1000~~ —

③. 1000 — 750 125 h

④ 750 — 54 5 h

193.5 h /24 = 8 day

Dec 8. 5:30 pm

big pt crucible : $(La_{0.85}Ba_{0.15})_2CuO_4$

Small pt $(La_{0.9}Ba_{0.1})_2CuO_4$

1000 (12h 0 → 1000 °C) ~~Keep~~ Keep 24 hr

Dec 9

$Ba_{0.75}La_{4.25}Cu_5O_{5(3-y)}$

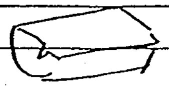
① 700 °C (925) 6 – 8 hours powder
② 500 °C (925) 6 – 8 hours powder

③ 900 °C (925) 24 hours pressure 4000 kb
15μ O_2 3/16" ⌀

Dec 9 1986

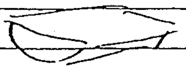
J-7 $(La_{0.85}Ba_{0.15})_2CuO_4$

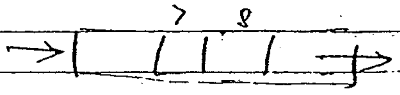
1000 24 hs in air
J-7-1 400 annealing in 2000 μ O_2 8 hrs.



J-8 $(La_{0.9}Ba_{0.1})_2CuO_4$

1000 24 hrs in air
J-8-1 400 annealing in 2000μ O_2 8 hrs.





9. Dec. 1986

NO.	Composition	First heatment		Second time		Third time		O_2	binder material
		T°C	hrs	°C	hrs	°C	hrs		
#1	$Ba_{0.75}La_{4.25}Cu_5O_5$	900	4	900	8	925	26	15μ	$NaSiO_3$
#8								0.2×10^{-4}	
#2	$BaLa_5Cu_5O_5$	900	4	900	8	925	26	15μ	$NaSiO_3$
#3	$Ba_{0.75}La_{4.25}Cu_5O_5$	900	4	900	8	900	26	15μ	$NaSiO_3$
#4	$BaLa_5Cu_5O_5$	900	4	900	8	900	26	15μ	$NaSiO_3$
#5	$BaLa_4Cu_5O_{5(3-y)}$	900	4	900	8	925	26	15μ	O-Glue
#6	$Ba_{0.75}La_{4.25}Cu_5O_{5(3-y)}$	900	4	900	8	925	26	15μ	O-Glue
#7	$Ba_{0.75}La_{4.25}Cu_5O_{(3-y)}$	900	4	900	8	925	26	15μ	$NaSiO_3$
#8	$BaLa_4Cu_5O_{5(3-y)}$	900	4	900	8	925	26	15μ	$NaSiO_3$
*9	$BaLa_4Cu_5O_{5(3-y)}$	900	4	900	8	925	30	15μ	$NaSiO_3$
J-1	$(La_{0.9}Ba_{0.1})_2CuO_4$	900	4	900	8	~~925~~	~~24~~	Air	
J-2	$La_{0.6}Ba_{0.4})_2CuO_4$	900	4	900	8	~~925~~	~~24~~	Air	
J-3	$(La_{0.7}Ba_{0.3})_2CuO_4$	900	4	900	8	~~925~~	~~24~~	Air	
J-4	$(La_{0.8}Ba_{0.2})_2CuO_4$	900 Air	4	900 Air	8	925	24	Air	
J-5	$(La_{0.85}Ba_{0.15})_2CuO_4$	900 Air	4	900 Air	8	925	24	Air	
J-6	$(La_{0.9}Ba_{0.1})_2CuO_4$	900 Air	4	900 Air	8	925	24	Air	
J-7	$(La_{0.85}Ba_{0.15})_2CuO_4$	1000 Air	24						
J-8	$La_{0.9}Ba_{0.1})_2CuO_4$	1000 Air	24						
J-7-1	$(La_{0.85}Ba_{0.15})CuO_4$	J-7 →		400	8	O_2 2000μ			
J-8-1	$(La_{0.9}Ba_{0.1})_2CuO_4$	" J-8 →		400	8	2000μ			

NO	Composition	First time T°C	First time Time	First time atm	Second time T°C	Second time Time	Second time atm	third time T°C	third time Time	third time atm	four time T°C	four time Time	four time atm	
J-7-2	$La_{0.85}$-$Ba_{0.15}$	1000	24	Air	400	5	2000μ	900	~~5~~	2000μ	400 + 900			
J-8-2	$La_{0.9}$ $Ba_{0.1}$	〃	〃	〃	〃	〃	〃	〃	〃		400 + 900			
J-7-3	$La_{0.85}$-$Ba_{0.15}$	1000	24	Air	900	5h	2000μ	(400 5h + 900h)						
J-8-3	$La_{0.9}$ $Ba_{0.1}$	〃	24	Air	900	5h	2000μ	(450 5h + 900h)						
J-4-2	$La_{0.8}$ $Ba_{0.2}$	900	4	Air	900	8h	Air	925	24	Air	400	5	2000μ O_2	
J-5-2	$La_{0.85}$ $Ba_{0.15}$	900	4	Air	900	8	Air	925	24	Air	400	5	2000μ O_2	
J-6-2	$La_{0.9}$ $Ba_{0.1}$	900	4	Air	900	8	Air	925	24	Air	400	5	2000μ O_2	
J-4-3	$La_{0.8}$ $Ba_{0.2}$	900	4	Air	900	8	Air	925	24	Air	400	2000μ 5h	2000μ 900	5h
J-5-3	$La_{0.85}$ $Ba_{0.15}$	900	4	Air	900	8	Air	925	24	Air	400	2000μ 5h	900	5h
* J-6-3	$La_{0.9}$ $Ba_{0.1}$	900	4	Air	900	8	Air	925	24	Air	400	2000μ 5h	2000μ 900	5h
J-9	$La_{0.8}$ $Ba_{0.2}$	900	4	15μ O_2	900	8	15μ O_2	Color is not Black.						
J-10	$La_{0.85}$ $Ba_{0.15}$	900	4	15μ O_2	900	8	O_2							
J-11	$La_{0.9}$ $Ba_{0.1}$	900	4	15μ O_2	900	8	O_2							
J-12	$La_{0.8}$ $Ba_{0.2}$ (J-6)	900	4	Air	900	8	Air	925	24	Air	400	1h 2000μ	900	2000μ
J-13	Be $La_{0.85}$ $Ba_{0.15}$	900	4	Air	900	8	Air	925	24	Air	400	1h 2000μ	900	2000μ
J-14	$La_{0.9}$ $Ba_{0.1}$	900	4	Air	900	8	Air	925	24	Air	400	1h 2000	900	2000μ

9hr from 900 → room temperature.

J-12, J-13 > Sample ~~after~~ 1h explode ~~in Air Two hour late become~~ ~~powder~~ into powder after Two hour in Air

J-14 still ~~[illegible]~~ good after over night in air.

NO.	Composition	First time			Second time			third time		
J-15	$La_{0.925}Ba_{0.075}$	900	4	Air	900	8	Air	925	24	Air
J-16	$La_{0.95}Ba_{0.05}$	900	4	Air	900	8	Air	925	24	Air
~~J-17~~	~~$La_{0.94}Ba_{0.06}$~~									
J-17	$La_{0.925}Ba_{0.075}$	1100	26	Air						
J-18	~~$La_{0.925}Ba_{0.075}$~~ $La_{0.9}Ba_{0.1}$	NO.2 1100	30	Air						
J-19	$La_{0.95}Ba_{0.05}$	NO.3 1100	30	Air						
J-17-1	$La_{0.925}Ba_{0.075}$	1100	26	Air	950	4	Air			
J-17-2	$La_{0.925}Ba_{0.075}$	1100	26	Air	950	4	O_2 2000μ			
J-20	La_2CuO_4	1100	30	Air						
J-21	$La_{0.925}Ba_{0.075}$	1100	30	Air						
J-22	$(La_{0.925}Ba_{0.075})_2CuO_4$	1100	26	Air						
J-23	$(La_{0.925}Ba_{0.075})_2CuO_4$	~~1100~~ 900	4	Air	900	8	Air	925	24 Air	Air
J-24	$La_{0.9}Ba_{0.1}$	1100	26	Air_p						
J-25	$La_{0.9}Ba_{0.1}$	900	4	Air_p	900	8	Air_p			
~~SL-1~~										
LS-1										

3rd Jan ~~1986~~ 1987

Time	T°c	O_2	Time	T°c	O_2
3:40	200/7.96	60	5:20	30.4	60
3:45	200/7.96	50	5:21	31.2	70
4:10	300	20	5:22	31.9	85
4:15	400/15.17	30	5:23	32.2	86
4:20	500/19.76	30	5:24	32.2	80
4:25	600/23.9	25	5:24	32.6	
4:26	688/~~30~~	26.1	5:25	33.5	90
4:27	636/26.7	36.0	5:25	34.4	100
4:30	/26.7	35.0	5:27	34.4	90
4:30	/26.9	38	5:30	34.7	80
4:31	/27	40	5:31	35.6	100
4:31	27	42	5:32	36.3	160
	27.1	44	5:32	36.7	150
4:35	27.2	45	5:33	36.8	120
4:35	27.2	43	5:34	37.0	100
	27.4	46	5:35	37.1	75
4:40	27.6	47	5:37	37.2	30
	28	60	5:38	37.4	18
	28.2	65	5:39	37.9	13
	28.2	70	5:40	38.2	10
	28.3	75	5:40	38.4	0 ?
	28.5	80	5:40	38.7	5
	28.5	81-82	5:41	38.9	8
4:41	28.6	84	5:43	38.9	10
4:42	28.6	80		(943)	
4:43	28.6	75	5:45	39	15
4:45	28.7	70	5:46	39.1	15
47	28.7	65	5:47	39.0	15
48.5	28.8	60	5:53	37.6	15
51	28.8	55			
55	28.8	50			
5:00	28.8	45			
5:05	28.8	40			
5:08	29.1	45			
5:09	29.9	70			
5:10	30.2	80			
5:13	30.4	25			
5:16	30.4	65			

J-2. $(La_{0.6}Ba_{0.4})_2CuO_4$

La_2O_3 6000 La : 5116.2

Ba : 5116.2 : 41.25 = x : 27.19 x = 3372.35

$BaCO_3$ 3372.35 : 69.59 = x : 100
x = 4846

Cu : 5116.2 : 41.25 = x : 15.72 x = 1949.73

CuO 1949.73 : 79.88 = x : 100 x = 2440.8.

J-1. $(La_{0.4}Ba_{0.6})_2CuO_4$

La_2O_3 ~~3000~~ 2000 × 85.27 x = 1705.4

Ba : 1705.4 : 27.54 = x : 40.85 x = 2529.6

$BaCO_3$ 2529.6 : 69.59 = x : 100 x = 3635

Cu : 1705.4 : 27.54 = x : 15.75 x = 2686

CuO : 2686 : 79.88 = x : 100 x = 3362.54

CHU EXHIBIT B
WU ET AL V. CHU
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16 NOV 1986

<1> J-4

$(La_{1.8}Ba_{0.2})_2 CuO_4$

La_2O_3 3000 mg × 85.27 = 2558.1 mg La (×2)

Ba 2558.1 : 54.92 = x : 13.57 x = 632.072.

$BaCO_3$:

632.07 : 69.59 = x : 100

x = 908.27 ($BaCO_3$ (×2))

Cu : 2558.1 : ~~[illegible]~~ 54.92 = x : 15.70 x = 731.28

CuO 731.28 : 79.88 = x : 100 x = 915.47×2 = 1830.95

<2> J-5 $La_{0.85}Ba_{0.15}CuO_4$

La_2O_3 5000 mg

La 5000 × 85.27 = 4263.5

Ba : 4263.5 : 58.32 = x : 10.18

x = 744.21

$BaCO_3$ 744.21 : 69.59 = x : 100

x = 1069.42

Cu : 4263.5 : 58.32 = x : 15.69

x = 1147.02.

CuO 1147.02 : 79.88 = x : 100

x = 1435.93.

3000 × 85.27 = 2558.10

2558.1 : 58.32 = x : 10.1

$BaCO_3$ x = 445.5

$BaCO_3$ 446.5 : 69.54 = x : 100.

x = 642.

Cu : 2558 : 58.32 = x : 15.

x = 686.52,

CuO.

686.52 : 79.88 = x : 100

x = 859.44

J-4 large pt
J-3 small pt

J-6 →


J-7 → longest one

J-6. $(La_{0.9}Ba_{0.1})_2CuO_4$

La_2O_3 6060 La : 5116.20 3000 mg

Ba : 5116.20 : 61.73 = x : 6.78

Ba : 561.92

$BaCO_3$ 561.92 : 69.59 = x : 100

x = 807.47 403.735 mg

Cu : 5116.20 : 61.73 = x : 15.69

Cu : 1300.39

CuO : 1300.39 : 79.88 = x : 100

1627.93 813.97 mg

J-3 $(La_{0.7}Ba_{0.3})_2CuO_4$

La_2O_3 5000 x 85.27 = 4263.5

Ba : 4263.5 : 48.09 = x : 20.38 , x = 1806.82

$BaCO_3$ 1806.82 : 69.59 = x : 100 x = 2596.38

Cu : 4263.5 : 48.09 = x : 15.71 x : 1392.80

CuO : 1392.80 : 79.88 = x : 100 x = 1743.62

No.	composition	First time			second time			Third time			Annealing-1			Annealing-2			Tc(1)	Tc(2)	R-T	Ratio	D	X
		T°C	hrs	atm	T°C	hrs	atm	T°	hrs	atm	T°C	hrs	atm	T°C	hrs	atm						
SL-1	$(La_{0.925}Sr_{0.075})_2CuO_4$	1175	4	Air c	1100	22	Air P															B.L
		transformer broke															45	28	M-S	∞		16.9
SL-2	$(La_{0.9}Sr_{0.1})_2CuO_4$	1125	4	Air p	1100	22	Air-p										~39	small x all	M-S-M			0
SL-3	$(La_{0.85}Sr_{0.15})_2CuO_4$	1125	4	Air-p	1100	22	Air-p															4.6
SL-4	$(La_{0.885}Sr_{0.115})_2CuO_4$	1175	4	Air-p	11.00	22	Air-p															5
SL-5	$(La_{0.865}Sr_{0.135})_2CuO_4$	1125	4	Air-p	1100	2.2	Air-p															
SL-6	$(La_{0.9}Sr_{0.1})_2CuO_4$	1110	24	Air-0																		
7. Jan																	39.4 ~39	18 28	M-S	▬	M	
SL-7	$(La_{0.925}Sr_{0.075})_2CuO_4$	1100	30	Air...													~3.8	70	S-I	∞		
SL-8	$(La_{0.9}Sr_{0.1})_2CuO_4$	11.00	30	Air...													~39	>20 a.r. Λ4.2				
SL-9	$(La_{0.885}Sr_{0.115})_2CuO_4$	11.00	30	Air...													26	23	M-S	∞	M	
SL-10	$(La_{0.9}Sr_{0.1})_2CuO_4$	1100	24	Air	quench in		LN2															
SL-10A	$(La_{0.9}Sr_{0.1})_2CuO_4$	1100	24			-	Air										35	22.3	M-S			
SL-11	$(La_{0.85}Sr_{0.15})_2CuO_4$	1200	24	Air B			—												I			
SL-12	$(La_{0.9}Sr_{0.1})_2CuO_4$	1100	24	Air B													33	Q	I-			40
SL-13	$(La_{0.9}-Sr_{0.1})_2CuO_4$	1000	8	Air-P	1100	24	Air B															
																	30	16.5			N	
CL-1	$(La_{0.9}Ca_{0.1})_2CuO_4$	1100	24	Air B	1100	14	Air B												T			
CL-2		1000	9	Air-p	1100	14	Air B															
CeS-1	$(Ce_{0.9}Sr_{0.1})_2CuO_4$																					
CeS-2	$(Ce_{0.85}Sr_{0.15})_2CuO_4$																					
~~CeS-3~~																						
CeB-1	$(Ce_{0.9}Ba_{0.1})_2CuO_4$																					
CeB-2	$(Ce_{0.85}Ba_{0.15})_2CuO_4$																					
ML-1	$(La_{0.9}Mg_{0.1})_2CuO_4$	1100	24	Air B																		
PL-1	$(La_{0.9}Pb_{0.1})_2CuO_4$	1100	24	Air B																	I	
Ys-1	$(Y_{0.9}Sr_{0.1})_2CuO_4$	1100	24	Air B																		
		1100 -	6h→20	-1100°C																	I	
Yb-1	$(Y_{0.9}Ba_{0.1})_2CuO_4$	1100	24	Air B																		
		1175 -	6h→20	→ 1100°C																	I	
LuS-1	$(Lu_{0.9}Sr_{0.1})_2CuO_4$	1100	24	Air B																		
		1100 -	6h-20	→ 1100°C																	I	
LuB-1	$(Lu_{0.9}Ba_{0.1})_2CuO_4$	1100	24	Air B																		
		1100 -	6h→20	— 1100°C																		

CHU EXHIBIT C
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18 Jan 87

										T	T	R:T	R:t	χ	ρ
J-46	$(La_{.9}Ba_{.1})_2CuO_4$	1100	24	Air								M-I		15.6	
J-47	$(La_{0.925}Ba_{0.075})_2CuO_4$	1100	24	Air						22.7	9.8	M-1.5		56.6	
J-48	La_2CuO_4	1100	24							30				0	
J-49	$(La_{0.925}Ba_{0.075})_2CuO_4$ (J-15)	900		Air	900		Air	1100	24	29	6			3.4	
	target									33	22			93.6	
SL-14	$La_{1.85}Sr_{.15}CuO_4$ 0.815 1.185	1100	24	Air										-2.78	
SL-15	$(La_{0.925}Sr_{0.075})_2CuO_4$	1100	24	Air						37	15			343	
SL-16	$La_{1.85}Sr_{0.15}CuO_4$	1100	24	Air										4.5	
SL-17	$La_{1.8}Sr_{0.2}CuO_4$	1100	24	Air						37	28			32	
CL-3	CL-1	1100	24	Air	1100	24									
CL-4	$Ca_{1.85}Ca_{0.075}CuO_4$	1100	24	Air											
CL-5	$La_{0.85}Ca_{0.075}CuO_4$	1100	24	Air											
CL-6	$(La_{0.925}Ca_{0.075})_2CuO_4$	1000	12	Air	1100	18	Air								
CL-7	$(La_{0.925}Ca_{0.075})_2CuO_4$	1000	12	Air	1100	18	Air							H	479

CHU EXHIBIT D
WU ET AL V. CHU
INTERFERENCE NO. 102,447

NO.	Composition	First T	hours	Atm	Second time T	hours	Atm	T1	T2	R-T	Ratio	ρ	χ	
SL-18	SL_2	900	20	O_2										
SL-19	$(La_{0.9}Sr_{0.1})_2CuO_4$	1100	24	Air	900	20	O_2							
SL-20	$(La_{0.975}Sr_{0.025})_2CuO_4$	1100	24	Air	900	20	O_2							
SL-21	$(La_{0.95}Sr_{0.05})_2CuO_4$	1100	24	Air				36.2	26.6	M				
SL-22	$La_{4.5}Sr_{0.5}Cu_5O_5$	900	24	O_2 15M				39.2	32	M				
SL-23	$La_{4.6}Sr_{0.4}Cu_5O_5$	900	24	O_2 15m				40.6	32.7					
SL-22-1	SL-22	~~950~~ 900	24	O_2 15				42.5	30.3	M				
SL-23-1	SL-23	~~950~~ 900	24	O 15m				~~[illegible]~~ 44.3 →	~~[illegible]~~ 31.5					
SL-20-1	SL-20	900	18	O_2										
SL-21-1	SL-21	900	18	O_2				38.8	19.8					
SL-24	$(La_{0.9}Sr_{0.1})_2CuO_4$	1000	24	Air_P	1100	~~18~~	Air_B							Single cry.
SL-25	$(La_{0.975}Sr_{0.025})_2CuO_4$	1000	24	Air_P	1100	18	Air_B							
SL-26	$La_{4.6}Sr_{0.4}Cu_5O_5$	900	24	O_2 15m										
SL-27	$La_{4.5}Sr_{0.5}Cu_5O_5$	900	24	O_2 15m										
SL-24-2 ~~SL-24-3~~	SLØ-24	1150	~~17~~ 13	Air										
SL-24-L	SLØ-24	1200	18	Air										
SL-28	$(La_{0.9}Sr_{0.1})_2CuO_4$	950	12	O_2										
SL-29	$(La_{0.9}Sr_{0.1})_2CuO_4$	1150	16	Air				37	27.3				H	477
SL-30	"	"	20	"				36.3	27.3					
SL-31	"	1150	24	Air				36.3	27.3					

(SL-32 — 36

CHU EXHIBIT E
WU ET AL V. CHU
INTERFERENCE NO. 102,447

YS-2 15 Jan ~~1988~~ 1987

(中) $(Y_{0.85}\ Sr_{0.15})_2\ CuO_4$

[illegible] $Y_{\cancel{0.67}\ 0.925}\ Sr_{\cancel{0.33}\ 0.075}\ CuO_4$ ~~1.67~~

SY-3

$(Y_{0.6}\ Ba_{0.4})_2\ CuO_4$

SB-2 $(Y_{0.85}\ Ba_{0.15})_2\ CuO_4$

SB-3 $(Y_{\cancel{1.67}\ 0.925}\ Ba_{\cancel{0.33}\ 0.075})_2\ CuO_4$

[I] $(Y_{0.85}\ Sr_{0.15})_2\ CuO_4$

YS-2

Y	Sr	Cu	O
47.25	12.88	19.87	0.20

Y_2O_3 1000

$SrCO_3$: 361.59

CuO : 414.52

(II) $Y_{0.925}\ Sr_{0.075}\ CuO_4$

YS-3

CHU EXHIBIT F
WU ET AL V. CHU
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29 Jan 1986

① $(Y_{0.8} Ba_{0.2})_2 cuO_4$

② $(Y_{0.6} Ba_{0.4})_2 cuO_4$

③ $(Y_{0.4} Ba_{0.6})_2 cuO_4$

④ $(Y_{0.2} Ba_{0.8})_2 cuO_4$

✓ ⑤ $(Lu_{0.8} Ba_{0.2})_2 cuO_4$

⑥ $(Lu_{0.6} Ba_{0.4})_2 cuO_4$

⑦ $(Lu_{0.4} Ba_{0.6})_2 cuO_4$

⑧ $(La_{0.2} Ba_{0.8})_2 cuO_4$

⑨ $Sc_{0.8} Ba_{0.2}$

⑪ $Sc_{0.6} Ba_{0.4}$

⑫ $Sc_{0.4} Ba_{0.2}$

⑬ $Sc_{0.2} Ba_{0.8}$

⑭ $Y_{0.8} pb_{0.2}$

⑮ $Y_{0.6} pb_{0.4}$

⑯ $Y_{0.4} pb_{0.6}$

⑰ $Y_{0.2} pb_{0.8}$

⑱ $(Lu_{0.8} pb_{0.2})_2 cuO_4$

⑲ $(Lu_{0.6} pb_{0.4})_2 cuO_4$

⑳ $(Lu_{0.4} pb_{0.6})_2 cuO_4$

㉑ $(Lu_{0.2} pb_{0.8})_2 cuO_4$

㉒ $Sc_{0.8} pb_{0.2}$

㉓ $Sc_{0.6} pb_{0.4}$

㉔ $Sc_{0.4} pb_{0.6}$

㉕ $Sc_{0.2} pb_{0.8}$

㉖ $(Y_{0.3} Ba_{0.7})_2 CuO_4$

CHU EXHIBIT G
WU ET AL V. CHU
INTERFERENCE NO. 102,447

29—30 Jan 1987

① $[La_{0.9}(Y_{0.155}Ba_{0.845})_{0.1}]_2cuO_4$ ✓

② $[La_{0.9}(Y_{0.26}Ba_{0.74})_{0.1}]_2cuO_4$

③ $[La_{0.9}(Y_{0.378}Ba_{0.622})_{0.1}]_2cuO_4$

④ $[La_{0.95}(Y_{0.155}Ba_{0.845})_{0.15}]_2cuO_4$

Y_2O_3

① ~~$La_{0.3}$ [illegible] $Ba_{0.168}$ [illegible] cuO_4~~ 0.031

~~LAM8~~

⑤ $[La_{0.95}(Y_{0.155}Ba_{0.845})_{0.05}]_2cuO_4$

Y_2O_3 78.74 ①

LYB-1 $[La_{0.9}(Y^{b}_{0.155}Ba_{0.845})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
61.96020	0.683	5.752	15.745	15.859

La_2O_3 : 1000 mg

Y_2O_3 : 11.937 mg

$BaCO_3$: 113.782 mg

CuO : 271.256 mg

52 H

CHU EXHIBIT H
WU ET AL V. CHU
INTERFERENCE NO. 102,447

② LYB-2 $[La_{0.9}(Y^{b}_{0.26}Ba_{0.74})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
62.117	1.149	5.050	15.785	15.900

La_2O_3 :	2000 mg	1000 mg
Y_2O_3 :	40.062 mg	20.031 mg
$BaCO_3$:	199.199 mg	99.600 mg
CuO :	542.515 mg	271.258 mg

③ LYB-3 $[La_{0.9}(Y_{0.378}Ba_{0.622})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
62.294	1.675	4.257	15.830	15.945

La_2O_3 :	1000 mg	2000 mg
Y_2O_3 :	29.118 mg	58.236 mg
$BaCO_3$:	83.721 mg	167.442 mg
CuO :	271.258 mg	542.516 mg

④ LYB-4 $[La_{0.85}(Y_{0.165}Ba_{0.845})_{0.1}]_2CuO_4$

La	Y	Ba	Cu	O
60.604	0.707	5.957	16.307	16.425

La_2O_3 :	2000 mg	1000 mg
Y_2O_3 :	25.266 mg	12.633 mg
$BaCO_3$:	240.843 mg	120.422 mg
CuO :	H 574.448 mg	287.224 mg H

⑤ LYB-5 $[La_{0.95}(Y_{0.155}Ba_{0.845})_{0.05}]_2CuO_4$

La	Y	Ba	Cu	O
65.256	0.341	2.869	15.710	15.824

La_2O_3 :	1000 mg	2000 mg
Y_2O_3 :	5.659 mg	11.318 mg
$BaCO_3$:	53.863 mg	107.725 mg
CuO :	256.987 mg	513.965 mg

Lu_2O_3

Lu : 87.93

⑥ LLB-1 $[La_{0.9}(Lu_{0.149}Ba_{0.851})_{0.1}]_2CuO_4$

La	Lu	Ba	Cu	O
61.560	1.284	5.755	15.644	15.757

La_2O_3 :	2000 mg	1000 mg
Lu_2O_3 :	40.448 mg	20.224 mg
$BaCO_3$:	229.062 mg	114.531 mg
CuO :	542.534 mg	271.267 mg

⑦ LLB-2 $[La_{0.95}(Lu_{0.149}Ba_{0.851})_{0.05}]_2CuO_4$

La	Lu	Ba	Cu	O
65.045	0.643	2.880	15.659	15.773

La_2O_3 : 2000 mg

Lu_2O_3 : 19.171 mg

$BaCO_3$: 108.489 mg

CuO : 513.959 mg

⑧ $[La_{0.95} Y_{0.05}]_2 CuO_4$

La	Y	Cu	O
65.923	2.221	15.871	15.986

La_2O_3 : 1000 mg

Y_2O_3 : 36.484 mg

CuO : 256.989 mg

⑨ $[La_{0.99} Ba_{0.01}]_2 CuO_4$

La	Ba	Cu	O
67.856	0.678	15.676	15.790

La_2O_3 :	1000 mg	2000 mg
$BaCO_3$:	12.241 mg	24.482 mg
CuO :	246.601 mg	493.202 mg

: Sinter 7 hours 1100 °C.

LuB-102 $(Lu_{0.6}Ba_{0.4})_2CuO_4$

Lu	Ba	Cu	O
46.932	24.559	14.203	14.306

Lu_2O_3 :	1000 mg	300 mg
$BaCO_3$:	661.202 mg	198.361 mg
CuO :	333.141 mg	99.942 mg

✓ LuB-103 $(Lu_{0.4}Ba_{0.6})_2CuO_4$

Lu	Ba	Cu	O
32.378	38.121	14.697	14.804

Lu_2O_3 :	1000 mg	300 mg
$BaCO_3$:	1487.670 mg	443.601 mg
CuO :	499.684 mg	149.905 mg

✓ LuB-104 $(Lu_{0.2}Ba_{0.8})_2CuO_4$

Lu	Ba	Cu	O
16.773	52.662	15.227	15.338

Lu_2O_3 : 300 mg

$BaCO_3$: 1190.146 mg

CuO : 299.807 mg

✓

YB-101 $(Y_{0.8}Ba_{0.2})_2CuO_4$

Y	Ba	Cu	O
43.806	16.918	19.567	19.709

Y_2O_3 :	300 mg	100
$BaCO_3$:	131.09 mg	43.686
CuO :	132.088 mg	44.029

YB-102 $(Y_{0.6}Ba_{0.4})_2CuO_4$

Y	Ba	Cu	O
31.005	31.930	18.466	18.599

Y_2O_3 : 300mg

$BaCO_3$: 349.555 mg (243.267.

CuO : 176.122mg

YB-103 : $(Y_{0.4}Ba_{0.6})_2CuO_4$

Y	Ba	Cu	O
19.558	45.343	17.481	17.608

Y_2O_3 : 300.00 mg

$BaCO_3$: 786.525 mg

CuO : 264.176 mg

YB-104 : $(Y_{0.2}Ba_{0.8})_2CuO_4$

Y	Ba	Cu	O
9.289	57.397	16.597	16.717

Y_2O_3 : 300.00 mg

$BaCO_3$: 2097.342 mg

CuO : 528.365 mg

YP-101 $(Y_{0.8}Pb_{0.2})_2CuO_4$

Y	Pb	Cu	O
40.335	23,500	18,017	18,148

Y_2O_3 : 300.00 mg

PbO_2 : 158.888 mg

CuO : 132.091 mg

BaO = 99.88

(BaO = 243.56 mg)

YB - 1.

Y_2O_3 1000 mg

$BaCO_3$: 194.195

CuO : 391.381

YB-105 : $(Y_{0.3} Ba_{0.7})_2 Cu O_4$

Y	Ba	Cu	O
14.295	51.527	17.028	17.151

Y_2O_3 : 300mg 100

$BaCO_3$: 1223.488mg 407.829

CuO : 352.252mg 117.417

$Yb_{1.2} Ba_{0.8} Cu O_4$

1.1 0.9

1.3 0.7

YbB-102 … $Yb_{1.2} Ba_{0.8} Cu O_4$

Yb	Ba	Cu	O
46.656	24.687	14.277	14.380

Yb_2O_3 : 300 mg

$BaCO_3$: 200.305 mg

CuO : 100.922mg

YbB-101 $Yb_{1.1} Ba_{0.9} Cu O_4$

Yb	Ba	Cu	O
43.114	27.997	14.392	14.496

Yb_2O_3 : 300mg

$BaCO_3$: 245.824 mg

CuO : 110.093 mg

YbB - 107 $Yb_{1.3}Ba_{0.7}CuO_4$

Yb	Ba	Cu	O
50.142	21.429	14.163	14.266

Yb_2O_3 : 300 mg

$BaCO_3$: 161.782 mg

CuO : 93.156 mg

YB - 105 $(Y_{0.5}Ba_{0.5})_2CuO_4 = Y_1Ba_1CuO_4$

Y	Ba	Cu	O
25.129	38.821	17.959	18.090

YB - 106 $(Y_{0.7}Ba_{0.3})_2CuO_4$

$Y_{1.4}$	$Ba_{0.6}$	CuO_4
~~[illegible]~~ 37.220		

Y	Ba	Cu	O
37.220	24.641	19.001	19.138

✓ LuB - 101 $(Lu_{0.8}Ba_{0.2})_2CuO_4$

Lu	Ba	Cu	O
60.540	11.880	13.741	13.840

Lu_2O_3:	1000 mg	300 mg
$BaCO_3$:	247.951 mg	74.385 mg
CuO:	249.870 mg	74.961 mg

✓ YP-102 $(Y_{0.6}Pb_{0.4})_2CuO_4$

Y	Pb	Cu	O
26.673	41.440	15.886	16.001

Y_2O_3 : 300 mg

PbO_2 423.695 mg

CuO : 176.123 mg

✓ YP-103 $(Y_{0.4}Pb_{0.6})_2CuO_4$

Y	Pb	Cu	O
15.901	55.585	14.205	14.308

Y_2O_3 : 300 mg

PbO_2: 953.319 mg

CuO : 264.174 mg

✓ YP-104 $(Y_{0.2}Pb_{0.8})_2CuO_4$

Y	Pb	Cu	O
7.190	67.024	12.847	12.940

Y_2O_3 : 300 mg

PbO_2 : 2542.181 mg

CuO : 528.380 mg

LuP-101 $(Lu_{0.8}Pb_{0.2})_2CuO_4$

Lu	Pb	Cu	O
57.090	16.901	12.958	13.051

Lu_2O_3 : 300 mg

PbO_2 : 90.162 mg

CuO : 74.958 mg

LuP-102 $(Lu_{0.6}Pb_{0.4})_2CuO_4$

Lu	Pb	Cu	O
41.721	32.936	12.626	12.717

Lu_2O_3 : 300 mg

PbO_2 : 240.428 mg

CuO : 99.942 mg

LuP-103 $(Lu_{0.4}Pb_{0.6})_2CuO_4$

Lu	Pb	Cu	O
27.120	48.170	12.311	12.400

Lu_2O_3 : 300 mg

PbO_2 : 540.949 mg

CuO : 149.914 mg

LuP-104 $(Lu_{0.2}Pb_{0.8})_2CuO_4$

Lu	Pb	Cu	O
13.229	62.662	12.011	12.098

Lu_2O_3 : 300 mg

PbO_2 : 1442.603 mg

CuO !! 299.840 mg

$BaCO_3$ 69.60
CuO 79.88
Y_2O_3 78.74

* Feb. 1987

(I) YB 106

$(Y_{0.5}Ba_{0.5})_2CuO_4$

Y	Ba	Cu	O
25.129	38.821	17.959	18.092

Y_2O_3 400 mg
$BaCO_3$ 609.12 mg
CuO 281.786 mg

(II) YB 107

$(Y_{0.55}Ba_{0.45})_2CuO_4$

Y	Ba	Cu	O
28.026	35.423	18.209	18.342

Y_2O_3 3.00 mg
$BaCO_3$: 428.974 mg
CuO : 192.133

III YB – 108

$(Y_{0.65}Ba_{0.35})_2CuO_4$

Y	Ba	Cu	O
34.068	22.338	18.729	18.865

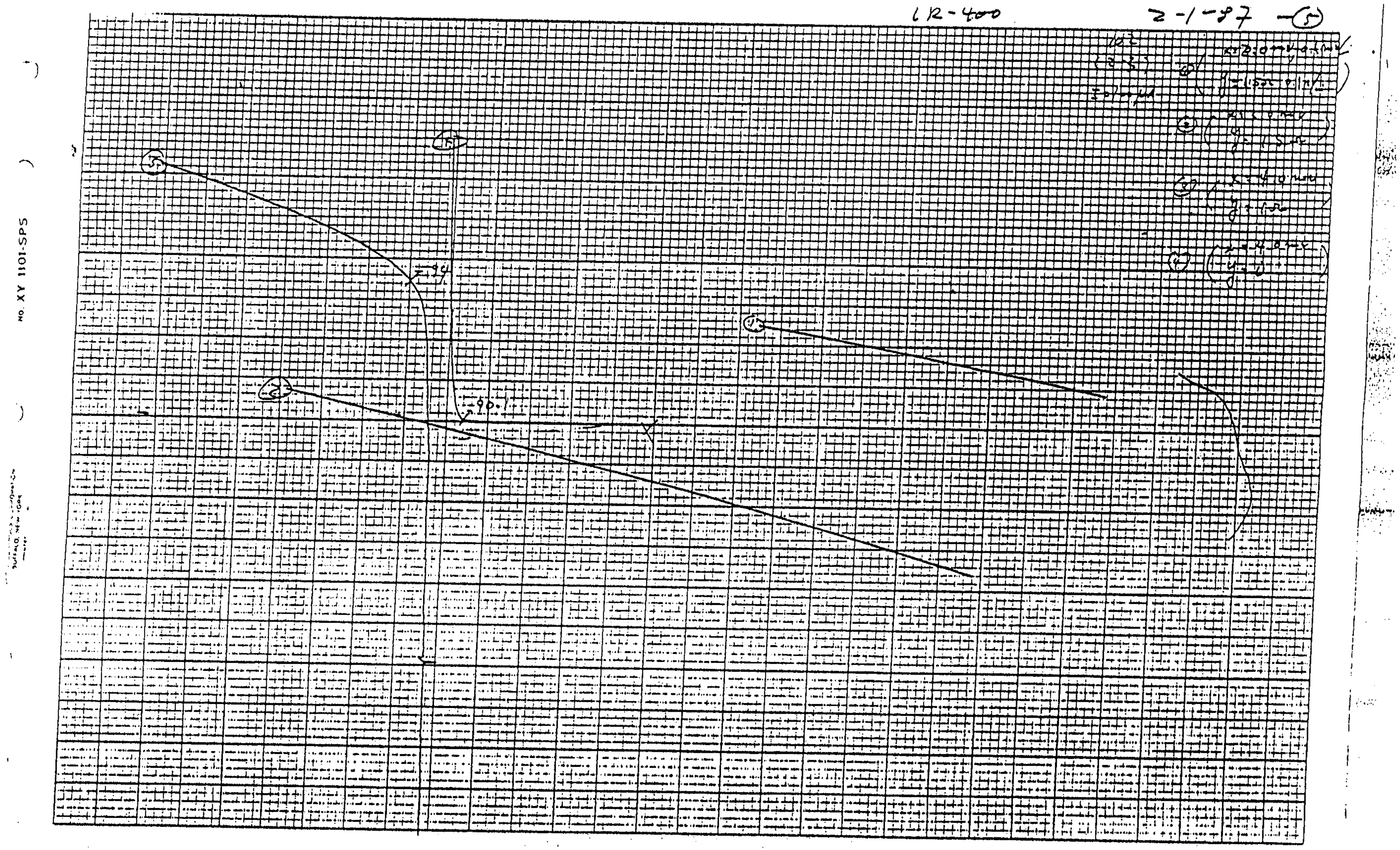
Y_2O_3 : 300 mg   Y : 236.22
$BaCO_3$: 222.54
CuO : 162.57

IV YB – 108 (YB – 105) $(Y_{0.7}Ba_{0.3})_2CuO_4$ H - 61

Y/37.22   Ba/24.641   Cu/19.001   O/19.138

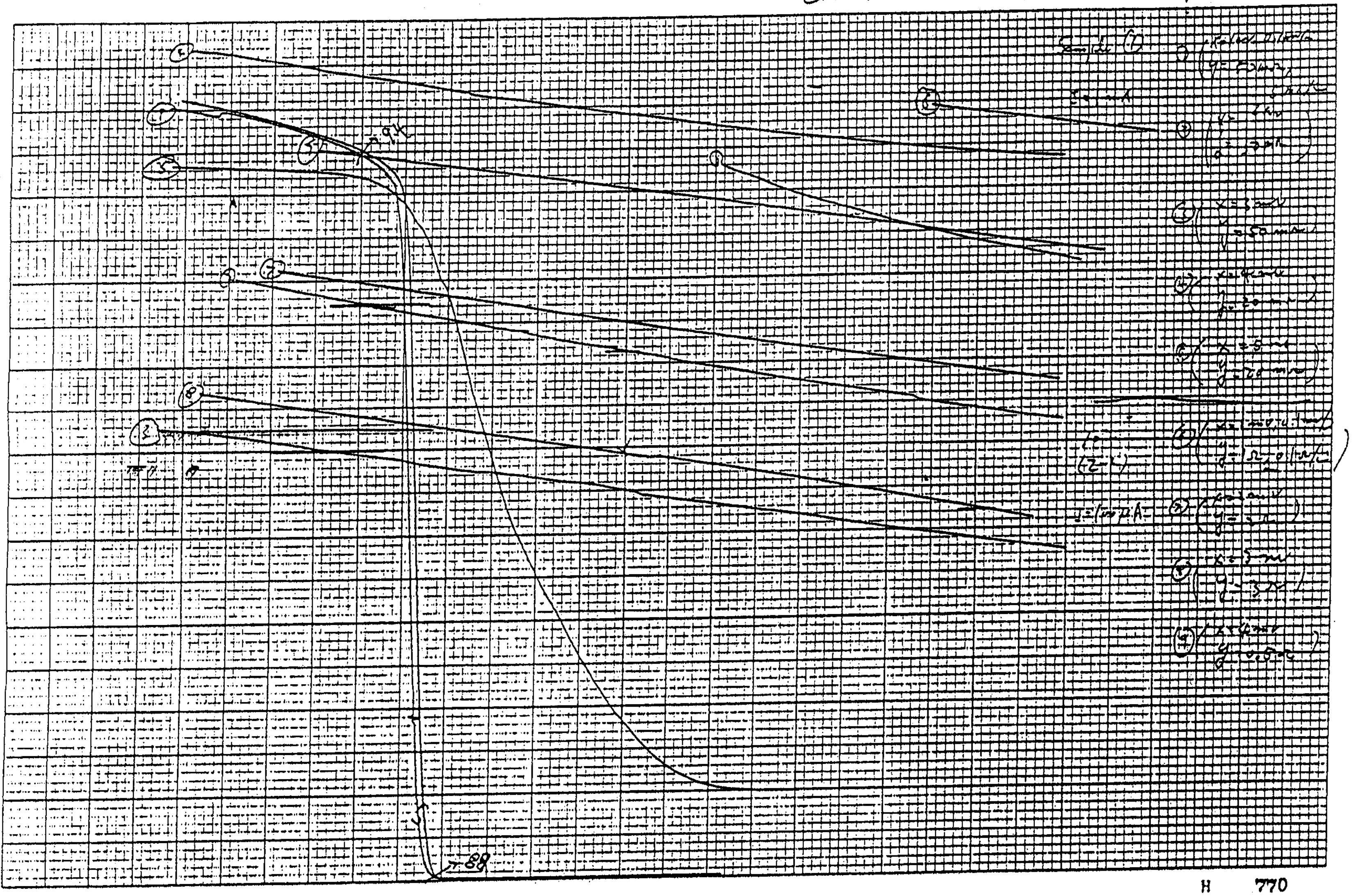
Y_2O_3 : 300 mg $BaCO_3$ 224.69   CuO : 150.97

CHU EXHIBIT I
WU ET AL V. CHU
INTERFERENCE NO. 102,447



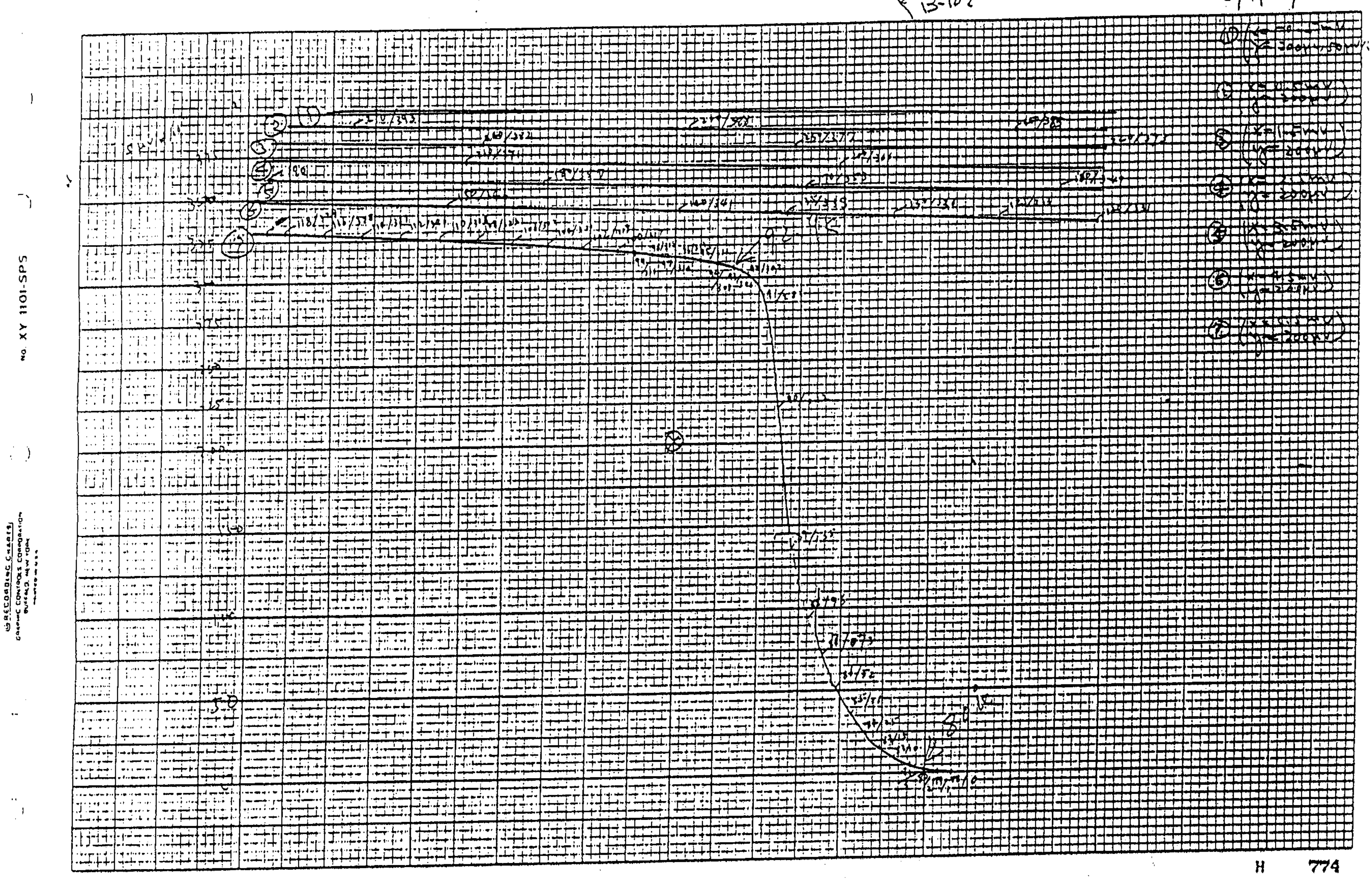
No XY 1101-5PS

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK



2/1/87

13-102


H 774
NO. XY 1101-SPS
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK

4 Feb 1987.

1) Y-B 102 (1-2) Sample.

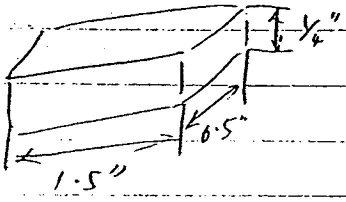
T_o^c 94 → 89.

~~pom~~ presure: 250 pounds

Φ 3/16

heat 20'

cooling on Al plat 2"x 7/8



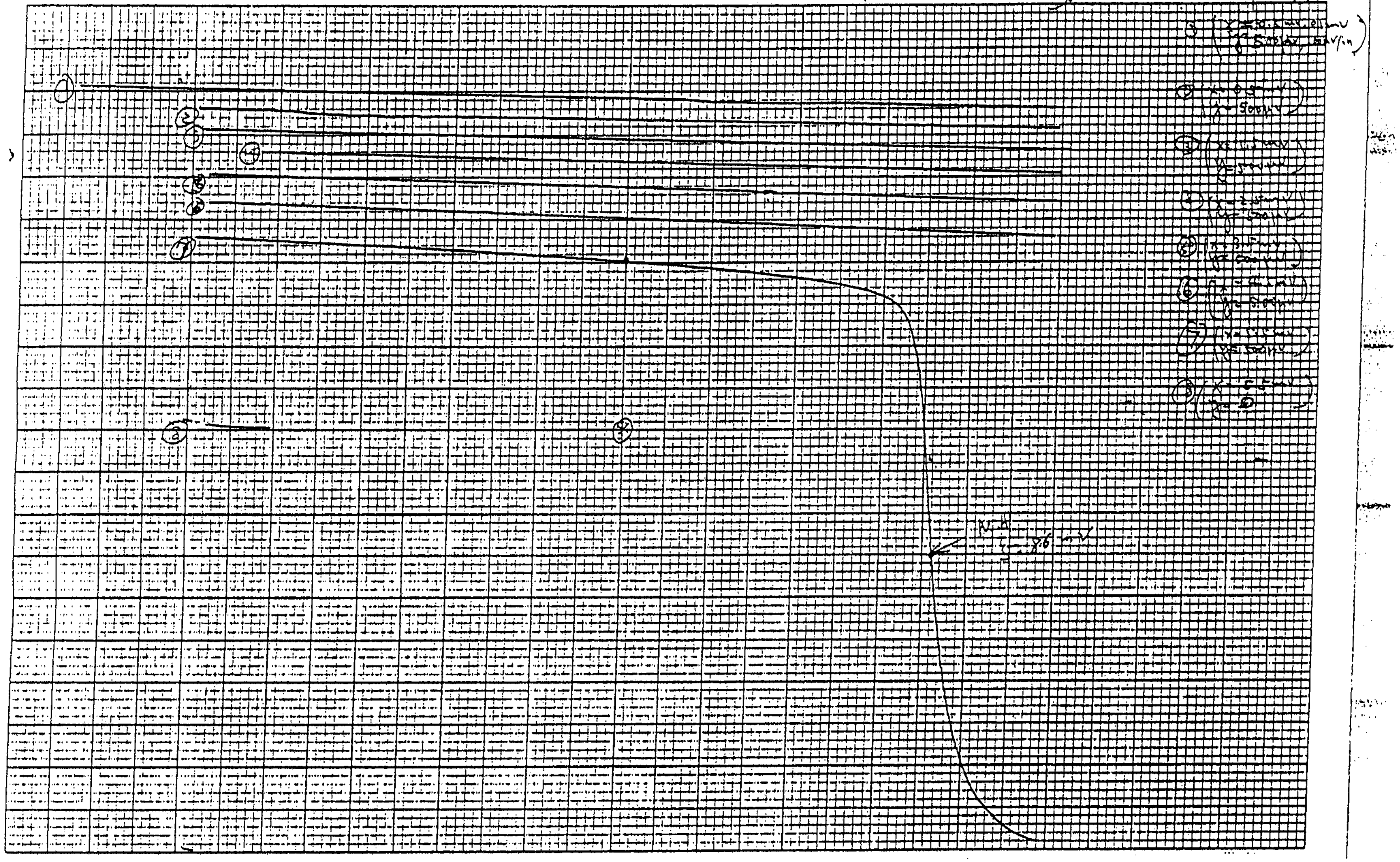
② YB 102 (2-3)

The same condition

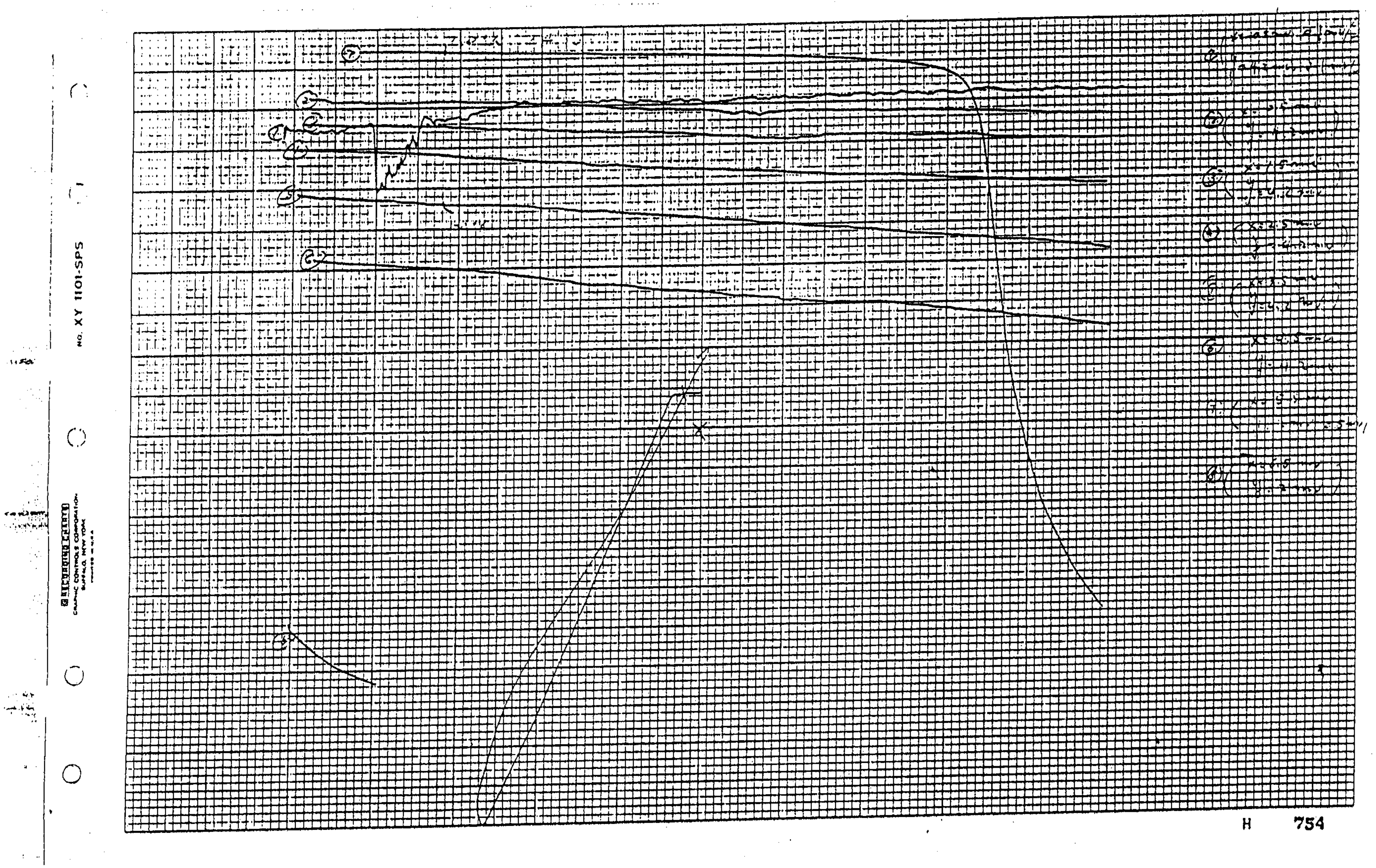
T_c 94-90.1

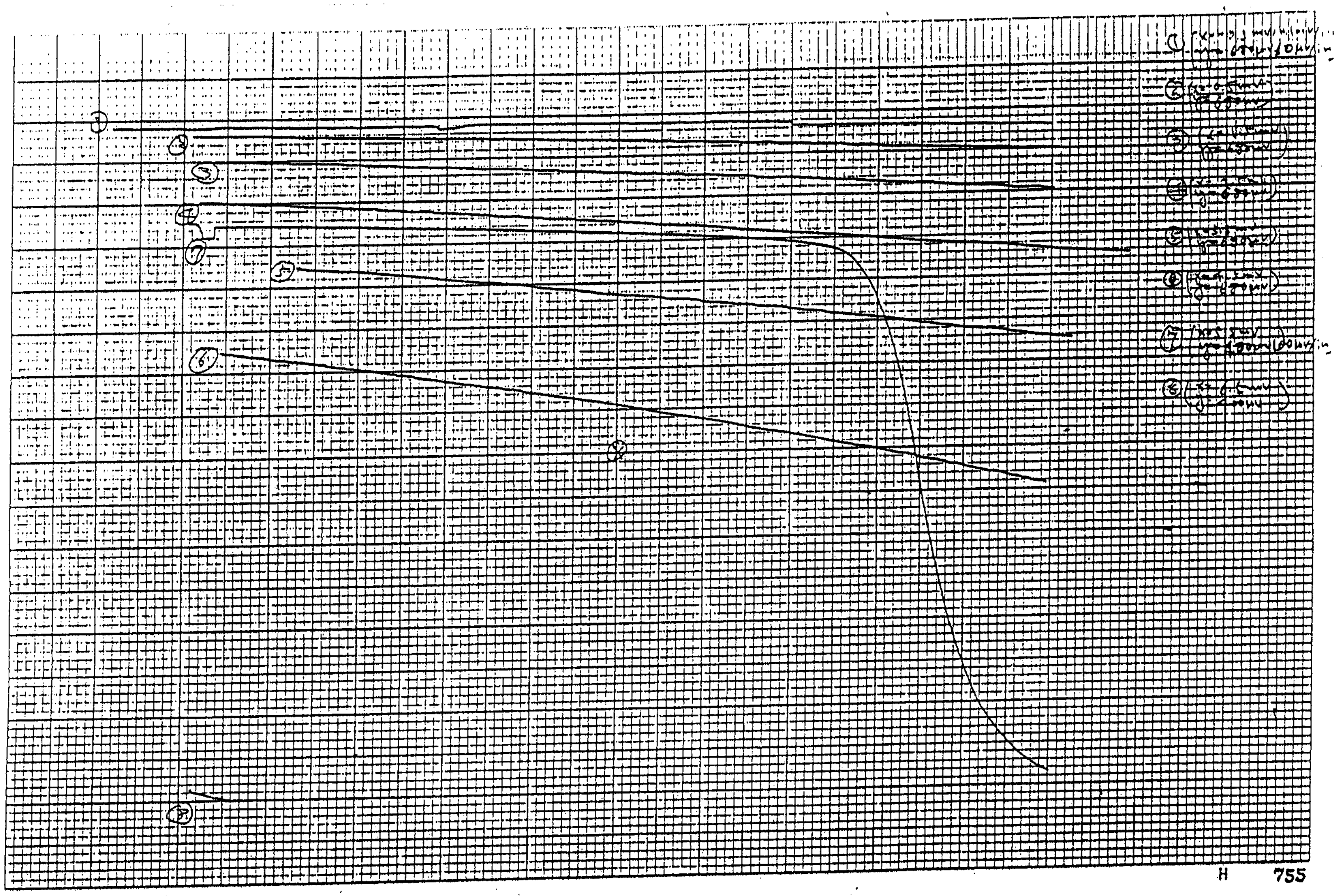
CHU EXHIBIT J
WU ET AL V. CHU
INTERFERENCE NO. 102,447

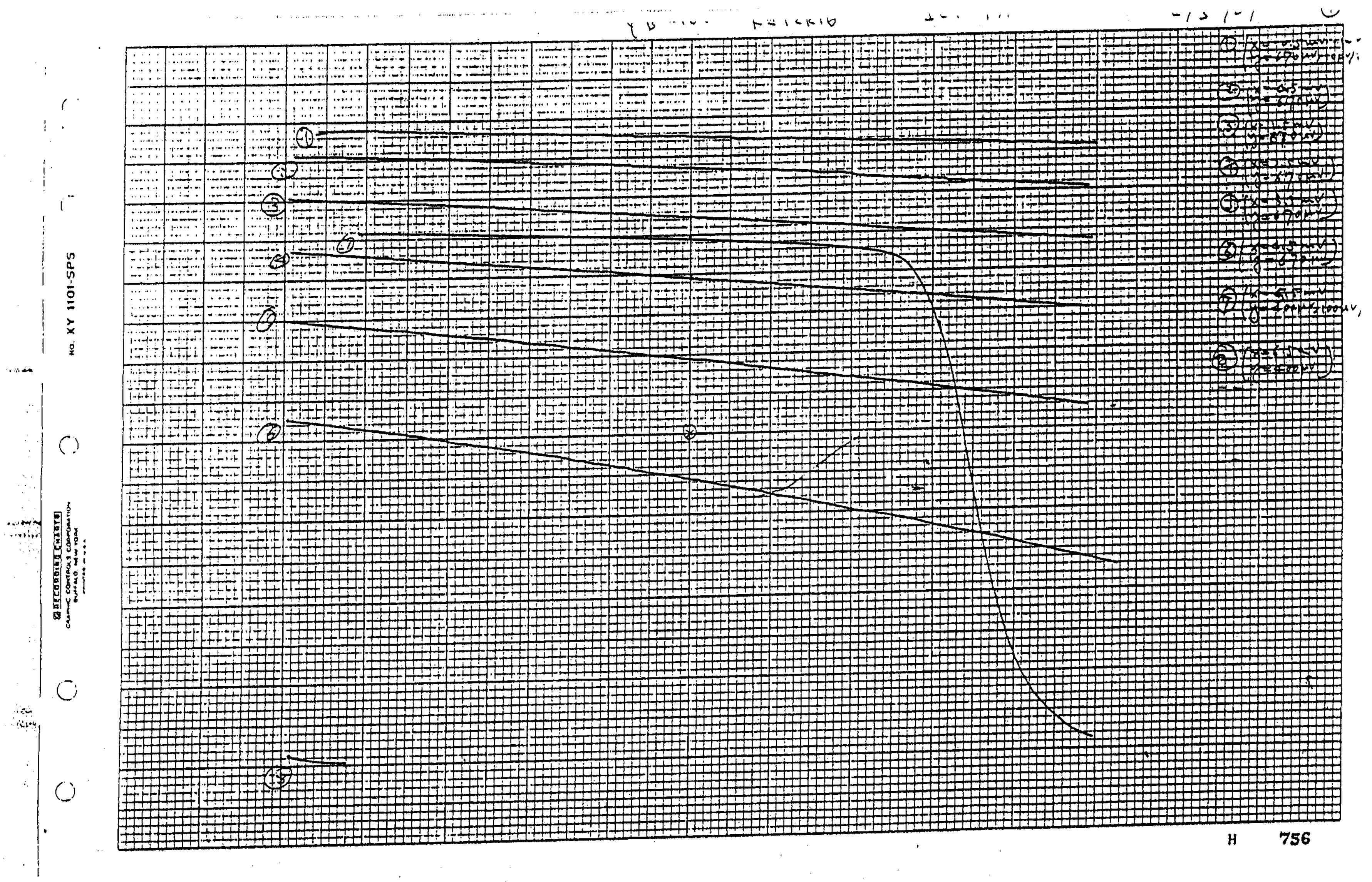
F=5410 I=100mA YB-102 2/2/97 (2)

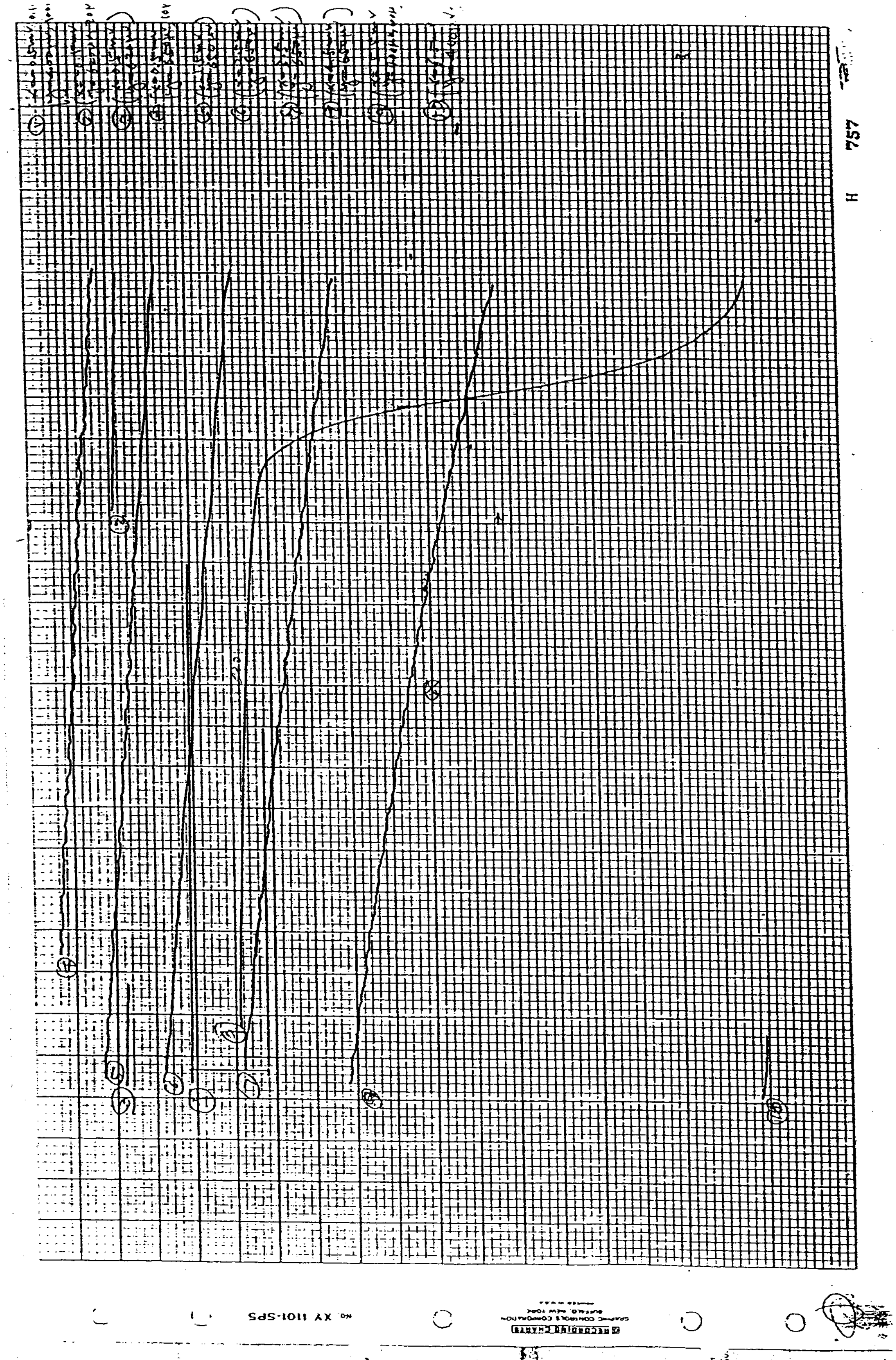


CHU EXHIBIT K
WU ET AL V. CHU
INTERFERENCE NO. 102,447


NO. XY 1101-SPS
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
H 754


①
②
③
④
⑤
⑥
⑦
⑧
H 755
NO. XY 1101-SPS
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK


①
③
100uV
H 756
NO. XY 1101-SPS


H 757
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2
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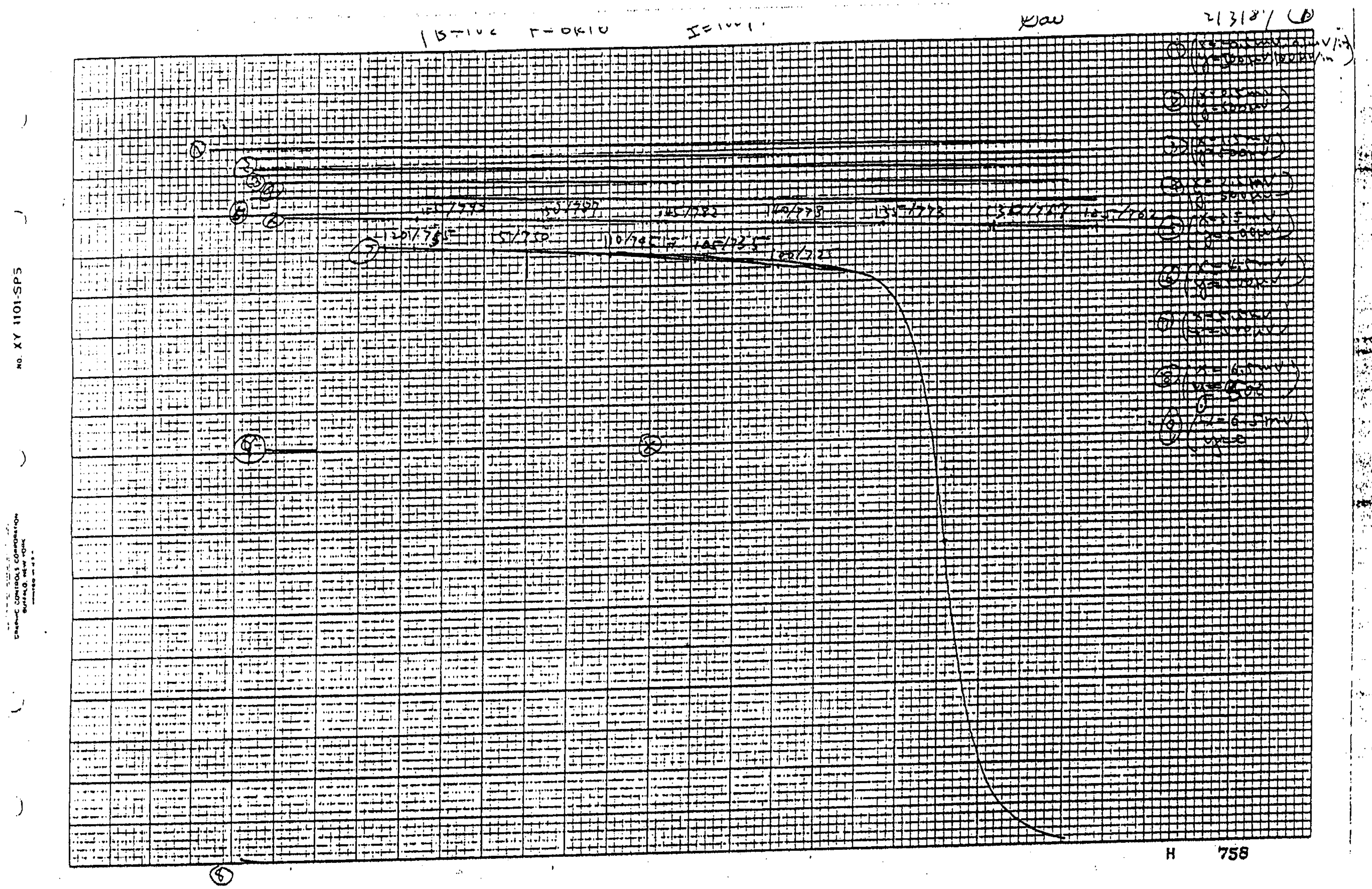
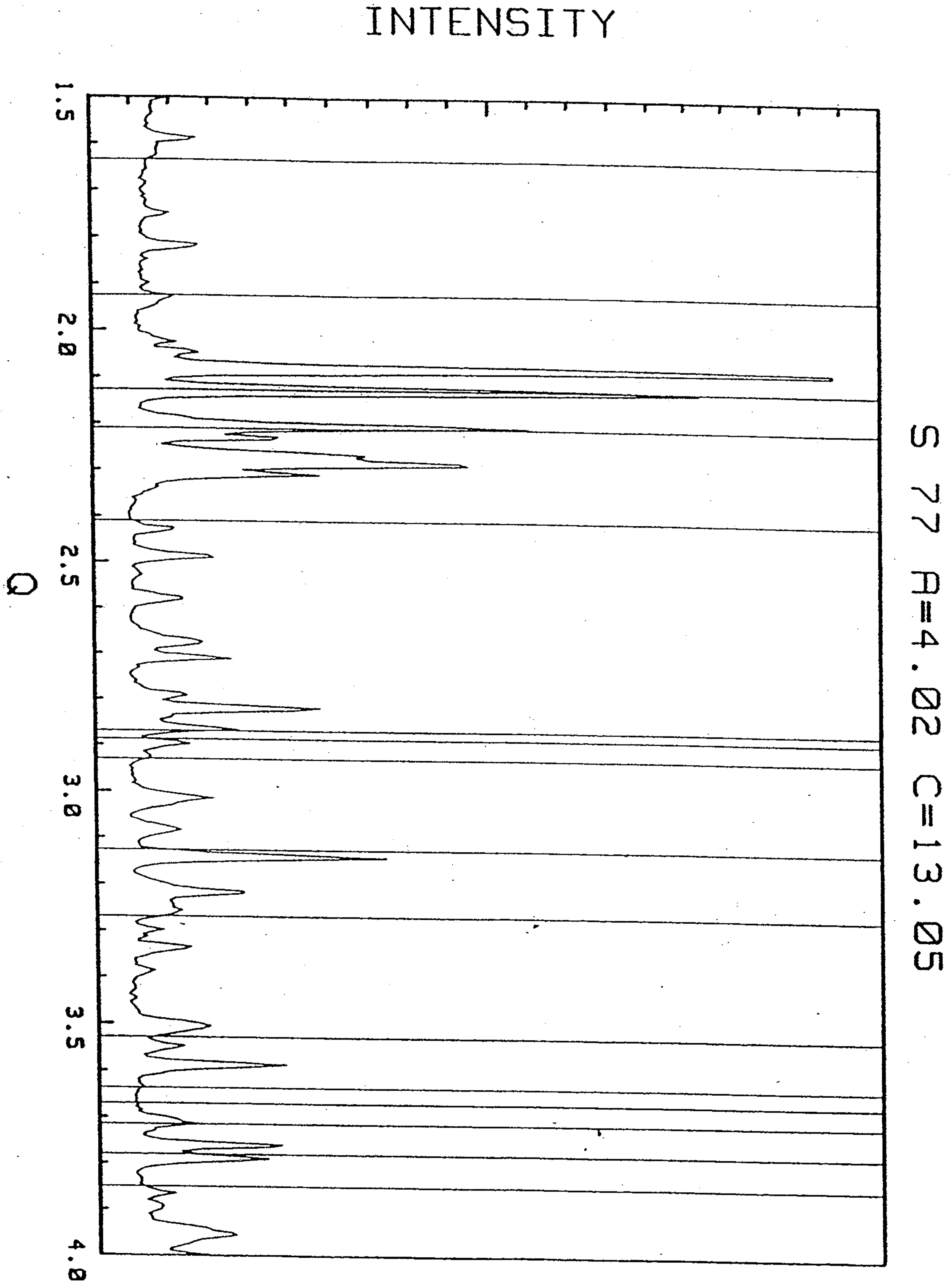
NO. XY 1101-SPS
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK

RLM1301

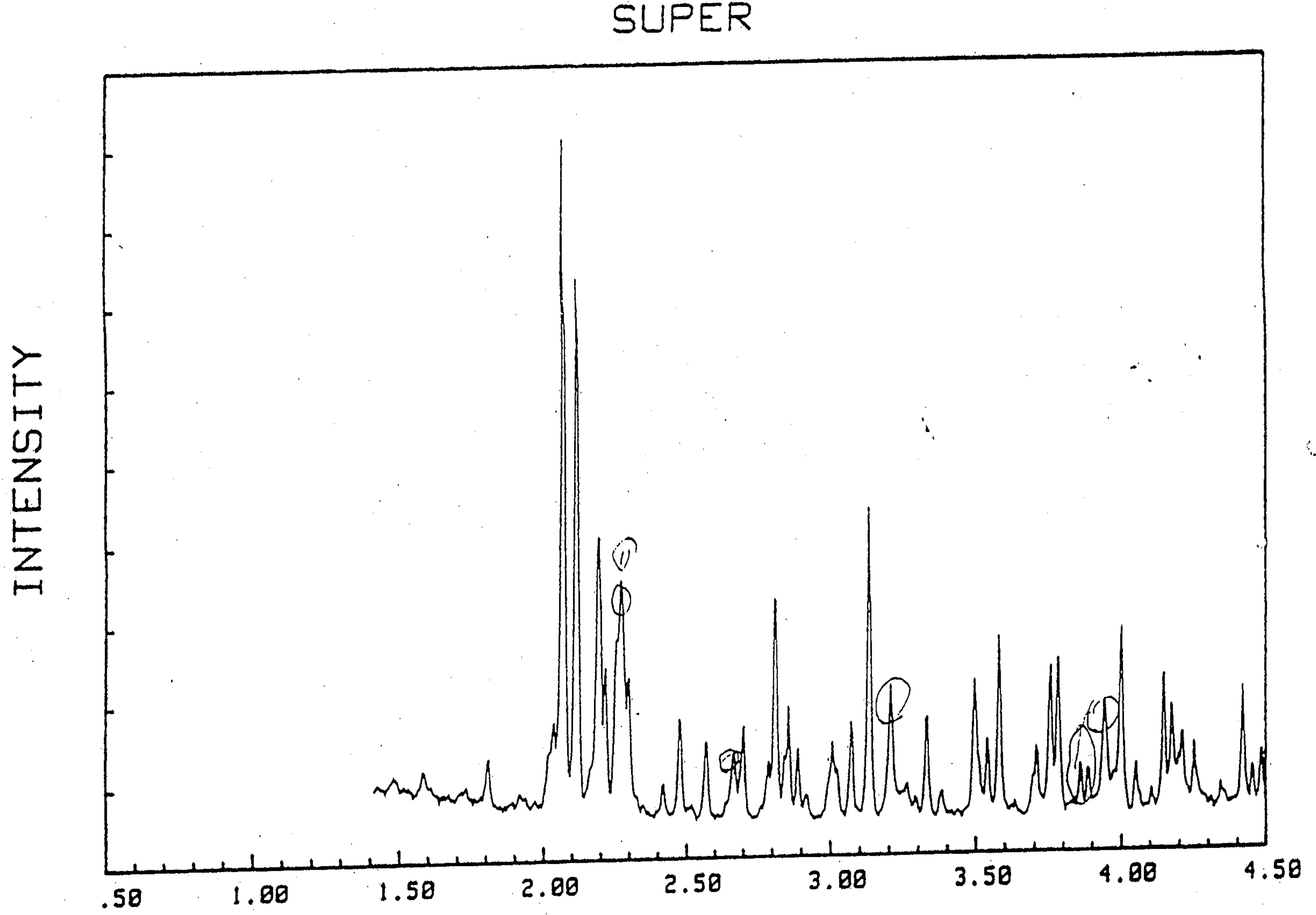

2/3/87
H 758
120/755
151/750
110/745
125/735
120/725
125/772
140/778
135/773
130/767
125/762
NO. XY 1101-SP5
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK



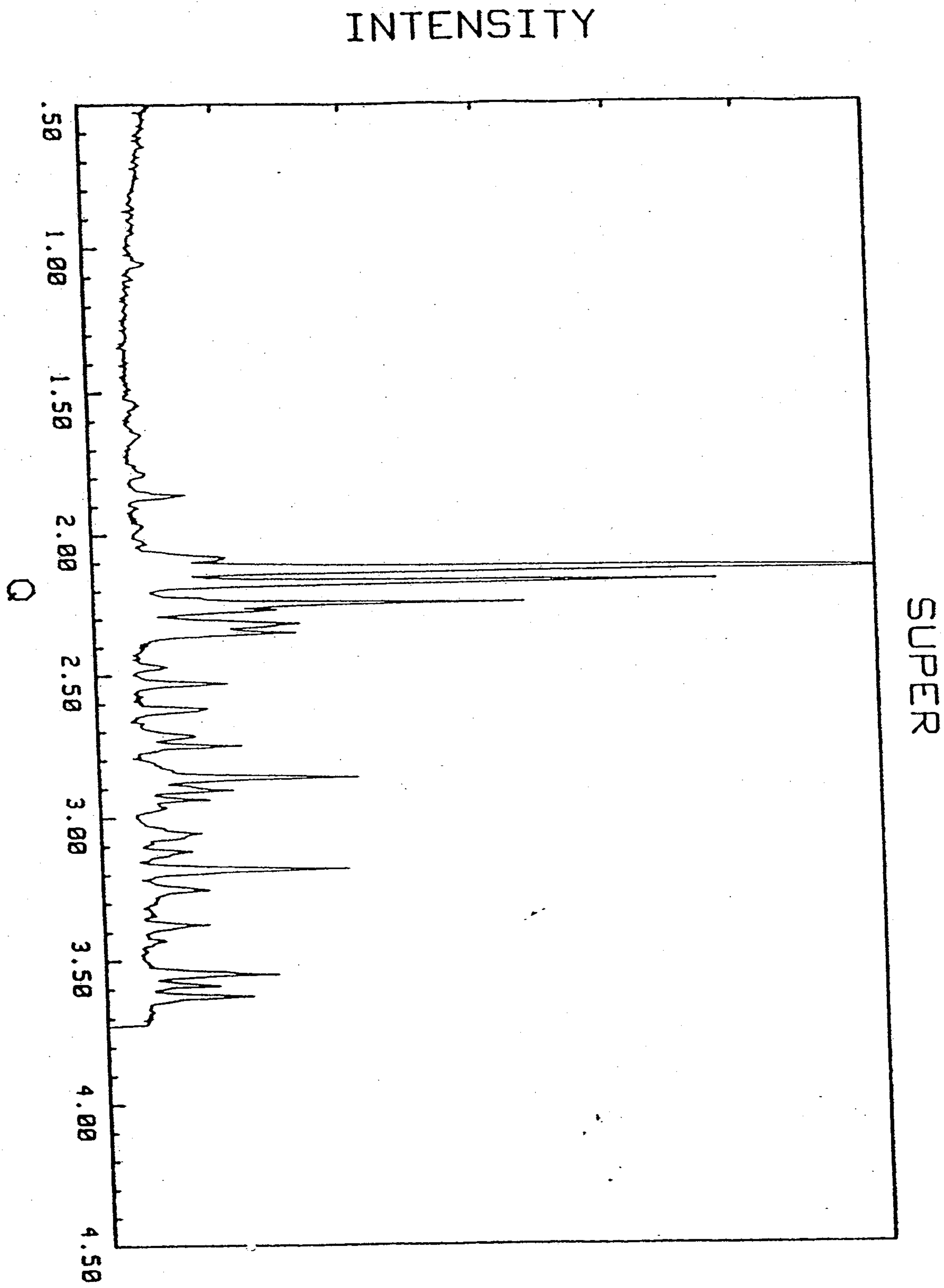
Fed. 1-2 198

CHU EXHIBIT L
WU ET AL V. CHU
INTERFERENCE NO. 102.447

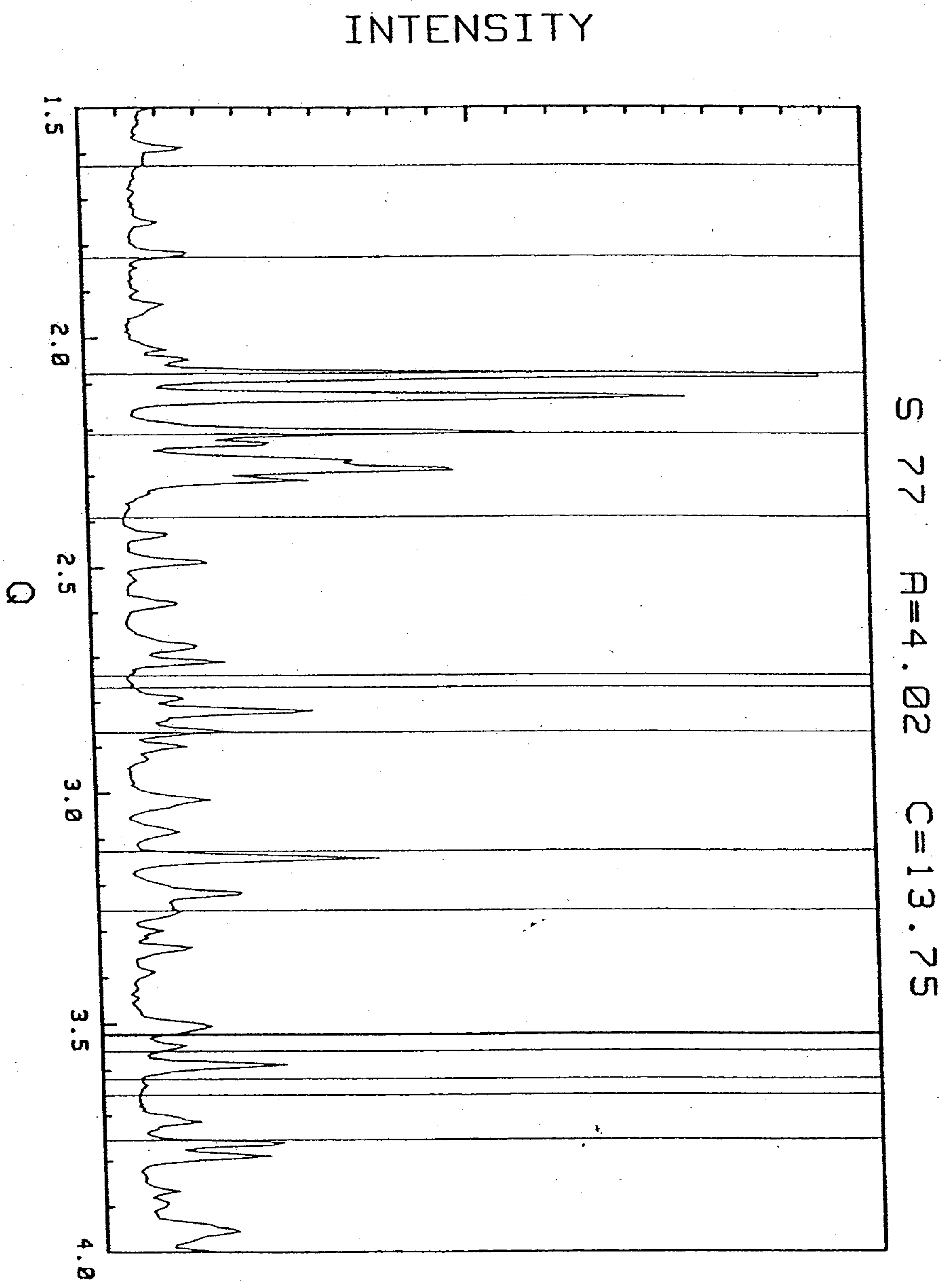
Feb 2 1987



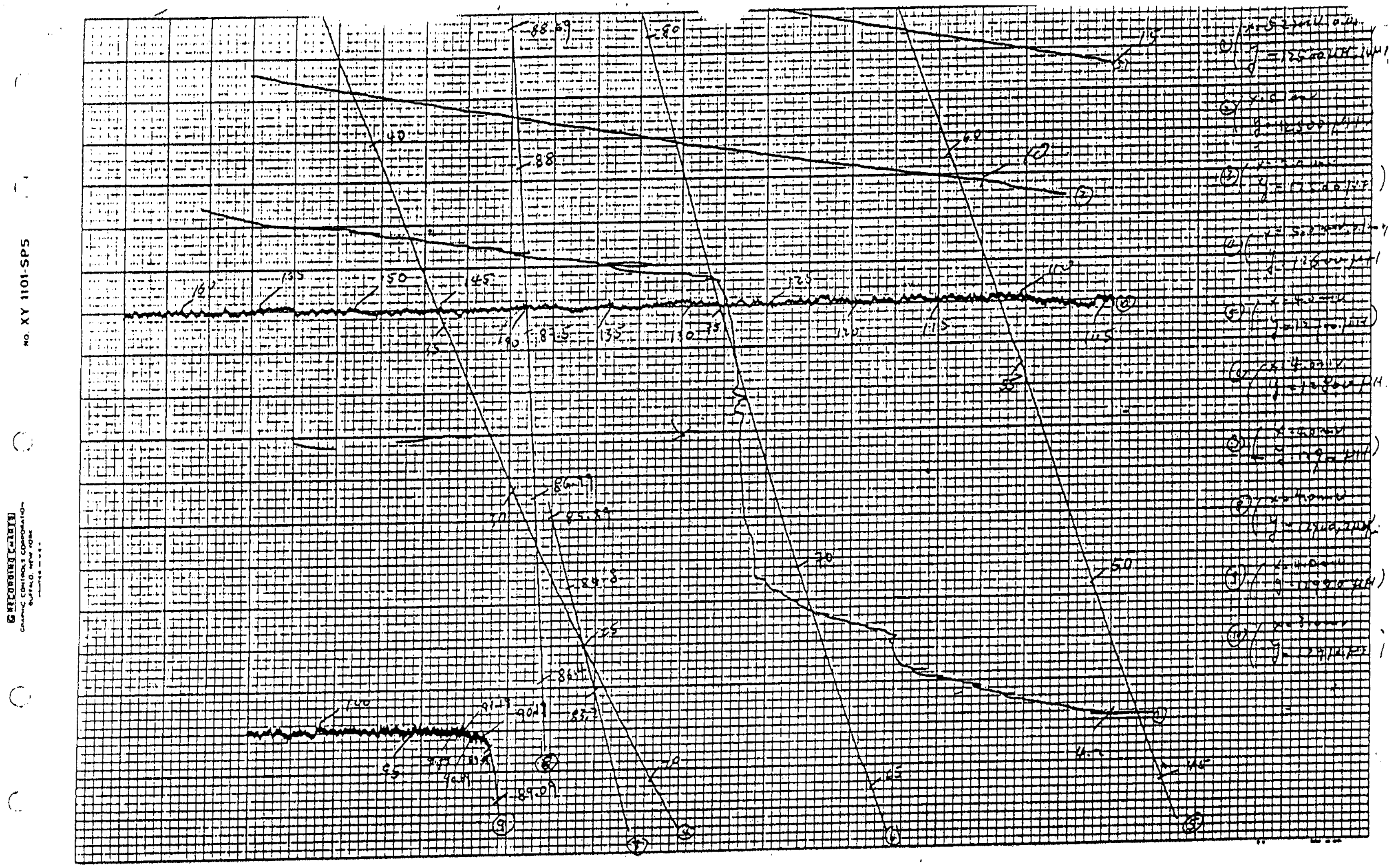
$Q = \frac{4\pi \sin\theta}{\lambda}$ $2 \arcsin\left(\frac{\lambda Q}{4\pi}\right) = 2\theta$



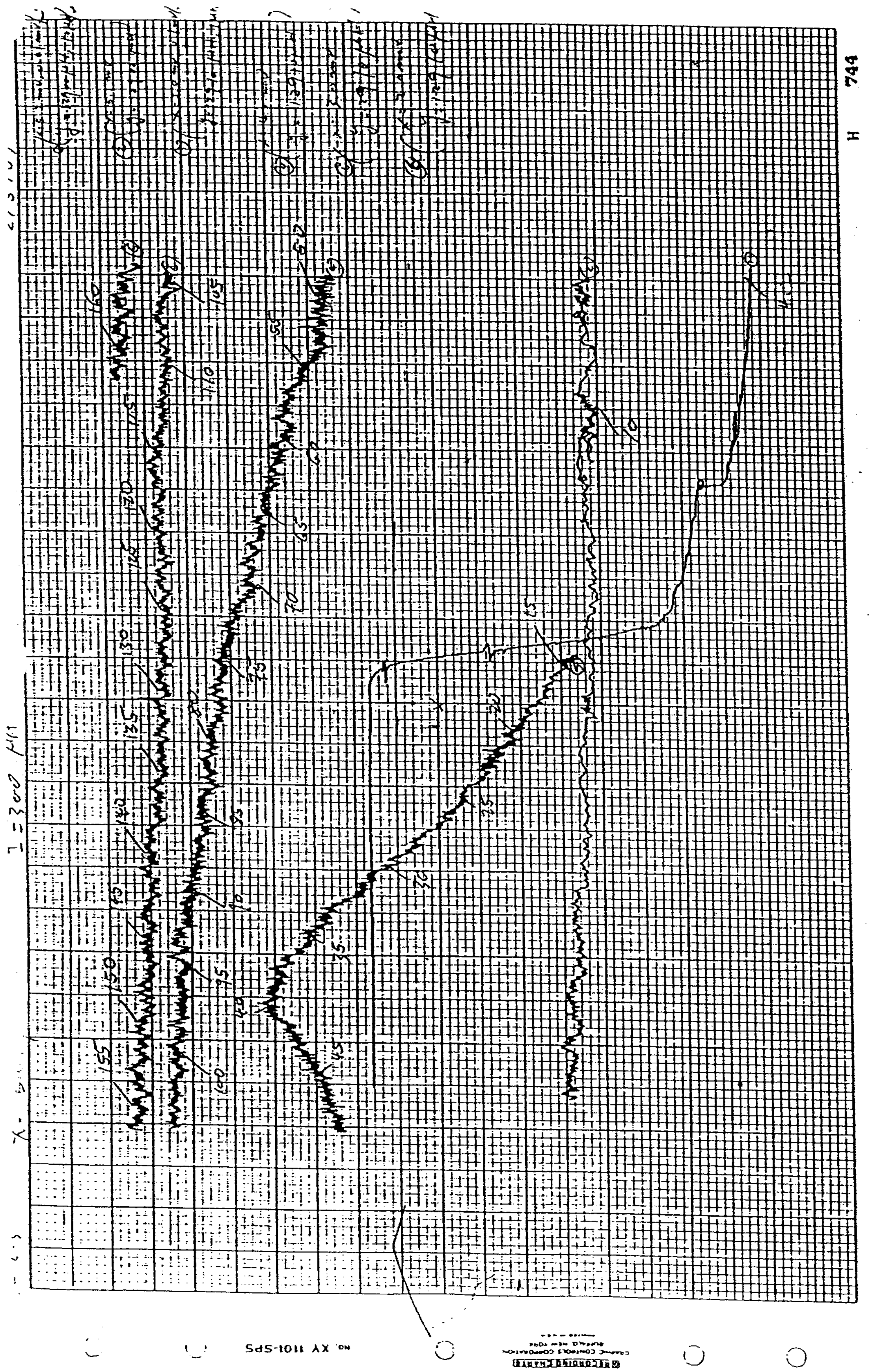
Feb. 4 1987



Fil 4 S7



CHU EXHIBIT M
WU ET AL V. CHU
INTERFERENCE NO. 102,447


H 744
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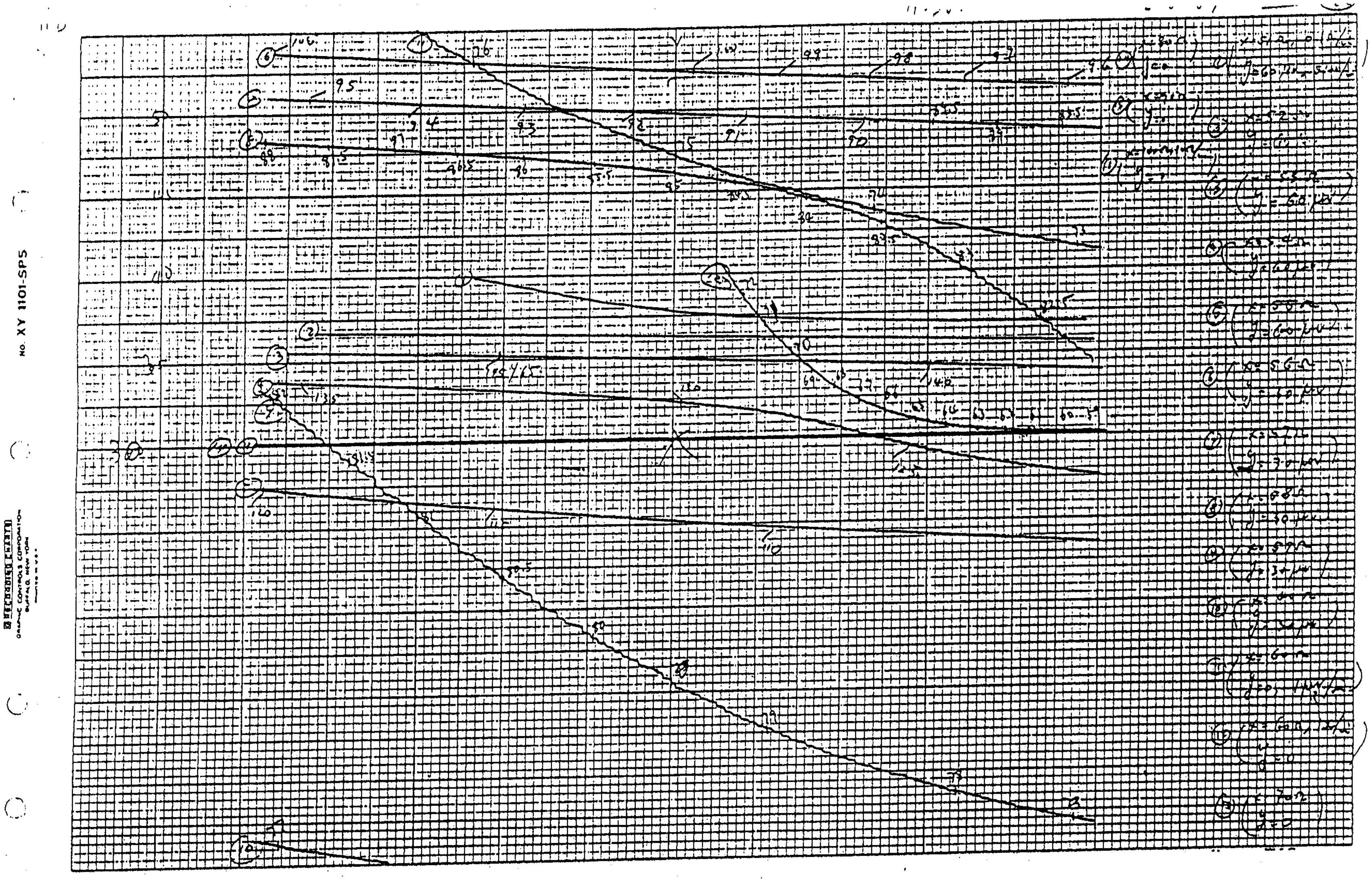
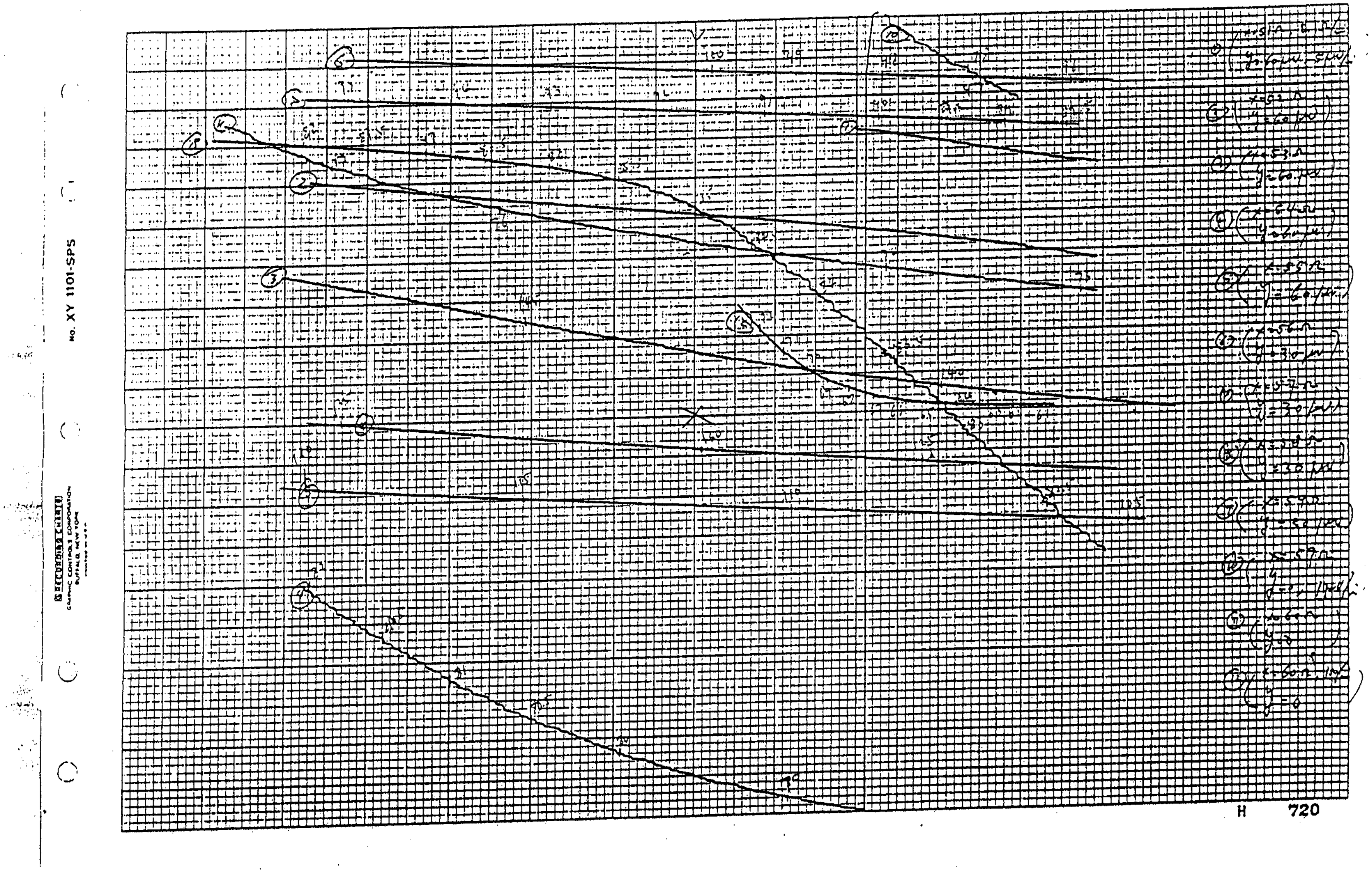
NO. XY 1101-SPS
RECORDING CHARTS
BUFFALO, NEW YORK



CHU EXHIBIT N
WU ET AL V. CHU
INTERFERENCE NO. 102,447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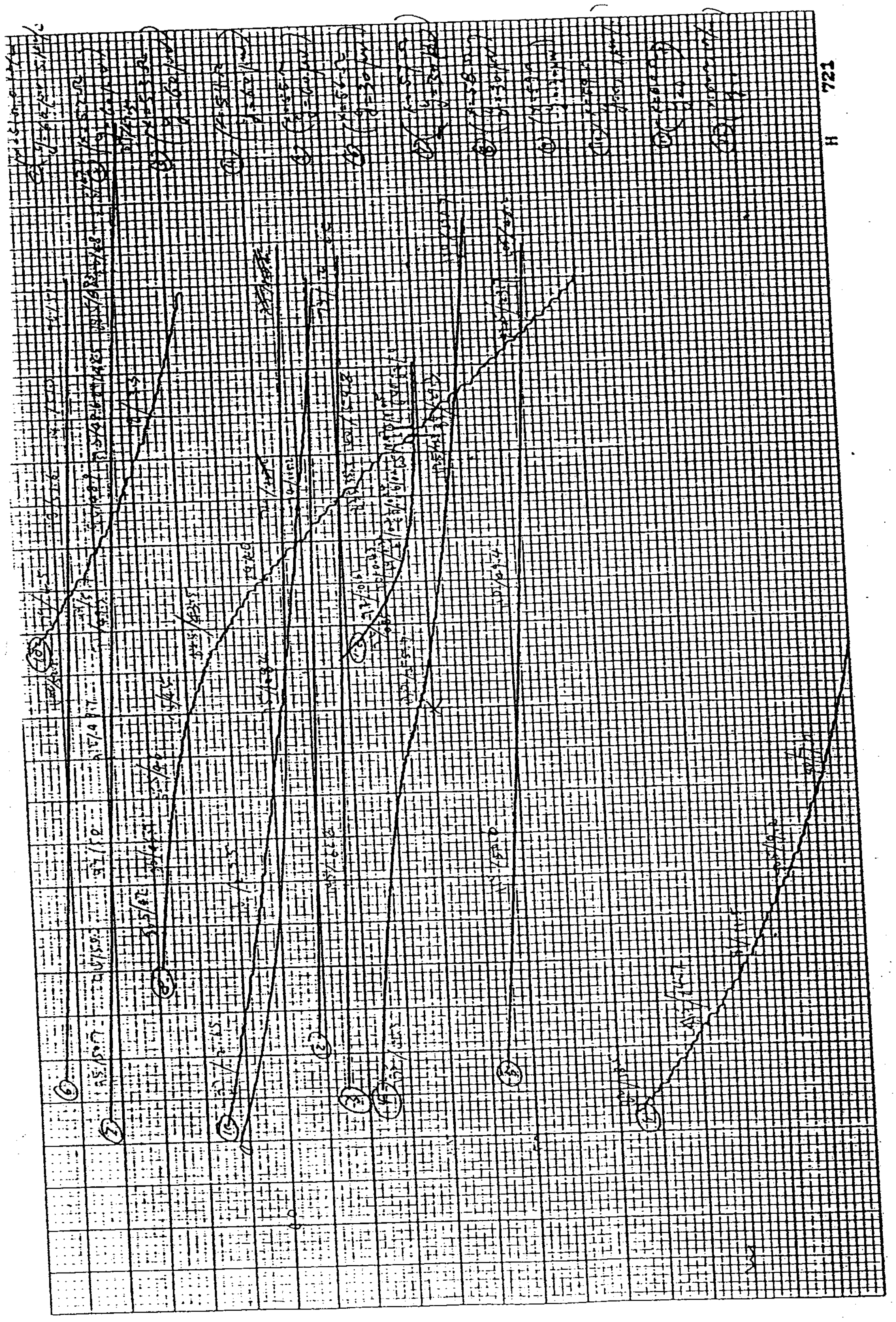
y=60μV
③ x=53Ω
y=60μV
④ x=54Ω
y=60μV
⑤ x=55Ω
y=60μV
⑥ x=56Ω
y=30μV
⑦ x=57Ω
y=30μV
⑧ x=58Ω
y=30μV
⑨ x=59Ω
y=30μV
⑩ x=59Ω
y=-1.1μV
⑪ x=60Ω
y=0
⑫ x=60Ω, 1.1
y=0
H 720
RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
NO. XY 1101-SPS



NO. XY 1101-SPS

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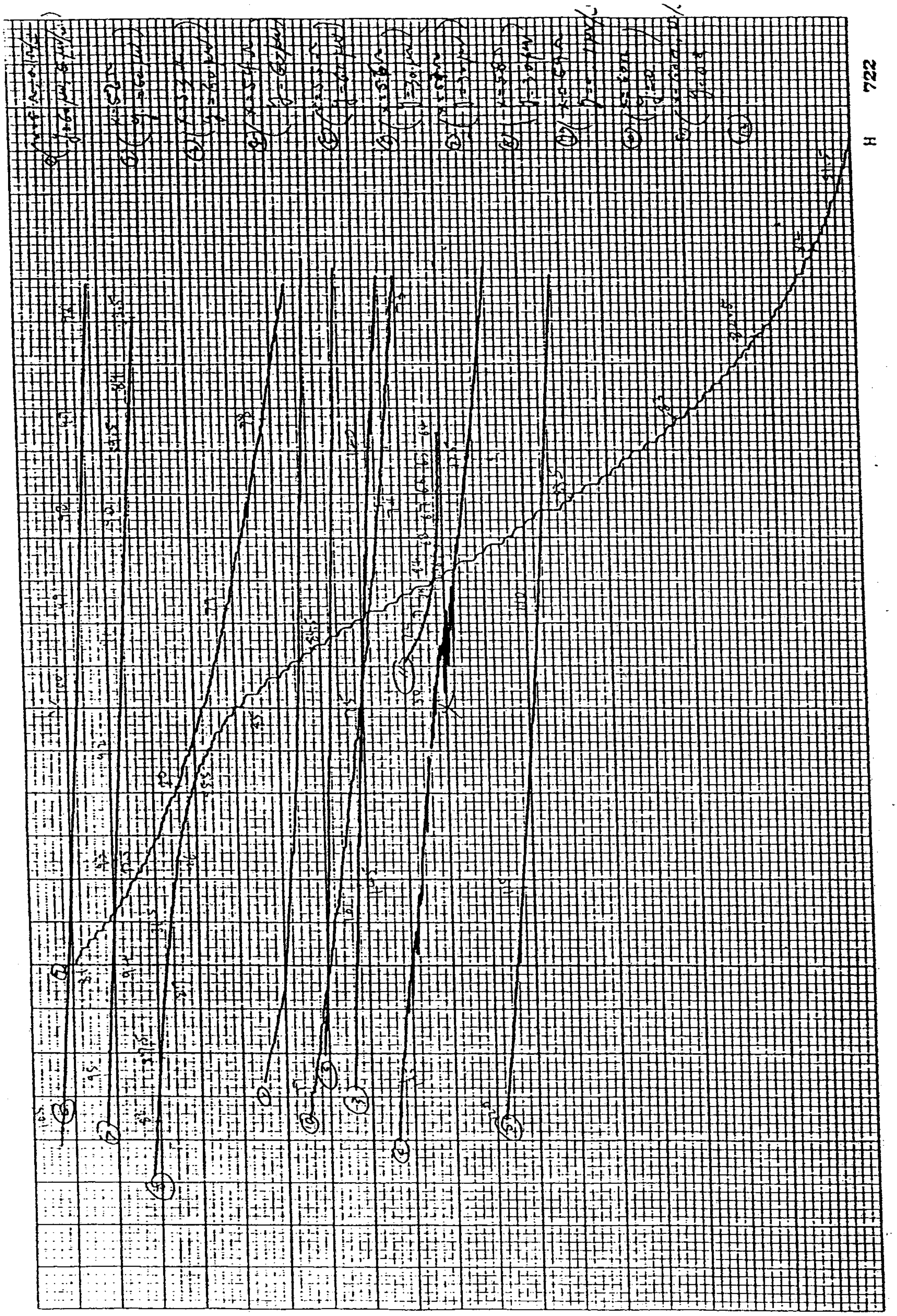
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK



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GRAPHIC CONTROLS CORPORATION
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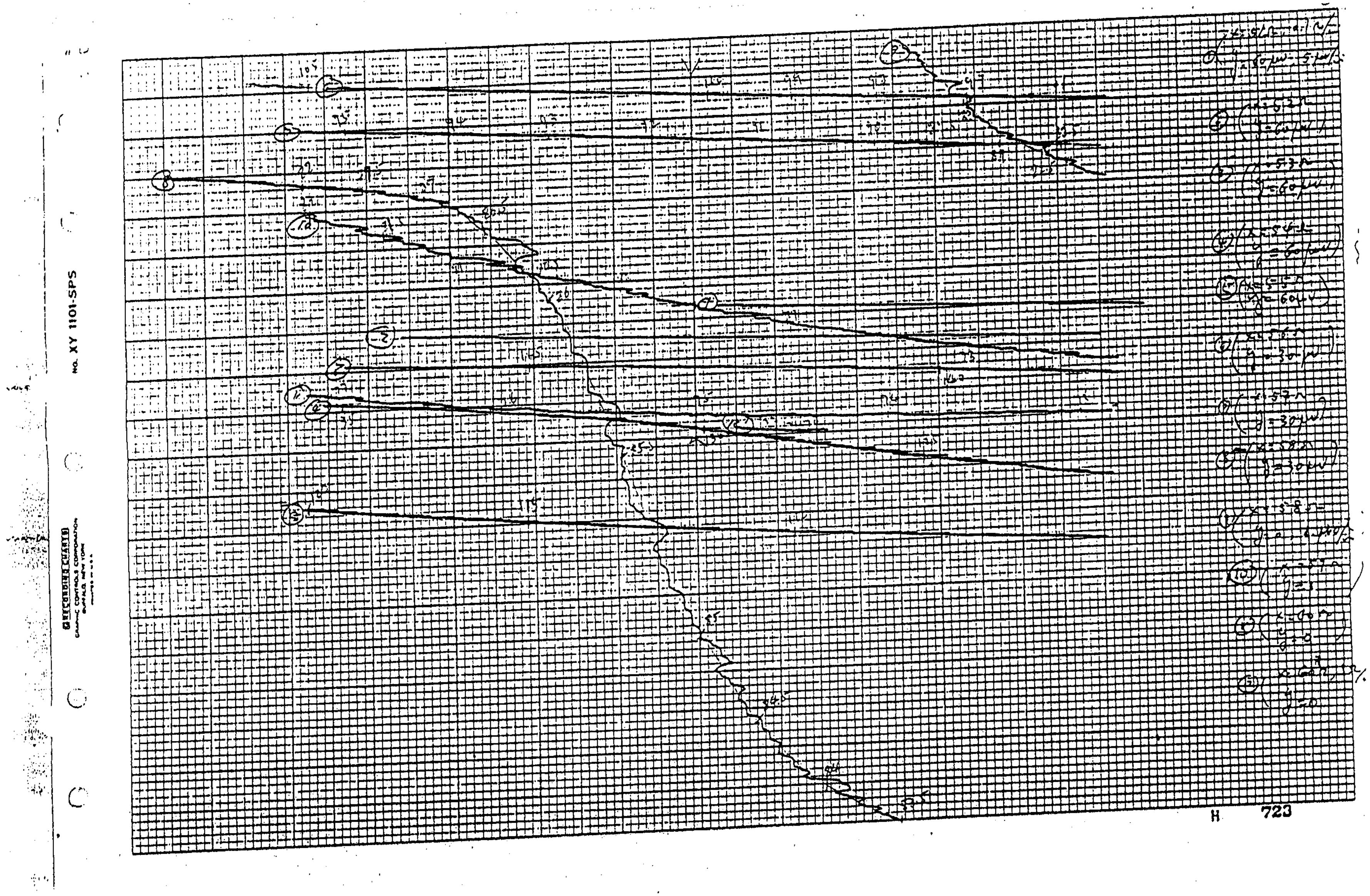
NO. XY 1101-SPS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H
723
NO. XY 1101-SPS
RECORDING CHARTS
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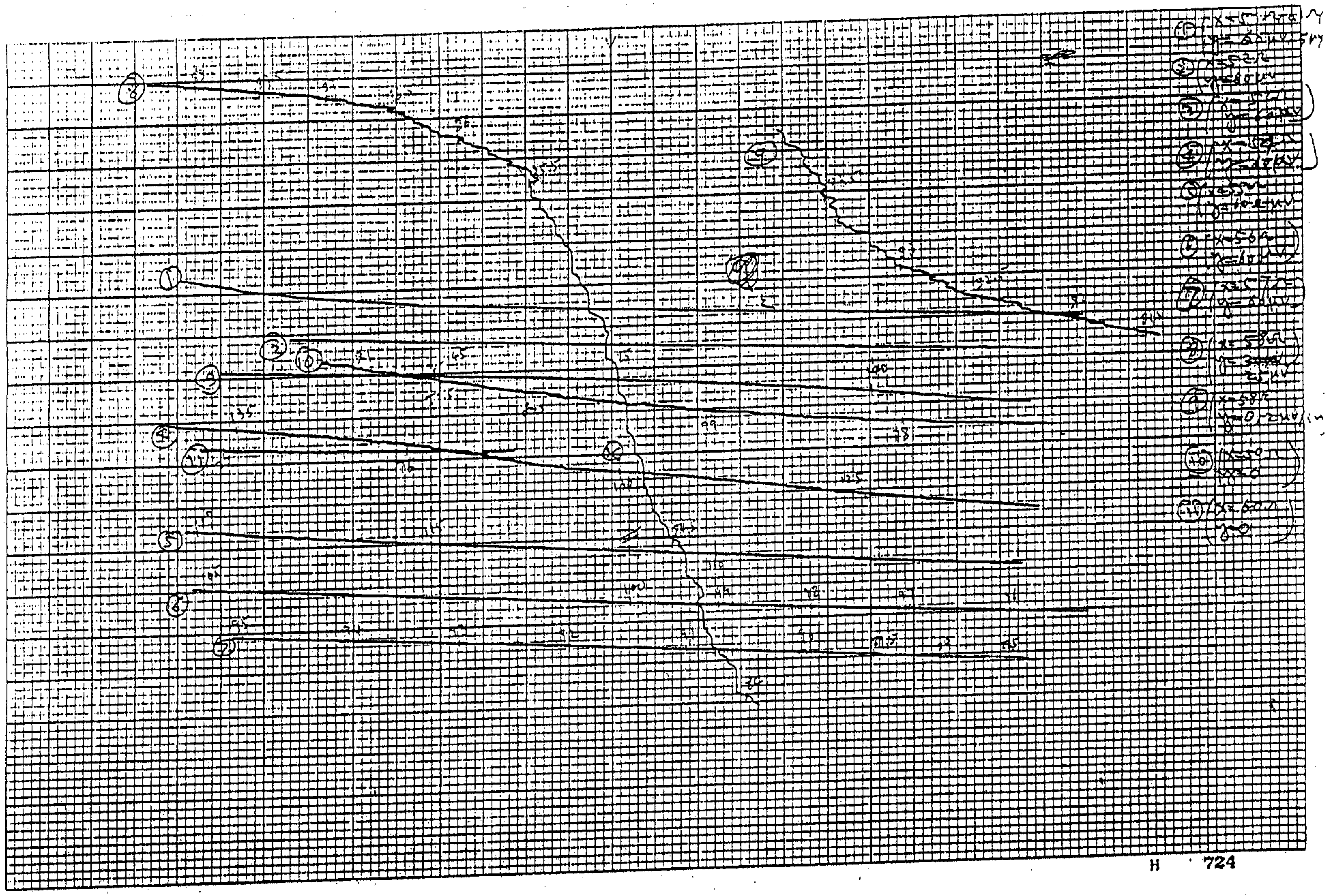
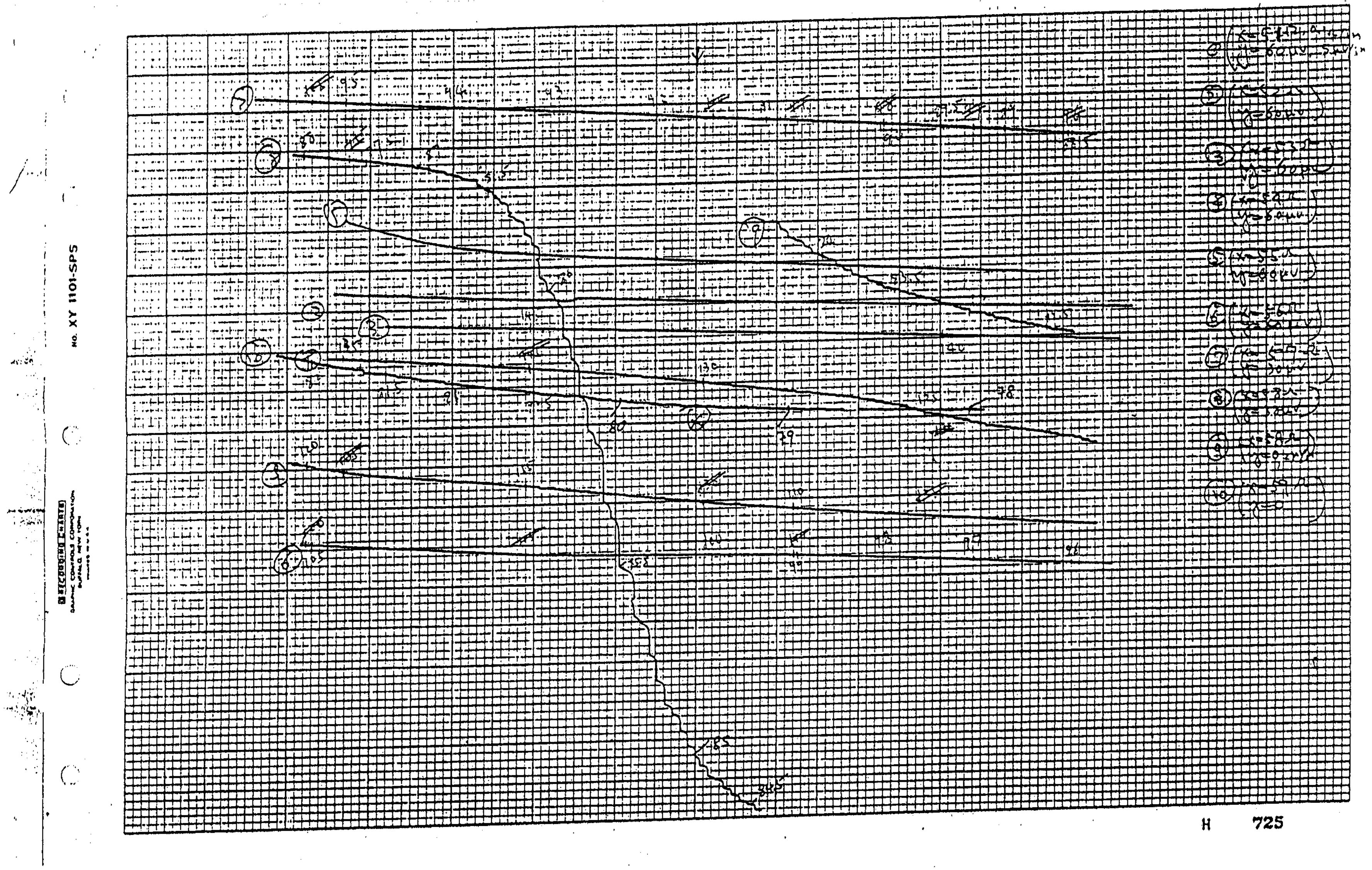
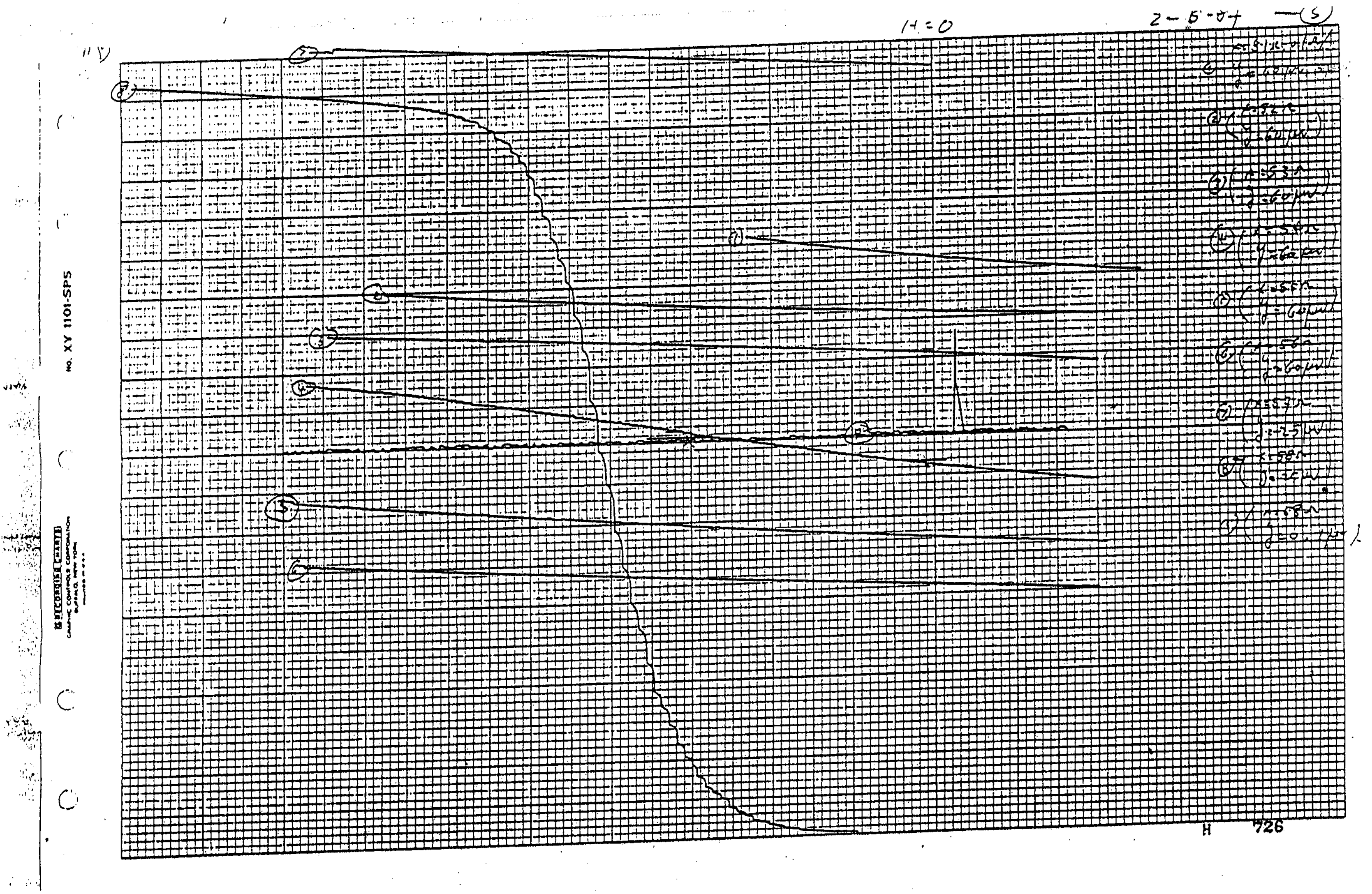


NO. XY 1101-SPS


NO. XY 1101-SPS
RECORDING CHARTS
H 725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2-8-04
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③ x=.53Ω y=.64μw
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⑤ x=.55Ω y=.64μw
⑥ x=.56Ω y=.60μw
⑦ x=.57Ω y=.25μw
⑧ x=.58Ω y=.2μw
⑨ x=.58Ω y=0.1μw
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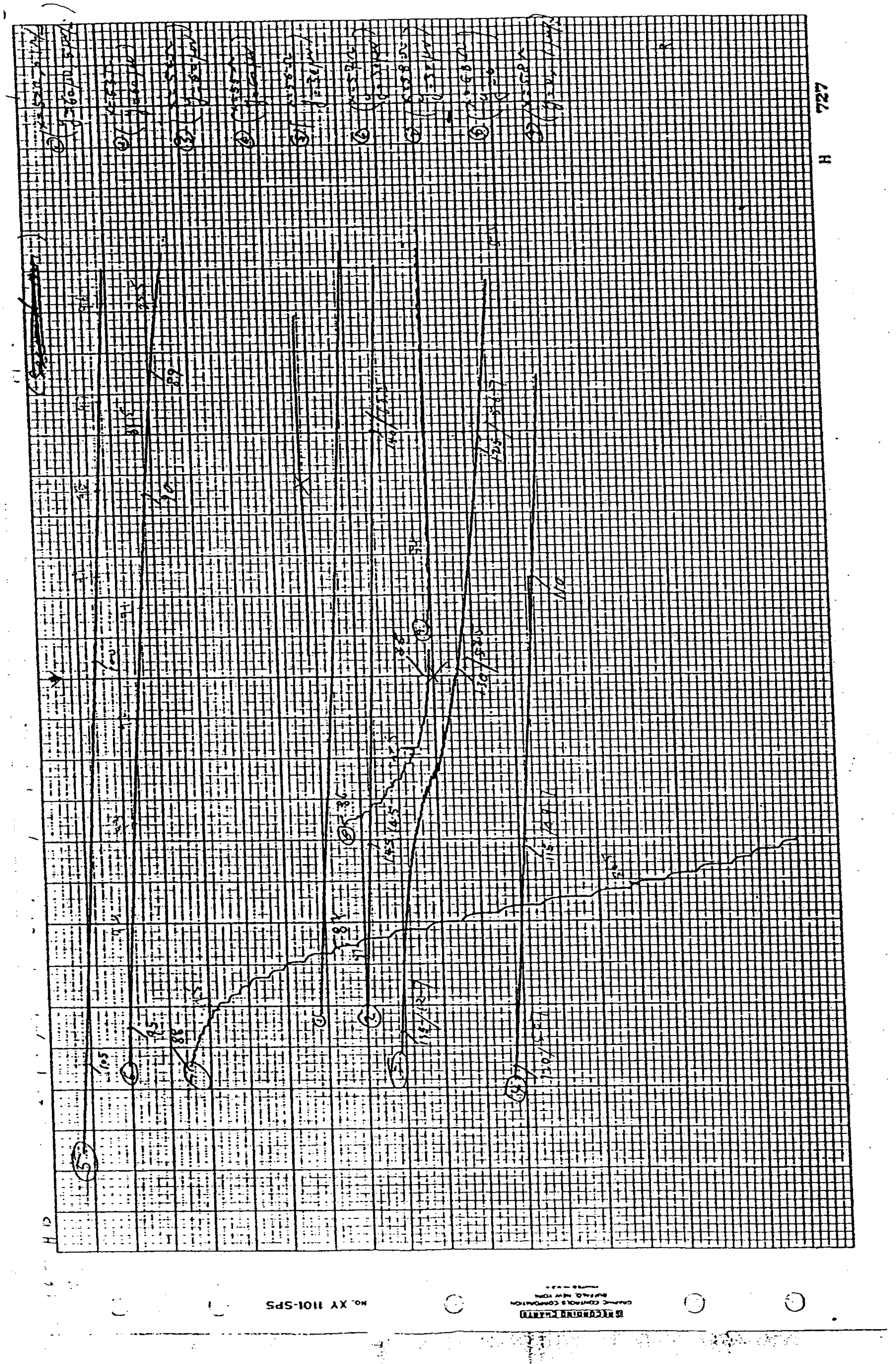
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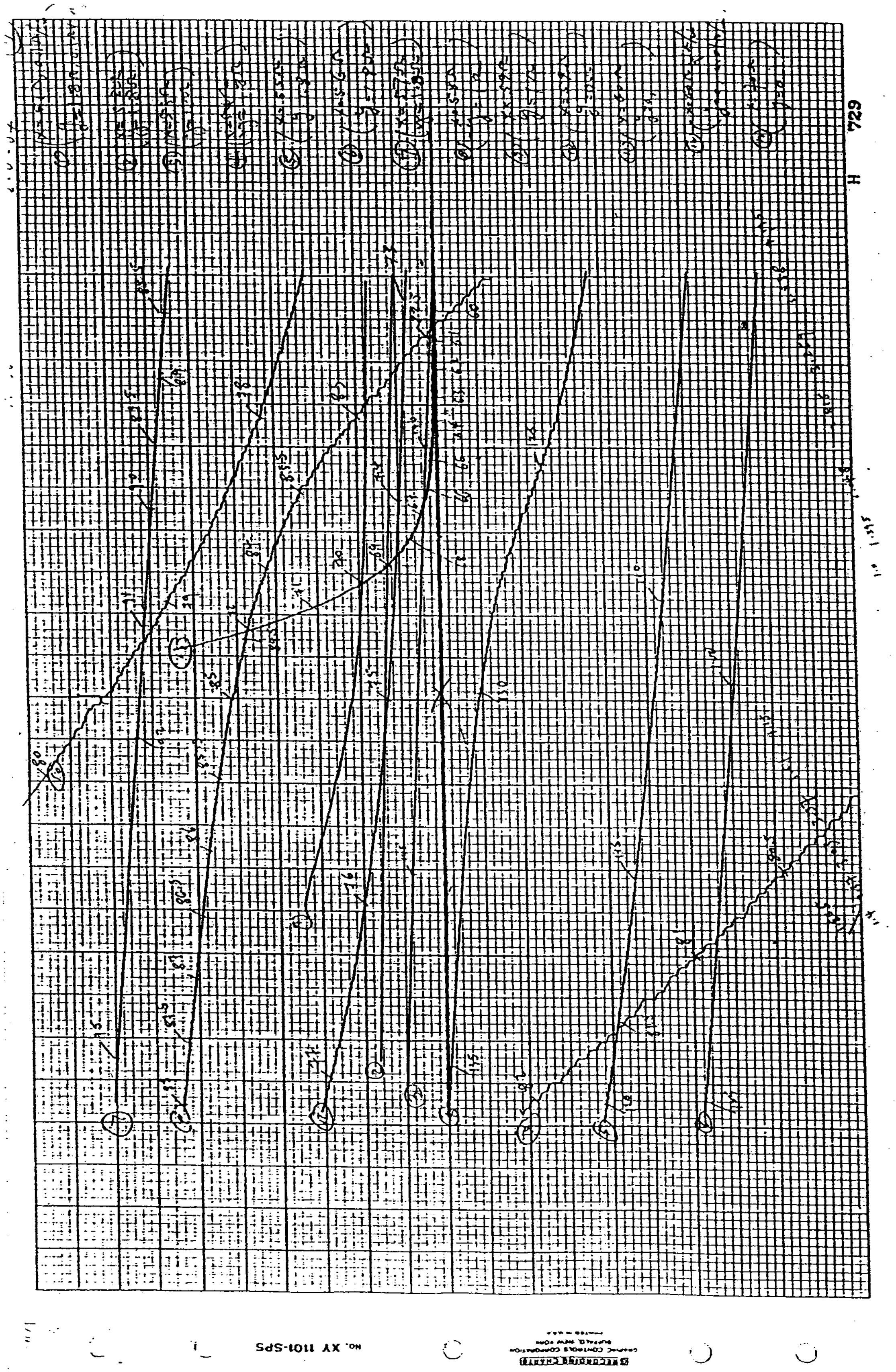
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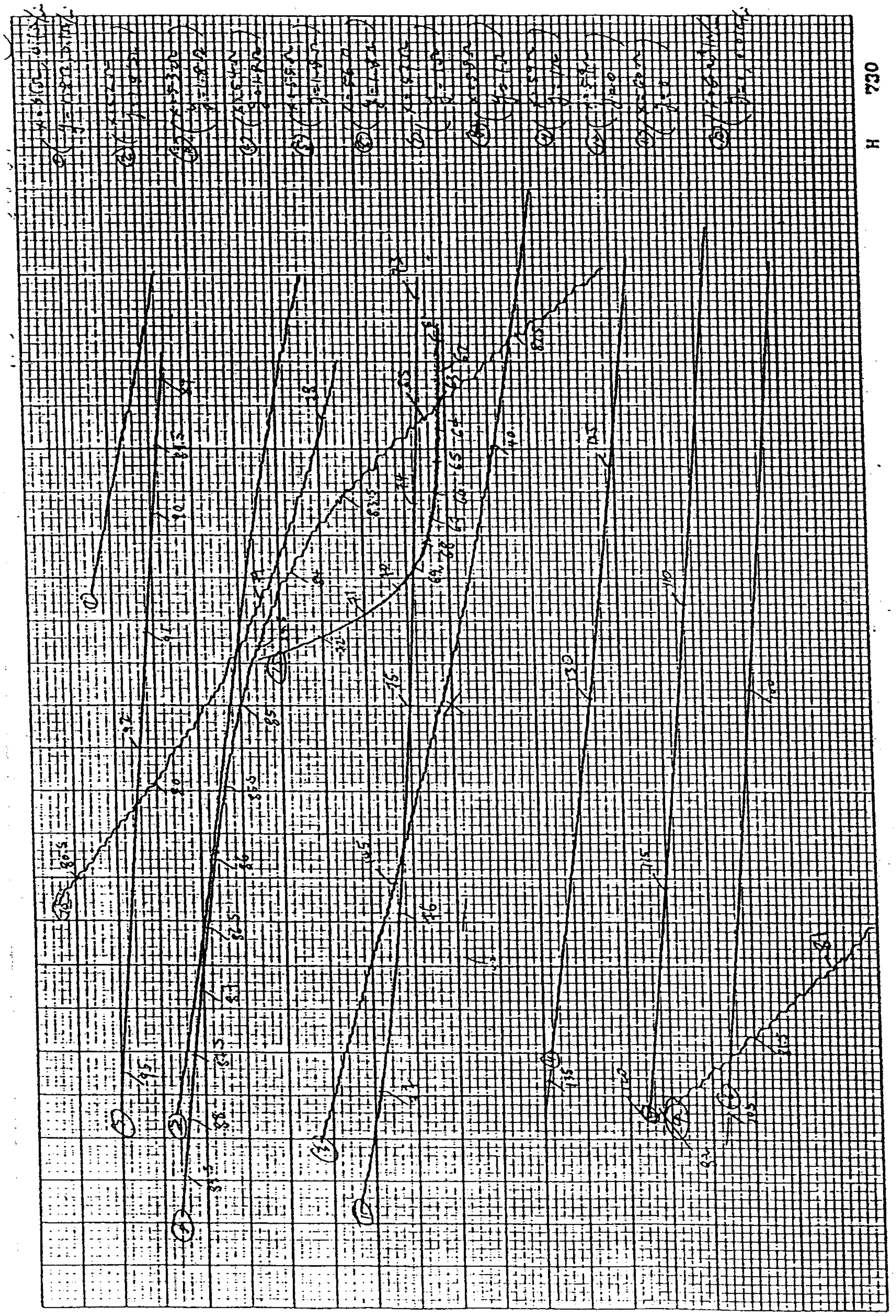

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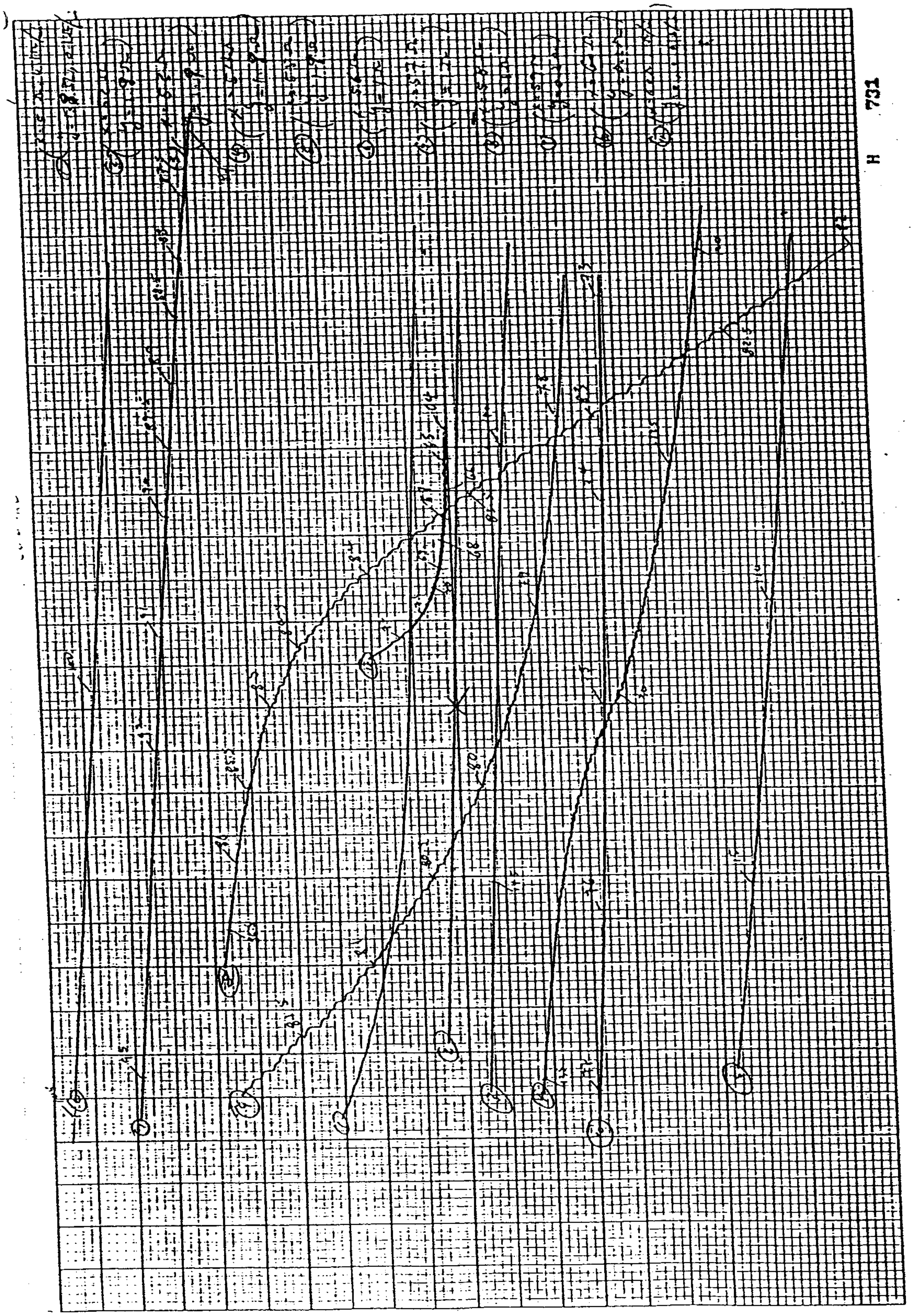

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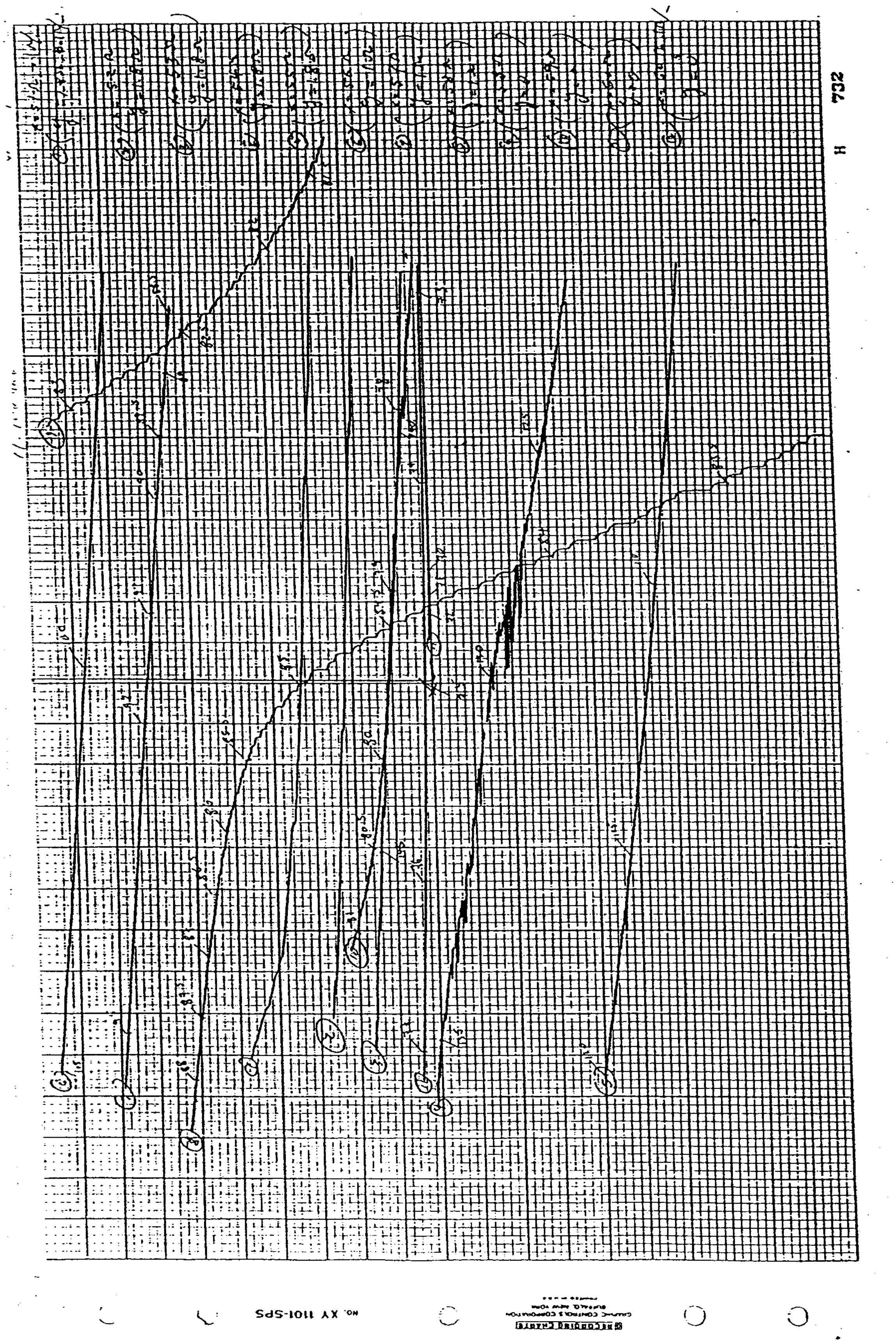
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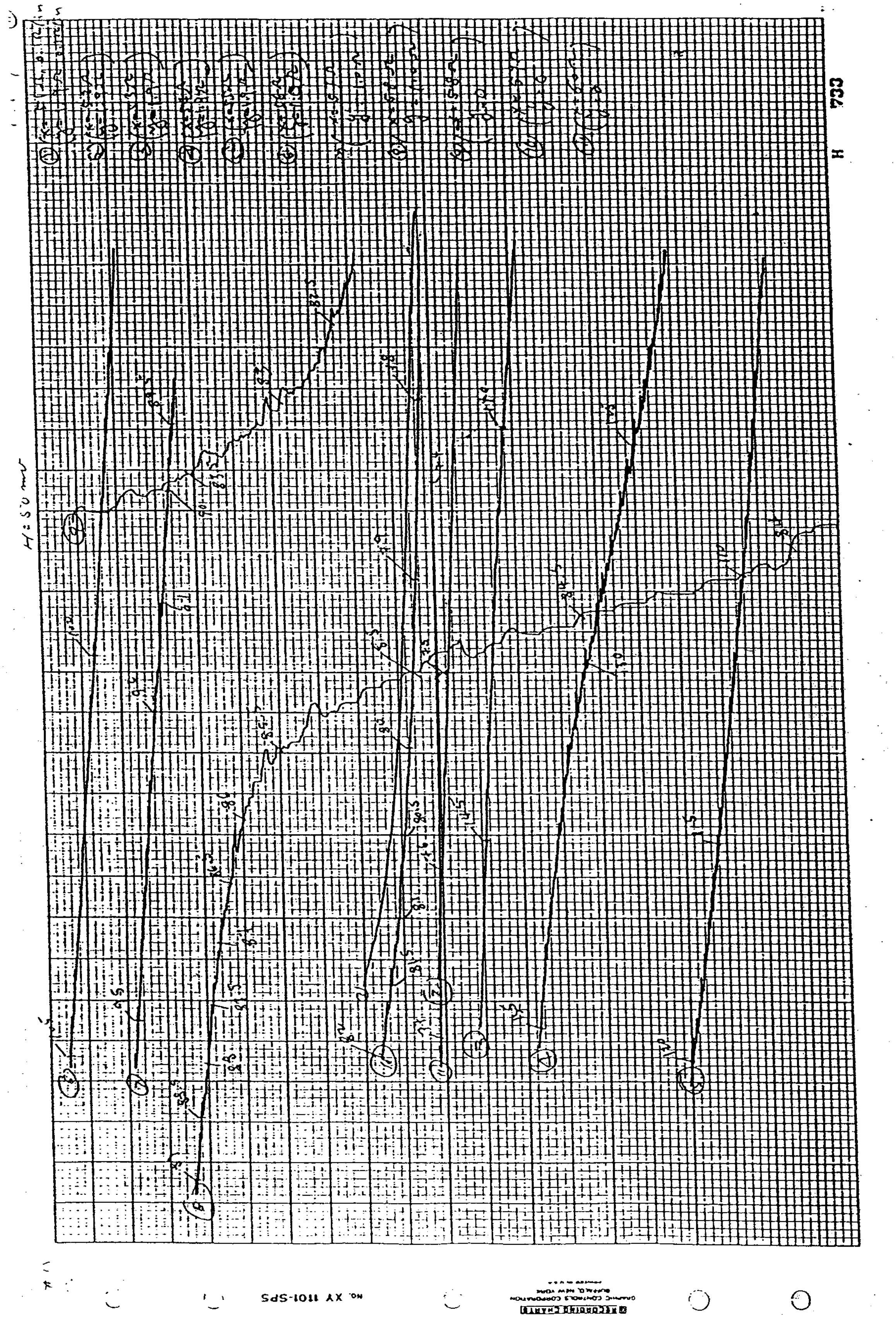
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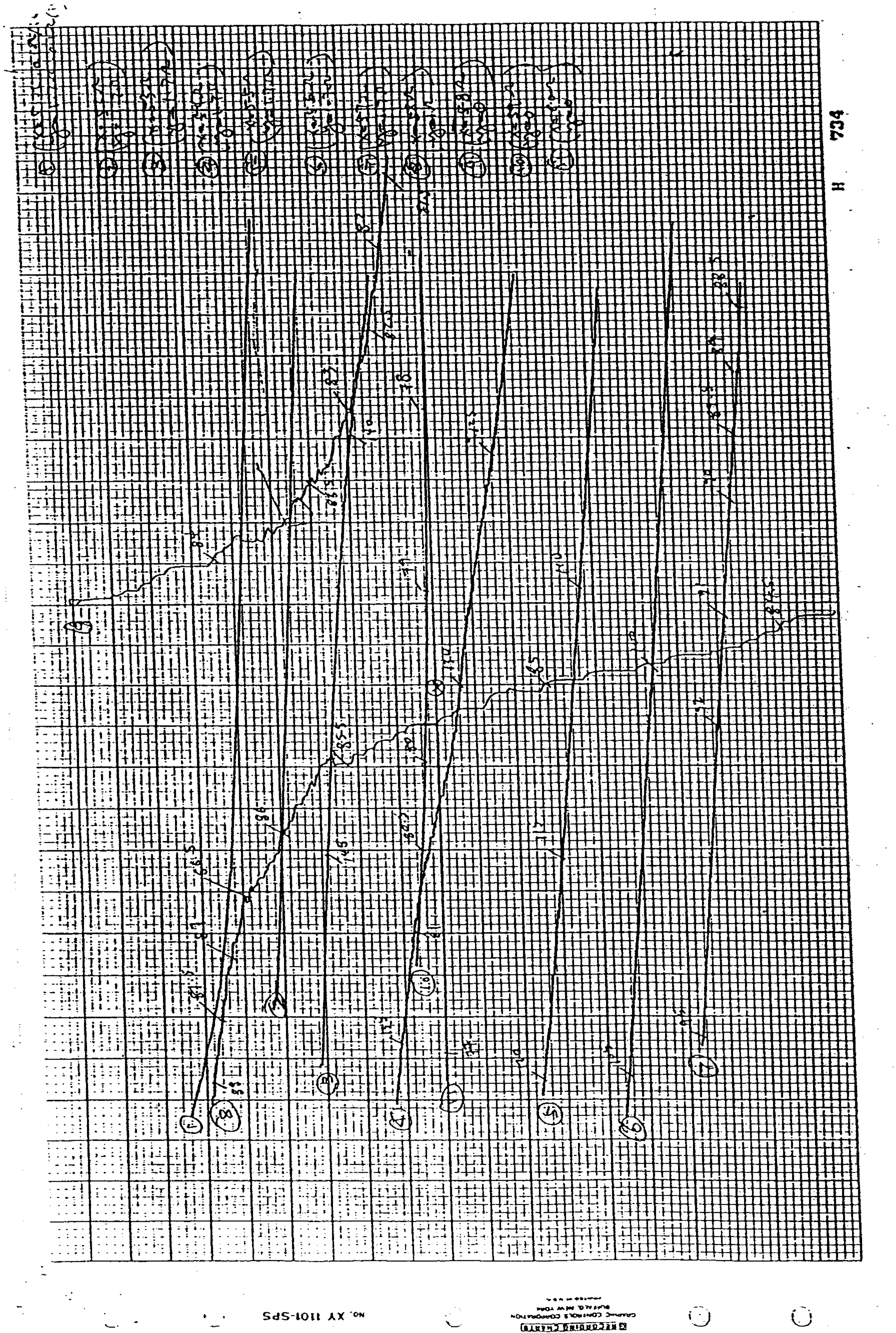

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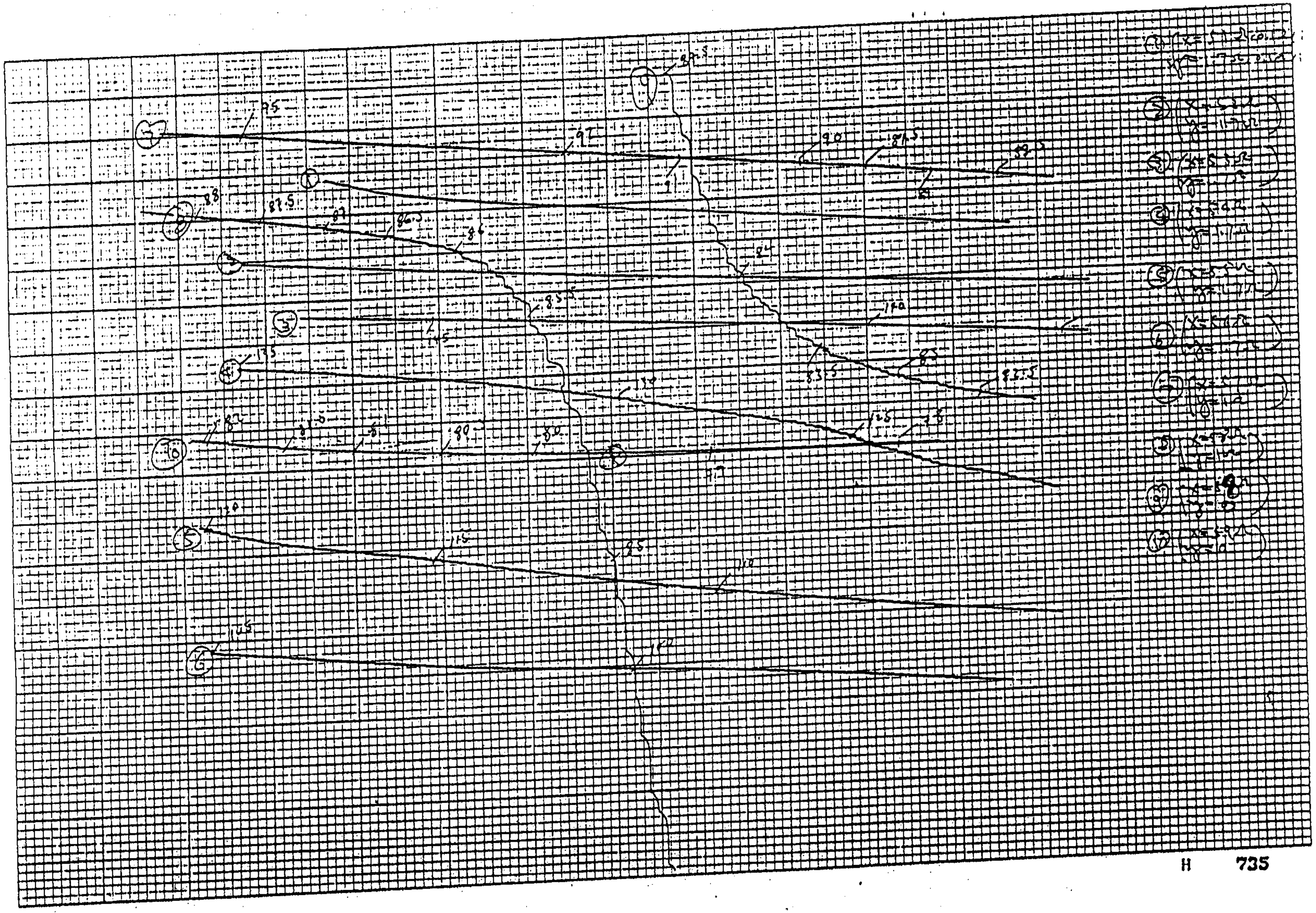

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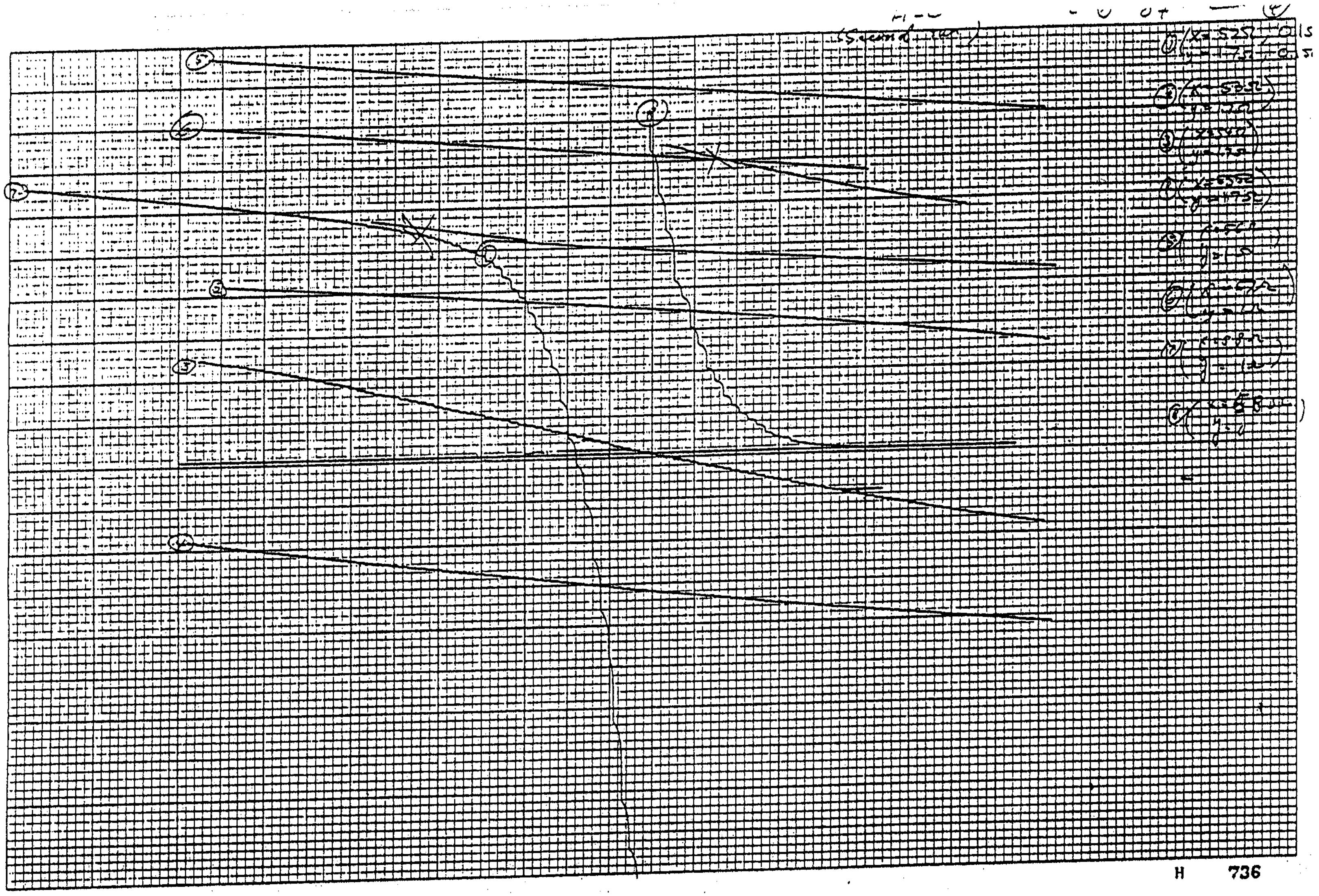

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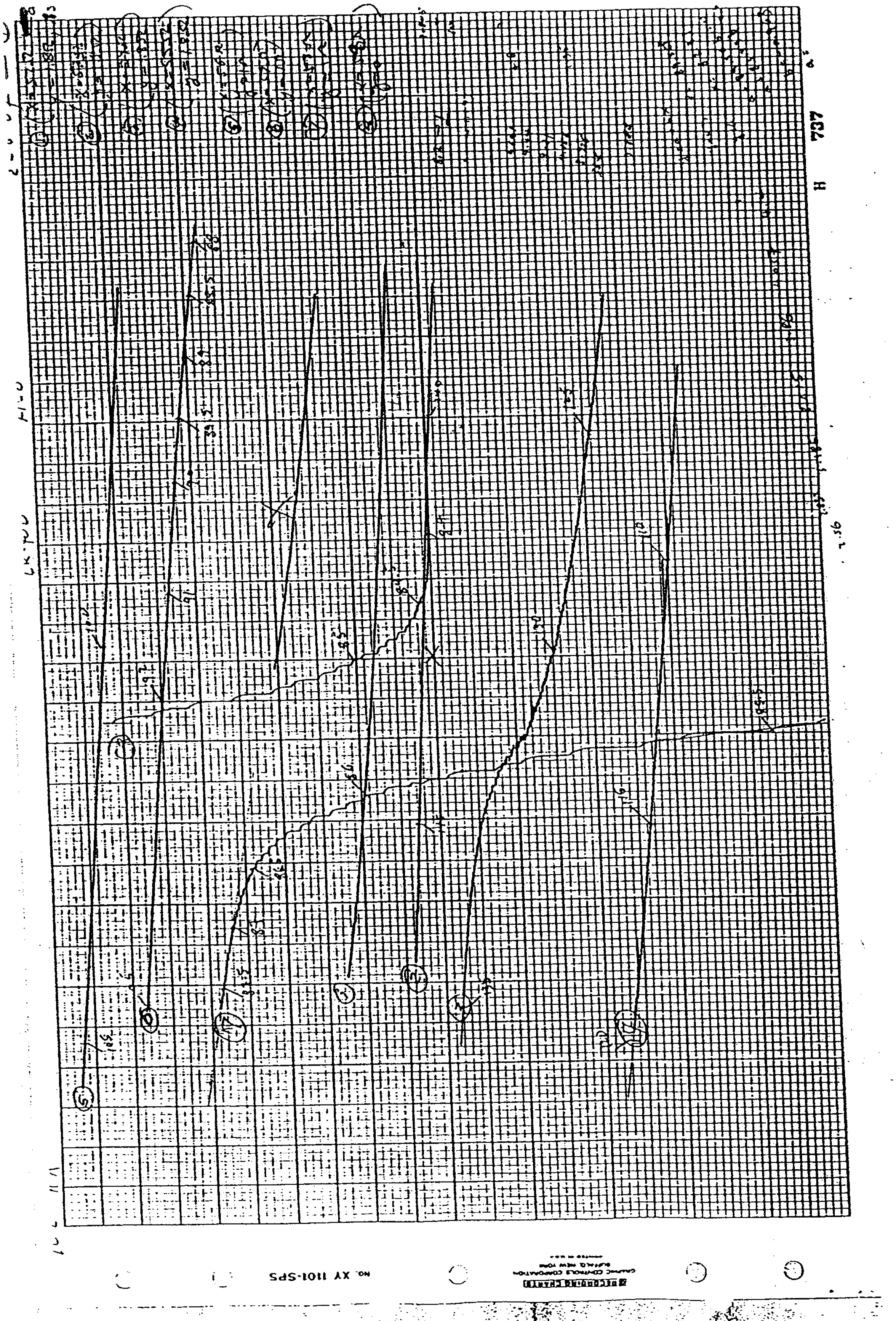
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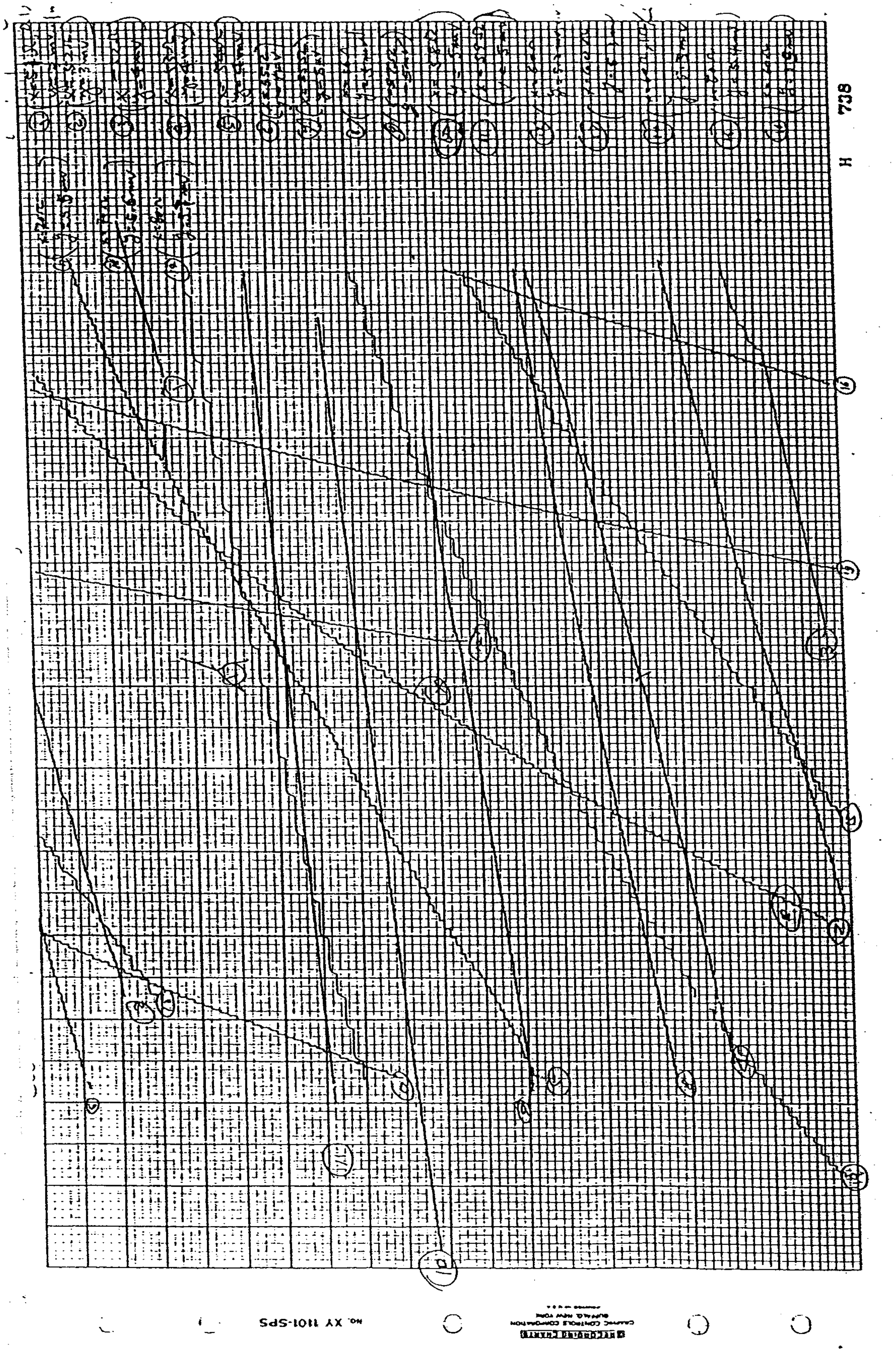
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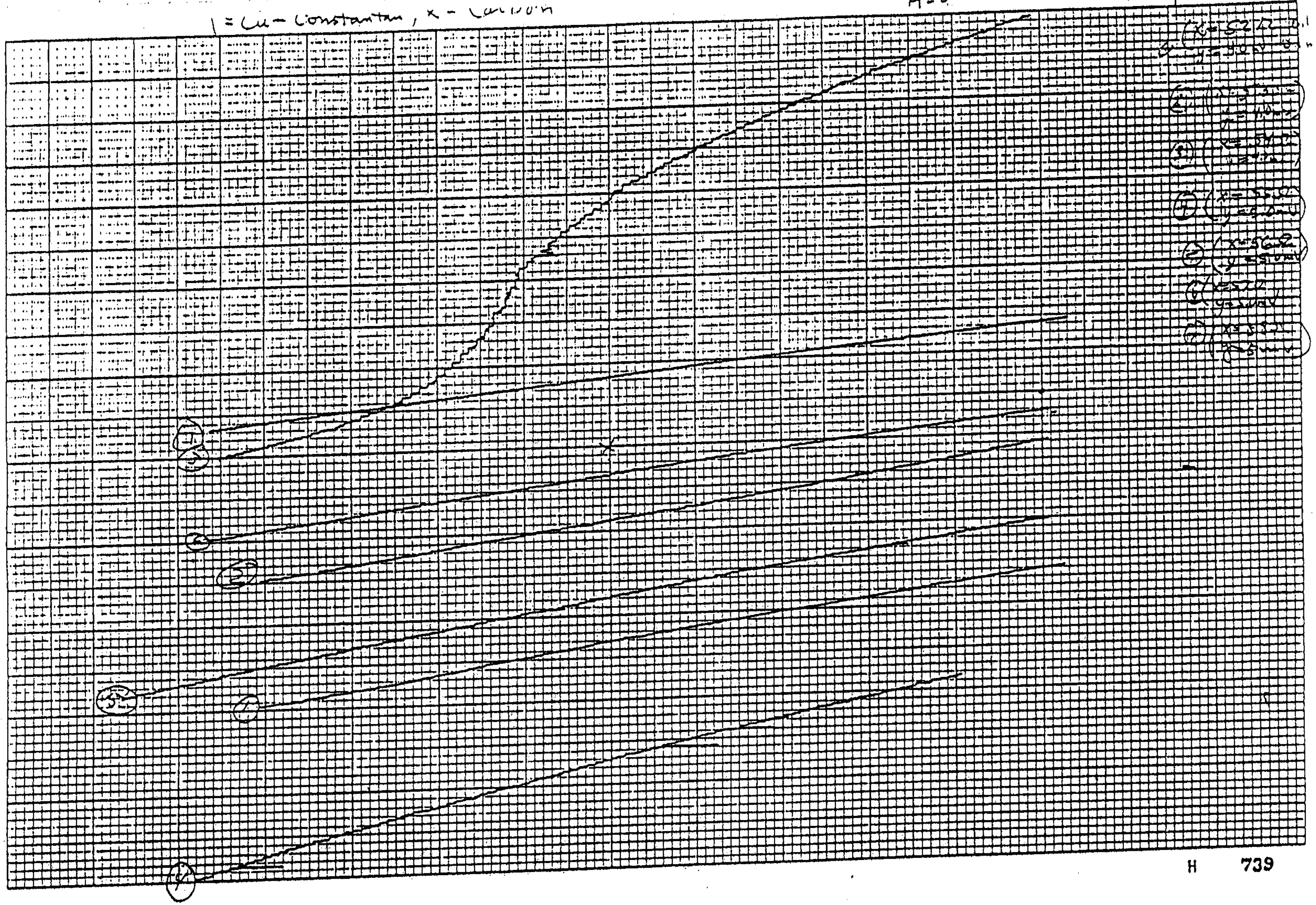

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AFFIDAVIT OF RULING MENG

THE STATE OF TEXAS)

COUNTY OF HARRIS)

On this the 6th, day of March, 2006, before me, a Notary Public in and for the State of Texas, personally appeared Ruling Meng, who, being duly sworn, upon oath deposes and says:

That I am of full legal age, have never been convicted of a felony or a crime involving moral turpitude and am in all respects competent to make this affidavit; that I reside in Houston, Harris County, Texas and that my business address: Superconductivity Center, Houston Science Center, Houston, Texas 77204.

- I am a material scientist. Before I came to the U.S. I was a research Scientist at The Chinese Academy science, Institute of Physics in Beijing, China.
- I started my research on superconducting materials since 1976.
- In 1979 I was invited by Dr.C.W. Paul Chu to join to his group as a visiting scholar in the Department of Physics at the University of Houston until 1981.
- Before I returned to China, in 1982, I was invited by Prof. Ernst Bucher at University of Konstanz, Germany and spent half year in their lab. My research projects were superconductor's single crystal growth. During this period I continued the collaboration with Dr. Chu. By sending him superconducting Single crystal for his studies.
- In mid 1982 I return to the Institute of physics in Bejing China and continued the collaboration on superconducting materials with Dr.C.W. Paul Chu
- In July of 1984 I was invited again by Dr. Chu and came back to the UH. and joined his group as a visiting scientist. My responsibility in this group was to research and study superconducting and related materials. I synthesized and characterized various compounds myself independently and supervise students on their materials studies.
- In 1986, Dr.C.W.Chu was on leave and served at the National Science Foundation in Washington D.C. He only came back Houston on

weekend to discuss research activity in the lab. At mid-November of 1986 I learned from my friend in China, Professor Z.X. Zhao about the paper "Possible High T_c Superconductivity in the Ba – La – Cu – O System," by J.G. Bednorz and K.A. Muller. I asked a graduate student Li Gao to go to the library to copy the paper on a Friday afternoon. Then I put a copy of the paper on Dr. Chu's desk. [Reference 1, on the paper with my hand writing note] On Saturday morning I came in and discussed the paper with him. The paper reported that they used the wet-chemical method and it also indicated that the solid-state reaction processing might be difficult to obtain the superconducting phase. I told Dr. Chu that I believed the solid-state reaction method could be used to synthesize this material. My expertise was not in wet-chemistry and I felt more confident with using the solid-state method.

- After this discussion, on the 14th of November I began to synthesize the first LaBaCuO compound with composition $La_{4.25}Ba_{0.75}Cu_5O_3$. And successfully repeated Dr.Bednorz and Muller's results. [Reference 2]
- In late November we began to apply pressure to the La-Ba-Cu-O compounds. The transition temperature increased from 35 to 57 K and leveled off. We realized that simulating the pressure effect we would have to substitute a small size element for Ba. Therefore, we began to substitute Sr for Ba in early December. However Dr. Chu asked me to stop the Sr substitution experiment in our lab because he had asked M.K. Wu (Alabama) to do this. He said that M.K.Wu couldn't compete with us. I therefore to replace Ba with Ca which has a smaller atoms size than Sr. at the same time, we learned that Bell lab has reported that LaCaCuO display a transition temperature which was lower than LaSrCuO. During this time Dr. Chu called back from Washington, D.C. every day to ask about the new results and set up the contact with outside corporations.
- On November 25th We observed a transition temperature around 70 K in a LaBaCuO sample made by Pei Hor. Unfortunately, the sample was not stable and we would not repeat the results. The results indicated that there were higher temperature superconductors existed.
- On December 30th Dr. M.K. Wu and his student brought his sample La-Sr-Cu-O to Houston for magnetic measurements. During his visit we had a discussion among Pei Hor, M.K. Wu, Li Gao and myself in Pei's office on Jan 1st (or 2 rd) 1987. Since the LaSrCuO indeed displayed a higher transition temperature at 40-45 K. while the Ca

substituted lower the transition temperature, we realized that we should substitute La by other elements. During the discussion Pei Hor suggested that we should replace La with Y (Yttrium). I suggested that we also replace La By Lu (Lutetium) because it has a smaller atomic radius.

- Two days later (around 3 or 4 of January) M.K. Wu returned to Alabama. Before his leaving our lab, I suggested him to go back to Alabama NASA 's lab to get Y_2O_3 and made the Y substitution compound. This could speed up the process, because we do not have Y_2O_3 and it if I placed the order the next day, it would take two weeks for us to get our order.
- From December 1986 to January 1987, I continued studying the La BaCuO compounds to optimize the composition and preparation condition. On January 11th we obverses a transition temperature up to 90K at the LaBaCuO sample that I made with formulas $(La_{0.4}Ba_{0.6})_2CuO_4$ (J2). [Reference 3] and X-ray data shown almost pure 123 structures. Unfortunately, I do not know the 123 phase yet and misidentify as 214 phase with impurity phase. Again the sample was not stable. [Reference 3,4].
- On January 13 we received our order of Y_2O_3 and Lu_2O_3 and then we began to work on substituting La with Y. But most of my effort still on LaBaCuO in order to repeat the 90 K result and I was under great pressure of providing outside groups with L:aBaCuO samples.
- In 29th of January 1987 Dr.Chu received a phone call from M.K.Wu said that he got a sample with a transition temperature up to 90 K and Dr. Chu asked him to bring the sample to our lab. For magnetic measurement to confirm the results.
- The sample with 90K is YBaCuO was mix phase and was in green color.
- For future application and academic study, it is important to separate the mix phase and identify the phase which contribute to the high temperature superconducting. By 27th of Feb. I successfully separate black and green crystals from the mixed phase by studied a set of YBCO sample with difference composition [reference 5] .Pei Hor and students did the magnetic measurement and identified the green phase was non-superconducting with rich Y content. And the phase contributed to superconducting is Black color $YBa_{1.8}Cu_3O$. This sample was sent to Dr. H.k.Mao at Geophysical Laboratory in

Washington. D.C for the crystal structure characterization and identifying the correct formula.

- In March 8th 1987, based on our green and black samples and the information we provided Dr.Robert M Hazen and H.K Mao at Geophysical Laboratory at Washington identify the high temperature superconductor YBCO 's formula is :$YBa_2Cu_3O_{6.7}$ with tetragonal structure.(So call 123 phase).
- Within half months from Feb.22th to March 15th. I had successful synthesized the entire substitute La by rare earth elements RBaCuO (R= rare earth) except Preseodymium and Cerium.

- In 1987, I attended a meeting with Dr.Chu, Pei Hor and attorney Charles M. Cox. During the meting Charles Cox asked who actually suggested to replace La by Y ? Dr. Chu immediately Point to me and said Ruling, remember I call you and told you to replace La by Y .I was shocked and did not know what to told. Because I clearly remember it was Hor suggested to substitute La by Y. during the discussion and Dr. Chu was not in the discussion. I am his employee and do not want to make him mad and instead stated " I do not remember."
- May be a couple of months later (I could not remember the exact date). Charles Cox called me and asked me again. that whether I remember Dr.Chu had called and directed me to replace La by Y. I did not answer and he said if you would not identify Dr.Chu told to you about his idea about the substitution of La by Y. Then the University of Houston would lose the patent to University of Alabama. I immediately said no this was our (UH) idea and they learned from us. Then Charles said then we need to identify Dr. Chu, he represents UH. I knew, if I say yes! I was lying. I asked Cox. whether I had to go to court? He said, "No, no, you would not go to the court" I knew this patent should be ours (UH). I would do every thing to help UH to earn the patent. Therefore, I said, "maybe Dr. Chu had called me and talk about the substitution. "
- One day, unexpectedly, Charles brought me the declaration writing by him or Chu and asked me to sign. All the detail and date was written and by Cox or Chu all I did was signing my signature. After that Dr. Chu thanked me for helping him in the critical time.
- In 1993, I was asking to make a deposition for U.H against the Uni. Of Alabama. I do not have any choice but continued to lie by

testifying Dr. Chu had called and told me about the substitution of La with Y. I feel very uncomfortable about this. But I think I did it for UH. Beside this all of my other statements in the deposition are truth. Indeed, in the pasts between 1986 to 1990 I made numerous high temperature Superconducting materials, helped to collect data and thou provided evidence for the patent,. I always thought the patent on high temperature superconductors was the join effort of our group.

- I did make a lie about the discovery of YBCO. I was a law illiterate. In 1987 I came to U.S from China where we could only obeying to the head of group, and the leader of the party. Whatever they said was the law. I do not understand any thing about declaration or deposition. I thought I did for the University. In addition I was Dr. Chu's employee and I trust him. and do not want to make him mad of me if not lying..
- However, no matter what was the reason, I should not have lied. The guilty feeling haunted me for about 20 years. Due to my health situation. I am planning to retire soon, I do not want to carry this guilty feeling to my retirement life. I want to have a peaceful mind. After a long mind struggling . Finally on Jan. 2006, I went to tell Pei Hor about how Cox asked me to testified Dr, Chu had called me and asked me to substitute La with Y. I apologized to him for what I have been wrong doing. I also told him that recently Dr.Chu mention our patent will be issued soon. Hor asked me, do you know we are also inventors? I said I think we should but I do not know, I never asked. Hor suggested me to find out. I went to asked John P. Warren the Associate Vice Chancellor for intellectual property management about the inventorship for the YBCO patent, and found out that Dr. Chu is a solo inventor for U.H. YBCO patent. We were shocked, disappointed and angry. We decided to talk to Mr.Warren and let him know that we are fully justified as this patent's inventors. We required and deserved fair treatment.

  Dr.Chu came back from Hong Kong the next week, He want to talk to me about this matters. I was sick and do not want to talk to him. On Feb. 9th Dr. Jacobson (the director for Texas Center for Superconductivity at the University of Houston) talked to me about this issue and he said that Dr. Chu said Pei and I are not the some case and should be treated differently. Dr. Chu is willing and prepared to compensate me as recognition for my contribution to the high temperature superconductor invention.

FURTHER, AFFIANT SAYETH NAUGHT.

Ruling Meng

SUBSCRIBED AND SWORN TO BEFORE ME this 6th day of March

Notary Public

D. Andra Black

DEANDRA LAINE BLACK
NOTARY PUBLIC, STATE OF TEXAS
MY COMMISSION EXPIRES
SEPT. 15, 2009

Z. Phys. B - Condensed Matter 64, 189–193 (1986)

Condensed Matter
Zeitschrift für Physik B

Reference 1

Ba La_4 Cu_5 $O_{5(3-y)}$

Ba $La_{4.25}$ Cu_5 O_{10}

Possible High T_c Superconductivity in the Ba–La–Cu–O System

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ have been prepared in polycrystalline form. Samples with $x=1$ and 0.75, $y>0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, bute possibly also from $2D$ superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of A 15 (Nb_3Sn) and B 1 (NbN) structure have so far shown the highest superconducting transition temperatures. Among many A 15 compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c = 23.3$ K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high T_c [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, n. In Nb-doped $SrTiO_3$, with $n = 2 \times 10^{20}$ cm^{-3}, the plasma edge is below the highest optical phonon, which is therefore unshielded [6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $BaPb_{1-x}Bi_xO_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n = 2$–4×10^{21} cm^{-3} [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1}, whose intensity is proportional to T_c, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe^{4+}, Ni^{3+} and Cu^{2+} in octahedral oxygen environment show strong Jahn-Teller (J.T.) effects [13]. While SrFe(VI)O_3 is distorted perovskite insulator, LaNi(III)O_3 is a J.T. undistorted metal in which the transfer energy b_π of the J.T. e_g electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba – La – Cu – O system. This system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T. Cu^{3+} and the J.T. Cu^{2+} ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

II. Experimental

1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECPURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 5 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIEMENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2θ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the K_2NiF_4 structure ($a = 3.79$ Å and $c = 13.21$ Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller x(Ba). The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite ($La_3Ba_3Cu_6O_{14}$) as described by Michel and Raveau [16].

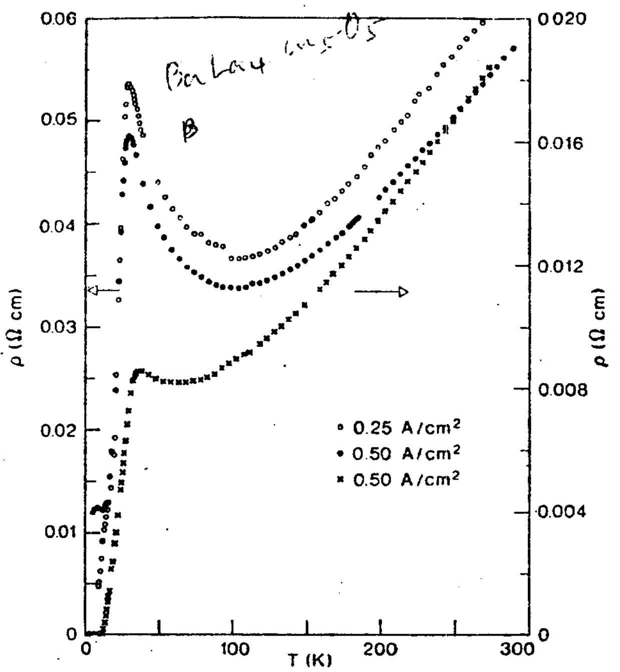

Fig. 1. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ for samples with x(Ba) = 1 (upper curves, left scale) and x(Ba) = 0.75 (lower curve, right scale). The first two cases also show the influence of current density

3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by In wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Hereaus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with $x(\text{Ba}) \leq 1.0$, the conductivity measurements, involving typical current densities of 0.5 A/cm², generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (>90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and O_2 partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted

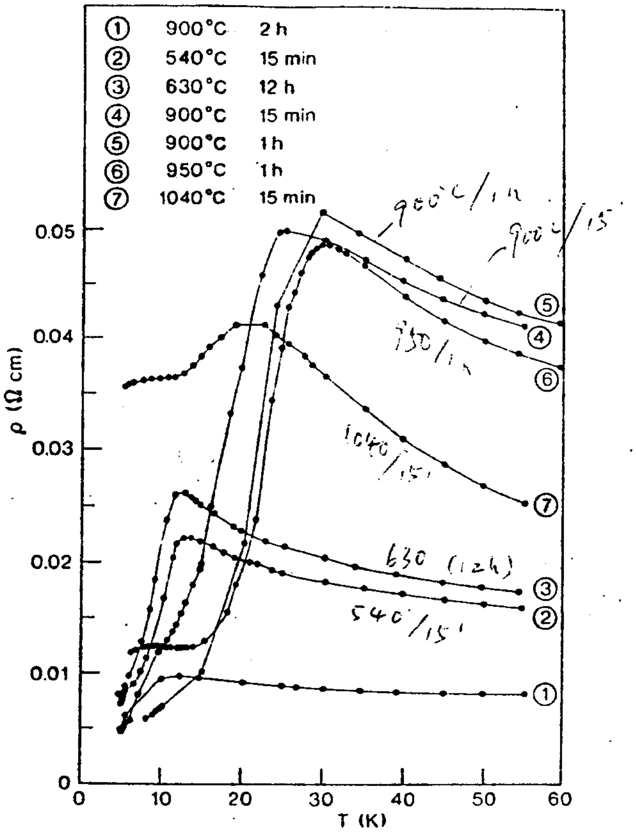

Fig. 2. Low-temperature resistivity of samples with x(Ba) = 1.0, annealed at O_2 partial pressure of 0.2 bar (curve ①) and 0.2×10^{-4} bar (curves ② to ⑦)

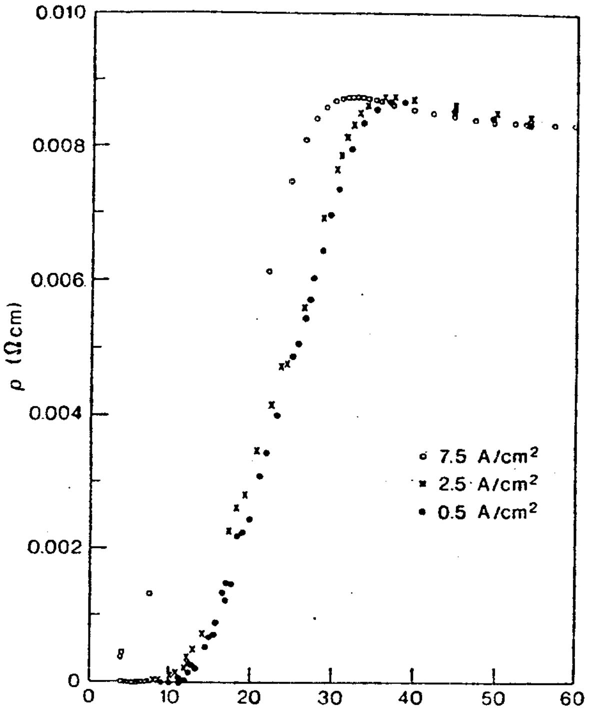

Fig. 3. Low-temperature resistivity of a sample with x(Ba) = 0.75, recorded for different current densities

towards the 30 K region. Curves ④ and ⑤, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve ⑥. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li – Ti – O system, and in superconducting $BaPb_{1-x}Bi_xO_3$ polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of $\rho(T)$, then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in $\rho(T)$ with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In $BaPb_{1-x}Bi_xO_3$, the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li – Ti – O [5] or in our Ba – La – Cu – O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba – La – Cu – O phases exhibits this behaviour. Therefore, under the above premises, the peak in $\rho(T)$ at 35 K, observed for an x(Ba) = 0.75 (Fig. 1), has to be identified as the start to superconductive cooperative phenomena in the isolated grains. It should be noted that in granular Al. Cooper pairs in coupled grains have been shown to exist already at a point where $\rho(T)$ upon cooling has decreased by only 20% of its highest value. This has been proven qualitatively [19] and more recently also quantitatively [20] by the negative frequency shift occurring in a microwave cavity. In 100 Å films, a shoulder in the frequency shift owing to $2D$ fluctuations was observed above the T_c of the grains. In our Ba – La – Cu – O system, a series of layer-like phases with considerable variety in compositions are known to exist [16, 21], and therefore $2D$ correlations can be present.

The granularity of our system can be justified from the structural information, and more quantitatively from the normal conductivity behaviour. From the former, we know that more than one phase is present and the question arises how large are the grains. This can be inferred from the logarithmic fingerprint in resistivity. Such logarithmic increases are usually associated with beginning of localization. A most recent example is the Anderson transition in granular Sn films [22]. Common for the granular Sn and our samples is also the resistivity at 300 K, lying in the range of 0.06 to 0.02 Ωcm, which is near the microscopic critical resistivity of $\rho_c = 10\ L_0 \hbar/e^2$ for localization. From the latter formula, an interatomic distance L_0 in the range of 100 Å is computed, thus a size of superconducting grains of this order of magnitude must be present. Upon cooling below T_c, Josephson junctions between the grains phase-lock progressively [23] and the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2 (Fig. 1). At larger current densities, the weaker Josephson junctions switch to normal resistivity, resulting in a temperature shift of the drop, as shown in Fig. 3. The plateau in resistivity occurring below the 80% drop (Fig. 1) for the higher current density of 0.5 A/cm^2, and Fig. 2 curve ⑥) may be ascribed to switching of junctions to the normal state.

The way the samples have been prepared seems to be of crucial importance: Michel et al. [21] obtained a single-phase perovskite by mixing the oxides of La and Cu and $BaCO_3$ in an appropriate ratio and subsequent annealing at 1,000 °C in air. We also applied this annealing condition to one of our samples, obtained by the decomposition of the corresponding oxalates, and found no superconductivity. Thus, the preparation from the oxalates and annealing below 950 °C are necessary to obtain a non-perovskite-type phase with a limited temperature range of stability exhibiting this new behaviour. The formation of this phase at comparatively low temperatures is favoured by the intimate mixture of the components and the high reactivity of the oxalates owing to the evolution of large amounts of H_2O and CO_2 during decomposition.

IV. Conclusion

In the concentration range investigated, compounds of the Ba – La – Cu – O system are metallic at high temperatures, and exhibit a tendency towards localization upon cooling. Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K. The system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress. An identification of that phase may allow growing of single crystals for studying the Meissner effect, and collecting specific-heat data to prove the presence of high T_c bulk superconductivity.

The authors would like to thank H.E. Weibel for his help in getting familiar with the conductivity measurement system, E. Courtens and H. Thomas for discussions and a critical reading of the manuscript.

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K.A. Müller
IBM Zürich Research Laboratory
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CH-8803 Rüschlikon
Switzerland

Note Added in Proof

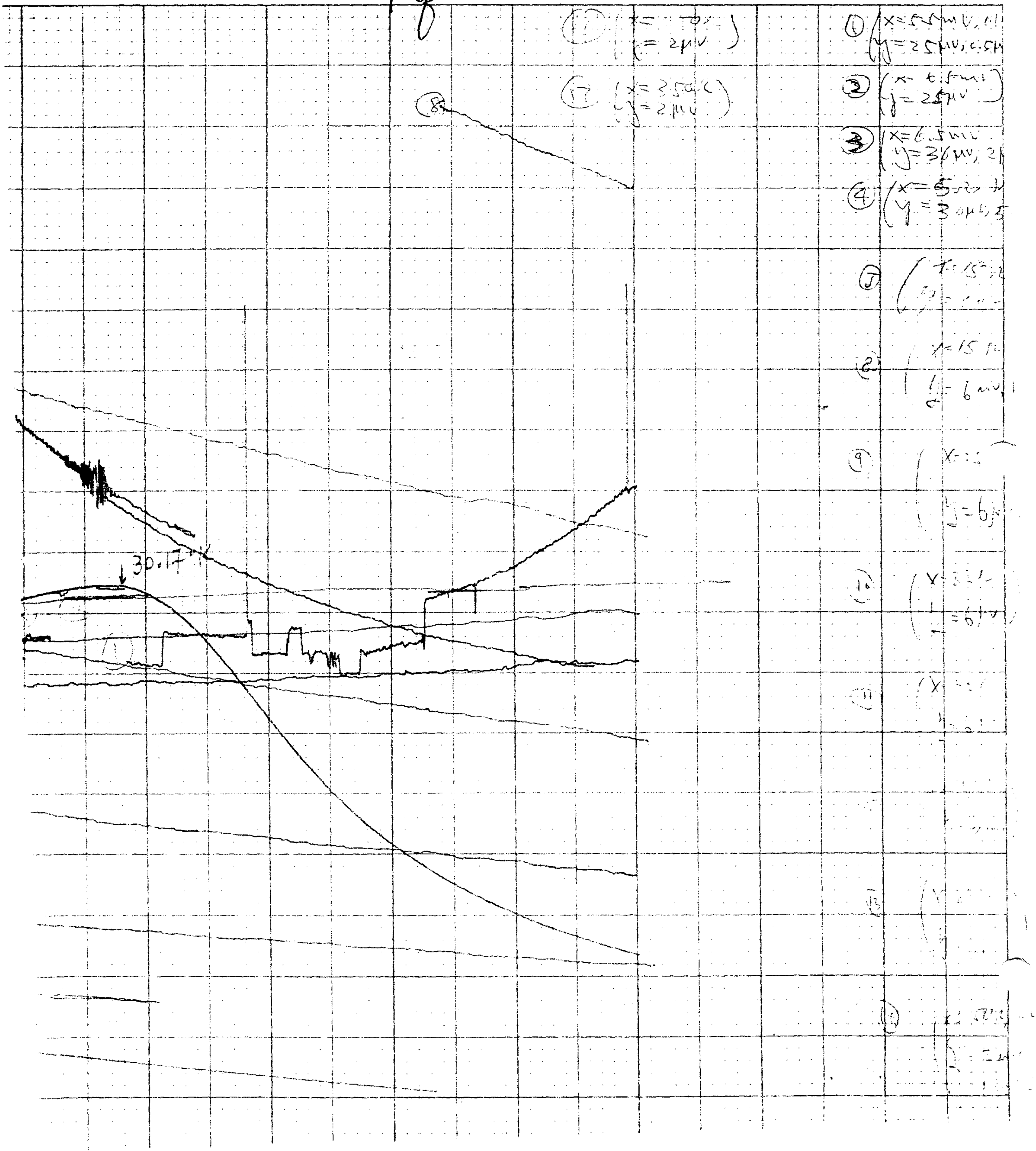
Chemical analysis of the bulk composition of our samples revealed a deviation from the ideal La/Ba ratios of 4 and 5.66. The actual ratios are 16 and 18, respectively. This is in agreement with an identification of the third phase as CuO.

[redacted]

ick Check

Reference 2.

11/21/86



First Clear Evidence of 90 K Superconductivity

Proc. Natl. Acad. Sci. USA
Vol. 84, pp. 4681–4682, July 1987
Symposium Paper

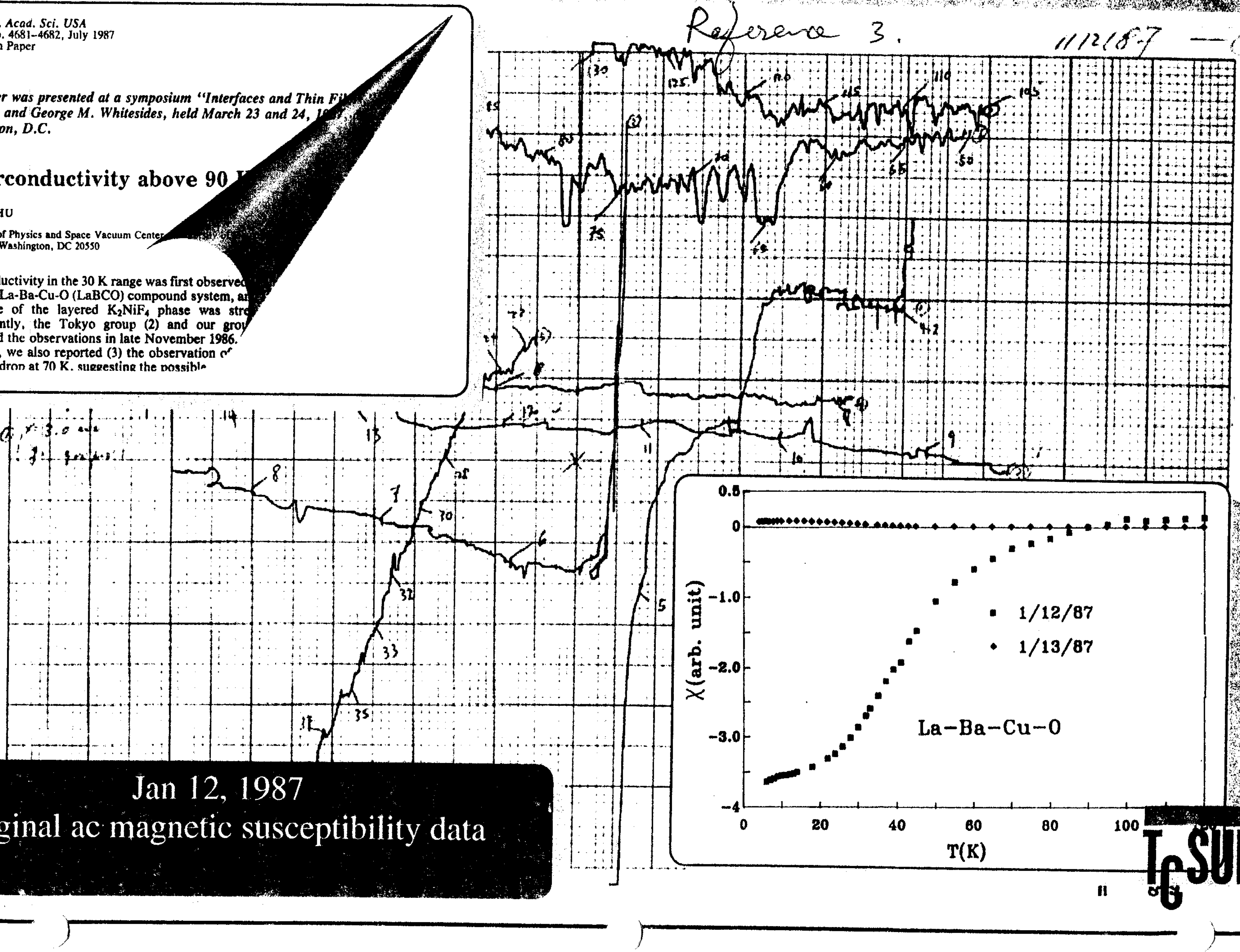
This paper was presented at a symposium “Interfaces and Thin Fi
Eastman, and George M. Whitesides, held March 23 and 24, 1
Washington, D.C.

Superconductivity above 90

C. W. Chu

Department of Physics and Space Vacuum Center
Foundation, Washington, DC 20550

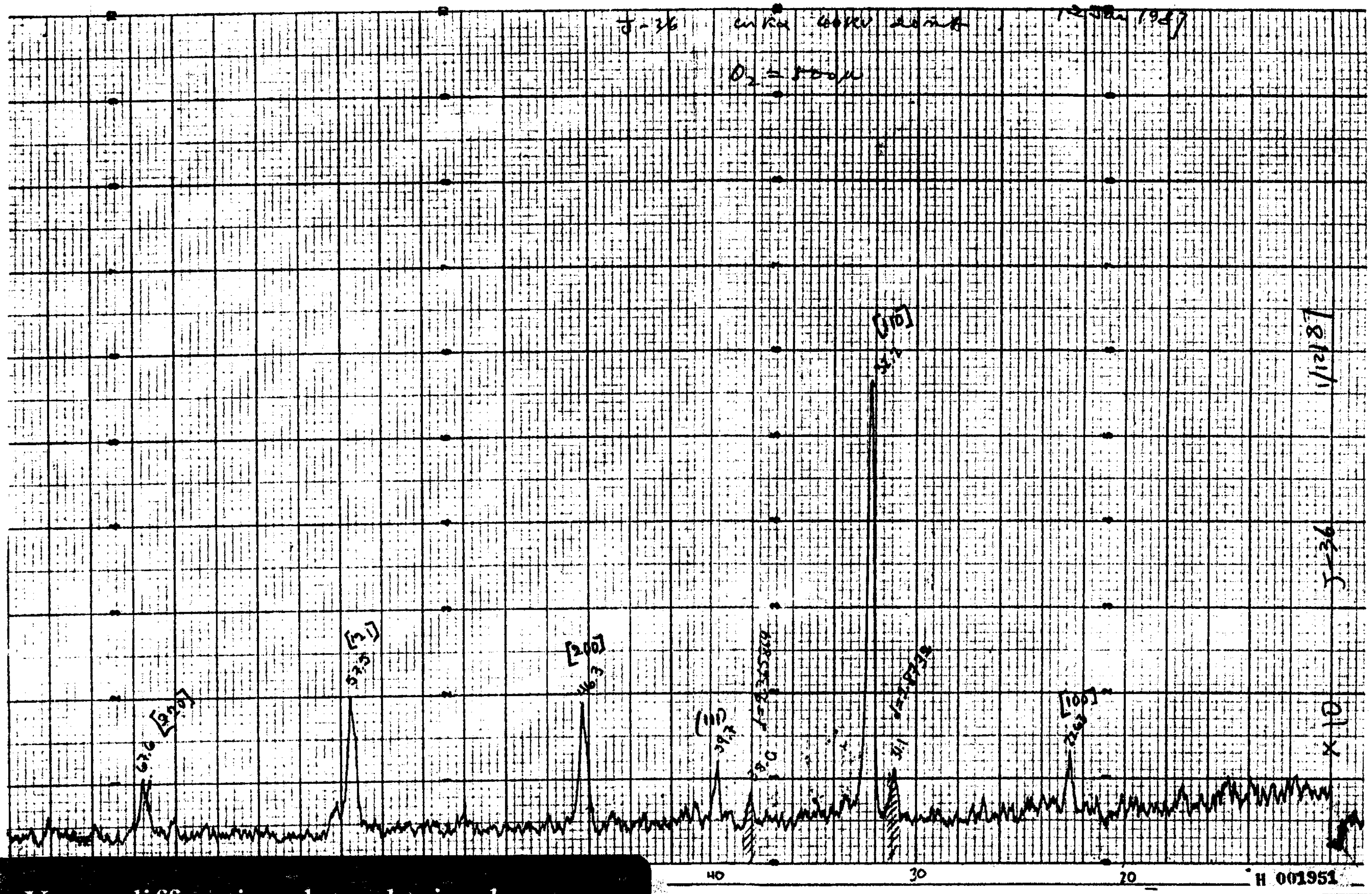
Superconductivity in the 30 K range was first observed
the mixed La-Ba-Cu-O (LaBCO) compound system, an
importance of the layered K_2NiF_4 phase was stre
Independently, the Tokyo group (2) and our grou
reproduced the observations in late November 1986.
same time, we also reported (3) the observation o
resistance drop at 70 K, suggesting the possible



Jan 12, 1987
Original ac magnetic susceptibility data

TcSUH

La-Ba-Cu-O with 123-Structure is Already Obtained



X-ray diffraction data obtained on
Jan. 12, 1987, indexed in Mar. 1987.

Reference 4.

TcSUH

Reference 5.

28 - Feb 1987.

① Y_1 ($Ba_{1.4}$ $Cu_{1.4 \times 1.425}$)

② Y_1 ($Ba_{1.5}$ $Cu_{1.5 \times 1.425}$)

③ Y_1 ($Ba_{1.6}$ $Cu_{1.6 \times 1.425}$)

① 50 H 250
500
1000
1500

J_c [illegible]

27 Feb. 1986.

Reference 4

① index : 2:00 pm.

② Cu + Sample.

Reference 5

③ Y + Ba + Cu + O.

Ba − Cu

④ 0.01 and 0.05 ⇒ $Y_{0.99}$, $Y_{0.95}$

Gd

Ce

✓ Nd

pr

Sm

Eu

Tb

Dy

Ho

Er

Tm

✓ Yb

✓ Lu

$[(La_{0.99}A_{0.01})_{0.9}Ba_{0.1}]_2CuO_4$

$La_{0.95}$ ~~Ba~~ $A_{0.05})_{0.9}Ba_{0.1}]$

J_{Dy} −

SL

152

H 557

Reference 5

Green :

$Y_1 (Ba_x Cu_{1-x})_1 O_3 \leftarrow$

$x = 0.0,\ 0.2,\ \underbrace{0.4,\ 0.5,\ 0.6}_{x \rightarrow},\ 0.8,\ 1.0.$

Black :

$Y_1 Ba_x Cu_y O$

$y = \underline{x \times 1.425}$

x	y
0.6	0.855
0.7	0.998
0.8	1.14
0.9	1.283
1.0	1.425

0.112

AFFIDAVIT OF RULING MENG

THE STATE OF TEXAS)

COUNTY OF HARRIS)

On this the 25thth, day of May, 2006, before me, a Notary Public in and for the State of Texas, personally appeared Ruling Meng, who, being duly sworn, upon oath deposes and says:

That I am of full legal age, have never been convicted of a felony or a crime involving moral turpitude and am in all respects competent to make this affidavit; that I reside in Houston, Harris County, Texas and that my business address is Superconductivity Center, Houston Science Center, Houston, Texas 77204.

1. In late 1986 and January 1987, Pei Hor and I collaborated at the University of Houston to invent and develop a "high temperature" superconductivity technology using Yttrium and known as the YBCO invention.
2. Dr. Paul Chu, as group leader, assured us (Dr. Hor and me), based on our actual inventive contributions, that we would be listed as co-inventors on all patent applications for YBCO. Consistent with that assurance, and our inventive contributions and my clear understanding, I was paid $137,000 in 1987 by the University of Houston as my initial share of licensing fees paid by Dupont for the YBCO invention. A true and correct copy of my W-2 for this exceptional compensation, along with the W-2 for my regular salary, is attached hereto as Exhibit "A".
3. It was not until February of 2006 that I learned from Mr. John P. Warren, Jr., (Associate Vice Chancellor for Intellectual Property Management) that Dr. Hor and I were not listed on any YBCO patent applications as at least "co-inventors". Mr. Warren said that that Dr. Paul Chu was the sole listed inventor on the applications. I feel this is wrong because Dr. Chu only minimally participated in inventing the YBCO technology.
4. Any statements made by me, under oath or otherwise, contrary to the paragraphs above were made to protect the University of Houston at

the urging of attorney Charles Cox, outside counsel for the University.

FURTHER, AFFIANT SAYETH NAUGHT.

Ruling Meng, Affiant

SUBSCRIBED AND SWORN TO BEFORE ME this 25th of May 2006

Notary Public

TRAVIS WOFFORD
NOTARY PUBLIC, STATE OF TEXAS
MY COMMISSION EXPIRES
SEP[illegible] 5, 2009

Wage and Tax Statement OMB No. 1545-0008

Copy C For employee's records

This information is being furnished to the IRS and appropriate State officials.

Year 1988

EMPLOYER: [illegible] STEM [illegible]

Advance EIC payment

Employee's social security number 459-47-6704	9 Federal income tax withheld 27,400.00	10 Wages, tips, other compensation 137,000.00	Soc. sec. tax withheld 496.84	Soc. sec. wages 6,615.00
		Pension plan coverage? Yes/No No	Allocated tips	Soc. sec. tips

Employee's name

Neng Ru-Ling
3515 Gannett
Houston, TX 77025

Employee's address and ZIP code

State or local tax withheld	State or local wages	State or locality
State or local tax withheld	State or local wages	State or locality

Supplemental W-2

The social security rate of % for retirement, survivors, and disability insurance, and % for hospital insurance benefits, totals %.

Department of the Treasury - Internal Revenue Service

Form

Wage and Tax Statement OMB No. 1545-0008

Copy C For employee's records

This information is being furnished to the IRS and appropriate State officials.

Year 1988

EMPLOYER:

UNIVERSITY OF HOUSTON SYSTEM
4800 [illegible]
[illegible]

74-6001399 67-0740031

Advance EIC payment

Employee's social security number 459-47-6704	9 Federal income tax withheld 4,831.87	10 Wages, tips, other compensation 30,490.30	Soc. sec. tax withheld 2,882.66	Soc. sec. wages 38,384.20
	DEF-COMP: YES	Pension plan coverage? Yes/No YES	Allocated tips	Soc. sec. tips

Employee's name

MENG RU-LING
3515 GANNETT
HOUSTON TX 77025

State or local tax withheld	State or local wages	State or locality
State or local tax withheld	State or local wages	State or locality

Department of the Treasury - Internal Revenue Service

EXHIBIT
"A"

GORDON G. WAGGETT, P.C.

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October 26, 2006

Via United State Express Mail No. EV 459408878 US

Mr. Lester L. Hewitt
Akin Gump Strauss Hauer & Feld LLP
1111 Louisiana Street, 44th Floor
Houston, Texas 77002-5800

Re: YBCO Patent Inventorship Issues

Dear Les,

As you know, I have been retained by Dr. Ruling Meng (Dr. Meng) to represent her rights as a coinventor of certain inventions arising from her work at The University of Houston (UH). Based on my review of the evidence thus far, Dr. Meng is clearly entitled to be named as a coinventor of U.S. Patent No. 7,056,866 ("the '866 patent"), and its progeny, including, without limitation, U.S. Patent Application Serial No. 07/300,063, and 163,956 (and any non-U.S. counterpart patents/applications, such as, e.g., the 35 family members for the '866 patent identified on INPADOC derived from 22 applications, and WO 89/08076 (PCT/US89/00685)).

Further to my letter of July 5, 2006, I have not yet received from you any input regarding my request for the progress of your investigation into this matter and the steps you have taken on behalf of UH and Dr. Ching-Wu Chu (Dr. Chu) with the U.S. Patent & Trademark Office (USPTO) to address these coinventorship issues relating to my client. In the meantime, however, I have had the opportunity to review documentary evidence that pertains specifically to my client showing her entitlement to be a named as a coinventor along with Dr. Chu. I am providing a synopsis of this evidence herein, along with a PowerPoint® presentation found on the enclosed CD.

In view of clear and convincing documentary evidence that exists showing and corroborating Dr. Meng's entitlement to be named as a coinventor of the claimed inventions, Dr. Meng hereby respectfully requests the following from Dr. Chu and UH:

I. Certification of Correction of U.S. Patent No. 7,056,866

Pursuant to 35 U.S.C § 256, 37 C.F.R. § 1.324, Dr. Meng seeks the agreement of Dr. Chu and UH to submit a joint application with her to the Director of the USPTO seeking a Certificate of Correction of Inventorship to add Dr. Meng as a named coinventor of U.S. Patent No. 7,056, 866 ("the '866 patent") along with Dr. Chu.[1]

35 U.S.C § 256 provides in pertinent part:

> Whenever … through error an inventor is not named in an issued patent and such error arose without any deceptive intention on his part, the Director may, on application of all the parties and assignees, with proof of the facts and such other requirements as may be imposed, issue a certificate correcting such error.
>
> The error of omitting inventors or naming persons who are not inventors shall not invalidate the patent in which such error occurred if it can be corrected as provided in this section.

Pursuant to 37 C.F.R. § 1.324(b)(1), Dr. Meng will provide a statement that the inventorship error occurred without any deceptive intention on her part – a position that neither Dr. Chu nor UH would dispute.[2] Pursuant to 37 C.F.R. § 1.324(b)(2), Dr. Meng

---

[1] It should be without dispute that Dr. Meng has standing to assert her rights as a coinventor and to seek correction of inventorship with Dr. Chu and UH. See Chou v. University of Chicago, 254 F.3d 1347, 1359-60 (Fed. Cir. 2001).

[2] Correction of inventorship under section 256 "only requires an inquiry into the intent of the nonjoined inventor". Stark v. Advanced Magnetics, Inc., 119 F.3d 1551, 1552 (Fed. Cir. 1997).

seeks from Dr. Chu a statement either agreeing to the change of inventorship or stating that he has no disagreement in regard to the requested change. Pursuant to 37 C.F.R. § 1.324(b)(3), Dr. Meng seeks from UH (and any other assignees of the '866 patent) a statement, made in compliance with 37 C.F.R. § 3.73(b), agreeing to the change of inventorship in the '866 patent.[3]

II. Certification of Correction of U.S. Patent Application Serial No. 07/300,063

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 07/300,063 ("the '063 application")(and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.[4]

35 U.S.C § 116 provides in pertinent part:

> Whenever … through an error an inventor is not named in an application [for patent], and such error arose without any deceptive intention on his part, the Director may permit the application to be amended accordingly, under such terms as he prescribes.

In this connection, Pursuant to 37 C.F.R. § 1.48(a)(2) Dr. Meng will provide a statement that the error in inventorship occurred without deceptive intention on her part – a position that neither Dr. Chu nor UH would dispute.[5] Pursuant to 37 C.F.R. § 1.48(a)(3) Dr. Meng will also provide an oath or declaration as required by 37 C.F.R. § 1.63. Pursuant to

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[3] See also MPEP 1412.04.

[4] See footnote 1.

[5] See footnote 2.

37 C.F.R. § 1.48(a)(5), Dr. Meng seeks from UH (and any other assignees of this application) written consent to this change in inventorship.[6]

III. Certification of Correction of U.S. Patent Application Serial No. 163,956 filed March 3, 1988

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 163,956 ("the '956 application")(and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.[7]

In this connection, Pursuant to 37 C.F.R. § 1.48(a)(2) Dr. Meng will provide a statement that the error in inventorship occurred without deceptive intention on her part – a position that neither Dr. Chu nor UH would dispute.[8] Pursuant to 37 C.F.R. § 1.48(a)(3) Dr. Meng will also provide an oath or declaration as required by 37 C.F.R. § 1.63. Pursuant to 37 C.F.R. § 1.48(a)(5), Dr. Meng seeks from UH (and any other assignees of this application) written consent to this change in inventorship.[9]

IV. Correction of Inventorship in all Non-US Counterpart Patents and Patent Applications

Dr. Meng claims entitlement to be named as a coinventor on all applicable non-U.S. counterpart patent applications as well. Dr. Meng is presently aware of the existence of non-U.S. counterpart applications, but does not have a complete identification of these applications. Since inventorship on such applications normally follows the inventorship

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[6] See also MPEP 201.03. Alternatively, Dr. Meng could be added as a coinventor in a continuing application under 37 CFR 1.53.

[7] See footnote 1.

[8] See footnote 2.

[9] See also MPEP 201.03. Alternatively, Dr. Meng could be added as a coinventor in a continuing application under 37 CFR 1.53.

designation in the originating country, Dr. Meng requests that Dr. Chu and UH take appropriate action to change the inventorship designation on all applicable non-US counterpart patents and patent applications. *See, e.g.,* PCT Receiving Office Guidelines, PCT Gazette Ch. XVI, ¶¶ 309-311 (World Intellectual Property Organization Aug. 28, 1998) (setting forth the procedures for recording a change in the applicant or inventor of PCT applications).[10]

V. Receipt of All Benefits Given to a UH Coinventor

As a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr. Meng also has a reputational interest in being recognized as a coinventor.

VI. Background and Discussion

A. Legal Standards

A review of the relevant facts in view of controlling Federal Circuit decisional law relating to section 256 clearly supports Dr. Meng's claim to coinventorship. For example, in Linear Technology Corp. v. Impala Linear, the Federal Circuit stated:

> A party seeking correction of inventorship must provide clear and convincing evidence of inventorship. Hess [v. Advanced Cardiovascular Sys., Inc.], 106 F.3d at 979-80 [(Fed. Cir. 1997)]; Ethicon, Inc. v. U.S. Surgical Corp., 135 F.3d 1456, 1461 (Fed. Cir. 1998). To meet the clear and convincing evidentiary burden, the alleged co-inventors must prove their contribution to the conception with more than their own testimony concerning the relevant facts. Trovan, Ltd. v. Sokymat SA, 299 F.3d 1292, 1302 (Fed. Cir. 2002) (citing Price v. Symsek, 988 F.2d 1187, 1194 (Fed. Cir. 1993)). Whether the co-inventor's testimony has been sufficiently corroborated is evaluated under a "rule of reason analysis," which requires that an "evaluation of all pertinent evidence must be made so that a sound determination of the credibility of the inventor's story may be reached." Price, 988 F.2d at 1195.

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[10] See Chou v. University of Chicago, 254 F.3d at 1360.

> Corroborating evidence may take many forms. Reliable evidence of corroboration preferably comes in the form of records made contemporaneously with the inventive process. Sandt Tech., Inc. v. Rosco Metal & Plastics Corp., 264 F.3d 1344, 1350-51 (Fed. Cir. 2001). Circumstantial evidence of an independent nature may also corroborate. Trovan, 299 F.3d at 1303. Additionally, oral testimony from someone other than the alleged inventor may corroborate. Id.

Linear Technology Corp. v. Impala Linear, 379 F.3d 1311, 1327 (Fed. Cir. 2004). See also Pannu v. Iolab Corp., 155 F.3d 1344, 1350 (Fed. Cir. 1998) ("[Section 256] is a savings provision. If a patentee demonstrates that inventorship can be corrected as provided for in section 256, a district court must order correction of the patent, thus saving it from being rendered invalid.").

Also, as outlined by the Federal Circuit in Eli Lilly And Company v. Aradigm Corp., 376 F.3d 1352, 1358-59 (Fed. Cir. 2004):

> Section 116 of Title 35 is the statutory locus of joint inventorship doctrine. It provides that a person not listed on a patent need not demonstrate that he made a contribution equal in importance to the contribution made by the listed inventors to claim his right to joint inventor status. See 35 U.S.C. § 116 (2000) ("Inventors may apply for a patent jointly even though (1) they did not physically work together or at the same time, (2) each did not make the same type or amount of contribution, or (3) each did not make a contribution to the subject matter of every claim of the patent."). In fact, section 116 "sets no explicit lower limit on the quantum or quality of inventive contribution required for a person to qualify as a joint inventor." Fina Oil & Chem. Co. v. Ewen, 123 F.3d 1466, 1473 (Fed. Cir. 1997). However a long line of decisions in this court holds that a person is a joint inventor only if he contributes to the conception of the claimed invention. See, e.g., C.R. Bard, Inc. v. M3 Sys., Inc., 157 F.3d 1340, 1352 (Fed. Cir. 1998); Fina Oil, 123 F.3d at 1473 ("The case law thus indicates that to be a joint inventor, an individual must make a contribution to the conception of the claimed invention that is not insignificant in quality, when that contribution is measured against the dimension of the full invention."); Sewall v. Walters, 21 F.3d 411, 415 (Fed. Cir. 1994); see also Burroughs Wellcome Co. v. Barr Labs., Inc., 40 F.3d 1223, 1227-28 (Fed. Cir. 1994) ("Conception is the touchstone of inventorship, the completion of the mental part of invention."). The line between actual contributions to conception and the remaining, more prosaic contributions to the inventive process that do not render the contributor a co-inventor is sometimes a difficult one to draw. Contributions to realizing an invention may not amount to a contribution to conception if they merely explain what was "then state of the art," Hess, 106 F.3d at 981, if they are too far

> removed from the real-world realization of an invention, see, e.g., Garret Corp., 422 F.2d at 881 ("One who merely suggests an idea of a result to be accomplished, rather than means of accomplishing it, is not a joint inventor."), or if they are focused solely on such realization, see, e.g., Ethicon, 135 F.3d at 1460 ("[O]ne does not qualify as a joint inventor by merely assisting the actual inventor after conception of the claimed invention.").
>
> It is however uncontroversial that the alleged joint inventor seeking to be listed on a patent must demonstrate that his labors were conjoined with the efforts of the named inventors. Joint inventorship under section 116 can only arise when collaboration or concerted effort occurs — that is, when the inventors have some open line of communication during or in temporal proximity to their inventive efforts:
>
> > What is clear is that the statutory word "jointly" is not mere surplusage. For persons to be joint inventors under Section 116, there must be some element of joint behavior, such as collaboration or working under common direction, one inventor seeing a relevant report and building upon it or hearing another's suggestion at a meeting. . . .
> >
> > [J]oint inventorship under Section 116 requires at least some quantum of collaboration or connection.
>
> Kimberly-Clark Corp. v. Procter & Gamble Distrib. Co., 973 F.2d 911, 917 (Fed. Cir. 1992).

Eli Lilly, 376 F.3d at 1358-59 (footnotes omitted).

B. Facts

A Review of the relevant facts will illustrate that Dr. Meng has clear and convincing evidence of her entitlement to be named as a coinventor of the '866 patent and its related applications and non-U.S. counterparts.

Dr. Meng is a materials scientist from China. Before she came to the U.S. she was a research scientist at the Chinese Academy of Science, Institute of Physics in Beijing, China (one of the top research institutes in China). In 1976, Dr. Meng began her research on superconducting materials in China. In 1979, Dr. Meng was invited by Dr. Chu to join his High Pressure Low Temperature research group at UH to serve as an independent materials scientist. During the time period 1979 to 1982, Dr. Meng set up the materials synthesis lab in Dr. Chu's group and began her independent synthesis of various types of materials and her studies of various superconducting compounds. Dr. Meng's expertise, in her capacity of visiting research scientist, permitted, for example, Dr. Chu's group to obtain materials samples directly from Dr. Meng, rather than being dependent upon other groups outside of UH to provide samples.

As a visiting scholar, Dr. Meng was required by her native country of China to return to China after 2 years. In 1981, Dr. Meng left UH at the invitation of Prof. Ernst Bucher to become a visiting scientist at the University of Konstanz, Germany. During this period, Dr. Meng continued her collaboration with Dr. Chu by providing him with more than 20 different types of superconducting single crystals for research. In mid 1982, Dr. Meng returned to the Institute of Physics in Beijing, China and continued the collaboration on superconducting materials with Dr. Chu for the next two years.

In July of 1984, Dr. Meng was invited again by Dr. Chu to return to UH as a visiting scientist. On her return to UH in July 1984 as a materials scientist, Dr. Meng independently conducted and supervised the research on superconducting and related materials, and she synthesized and characterized various compounds.

In mid-November of 1986, Dr. Meng learned from her colleague in China, Professor Z. X. Zhao, about the paper entitled: "Possible High Tc Superconductivity in the Ba-La-Cu-O System," by J.G. Bednorz and K.A. Muller. At that time, Dr. Chu was on leave and served at the National Science Foundation in Washington (he served there for about one year). Dr. Meng asked a graduate student, Li Gao, to go to the library to copy the paper on a Friday afternoon. Dr. Meng then placed a copy of the paper on Dr. Chu's desk. On Saturday morning Dr. Chu returned for a weekend visit to his office and discussed the paper with Dr. Meng. The paper reported that the wet-chemical method was used and it also indicated that the solid-state reaction processing might be difficult to obtain the superconducting phase. Dr. Ruling advised Dr. Chu that based on her knowledge and experience in the materials sciences (and with solid-state reactions), that a solid-state reaction method could be used to synthesize this material.

On November 14, 1986, Dr Meng was the first person to use the solid-state reaction methods to successfully repeat Dr. Bednorz' and Muller's results on Ba-La-Cu-O compounds. Subsequently, Dr. Meng optimized the processing conditions, such as the temperature, atmosphere, time and composition for this Ba-La-Cu-O system.

During 1987, the high temperature YBCO discovery took place within Dr. Chu's group. By February 27, 1987, Dr. Meng independently successfully separated black and green crystals from the mixed phase by studying a set of YBCO samples with different compositions. This work contributed to the conception of the High temperature YBCO formula and structure identified and claimed in the '866 patent. Subsequently, Dr. Meng continued to conduct high temperature superconductor material research within Dr. Chu's group and optimized the processing conditions for individual rare earth compounds and successfully synthesized a whole series of rare earth High temperature superconductors.

Additionally, in January 1988, Dr. Meng extended her work in the high Tc area on the Bi System ("BSCCO").

As illustrated in the accompanying PowerPoint presentation (on CD)("the presentation"), Dr. Meng's independent laboratory work clearly contributed to the conception of the claimed invention of the '866 patent (and the '956 application regarding BSCCO) in a manner that is not insignificant in quality, when that contribution is measured against the dimension of the full invention. The presentation highlights a direct correlation between Dr. Meng's laboratory notebook entries and the disclosure relied upon in the specification (Examples, etc.) and claims of the '866 patent. Dr. Meng's laboratory entries were contemporaneously made at relevant times just preceding the filing dates of the patent applications that ultimately issued as the '866 patent. These laboratory notebooks are of the most reliable type of evidence of corroboration of Dr. Meng's claim to be named a coinventor since her lab notebooks constitute records made contemporaneously with her inventive process. Sandt, 264 F.3d at 1350-51.

Dr. Chu was the head of his research group. As such, Dr. Meng worked in collaboration with Dr. Chu on a regular basis during this inventive process. Dr. Meng routinely shared with and reported to Dr. Chu her laboratory results, often on a daily basis, either in person or via telephone, and Dr. Chu provided input to Dr. Meng as well. This open line of communication existed during or in temporal proximity to their coinventive efforts and resulted in having Dr. Meng's laboratory work form a substantive contribution to the specifications as filed, and the conception of the claims as issued (or filed), in the applications leading to the '866 patent (and the pending '956 application).

Dr. Chu has always been the head of this research group at UH, and Dr. Meng has always worked in this group while employed at UH. However, Dr. Meng's research has always been independently conducted. She brought to UH a unique expertise in her field that was not otherwise found within Dr. Chu's group. Although Dr. Meng worked within Dr. Chu's research group, and Dr. Chu was technically her "boss" she was not "merely assisting" Dr. Chu, but instead was actively working in connection with Dr. Chu to jointly conceive of this invention. In other words, Dr. Meng is not merely another pair of hands for Dr. Chu, but instead her labors were conjoined with the efforts of Dr. Chu.

Dr. Meng has already been recognized on numerous occasions to be a coinventor with Dr. Chu. Thus far, Dr. Chu has seven (7) U.S. patents issued naming him as an inventor (in each case, as the first named inventor):

U.S. Patent No.	Filing Dates	Inventors	Patent counsel
7,056,866	12 Jan 87 26 Jan 87 6 Feb 87 26 Mar 87	Chu	Akin Gump
6,329,325	9 Jul 88	Chu, **Meng** & Xue	Akin Gump
5,563,564	22 Apr 93	Chu, Xue, Gao, **Meng** & Ramirez	Fulbright & Jaworski
5,578,551	28 Jul 93	Chu, **Meng** & Wang	Fulbright & Jaworski
6,025,769	7 Oct 96	Chu, Xue, Gao & **Meng**	Fulbright & Jaworski
5,906,964	15 Jun 97	Chu, **Meng** & Xue	Flehr …
6,239.080	6 Jul 99	Chu, Xue & Du	Akin Gump

Over the course of 12+ years, Dr. Meng was listed as a co-inventor with Dr. Chu on 5 of these 7 patents. Dr. Meng's level of inventive contribution as an independent materials scientist was recognized by Dr. Chu and three different sets of patent counsel. Dr. Meng's level of inventive contribution to the '866 patent appears to have been overlooked, perhaps owing to the fact that this was the very first patent application filed out of Dr. Chu's research group at UH. Back in early 1987, Dr. Meng thought she was to be a coinventor of the YBCO invention, but was totally unfamiliar with US patent law and USPTO procedures and as such, did not know she was left off of this application (or the '956 application) until recently.

Dr. Meng has approximately 237 peer-reviewed publications (2 being in press). Dr. Meng has served as a sub-editor for many conference proceedings and numerous invited talks delivered at domestic and international conferences. She is already recognized as a Coinventor with Dr. Chu on five U.S. patents. A current copy of Dr. Meng's CV is contained on the CD.

Dr. Meng, who is well recognized in her field, is Ranked 25th out of the 1000 most cited physicists from 1981-June 1997 by the Institute for Scientific Information (ISI) (http://www.sst.nrel.gov). She was identified as one of the world's most cited authors (less than 1/2 of 1 percent of all publishing researchers) by ISI Current Contents-2000, an updated list based on important scientific developments of the last two decades.

VII. Conclusion

In view of the foregoing facts, Dr. Meng's claim to being named a coinventor under the '866 patent and related applications and counterparts is well grounded under the law and supported by clear and convincing evidence. Although the pending related, unpublished applications other than the '956 CIP application, (e.g., the '063 application) have not been analyzed as of yet, Dr. Meng believes that for the reasons set out herein, the related applications likewise contain the joint inventive contributions and conceptions of Dr. Meng entitling her to be named as a joint inventor.

Based on the foregoing, Dr. Meng rightfully claims entitlement to be named as a co-inventor with Dr. Chu for the patents that were applied for by Dr. Chu during this time period relating to high temperature superconductors, such as, U.S. Patent No. 7,056,866, U.S. Patent Application Serial Nos. 07/300,063, and 163,956 and any other related U.S. or non-U.S. patents or patent applications.

In this connection, as a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr.

Meng is aware that certain revenue-generating transactions (be they assignments or licenses) have occurred in the past respecting these patents and patent applications and hereby requests an accounting to her for her fair share of such proceeds. Dr. Meng also has a reputational interest in being recognized as a coinventor.

I look forward to hearing from you at your earliest possible time to discuss moving forward with the above requested procedures and accounting. Dr. Meng stands ready to cooperate with UH and Dr. Chu in any filings required with the USPTO regarding her requests noted herein and is available to provide feedback on the correction of typographical errors in the '866 patent.

Very truly yours,

Gordon G. Waggett

Enclosures:

CD containing the following files:
(1) "Ruling Meng's Inventorship Presentation re '866 patent (26 Oct 06)" (.pfd format)
(2) "Ruling Meng's Inventorship Presentation re '866 patent (read only)(26 Oct 06)" (PowerPoint format)
(3) CV of Dr. Meng (.pdf format)

cc: Dr. Ruling Meng (with enclosures)

RULING MENG

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Education:

B.S. Central South University, Hunan, P.R. China (1958)

Employment History:

2002-present	Editorial Board of the Central European Journal of Physics.
1987-present	Senior Research Scientist, Department of Physics, Texas Center for Superconductivity at the University of Houston, Houston TX U.S.A.
1984-1986	Research Associate, Department of Physics, University of Houston, Houston TX
1982-1984	Research Associate, Institute of Physics, Academy of Science, Beijing, P. R. China
1981	Visiting Scholar, Department of Physics, University of Konstanz, West Germany
1979-1981	Research Associate, Department of Physics, University of Houston TX
1973-1979	Research Associate, Institute of Physics, Chinese Academy of Science, Beijing
1959-1973	Research Assistant, Metallurgy and Materials Science Division, Institute of Mining and Metallurgy, Academy of Science, P. R. China
1958-1959	Instructor, Central South University of Technology, Hunan, P. R. China

Honors and Awards:

Ranked 25th out of the 1000 most cited physicists from 1981- June 1997 by the Institute for Scientific Information (ISI) (http://www.sst.nrel.gov). Identified as one of the world's most cited authors (less than 1/2 of 1 percent of all publishing researchers) by *ISI Current Contents-2000,* updated list based on important scientific developments of the last two decades.

2004	Advisory Board member	Hainan University
2003	Honorary Professorship	Hainan Normal University.
2003	Honorary Professorship	Hainan University
1998	Honorary Professorship	Beijing Polytechnic University
1992	Honorary Professorship	Zhong-Shan University (Sun Yat-Sen University), P.R. China
1992	Honorary Professorship	Central South University of Technology, P.R. China
1992-	Senior Consultant	Chan-Sha Research Institute of Mining and Metallurgy, PRC

Member: Materials Research Society; Phi Beta Delta International Assn., Chinese Association of Professionals in Science and Technology (Houston: Founder/lst President)

Co-inventor on five patents

6,329,325 High temperature superconducting tape and method of manufacture

6,025,769 Strong high-temperature superconductor trapped field magnets

5,906,964 High temperature superconducting tape and method of manufacture

5,578,551 Method for synthesis of high-temperature Hg-Ba0ca-Cu-O(HBCCO) superconductors

5,563,564 Strong high-temperature superconductor trapped field magnets

Primary Research

Research Interests: Improving known high T_c superconductors and finding new compounds. Synthesis and characterization of alloy, intermetallic, and oxide superconductors in bulk and think film. Single crystal growth, tape and coated conductor processes.

Research Highlights:

- Primary research interests are in superconducting and other related materials.
- **1987** Major contribution on the discovery of the high temperature superconducting Y-Ba-Cu-O system.
- **1990** First to succeed in fabricating texturing Y-Ba-Ca-O bar.
- **1991** Obtained first record trapped field of 8 T at 4.2 k by 20 mm dia x 6mm YBCO disks.
- **1991** Obtained first record shielding field of >19 T at 4.2 k by 20mm x 6 mm YBCO disks.
- **1991** First to grow C-60 single crystal with no defect.
- **1993** First to develop and patent the processing techniques for highest transition superconducting temperature Hg-Ba-Ca-Cu-O, and co-developed the first Hg-1212 film.
- **1996** First to succeed in fabricating Hg-1223 tapes.
- **1998** First to succeed in fabricating Bi -Sr-Ca- Cu-O on a low cost Ni metal substrate.

Recent Research Highlights:

Primary research interests are in research for superconducting and other related materials.

- Study of Binary and pseudo-binary intermetallic compound with AIB_2 structure. Discovery two new intermetallic superconductors.
- Search for and study of Novel HTSg and Related Compounds. Such as: study the unconventional superconductivity and Electron correlation in Cobalt Oxyhydrate $NaO._{35}CoO_2.yH2O$.
- Investigated on the enhancement of flux pinning and critical currents in $YBa_2Cu_3O_x$ films by cation substitution.
- Enhance the flux pinning in YBCO films by pre-decoration of substrate surfaces with metal or oxide nano-scale partial .The critical current enhance a factor of 2-3.
- Develop a new and efficient method to obtain enhanced pinning and critical current density in $YBa_2Cu_3O_x$ films by grown on $Nd_{1/3}Eu_{1/3}Gd_{1/3}Ba_2Cu_3O_x$ with nano-undulated surface morphology. Clarify the origin of this pinning enhancement. The YBCO on NEG gives an enhancement in j_c of 50%-100% between 5 K and 77 K.

PUBLICATIONS

Total publications ~250. Sub-editor for many conference proceedings; numerous invited talks delivered at domestic and international conferences.

1. "The Research on Nb-Al-Ge Bulk Sample by Powder Sintered Method," R. L. Meng, Wuhan Conference, China (1974).

2. "Levitation Melting Method of Preparing A-15 Structure Nb_3Si," R. L. Meng, ACTA Physica Temperature Humilis Sinica, 27(5) (September 1978).

3. "A Better Sputtering Apparatus," R. L. Meng, G. Y. Gui, B. R. Zha, S. Q. Guo, L. Li, ACTA Physica Temperature Humilis Sinica, 2(4) (1980).

4. "Absence of Pressure-Induced Valence Charge in CeAs," A. Werner, H. O. Hoehhimer, R. L. Meng, E. Bucher, Physica Lett., 97A(5) (1983).

5. "High Pressure Study on CeSb and CeBi," P. H. Hor, R. L. Meng, S. Yomo, C. W. Chu, E. Bucher, P. H. Schmidt, Physica B 139 & 140, 378 (1986).

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7. "High Pressure Study on the Anomalous Rare-Earth Ternaries $Eu_{1.2}Mo_6S_8$ and $Eu_{1.2}Mo_6Se_8$," C. W. Chu, S. Z. Huang, J. H. Lin, R. L. Meng, M. K. Wu and P. H. Schmidt, Phys. Rev. Lett. 46, 276 (1981).

8. "The Peculiar Superconducting Properties in $Eu_{1.2}Mo_6S_8$ Under Pressure," C. W. Chu, S. Z. Huang, C. H. Lin, R. L. Meng, M. K. Wu and P. H. Schmidt, Ternary Superconductors (Amsterdam: North Holland, 1980), p. 103.

9. "The Exceptionally Corrosion-Resistant Alloys Mo-Ru-X (X = Fe, Co and Ni)," R. L. Meng, S. Z. Huang and C. W. Chu, Appl. Phys. Lett. 38, 339 (1981).

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13. "Pressure Induced Non-Bulk Superconductivity in $Eu_{1.2}Mo_6(S_{1-x}Se_x)_8$," R. L. Meng, T. H. Lin, M. K. Wu, C. W. Chu and S. Z. Huang, J. Low Temp. Phys. 48, 383 (1982).

14. "Distinct In T-Dependent Resistance of $Ce_{1.2}Mo_6S_8$ Under High Pressure," M. K. Wu, V. Diatschenko, P. H. Hor, S. Z. Huang, T. H. Lin, R. L. Meng, D. L. Zhang and C. W. Chu, Phys. Rev. 25, 3377 (1982).

15. "Specific Heat of V_3GaH_x," B. Gort, G. R. Stewart, S. Z. Huang, R. L. Meng and C. W. Chu, O. K. (Los Angeles, 1981); Phys. Rev. B 24, 4075 (1981).

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20. "High Pressure Study on Quasi-One-Dimensional Compounds $M_2Mo_6X_2$," P. H. Hor, R. L. Meng, C. W. Chu and J. M. Tarascon, Physica B 135, 245 (1985).

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42. “Electron Microscopy of a Gd-Ba-Cu-O Superconductor,” R. Ramesh, G. Thomas, R. L. Meng, P. H. Hor and C. W. Chu, J. Mater. Res. 4, 515 (1989).

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45. “Softening of Cu-O Vibrational Modes as a Precursor to Onset of Superconductivity in $EuBa_2Cu_3O_{7-\delta}$,” P. Boolchand, R. N. Enzweiler, Ivan Zitkovsky, Jack Wells, Wayne Bresser, Darl McDaniel, R. L. Meng, P. H. Hor, C. W. Chu and C. Y. Huang, Phys. Rev. B 37, 3766 (1988).

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Evidence Supporting Dr. Ruling Meng's Entitlement to be Named as a Coinventor with Dr. Chu on U.S. Patent No. 7,056,866 and its related applications and foreign counterparts

Submitted to:
The University of Houston and Dr. Ching-Wu (Paul) Chu
through their counsel, Lester L. Hewitt,
Akin, Gump, Akin Gump Strauss Hauer & Feld LLP
October 26, 2006
By:

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Dr. Meng Respectfully Requests the Following From UH and Dr. Chu:

I. Certification of Correction of U.S. Patent No. 7,056,866

Pursuant to 35 U.S.C § 256, 37 C.F.R. § 1.324, Dr. Meng seeks the agreement of Dr. Chu and UH to submit a joint application with her to the Director of the USPTO seeking a Certificate of Correction of Inventorship to add Dr. Meng as a named coinventor of U.S. Patent No. 7,056, 866 ("the '866 patent") along with Dr. Chu.

II. Certification of Correction of U.S. Patent Application Serial No. 07/300,063

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 07/300,063 ("the '063 application")(and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.

III. Certification of Correction of U.S. Patent Application Serial No. 163,956 filed March 3, 1988

Similarly, pursuant to 35 U.S.C § 116, 37 C.F.R. § 1.48(a), Dr. Meng seeks the agreement of Dr. Chu and UH to the filing with the USPTO of a request to correct the inventorship of pending U.S. Patent Application Serial No. 163,956 ("the '956 application")(and any other related pending application) to add Dr. Meng as a named coinventor along with Dr. Chu.

IV. Correction of Inventorship in all Non-US Counterpart Patents and Patent Applications

Dr. Meng claims entitlement to be named as a coinventor on all applicable non-U.S. counterpart patent applications as well. Dr. Meng is presently aware of the existence of non-U.S. counterpart applications, but does not have a complete identification of these applications. Since inventorship on such applications normally follows the inventorship designation in the originating country, Dr. Meng requests that Dr. Chu and UH take appropriate action to change the inventorship designation on all applicable non-US counterpart patents and patent applications.

V. Receipt of All Benefits Given to a UH Coinventor

As a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr. Meng also has a reputational interest in being recognized as a coinventor.

Dr. Meng is an Inventor

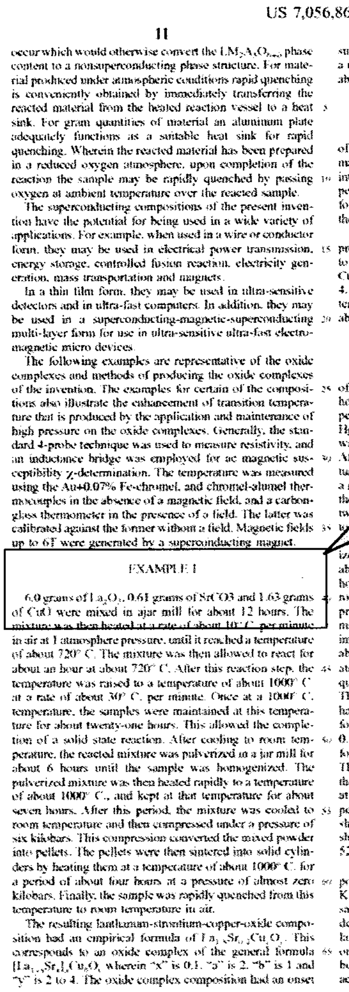
Dr. Meng has already been recognized on numerous occasions to be a coinventor with Dr. Chu. Thus far, Dr. Chu has seven (7) U.S. patents issued naming him as an inventor (in each case, as the first named inventor):

U.S. Patent No.	Filing Date	Inventors	Patent Counsel
7,056,866	26 Mar 87	Chu	AG
6,329,325	9 Jul 88	Chu, **Meng** & Xue	AG
5,563,564	22 Apr 93	Chu, Xue, Gao, **Meng** & Ramirez	F&J
5,578,551	28 Jul 93	Chu, **Meng** & Wang	F&J
6,025,769	7 Oct 96	Chu, Xue, Gao & **Meng**	F&J
5,906,964	15 Jun 97	Chu, **Meng** & Xue	Flehr …
6,239.080	6 Jul 99	Chu, Xue & Du	AG

Over the course of 12+ years, Dr. Meng was listed as a co-inventor with Dr. Chu on 5 of these 7 patents. Dr. Meng's level of inventive contribution as an independent materials scientist was recognized by Dr. Chu and three different sets of patent counsel. Dr. Meng's level of inventive contribution to the '866 patent appears to have been overlooked, perhaps owing to the fact that this was the very first patent application filed out of Dr. Chu's research group at UH. Back in early 1987, Dr. Meng thought she was to be a coinventor of the YBCO invention, but was totally unfamiliar with US patent law and USPTO procedures and as such, did not know she was left off of the '866 applications until recently.

Clear and Convincing Evidence of Coinventorship

Dr. Meng's independent laboratory work clearly contributed to the conception of the claimed invention of the '866 patent in a manner that is not insignificant in quality, when that contribution is measured against the dimension of the full invention. The following slides highlight a direct correlation between Dr. Meng's laboratory notebook entries and the disclosure relied upon in the specification (Examples, etc.) and claims of the '866 patent. Dr. Meng's laboratory entries were contemporaneously made at relevant times just preceding the filing dates of the patent applications that ultimately issued as the '866 patent.



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occur which would otherwise convert the $LM_2A_1O_{4-y}$ phase content to a nonsuperconducting phase structure. For material produced under atmospheric conditions rapid quenching is conveniently obtained by immediately transferring the reacted material from the heated reaction vessel to a heat sink. For gram quantities of material an aluminum plate adequately functions as a suitable heat sink for rapid quenching. Wherein the reacted material has been prepared in a reduced oxygen atmosphere, upon completion of the reaction the sample may be rapidly quenched by passing oxygen at ambient temperature over the reacted sample.

The superconducting compositions of the present invention have the potential for being used in a wide variety of applications. For example, when used in a wire or conductor form, they may be used in electrical power transmission, energy storage, controlled fusion reaction, electricity generation, mass transportation and magnets.

In a thin film form, they may be used in ultra-sensitive detectors and in ultra-fast computers. In addition, they may be used in a superconducting-magnetic-superconducting multi-layer form for use in ultra-sensitive ultra-fast electromagnetic micro devices.

The following examples are representative of the oxide complexes and methods of producing the oxide complexes of the invention. The examples for certain of the compositions also illustrate the enhancement of transition temperature that is produced by the application and maintenance of high pressure on the oxide complexes. Generally, the standard 4-probe technique was used to measure resistivity, and an inductance bridge was employed for ac magnetic susceptibility χ-determination. The temperature was measured using the Au+0.07% Fe-chromel, and chromel-alumel thermocouples in the absence of a magnetic field, and a carbon-glass thermometer in the presence of a field. The latter was calibrated against the former without a field. Magnetic fields up to 6T were generated by a superconducting magnet.

EXAMPLE I

6.0 grams of La_2O_3, 0.61 grams of SrCO3 and 1.63 grams of CuO were mixed in ajar mill for about 12 hours. The mixture was then heated at a rate of about 10° C. per minute in air at 1 atmosphere pressure, until it reached a temperature of about 720° C. The mixture was then allowed to react for about an hour at about 720° C. After this reaction step, the temperature was raised to a temperature of about 1000° C. at a rate of about 30° C. per minute. Once at a 1000° C. temperature, the samples were maintained at this temperature for about twenty-one hours. This allowed the completion of a solid state reaction. After cooling to room temperature, the reacted mixture was pulverized in a jar mill for about 6 hours until the sample was homogenized. The pulverized mixture was then heated rapidly to a temperature of about 1000° C., and kept at that temperature for about seven hours. After this period, the mixture was cooled to room temperature and then compressed under a pressure of six kilobars. This compression converted the mixed powder into pellets. The pellets were then sintered into solid cylinders by heating them at a temperature of about 1000° C. for a period of about four hours at a pressure of almost zero kilobars. Finally, the sample was rapidly quenched from this temperature to room temperature in air.

The resulting lanthanum-strontium-copper-oxide composition had an empirical formula of $La_{1.8}Sr_{0.2}Cu_1O_4$. This corresponds to an oxide complex of the general formula $[La_{1-x}Sr_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is 2 to 4. The oxide complex composition had an onset

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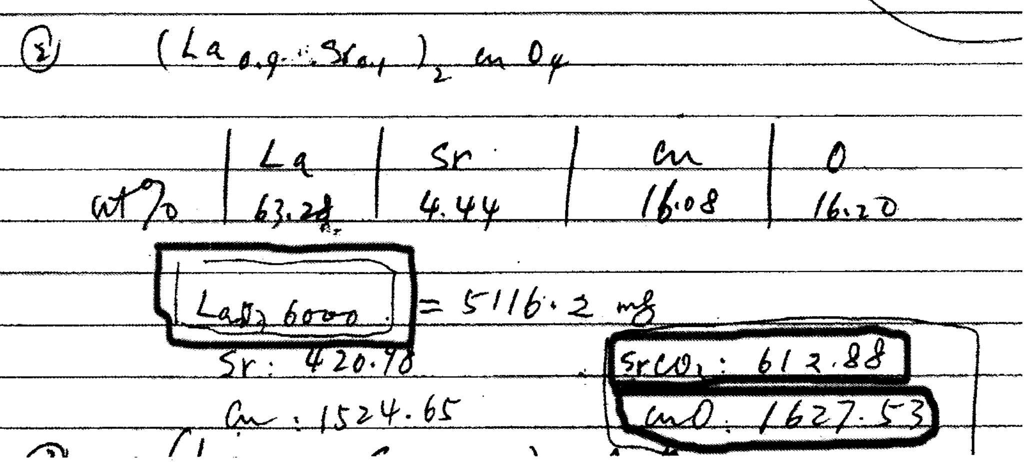
EXAMPLE I

"6.0 grams of La_2O_3, 0.61 grams of $SrCO_3$ and 1.63 grams of CuO were mixed in ajar mill for about 12 hours."

From p. H 12, Meng's Lab Notebook (23 Dec 86):



② $(La_{0.9}Sr_{0.1})_2CuO_4$

	La	Sr	Cu	O
wt%	63.28	4.44	16.08	16.20

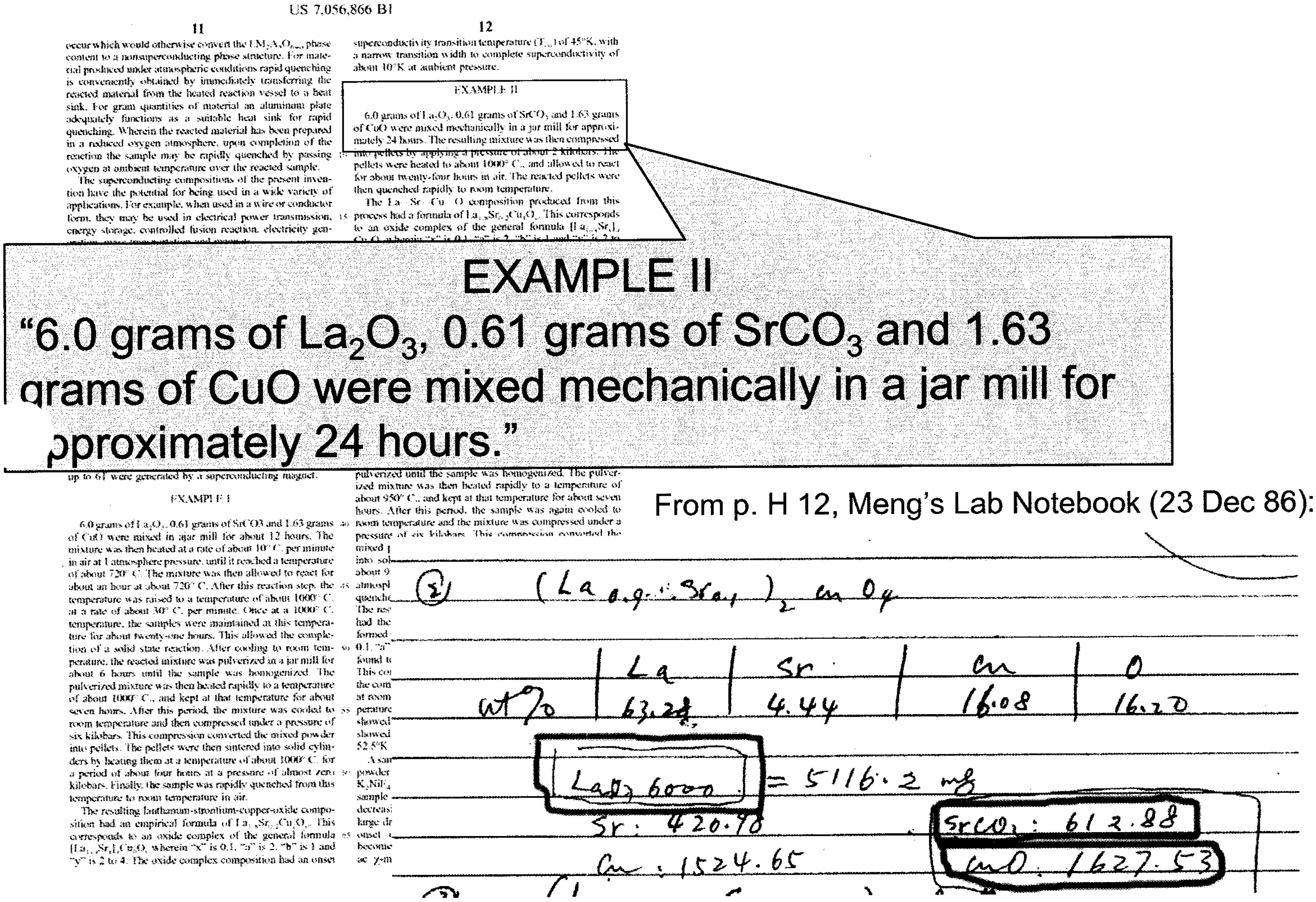
La_2O_3 6000 = 5116.2 mg

Sr: 420.78

$SrCO_3$: 612.88

Cu: 1524.65

CuO: 1627.53



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occur which would otherwise convert the LM_yA_xO phase content to a nonsuperconducting phase structure. For material produced under atmospheric conditions rapid quenching is conveniently obtained by immediately transferring the reacted material from the heated reaction vessel to a heat sink. For gram quantities of material an aluminum plate adequately functions as a suitable heat sink for rapid quenching. Wherein the reacted material has been prepared in a reduced oxygen atmosphere, upon completion of the reaction the sample may be rapidly quenched by passing oxygen at ambient temperature over the reacted sample.

The superconducting compositions of the present invention have the potential for being used in a wide variety of applications. For example, when used in a wire or conductor form, they may be used in electrical power transmission, energy storage, controlled fusion reaction, electricity gen-

up to 6T were generated by a superconducting magnet.

EXAMPLE I

6.0 grams of La_2O_3, 0.61 grams of SrCO3 and 1.63 grams of CuO were mixed in a jar mill for about 12 hours. The mixture was then heated at a rate of about 10° C. per minute in air at 1 atmosphere pressure, until it reached a temperature of about 720° C. The mixture was then allowed to react for about an hour at about 720° C. After this reaction step, the temperature was raised to a temperature of about 1000° C. at a rate of about 30° C. per minute. Once at a 1000° C. temperature, the samples were maintained at this temperature for about twenty-one hours. This allowed the completion of a solid state reaction. After cooling to room temperature, the reacted mixture was pulverized in a jar mill for about 6 hours until the sample was homogenized. The pulverized mixture was then heated rapidly to a temperature of about 1000° C., and kept at that temperature for about seven hours. After this period, the mixture was cooled to room temperature and then compressed under a pressure of six kilobars. This compression converted the mixed powder into pellets. The pellets were then sintered into solid cylinders by heating them at a temperature of about 1000° C. for a period of about four hours at a pressure of almost zero kilobars. Finally, the sample was rapidly quenched from this temperature to room temperature in air.

The resulting lanthanum-strontium-copper-oxide composition had an empirical formula of $La_{1.8}Sr_{0.2}Cu_1O_y$. This corresponds to an oxide complex of the general formula $[La_{1-x}Sr_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is 2 to 4. The oxide complex composition had an onset

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superconductivity transition temperature (T_{co}) of 45°K, with a narrow transition width to complete superconductivity of about 10°K at ambient pressure.

EXAMPLE II

6.0 grams of La_2O_3, 0.61 grams of $SrCO_3$ and 1.63 grams of CuO were mixed mechanically in a jar mill for approximately 24 hours. The resulting mixture was then compressed into pellets by applying a pressure of about 2 kilobars. The pellets were heated to about 1000° C., and allowed to react for about twenty-four hours in air. The reacted pellets were then quenched rapidly to room temperature.

The La–Sr–Cu–O composition produced from this process had a formula of $La_{1.8}Sr_{0.2}Cu_1O_y$. This corresponds to an oxide complex of the general formula $[La_{1-x}Sr_x]_a$

pulverized until the sample was homogenized. The pulverized mixture was then heated rapidly to a temperature of about 950° C., and kept at that temperature for about seven hours. After this period, the sample was again cooled to room temperature and the mixture was compressed under a pressure of six kilobars. This compression converted the

EXAMPLE II

"6.0 grams of La_2O_3, 0.61 grams of $SrCO_3$ and 1.63 grams of CuO were mixed mechanically in a jar mill for approximately 24 hours."

From p. H 12, Meng's Lab Notebook (23 Dec 86):

② $(La_{0.9}Sr_{0.1})_2CuO_4$

	La	Sr	Cu	O
wt%	63.28	4.44	16.08	16.20

La_2O_3 6000 = 5116.2 mg

Sr: 420.98

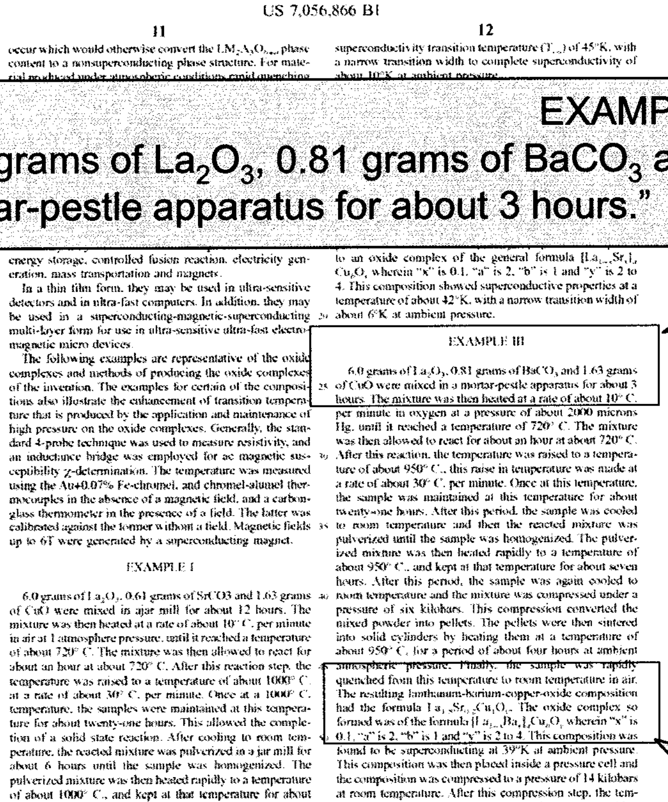
Cu: 1524.65

$SrCO_3$: 612.88

CuO: 1627.53

EXAMPLE III

"6.0 grams of La_2O_3, 0.81 grams of $BaCO_3$ and 1.63 grams of CuO were mixed in a mortar-pestle apparatus for about 3 hours."



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occur which would otherwise convert the $LM_2A_3O_{8\pm\delta}$ phase content to a nonsuperconducting phase structure. For mate-

energy storage, controlled fusion reaction, electricity generation, mass transportation and magnets.

In a thin film form, they may be used in ultra-sensitive detectors and in ultra-fast computers. In addition, they may be used in a superconducting-magnetic-superconducting multi-layer form for use in ultra-sensitive ultra-fast electromagnetic micro devices.

The following examples are representative of the oxide complexes and methods of producing the oxide complexes of the invention. The examples for certain of the compositions also illustrate the enhancement of transition temperature that is produced by the application and maintenance of high pressure on the oxide complexes. Generally, the standard 4-probe technique was used to measure resistivity, and an inductance bridge was employed for ac magnetic susceptibility χ-determination. The temperature was measured using the Au+0.07% Fe-chromel, and chromel-alumel thermocouples in the absence of a magnetic field, and a carbon-glass thermometer in the presence of a field. The latter was calibrated against the former without a field. Magnetic fields up to 6T were generated by a superconducting magnet.

EXAMPLE I

6.0 grams of La_2O_3, 0.61 grams of SrCO3 and 1.63 grams of CuO were mixed in a jar mill for about 12 hours. The mixture was then heated at a rate of about 10° C. per minute in air at 1 atmosphere pressure, until it reached a temperature of about 720° C. The mixture was then allowed to react for about an hour at about 720° C. After this reaction step, the temperature was raised to a temperature of about 1000° C. at a rate of about 30° C. per minute. Once at a 1000° C. temperature, the samples were maintained at this temperature for about twenty-one hours. This allowed the completion of a solid state reaction. After cooling to room temperature, the reacted mixture was pulverized in a jar mill for about 6 hours until the sample was homogenized. The pulverized mixture was then heated rapidly to a temperature of about 1000° C., and kept at that temperature for about seven hours. After this period, the mixture was cooled to room temperature and then compressed under a pressure of six kilobars. This compression converted the mixed powder into pellets. The pellets were then sintered into solid cylinders by heating them at a temperature of about 1000° C. for

superconductivity transition temperature (T_{c0}) of 45°K, with a narrow transition width to complete superconductivity of

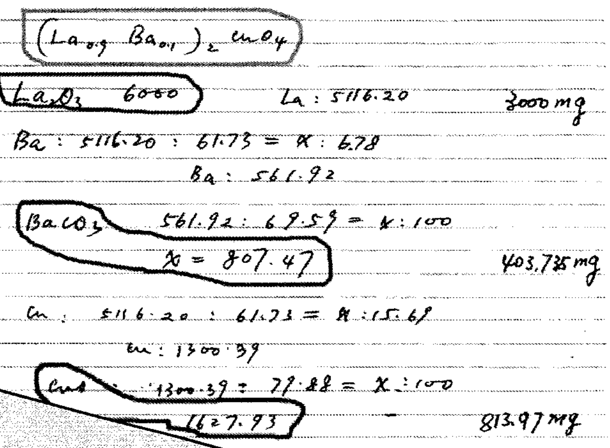
to an oxide complex of the general formula $[La_{1-x}Sr_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is 2 to 4. This composition showed superconductive properties at a temperature of about 42°K, with a narrow transition width of about 6°K at ambient pressure.

EXAMPLE III

6.0 grams of La_2O_3, 0.81 grams of $BaCO_3$ and 1.63 grams of CuO were mixed in a mortar-pestle apparatus for about 3 hours. The mixture was then heated at a rate of about 10° C. per minute in oxygen at a pressure of about 2000 microns Hg, until it reached a temperature of 720° C. The mixture was then allowed to react for about an hour at about 720° C. After this reaction, the temperature was raised to a temperature of about 950° C., this raise in temperature was made at a rate of about 30° C. per minute. Once at this temperature, the sample was maintained at this temperature for about twenty-one hours. After this period, the sample was cooled to room temperature and then the reacted mixture was pulverized until the sample was homogenized. The pulverized mixture was then heated rapidly to a temperature of about 950° C., and kept at that temperature for about seven hours. After this period, the sample was again cooled to room temperature and the mixture was compressed under a pressure of six kilobars. This compression converted the mixed powder into pellets. The pellets were then sintered into solid cylinders by heating them at a temperature of about 950° C. for a period of about four hours at ambient atmospheric pressure. Finally, the sample was rapidly quenched from this temperature to room temperature in air. The resulting lanthanum-barium-copper-oxide composition had the formula $La_{1.8}Sr_{0.2}Cu_1O_y$. The oxide complex so formed was of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is 2 to 4. This composition was found to be superconducting at 39°K at ambient pressure. This composition was then placed inside a pressure cell and the composition was compressed to a pressure of 14 kilobars at room temperature. After this compression step, the temperature was gradually reduced until the composition showed superconducting properties. This composition showed superconductivity properties at a temperature of 52.5°K at the applied pressure of 10 kilobars.

A sample prepared as described above exhibits only X-ray

From p. H 11, Meng's Lab Notebook:



J-6 $(La_{0.9}Ba_{0.1})_2CuO_4$

La_2O_3 6000 La : 5116.20 3000 mg

Ba : 5116.20 : 61.73 = x : 6.78

Ba : 561.92

$BaCO_3$ 561.92 : 69.59 = x : 100

x = 807.47 403.735 mg

Cu : 5116.20 : 61.73 = x : 15.69

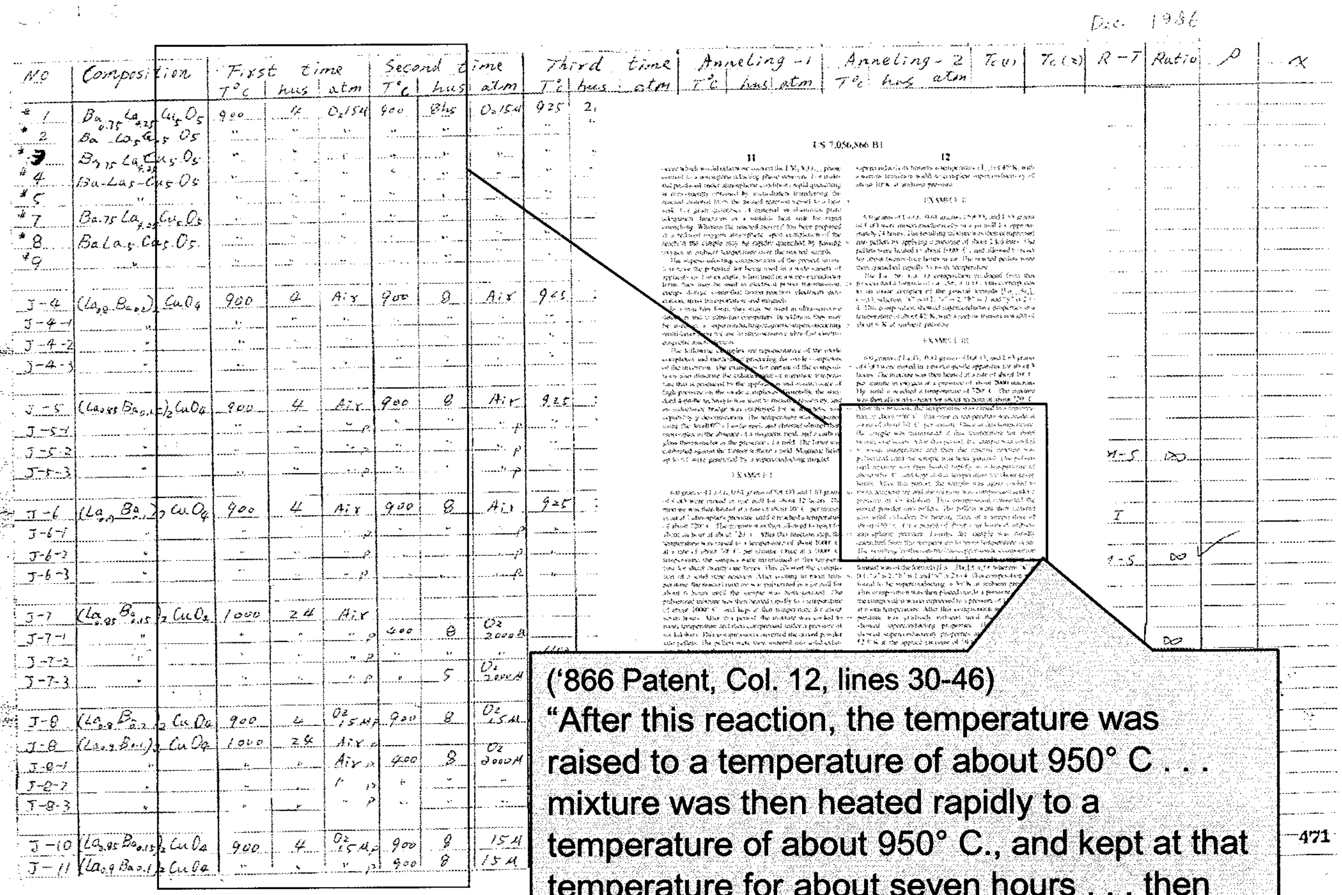
Cu : 1300.39

CuO : 1300.39 : 79.88 = x : 100

1627.93 813.97 mg

"The resulting lanthanum-barium-copper-oxide composition had the formula $La_{1.8}Sr_{0.2}Cu_1O_y$. The oxide complex so formed was of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is 2 to 4." (Sr should be Ba – typographical error)

From p. H 471, Meng's Lab Notebook:



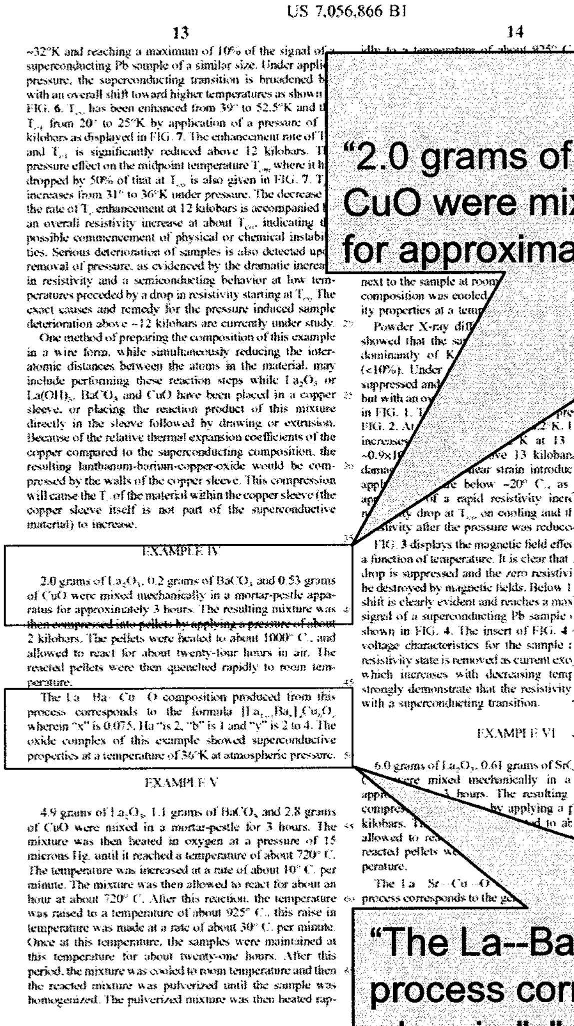
Dec. 1986

NO	Composition	First time T°C	hrs	atm	Second time T°C	hrs	atm	Third time T°C	hrs	atm	Anneling-1 T°C	hrs	atm	Anneling-2 T°C	hrs	atm	Tc(1)	Tc(2)	R-T	Ratio	ρ	α
*1	$Ba_{0.75}La_{4.25}Cu_5O_5$	900	4	O_2 15M	900	8hs	O_2 15M	925	2.													
*2	$Ba\ La_5Cu_5O_5$	"	"	"	"	"	"	"	"													
*3	$B_{.75}La_{4.25}Cu_5O_5$	"	"	"	"	"	"	"	"													
*4	$Ba\text{-}La_5\text{-}Cu_5O_5$	"	"	"	"	"		"	"													
*5	"		"	"	"	"		"														
*7	$Ba_{.75}La_{4.25}Cu_5O_5$			"	"	"																
*8	$BaLa_5Cu_5O_5$			"		"																
*9	"					"																
J-4	$(La_{0.9}Ba_{0.1})_2CuO_4$	900	4	Air	900	8	Air	925														
J-4-1	"	"	"	"		"		"														
J-4-2	"	"						"														
J-4-3	"	"		"	"			"														
J-5	$(La_{0.85}Ba_{0.15})_2CuO_4$	900	4	Air	900	8	Air	925														
J-5-1		"		" p	"	"	" p	"														
J-5-2	"			" p	"		" p	"											M-S	∞		
J-5-3	"	"	"	" p	"		" p															
J-6	$(La_{0.9}Ba_{0.1})_2CuO_4$	900	4	Air	900	8	Air	925											I			
J-6-1	"			" p	"	"	" p	"														
J-6-2	"	"	"	" p			" p												M-S	∞	✓	
J-6-3	"	"	"	" p			" p	"														
J-7	$(La_{0.85}Ba_{0.15})_2CuO_4$	1000	24	Air																		
J-7-1	"	"	"	" p	400	8	O_2 2000A													∞		
J-7-2	"	"	"	" p	"	"	"															
J-7-3	"	"	"	" p	"	5	O_2 2000A															
J-8	$(La_{0.8}Ba_{0.2})_2CuO_4$	900	4	O_2 15M,p	900	8	O_2 15M															
J-8	$(La_{0.9}Ba_{0.1})_2CuO_4$	1000	24	Air "			O_2 2000M															
J-8-1	"	"	"	Air "	400	8																
J-8-2	"	"	"	" p	"	"	"															
J-8-3	"	"	"	" p	"	"	"															
J-10	$(La_{0.85}Ba_{0.15})_2CuO_4$	900	4	O_2 15M,p	900	8	15M															
J-11	$(La_{0.9}Ba_{0.1})_2CuO_4$	"	"	" p	900	8	15M															

471

('866 Patent, Col. 12, lines 30-46)

"After this reaction, the temperature was raised to a temperature of about 950° C . . . mixture was then heated rapidly to a temperature of about 950° C., and kept at that temperature for about seven hours . . . then sintered into solid cylinders by heating them at a temperature of about 950° C. for a period of about four hours at ambient atmospheric pressure."



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~32°K and reaching a maximum of 10% of the signal of
superconducting Pb sample of a similar size. Under appli
pressure, the superconducting transition is broadened b
with an overall shift toward higher temperatures as shown
FIG. 6. T_{co} has been enhanced from 39° to 52.5°K and t
T_{c1} from 20° to 25°K by application of a pressure of
kilobars as displayed in FIG. 7. The enhancement rate of T
and T_{c1} is significantly reduced above 12 kilobars. T
pressure effect on the midpoint temperature T_{cm} where it h
dropped by 50% of that at T_{co} is also given in FIG. 7. T
increases from 31° to 36°K under pressure. The decrease
the rate of T_c enhancement at 12 kilobars is accompanied
an overall resistivity increase at about T_{co}, indicating t
possible commencement of physical or chemical instabi
ties. Serious deterioration of samples is also detected up
removal of pressure, as evidenced by the dramatic increa
in resistivity and a semiconducting behavior at low temperatures preceded by a drop in resistivity starting at T_{co}. The exact causes and remedy for the pressure induced sample deterioration above ~12 kilobars are currently under study.

One method of preparing the composition of this example in a wire form, while simultaneously reducing the interatomic distances between the atoms in the material, may include performing these reaction steps while La_2O_3 or $La(OH)_3$, $BaCO_3$ and CuO have been placed in a copper sleeve, or placing the reaction product of this mixture directly in the sleeve followed by drawing or extrusion. Because of the relative thermal expansion coefficients of the copper compared to the superconducting composition, the resulting lanthanum-barium-copper-oxide would be compressed by the walls of the copper sleeve. This compression will cause the T_c of the material within the copper sleeve (the copper sleeve itself is not part of the superconductive material) to increase.

EXAMPLE IV

2.0 grams of La_2O_3, 0.2 grams of $BaCO_3$ and 0.53 grams of CuO were mixed mechanically in a mortar-pestle apparatus for approximately 3 hours. The resulting mixture was then compressed into pellets by applying a pressure of about 2 kilobars. The pellets were heated to about 1000° C. and allowed to react for about twenty-four hours in air. The reacted pellets were then quenched rapidly to room temperature.

The La--Ba--Cu--O composition produced from this process corresponds to the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.075, "a" is 2, "b" is 1 and "y" is 2 to 4. The oxide complex of this example showed superconductive properties at a temperature of 36°K at atmospheric pressure.

EXAMPLE V

4.9 grams of La_2O_3, 1.1 grams of $BaCO_3$ and 2.8 grams of CuO were mixed in a mortar-pestle for 3 hours. The mixture was then heated in oxygen at a pressure of 15 microns Hg. until it reached a temperature of about 720° C. The temperature was increased at a rate of about 10° C. per minute. The mixture was then allowed to react for about an hour at about 720° C. After this reaction, the temperature was raised to a temperature of about 925° C., this raise in temperature was made at a rate of about 30° C. per minute. Once at this temperature, the samples were maintained at this temperature for about twenty-one hours. After this period, the mixture was cooled to room temperature and then the reacted mixture was pulverized until the sample was homogenized. The pulverized mixture was then heated rap-

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next to the sample at room
composition was cooled
ity properties at a temp

Powder X-ray diff
showed that the sa
dominantly of K
(<10%). Under
suppressed and
but with an ov
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FIG. 2. At
increase
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damag
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sivity after the pressure was reduc

FIG. 3 displays the magnetic field effe
a function of temperature. It is clear that
drop is suppressed and the zero resistivi
be destroyed by magnetic fields. Below
shift is clearly evident and reaches a max
signal of a superconducting Pb sample
shown in FIG. 4. The insert of FIG. 4
voltage characteristics for the sample
resistivity state is removed as current exc
which increases with decreasing temp
strongly demonstrate that the resistivity
with a superconducting transition.

EXAMPLE VI

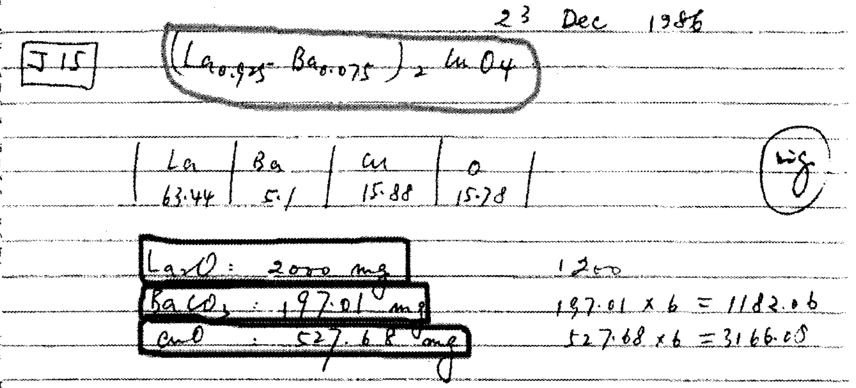
6.0 grams of La_2O_3, 0.61 grams of Sr
C were mixed mechanically in a
appr 3 hours. The resulting
compre by applying a
kilobars.
allowed to re hours in air. The
reacted pellets w room temperature.

The La--Sr--Cu--O
process corresponds to the ge

EXAMPLE IV

"2.0 grams of La_2O_3, 0.2 grams of $BaCO_3$ and 0.53 grams of CuO were mixed mechanically in a mortar-pestle apparatus for approximately 3 hours."

From p. H 14, Meng's Lab Notebook:



23 Dec 1986

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$(La_{0.925}Ba_{0.075})_2CuO_4$

La	Ba	Cu	O
63.44	5.1	15.88	15.78

mg

La_2O : 2000 mg

$BaCO_3$: 197.01 mg

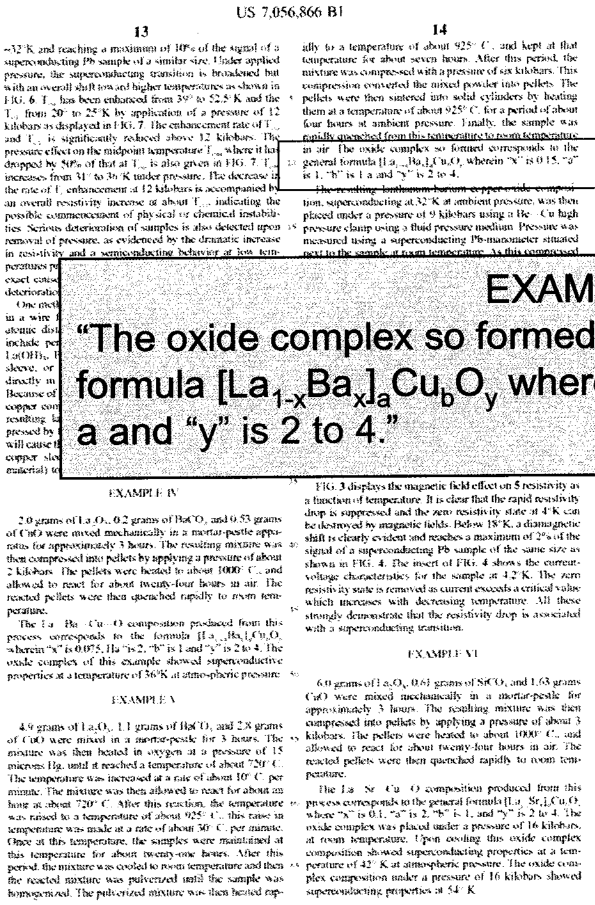
CuO : 527.68 mg

1200

197.01 x 6 = 1182.06

527.68 x 6 = 3166.08

"The La--Ba--Cu--O composition produced from this process corresponds to the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.075, "a" is 2, "b" is 1 and "y" is 2 to 4."



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~32°K and reaching a maximum of 10% of the signal of a superconducting Pb sample of a similar size. Under applied pressure, the superconducting transition is broadened but with an overall shift toward higher temperatures as shown in FIG. 6. T_{co} has been enhanced from 39° to 52.5°K and the T_{c1} from 20° to 25°K by application of a pressure of 12 kilobars as displayed in FIG. 7. The enhancement rate of T_{co} and T_{c1} is significantly reduced above 12 kilobars. The pressure effect on the midpoint temperature T_{cm} where it has dropped by 50% of that at T_{co} is also given in FIG. 7. T_{cm} increases from 31° to 36°K under pressure. The decrease in the rate of T_c enhancement at 12 kilobars is accompanied by an overall resistivity increase at about T_{co}, indicating the possible commencement of physical or chemical instabilities. Serious deterioration of samples is also detected upon removal of pressure, as evidenced by the dramatic increase in resistivity and a semiconducting behavior at low temperatures p

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EXAMPLE IV

2.0 grams of La_2O_3, 0.2 grams of $BaCO_3$ and 0.53 grams of CuO were mixed mechanically in a mortar-pestle apparatus for approximately 3 hours. The resulting mixture was then compressed into pellets by applying a pressure of about 2 kilobars. The pellets were heated to about 1000° C. and allowed to react for about twenty-four hours in air. The reacted pellets were then quenched rapidly to room temperature.

The La—Ba—Cu—O composition produced from this process corresponds to the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.075, "a" is 2, "b" is 1 and "y" is 2 to 4. The oxide complex of this example showed superconductive properties at a temperature of 36°K at atmospheric pressure.

EXAMPLE V

4.9 grams of La_2O_3, 1.1 grams of $BaCO_3$ and 2.8 grams of CuO were mixed in a mortar-pestle for 3 hours. The mixture was then heated in oxygen at a pressure of 15 microns Hg. until it reached a temperature of about 720° C. The temperature was increased at a rate of about 10° C. per minute. The mixture was then allowed to react for about an hour at about 720° C. After this reaction, the temperature was raised to a temperature of about 925° C., this raise in temperature was made at a rate of about 30° C. per minute. Once at this temperature, the samples were maintained at this temperature for about twenty-one hours. After this period, the mixture was cooled to room temperature and then the reacted mixture was pulverized until the sample was homogenized. The pulverized mixture was then heated rapidly to a temperature of about 925° C. and kept at that temperature for about seven hours. After this period, the mixture was compressed with a pressure of six kilobars. This compression converted the mixed powder into pellets. The pellets were then sintered into solid cylinders by heating them at a temperature of about 925° C. for a period of about four hours at ambient pressure. Finally, the sample was rapidly quenched from this temperature to room temperature in air. The oxide complex so formed corresponds to the general formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.15, "a" is 1, "b" is 1 a and "y" is 2 to 4.

The resulting lanthanum-barium-copper-oxide composition, superconducting at 32°K at ambient pressure, was then placed under a pressure of 9 kilobars using a Be—Cu high pressure clamp using a fluid pressure median. Pressure was measured using a superconducting Pb-manometer situated next to the sample at room temperature. As this compressed

FIG. 3 displays the magnetic field effect on 5 resistivity as a function of temperature. It is clear that the rapid resistivity drop is suppressed and the zero resistivity state at 4°K can be destroyed by magnetic fields. Below 18°K, a diamagnetic shift is clearly evident and reaches a maximum of 2% of the signal of a superconducting Pb sample of the same size as shown in FIG. 4. The insert of FIG. 4 shows the current-voltage characteristics for the sample at 4.2°K. The zero resistivity state is removed as current exceeds a critical value which increases with decreasing temperature. All these strongly demonstrate that the resistivity drop is associated with a superconducting transition.

EXAMPLE VI

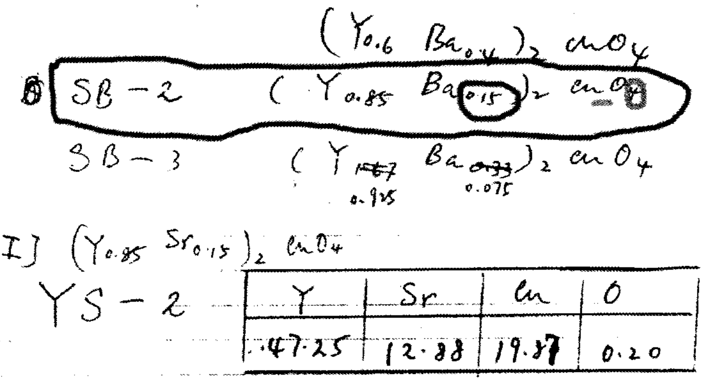
6.0 grams of La_2O_3, 0.61 grams of $SrCO_3$ and 1.63 grams CuO were mixed mechanically in a mortar-pestle for approximately 3 hours. The resulting mixture was then compressed into pellets by applying a pressure of about 3 kilobars. The pellets were heated to about 1000° C. and allowed to react for about twenty-four hours in air. The reacted pellets were then quenched rapidly to room temperature.

The La—Sr—Cu—O composition produced from this process corresponds to the general formula $[La_{1-x}Sr_x]_aCu_bO_y$ where "x" is 0.1, "a" is 2, "b" is 1, and "y" is 2 to 4. The oxide complex was placed under a pressure of 16 kilobars, at room temperature. Upon cooling this oxide complex composition showed superconducting properties at a temperature of 42° K at atmospheric pressure. The oxide complex composition under a pressure of 16 kilobars showed superconducting properties at 54° K

EXAMPLE V

"The oxide complex so formed corresponds to the general formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.15, "a" is 1, "b" is 1 a and "y" is 2 to 4."

From p. H 49, Meng's Lab Notebook:



$(Y_{0.6}\ Ba_{0.4})_2\ CuO_4$

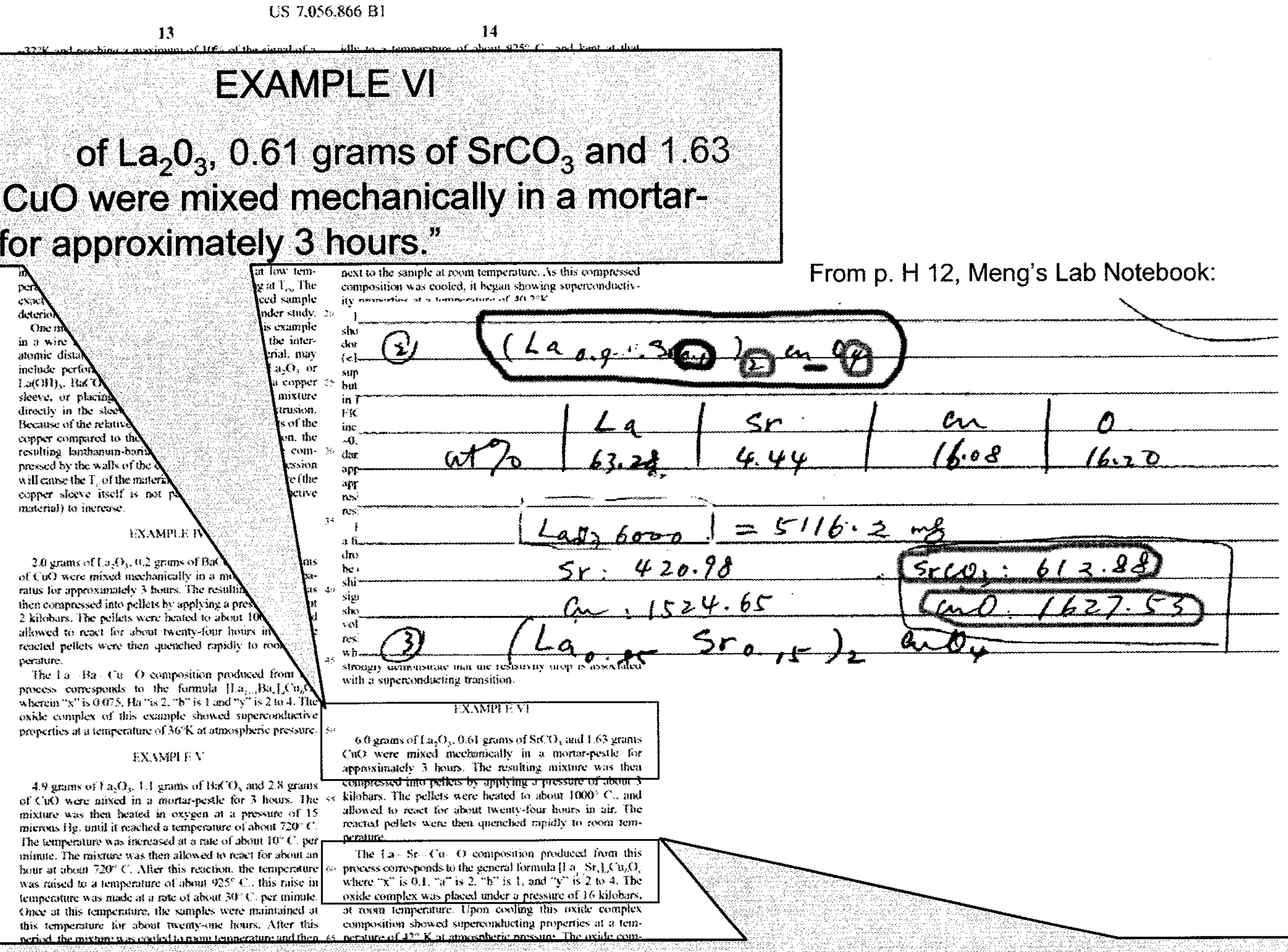
SB – 2 $(Y_{0.85}\ Ba_{0.15})_2\ CuO_4$

SB – 3 $(Y_{\cancel{1.67}\ 0.925}\ Ba_{\cancel{0.33}\ 0.075})_2\ CuO_4$

[I] $(Y_{0.85}\ Sr_{0.15})_2\ CuO_4$

YS – 2

Y	Sr	Cu	O
47.25	12.88	19.87	0.20



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EXAMPLE VI

“ of La_2O_3, 0.61 grams of $SrCO_3$ and 1.63 grams CuO were mixed mechanically in a mortar-pestle for approximately 3 hours.”

From p. H 12, Meng's Lab Notebook:

② $(La_{0.9}Sr_{0.1})_2Cu O_4$

	La	Sr	Cu	O
wt%	63.28	4.44	16.08	16.20

La_2O_3 6000 = 5116.2 mg

Sr : 420.98 $SrCO_3$: 613.88

Cu : 1524.65 CuO : 1627.53

③ $(La_{0.85}Sr_{0.15})_2CuO_4$

material) to increase.

EXAMPLE IV

2.0 grams of La_2O_3, 0.2 grams of BaC… of CuO were mixed mechanically in a m… ratus for approximately 3 hours. The resulti… then compressed into pellets by applying a pres… 2 kilobars. The pellets were heated to about 10… allowed to react for about twenty-four hours in… reacted pellets were then quenched rapidly to roo… perature.

The La-Ba-Cu-O composition produced from … process corresponds to the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is 0.075, "a" is 2, "b" is 1 and "y" is 2 to 4. The oxide complex of this example showed superconductive properties at a temperature of 36°K at atmospheric pressure.

EXAMPLE V

4.9 grams of La_2O_3, 1.1 grams of $BaCO_3$ and 2.8 grams of CuO were mixed in a mortar-pestle for 3 hours. The mixture was then heated in oxygen at a pressure of 15 microns Hg. until it reached a temperature of about 720° C. The temperature was increased at a rate of about 10° C. per minute. The mixture was then allowed to react for about an hour at about 720° C. After this reaction, the temperature was raised to a temperature of about 925° C., this raise in temperature was made at a rate of about 30° C. per minute. Once at this temperature, the samples were maintained at this temperature for about twenty-one hours. After this period the mixture was cooled to room temperature and then

next to the sample at room temperature. As this compressed composition was cooled, it began showing superconductivity properties at a temperature of 40.2°K.

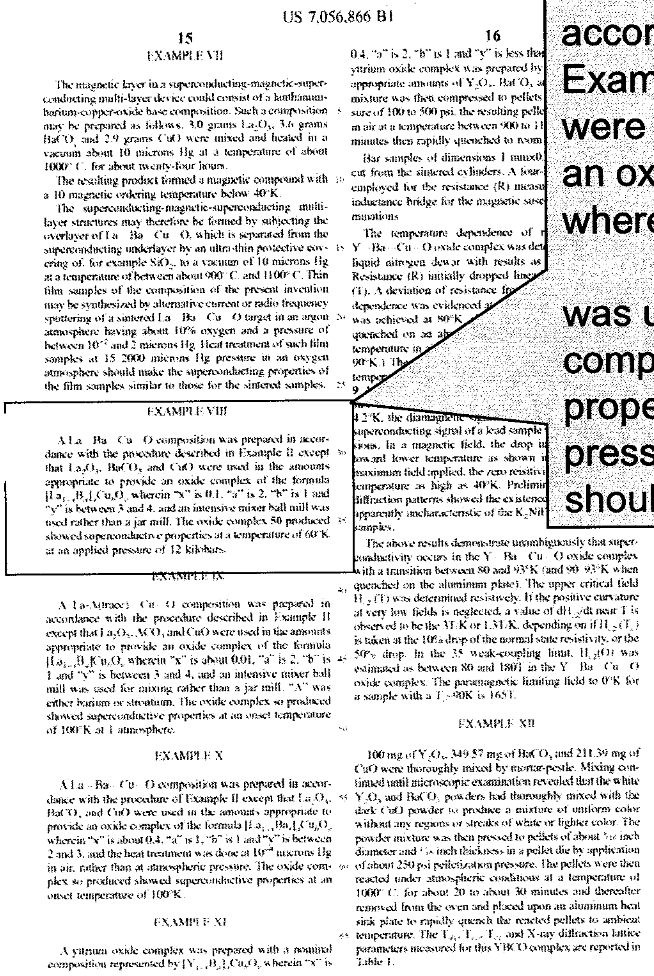
with a superconducting transition.

EXAMPLE VI

6.0 grams of La_2O_3, 0.61 grams of $SrCO_3$ and 1.63 grams CuO were mixed mechanically in a mortar-pestle for approximately 3 hours. The resulting mixture was then compressed into pellets by applying a pressure of about 3 kilobars. The pellets were heated to about 1000° C., and allowed to react for about twenty-four hours in air. The reacted pellets were then quenched rapidly to room temperature.

The La-Sr-Cu-O composition produced from this process corresponds to the general formula $[La_{1-x}Sr_x]_aCu_bO_y$ where "x" is 0.1, "a" is 2, "b" is 1, and "y" is 2 to 4. The oxide complex was placed under a pressure of 16 kilobars, at room temperature. Upon cooling this oxide complex composition showed superconducting properties at a temperature of 42° K at atmospheric pressure. The oxide com-

“The La Sr—Cu--O composition produced from this process corresponds to the general formula $[La_{1-x}Sr_x]_aCu_bO_y$ where “x” is 0.1, “a” is 2, “b” is 1, and “y” is 2 to 4.”



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EXAMPLE VII

The magnetic layer in a superconducting-magnetic-superconducting multi-layer device could consist of a lanthanum-barium-copper-oxide base composition. Such a composition may be prepared as follows. 3.0 grams La_2O_3, 3.6 grams $BaCO_3$ and 2.9 grams CuO were mixed and heated in a vacuum about 10 microns Hg at a temperature of about 1000° C. for about twenty-four hours.

The resulting product formed a magnetic compound with a 10 magnetic ordering temperature below 40°K.

The superconducting-magnetic-superconducting multi-layer structures may therefore be formed by subjecting the overlayer of La–Ba–Cu–O, which is separated from the superconducting underlayer by an ultra-thin protective covering of, for example SiO_2, to a vacuum of 10 microns Hg at a temperature of between about 900° C. and 1100° C. Thin film samples of the composition of the present invention may be synthesized by alternative current or radio frequency sputtering of a sintered La–Ba–Cu–O target in an argon atmosphere having about 10% oxygen and a pressure of between 10^{-2} and 2 microns Hg. Heat treatment of such film samples at 15 2000 microns Hg pressure in an oxygen atmosphere should make the superconducting properties of the film samples similar to those for the sintered samples.

EXAMPLE VIII

A La–Ba–Cu–O composition was prepared in accordance with the procedure described in Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_a]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is between 3 and 4, and an intensive mixer ball mill was used rather than a jar mill. The oxide complex 50 produced showed superconductive properties at a temperature of 60°K at an applied pressure of 12 kilobars.

EXAMPLE IX

A La-A(trace)–Cu–O composition was prepared in accordance with the procedure described in Example II except that La_2O_3, ACO_3 and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_x]Cu_bO_y$ wherein "x" is about 0.01, "a" is 2, "b" is 1 and "Y" is between 3 and 4, and an intensive mixer ball mill was used for mixing rather than a jar mill. "A" was either barium or strontium. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K at 1 atmosphere.

EXAMPLE X

A La–Ba–Cu–O composition was prepared in accordance with the procedure of Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is about 0.4, "a" is 1, "b" is 1 and "y" is between 2 and 3, and the heat treatment was done at 10^{-4} microns Hg in air, rather than at atmospheric pressure. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K.

EXAMPLE XI

A yttrium oxide complex was prepared with a nominal composition represented by $[Y_{1-x}B_x]_aCu_bO_y$ wherein "x" is

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0.4, "a" is 2, "b" is 1 and "y" is less tha
yttrium oxide complex was prepared by
appropriate amounts of Y_2O_3, $BaCO_3$ a
mixture was then compressed to pellets
sure of 100 to 500 psi, the resulting pelle
in air at a temperature between 900 to 1
minutes then rapidly quenched to room

Bar samples of dimensions 1 mmx0.
cut from the sintered cylinders. A four-
employed for the resistance (R) measu
inductance bridge for the magnetic susc
minations

The temperature dependence of
Y–Ba–Cu–O oxide complex was det
liquid nitrogen dewar with results as
Resistance (R) initially dropped line
(T). A deviation of resistance fr
dependence was evidenced a
was achieved at 80°K
quenched on an al
temperature in
90°K.) The
temper
9

4.2°K, the diamagnetic
superconducting signal of a lead sample
sions. In a magnetic field, the drop in
toward lower temperature as shown i
maximum field applied, the zero resistivi
temperature as high as 40°K. Prelimi
diffraction patterns showed the existenc
apparently uncharacteristic of the K_2NiF
samples.

The above results demonstrate unambiguously that superconductivity occurs in the Y–Ba–Cu–O oxide complex with a transition between 80 and 93°K (and 90–93°K when quenched on the aluminum plate). The upper critical field $H_{c2}(T)$ was determined resistively. If the positive curvature at very low fields is neglected, a value of dH_{c2}/dt near T is observed to be the 3T/K or 1.3T/K, depending on if $H_{c2}(T_c)$ is taken at the 10% drop of the normal state resistivity, or the 50% drop. In the 35 weak-coupling limit, $H_{c2}(O)$ was estimated as between 80 and 180T in the Y–Ba–Cu–O oxide complex. The paramagnetic limiting field to 0°K for a sample with a T_c~90K is 165T.

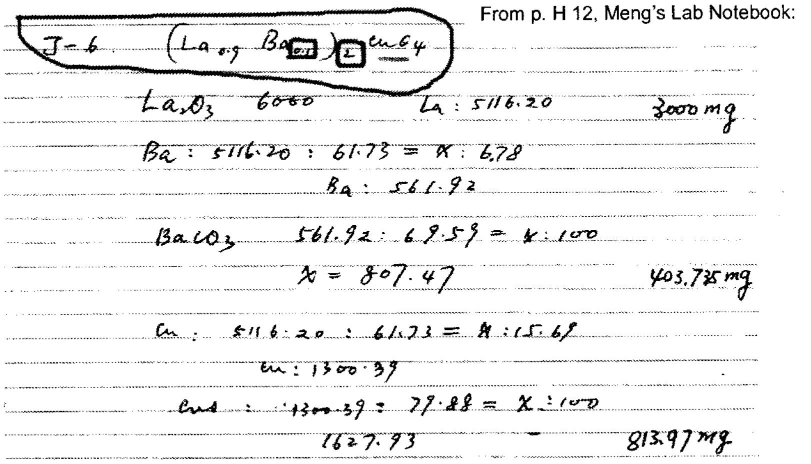
EXAMPLE XII

100 mg of Y_2O_3, 349.57 mg of $BaCO_3$ and 211.39 mg of CuO were thoroughly mixed by mortar-pestle. Mixing continued until microscopic examination revealed that the white Y_2O_3 and $BaCO_3$ powders had thoroughly mixed with the dark CuO powder to produce a mixture of uniform color without any regions or streaks of white or lighter color. The powder mixture was then pressed to pellets of about ⅜ inch diameter and 1/16 inch thickness in a pellet die by application of about 250 psi pelletization pressure. The pellets were then reacted under atmospheric conditions at a temperature of 1000° C. for about 20 to about 30 minutes and thereafter removed from the oven and placed upon an aluminum heat sink plate to rapidly quench the reacted pellets to ambient temperature. The T_{c0}, T_{c1}, T_{c2} and X-ray diffraction lattice parameters measured for this YBCO complex are reported in Table 1.

EXAMPLE VIII

"A La-Ba-Cu-O composition was prepared in accordance with the procedure described in Example II except that La_20_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_a]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and [illegible], and an intensive mixer ball mill was used rather than a jar mill. The oxide complex 50 produced showed superconductive properties at a temperature of 60°K at an applied pressure of 12 kilobars." $[La_{1-x}B_a]_a$ is a typo that should read: $[La_{1-x}Ba_x]_a$

From p. H 12, Meng's Lab Notebook:



J-6 (La 0.9 Ba $\boxed{0.1}$) $\boxed{2}$ Cu 6 4

La₂O₃ 6060 La : 5116.20 3000 mg

Ba : 5116.20 : 61.73 = x : 6.78

Ba : 561.92

BaCO₃ 561.92 : 69.59 = x : 100

x = 807.47 403.735 mg

Cu : 5116.20 : 61.73 = x : 15.68

Cu : 1300.39

CuO : 1300.39 : 79.88 = x : 100

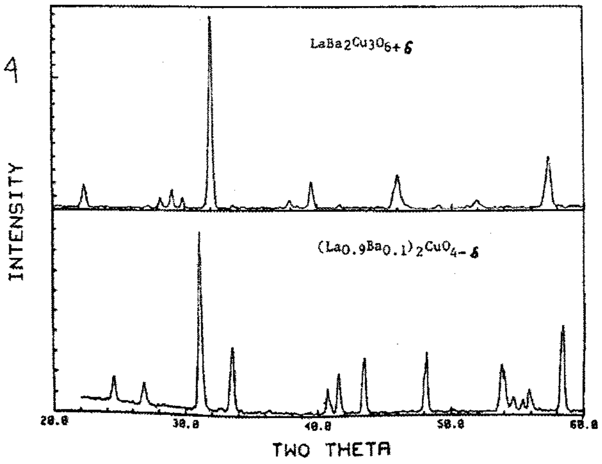
1627.93 – 813.97 mg

‘866 Patent, col 4, lines 32-35:

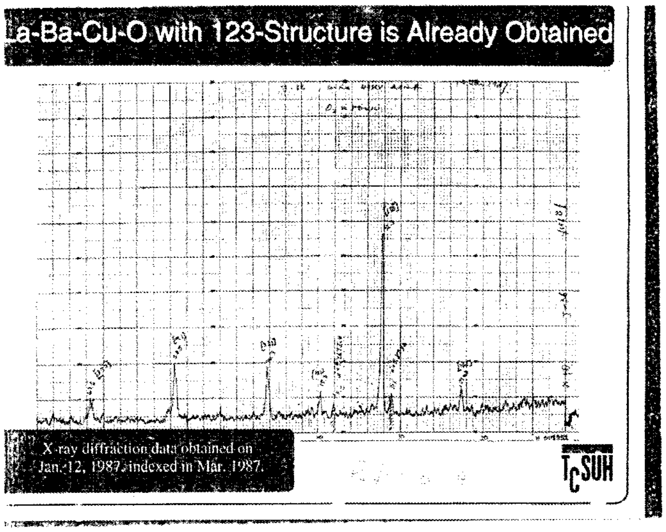
FIG. **14** is the X-ray diffraction patterns for a ($La_{0.9}Ba_{0.1}$) $CuO_{4-\partial}$ oxide complex as prepared according to Example VIII and for an $LaBa_2Cu_3O_{6+\partial}$ oxide complex as prepared according to Example XIII.

‘866 Patent:

FIG. 14

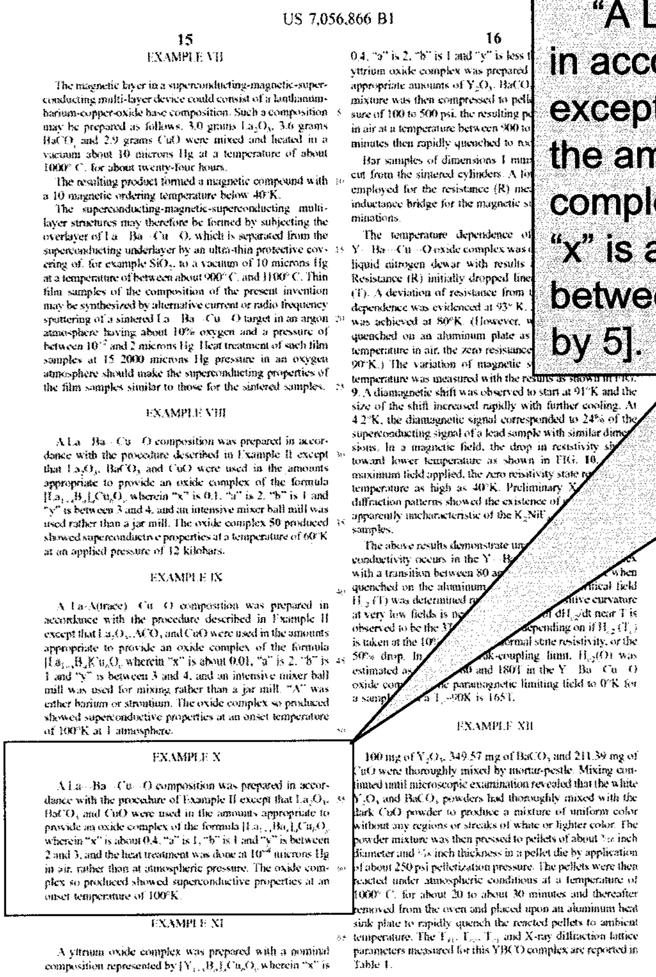


p. H 001951, Meng’s Data Book, Jan. 12, 1987


La-Ba-Cu-O with 123-Structure is Already Obtained

X-ray diffraction data obtained on Jan. 12, 1987, indexed in Mar. 1987.

Dr. Meng performed X-Ray diffraction that was referenced in the ‘866 patent. Here is one example.



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EXAMPLE VII

The magnetic layer in a superconducting-magnetic-superconducting multi-layer device could consist of a lanthanum-barium-copper-oxide base composition. Such a composition may be prepared as follows. 3.0 grams La_2O_3, 3.6 grams $BaCO_3$ and 2.9 grams CuO were mixed and heated in a vacuum about 10 microns Hg at a temperature of about 1000° C. for about twenty-four hours.

The resulting product formed a magnetic compound with a 10 magnetic ordering temperature below 40°K.

The superconducting-magnetic-superconducting multi-layer structures may therefore be formed by subjecting the overlayer of La—Ba—Cu—O, which is separated from the superconducting underlayer by an ultra-thin protective covering of, for example SiO_2, to a vacuum of 10 microns Hg at a temperature of between about 900° C. and 1100° C. Thin film samples of the composition of the present invention may be synthesized by alternative current or radio frequency sputtering of a sintered La—Ba—Cu—O target in an argon atmosphere having about 10% oxygen and a pressure of between 10^{-2} and 2 microns Hg. Heat treatment of such film samples at 15 2000 microns Hg pressure in an oxygen atmosphere should make the superconducting properties of the film samples similar to those for the sintered samples.

EXAMPLE VIII

A La—Ba—Cu—O composition was prepared in accordance with the procedure described in Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is between 3 and 4, and an intensive mixer ball mill was used rather than a jar mill. The oxide complex 50 produced showed superconductive properties at a temperature of 60°K at an applied pressure of 12 kilobars.

EXAMPLE IX

A La-A(trace)—Cu—O composition was prepared in accordance with the procedure described in Example II except that La_2O_3, ACO_3 and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_x]Cu_bO_y$ wherein "x" is about 0.01, "a" is 2, "b" is 1 and "y" is between 3 and 4, and an intensive mixer ball mill was used for mixing rather than a jar mill. "A" was either barium or strontium. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K at 1 atmosphere.

EXAMPLE X

A La—Ba—Cu—O composition was prepared in accordance with the procedure of Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is about 0.4, "a" is 1, "b" is 1 and "y" is between 2 and 3, and the heat treatment was done at 10^{-4} microns Hg in air, rather than at atmospheric pressure. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K.

EXAMPLE XI

A yttrium oxide complex was prepared with a nominal composition represented by $[Y_{1-x}B_x]_aCu_bO_y$ wherein "x" is

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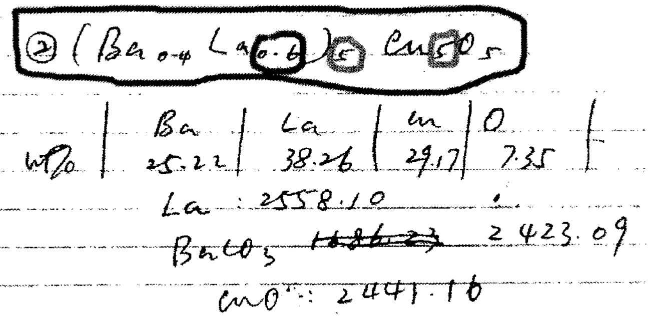
EXAMPLE XII

100 mg of Y_2O_3, 349.57 mg of $BaCO_3$ and 211.39 mg of CuO were thoroughly mixed by mortar-pestle. Mixing continued until microscopic examination revealed that the white Y_2O_3 and $BaCO_3$ powders had thoroughly mixed with the dark CuO powder to produce a mixture of uniform color without any regions or streaks of white or lighter color. The powder mixture was then pressed to pellets of about ⅜ inch diameter and 1/16 inch thickness in a pellet die by application of about 250 psi pelletization pressure. The pellets were then reacted under atmospheric conditions at a temperature of 1000° C. for about 20 to about 30 minutes and thereafter removed from the oven and placed upon an aluminum heat sink plate to rapidly quench the reacted pellets to ambient temperature. The T_{c0}, T_{c1}, T_{c2} and X-ray diffraction lattice parameters measured for this YBCO complex are reported in Table 1.

EXAMPLE X

"A La—Ba—Cu—O composition was prepared in accordance with the procedure of Example II except that La_2O_2, $BaCO_3$, and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is about 0.4, "a" is 1, "b" is 1 and "y" is between 2 and 3, ..." [Note: Divide "a" and "b" by 5].

From p. H 16, Meng's Lab Notebook:



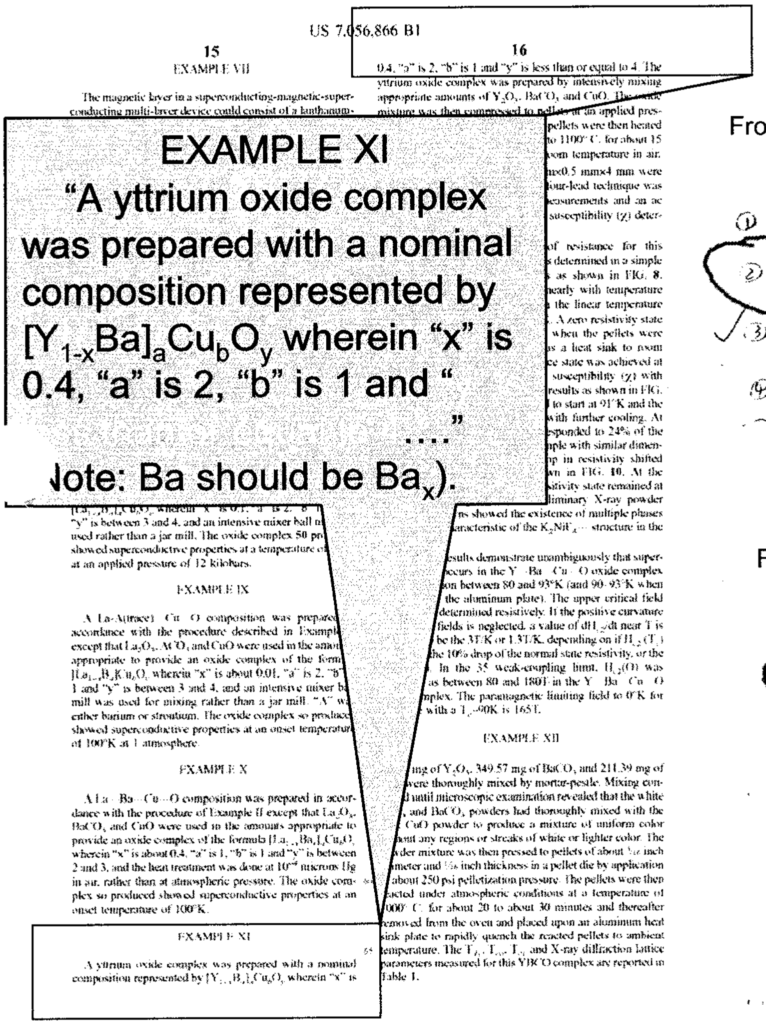
② $(Ba_{0.4}La_{0.6})_5Cu_5O_5$

	Ba	La	Cu	O
wt%	25.22	38.26	29.17	7.35

La : 2558.10

$BaCO_3$ ~~1686.23~~ 2423.09

CuO : 2441.16



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EXAMPLE VII

The magnetic layer in a superconducting-magnetic-superconducting multi-layer device could consist of a lanthanum-

EXAMPLE XI

"A yttrium oxide complex was prepared with a nominal composition represented by $[Y_{1-x}Ba]_aCu_bO_y$ wherein "x" is 0.4, "a" is 2, "b" is 1 and "

…."

Note: Ba should be Ba_x).

$[La_{1-x}B_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" … "y" is between 3 and 4, and an intensive mixer ball m… used rather than a jar mill. The oxide complex so pr… showed superconductive properties at a temperature o… at an applied pressure of 12 kilobars.

EXAMPLE IX

A La-A(trace)-Cu-O composition was prepared… accordance with the procedure described in Exampl… except that La_2O_3, ACO_3 and CuO were used in the amoun… appropriate to provide an oxide complex of the form… $[La_{1-x}B_x]Cu_bO_y$ wherein "x" is about 0.01, "a" is 2, "b"… 1 and "y" is between 3 and 4, and an intensive mixer b… mill was used for mixing rather than a jar mill. "A" wa… either barium or strontium. The oxide complex so produce… showed superconductive properties at an onset temperatur… of 100°K at 1 atmosphere.

EXAMPLE X

A La-Ba-Cu-O composition was prepared in accordance with the procedure of Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is about 0.4, "a" is 1, "b" is 1 and "y" is between 2 and 3, and the heat treatment was done at 10^{-4} microns Hg in air, rather than at atmospheric pressure. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K.

EXAMPLE XI

A yttrium oxide complex was prepared with a nominal composition represented by $[Y_{1-x}B_x]_aCu_bO_y$ wherein "x" is

16

0.4, "a" is 2, "b" is 1 and "y" is less than or equal to 4. The yttrium oxide complex was prepared by intensively mixing appropriate amounts of Y_2O_3, $BaCO_3$ and CuO. The oxide mixture was then compressed to pellets at an applied pres-… pellets were then heated … to 1100° C. for about 15 … room temperature in air. … mm×0.5 mm×4 mm were … four-lead technique was … measurements and an ac … susceptibility (χ) deter-…

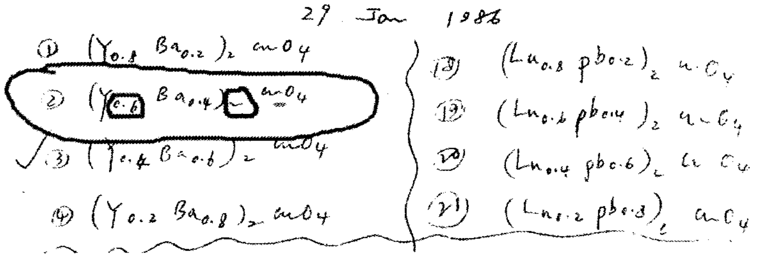
… of resistance for this … determined in a simple … as shown in FIG. 8. … nearly with temperature … the linear temperature … A zero resistivity state … when the pellets were … as a heat sink to room … ce state was achieved at … susceptibility (χ) with … results as shown in FIG. … to start at 91°K and the … with further cooling. At … sponded to 24% of the … mple with similar dimen- … up in resistivity shifted … wn in FIG. 10. At the … stivity state remained at … liminary X-ray powder … ns showed the existence of multiple phases … aracteristic of the K_2NiF_4 structure in the

… esults demonstrate unambiguously that super- … occurs in the Y-Ba-Cu-O oxide complex … on between 80 and 93°K (and 90-93°K when … the aluminum plate). The upper critical field … determined resistively. If the positive curvature … fields is neglected, a value of dH_{c2}/dt near T is … be the 3T/K or 1.3T/K, depending on if $H_{c2}(T_c)$ … the 10% drop of the normal state resistivity, or the … In the weak-coupling limit, $H_{c2}(0)$ was … as between 80 and 180T in the Y-Ba-Cu-O … mplex. The paramagnetic limiting field to 0°K for … with a T_c~90K is 165T.

EXAMPLE XII

… mg of Y_2O_3, 349.57 mg of $BaCO_3$ and 211.39 mg of … were thoroughly mixed by mortar-pestle. Mixing con-… d until microscopic examination revealed that the white … and $BaCO_3$ powders had thoroughly mixed with the … CuO powder to produce a mixture of uniform color … out any regions or streaks of white or lighter color. The … der mixture was then pressed to pellets of about 3/16 inch … meter and 1/16 inch thickness in a pellet die by application … about 250 psi pelletization pressure. The pellets were then … acted under atmospheric conditions at a temperature of … 000° C. for about 20 to about 30 minutes and thereafter … emoved from the oven and placed upon an aluminum heat sink plate to rapidly quench the reacted pellets to ambient temperature. The T_c, T_{c0}, T_{c1} and X-ray diffraction lattice parameters measured for this YBCO complex are reported in Table 1.

From p. H 50, Meng's Lab Notebook:



29 Jan 1986

① $(Y_{0.8}Ba_{0.2})_2CuO_4$

② $(Y_{\boxed{0.6}}Ba_{0.4})_{\boxed{2}}CuO_4$

✓ ③ $(Y_{0.4}Ba_{0.6})_2CuO_4$

④ $(Y_{0.2}Ba_{0.8})_2CuO_4$

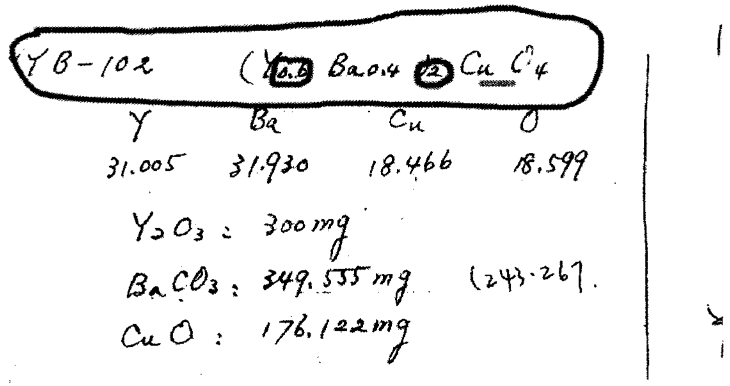
⑱ $(Ln_{0.8}pb_{0.2})_2CuO_4$

⑲ $(Ln_{0.6}pb_{0.4})_2CuO_4$

⑳ $(Ln_{0.4}pb_{0.6})_2CuO_4$

(21) $(Ln_{0.2}pb_{0.8})_2CuO_4$

From p. H 56, Meng's Lab Notebook:



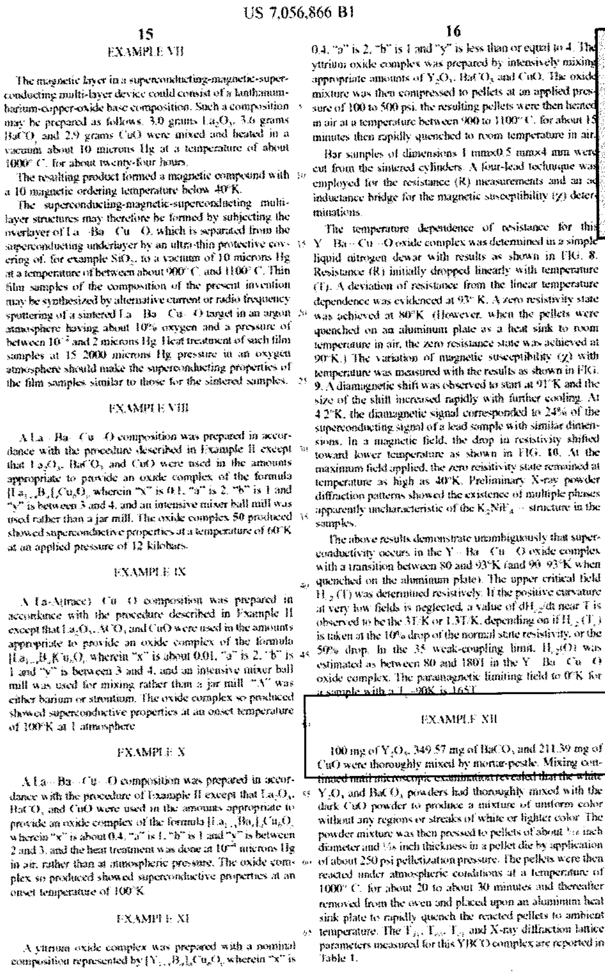
YB-102 $(Y_{\boxed{0.6}}Ba_{0.4})_{\boxed{2}}CuO_4$

Y	Ba	Cu	O
31.005	31.930	18.466	18.599

Y_2O_3 : 300mg

$BaCO_3$: 349.555mg (243.267.

CuO : 176.122mg



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EXAMPLE VII

The magnetic layer in a superconducting-magnetic-superconducting multi-layer device could consist of a lanthanum-barium-copper-oxide base composition. Such a composition may be prepared as follows. 3.0 grams La_2O_3, 3.6 grams $BaCO_3$ and 2.9 grams CuO were mixed and heated in a vacuum about 10 microns Hg at a temperature of about 1000° C. for about twenty-four hours.

The resulting product formed a magnetic compound with a 10 magnetic ordering temperature below 40°K.

The superconducting-magnetic-superconducting multi-layer structures may therefore be formed by subjecting the overlayer of La–Ba–Cu–O, which is separated from the superconducting underlayer by an ultra-thin protective covering of, for example SiO_2, to a vacuum of 10 microns Hg at a temperature of between about 900° C. and 1100° C. Thin film samples of the composition of the present invention may be synthesized by alternative current or radio frequency sputtering of a sintered La–Ba–Cu–O target in an argon atmosphere having about 10% oxygen and a pressure of between 10^{-2} and 2 microns Hg. Heat treatment of such film samples at 15 2000 microns Hg pressure in an oxygen atmosphere should make the superconducting properties of the film samples similar to those for the sintered samples.

EXAMPLE VIII

A La–Ba–Cu–O composition was prepared in accordance with the procedure described in Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_x]_aCu_bO_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is between 3 and 4, and an intensive mixer ball mill was used rather than a jar mill. The oxide complex 50 produced showed superconductive properties at a temperature of 60°K at an applied pressure of 12 kilobars.

EXAMPLE IX

A La-A(trace)-Cu-O composition was prepared in accordance with the procedure described in Example II except that La_2O_3, ACO_3 and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}B_x]_aCu_bO_y$ wherein "x" is about 0.01, "a" is 2, "b" is 1 and "y" is between 3 and 4, and an intensive mixer ball mill was used for mixing rather than a jar mill. "A" was either barium or strontium. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K at 1 atmosphere.

EXAMPLE X

A La–Ba–Cu–O composition was prepared in accordance with the procedure of Example II except that La_2O_3, $BaCO_3$ and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[La_{1-x}Ba_x]_aCu_bO_y$ wherein "x" is about 0.4, "a" is 1, "b" is 1 and "y" is between 2 and 3, and the heat treatment was done at 10^{-4} microns Hg in air, rather than at atmospheric pressure. The oxide complex so produced showed superconductive properties at an onset temperature of 100°K.

EXAMPLE XI

A yttrium oxide complex was prepared with a nominal composition represented by $[Y_{1-x}B_x]_aCu_bO_y$ wherein "x" is

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0.4, "a" is 2, "b" is 1 and "y" is less than or equal to 4. The yttrium oxide complex was prepared by intensively mixing appropriate amounts of Y_2O_3, $BaCO_3$ and CuO. The oxide mixture was then compressed to pellets at an applied pressure of 100 to 500 psi, the resulting pellets were then heated in air at a temperature between 900 to 1100° C. for about 15 minutes then rapidly quenched to room temperature in air.

Bar samples of dimensions 1 mm×0.5 mm×4 mm were cut from the sintered cylinders. A four-lead technique was employed for the resistance (R) measurements and an ac inductance bridge for the magnetic susceptibility (χ) determinations.

The temperature dependence of resistance for this Y–Ba–Cu–O oxide complex was determined in a simple liquid nitrogen dewar with results as shown in FIG. 8. Resistance (R) initially dropped linearly with temperature (T). A deviation of resistance from the linear temperature dependence was evidenced at 93° K. A zero resistivity state was achieved at 80°K. (However, when the pellets were quenched on an aluminum plate as a heat sink to room temperature in air, the zero resistance state was achieved at 90°K.) The variation of magnetic susceptibility (χ) with temperature was measured with the results as shown in FIG. 9. A diamagnetic shift was observed to start at 91°K and the size of the shift increased rapidly with further cooling. At 4.2°K, the diamagnetic signal corresponded to 24% of the superconducting signal of a lead sample with similar dimensions. In a magnetic field, the drop in resistivity shifted toward lower temperature as shown in FIG. 10. At the maximum field applied, the zero resistivity state remained at temperature as high as 40°K. Preliminary X-ray powder diffraction patterns showed the existence of multiple phases apparently uncharacteristic of the K_2NiF_4 structure in the samples.

The above results demonstrate unambiguously that superconductivity occurs in the Y–Ba–Cu–O oxide complex with a transition between 80 and 93°K (and 90–93°K when quenched on the aluminum plate). The upper critical field $H_{c2}(T)$ was determined resistively. If the positive curvature at very low fields is neglected, a value of dH_{c2}/dT near T is observed to be the 3T/K or 1.3T/K, depending on if $H_{c2}(T_c)$ is taken at the 10% drop of the normal state resistivity, or the 50% drop. In the 35 weak-coupling limit, $H_{c2}(O)$ was estimated as between 80 and 180T in the Y–Ba–Cu–O oxide complex. The paramagnetic limiting field to 0°K for a sample with a T_c ~90K is 165T.

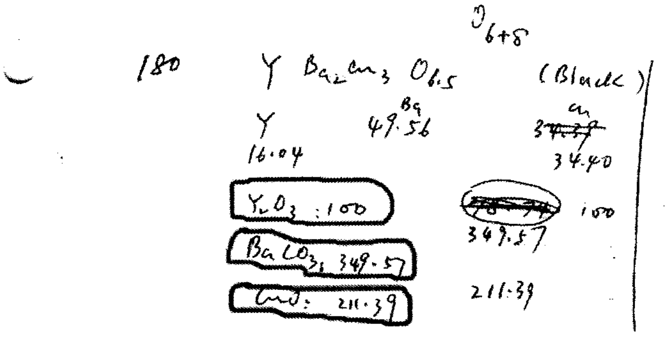
EXAMPLE XII

100 mg of Y_2O_3, 349.57 mg of $BaCO_3$ and 211.39 mg of CuO were thoroughly mixed by mortar-pestle. Mixing continued until microscopic examination revealed that the white Y_2O_3 and $BaCO_3$ powders had thoroughly mixed with the dark CuO powder to produce a mixture of uniform color without any regions or streaks of white or lighter color. The powder mixture was then pressed to pellets of about ½ inch diameter and ⅛ inch thickness in a pellet die by application of about 250 psi pelletization pressure. The pellets were then reacted under atmospheric conditions at a temperature of 1000° C. for about 20 to about 30 minutes and thereafter removed from the oven and placed upon an aluminum heat sink plate to rapidly quench the reacted pellets to ambient temperature. The T_{c0}, T_{cm}, T_{c1} and X-ray diffraction lattice parameters measured for this YBCO complex are reported in Table 1.

EXAMPLE XII

"100mg of Y_2O_3, 349.57mg of $BaCO_3$ and 211.39mg of CuO were thoroughly mixed by mortar-pestle. Mixing continued ...."

From p. H 87, Meng's Lab Notebook:



$O_{6+\delta}$

180 $YBa_2Cu_3O_{6.5}$ (Black)

Y 16.04

Ba 49.56

Cu ~~34.39~~ 34.40

Y_2O_3 : 100

$BaCO_3$: 349.57

CuO: 211.39

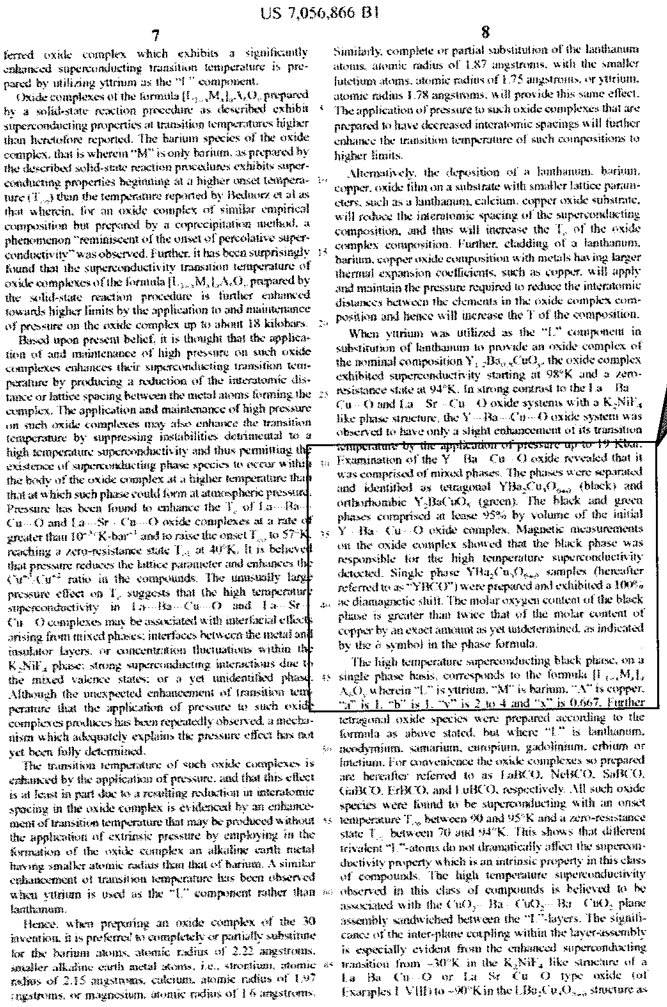
~~[illegible]~~ 100

349.57

211.39

Black Phase/Green Phase

By February 27, 1987, Dr. Meng independently successfully separated black and green crystals from the mixed phase by studying a set of YBCO samples with different compositions. This work contributed to the conception of the High temperature YBCO formula and structure identified and claimed in the ‘866 patent (and related applications).



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ferred oxide complex which exhibits a significantly enhanced superconducting transition temperature is prepared by utilizing yttrium as the "L" component.

Oxide complexes of the formula $[L_{1-x}M_x]_aA_bO_y$ prepared by a solid-state reaction procedure as described exhibit superconducting properties at transition temperatures higher than heretofore reported. The barium species of the oxide complex, that is wherein "M" is only barium, as prepared by the described solid-state reaction procedures exhibits superconducting properties beginning at a higher onset temperature (T_{co}) than the temperature reported by Bednorz et al as that wherein, for an oxide complex of similar empirical composition but prepared by a coprecipitation method, a phenomenon "reminiscent of the onset of percolative superconductivity" was observed. Further, it has been surprisingly found that the superconductivity transition temperature of oxide complexes of the formula $[L_{1-x}M_x]_aA_bO_y$ prepared by the solid-state reaction procedure is further enhanced towards higher limits by the application to and maintenance of pressure on the oxide complex up to about 18 kilobars.

Based upon present belief, it is thought that the application of and maintenance of high pressure on such oxide complexes enhances their superconducting transition temperature by producing a reduction of the interatomic distance or lattice spacing between the metal atoms forming the complex. The application and maintenance of high pressure on such oxide complexes may also enhance the transition temperature by suppressing instabilities detrimental to a high temperature superconductivity and thus permitting the existence of superconducting phase species to occur within the body of the oxide complex at a higher temperature than that at which such phase could form at atmospheric pressure. Pressure has been found to enhance the T_c of La—Ba—Cu—O and La—Sr—Cu—O oxide complexes at a rate of greater than 10^{-3}°K·bar^{-1} and to raise the onset T_{co} to 57°K, reaching a zero-resistance state T_{c1} at 40°K. It is believed that pressure reduces the lattice parameter and enhances the Cu^{+3}/Cu^{+2} ratio in the compounds. The unusually large pressure effect on T_c suggests that the high temperature superconductivity in La—Ba—Cu—O and La—Sr—Cu—O complexes may be associated with interfacial effects arising from mixed phases; interfaces between the metal and insulator layers, or concentration fluctuations within the K_2NiF_4 phase; strong superconducting interactions due to the mixed valence states; or a yet unidentified phase. Although the unexpected enhancement of transition temperature that the application of pressure to such oxide complexes produces has been repeatedly observed, a mechanism which adequately explains the pressure effect has not yet been fully determined.

The transition temperature of such oxide complexes is enhanced by the application of pressure, and that this effect is at least in part due to a resulting reduction in interatomic spacing in the oxide complex is evidenced by an enhancement of transition temperature that may be produced without the application of extrinsic pressure by employing in the formation of the oxide complex an alkaline earth metal having smaller atomic radius than that of barium. A similar enhancement of transition temperature has been observed when yttrium is used as the "L" component rather than lanthanum.

Hence, when preparing an oxide complex of the invention, it is preferred to completely or partially substitute for the barium atoms, atomic radius of 2.22 angstroms, smaller alkaline earth metal atoms, i.e., strontium, atomic radius of 2.15 angstroms, calcium, atomic radius of 1.97 angstroms, or magnesium, atomic radius of 1.6 angstroms.

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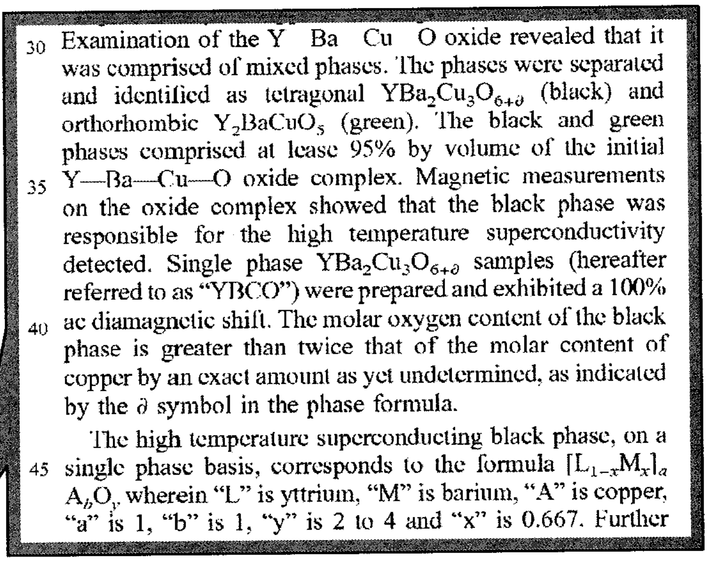
Similarly, complete or partial substitution of the lanthanum atoms, atomic radius of 1.87 angstroms, with the smaller lutetium atoms, atomic radius of 1.75 angstroms, or yttrium, atomic radius 1.78 angstroms, will provide this same effect. The application of pressure to such oxide complexes that are prepared to have decreased interatomic spacings will further enhance the transition temperature of such compositions to higher limits.

Alternatively, the deposition of a lanthanum, barium, copper, oxide film on a substrate with smaller lattice parameters, such as a lanthanum, calcium, copper oxide substrate, will reduce the interatomic spacing of the superconducting composition, and thus will increase the T_c of the oxide complex composition. Further, cladding of a lanthanum, barium, copper oxide composition with metals having larger thermal expansion coefficients, such as copper, will apply and maintain the pressure required to reduce the interatomic distances between the elements in the oxide complex composition and hence will increase the T of the composition.

When yttrium was utilized as the "L" component in substitution of lanthanum to provide an oxide complex of the nominal composition $Y_{1.2}Ba_{0.8}CuO_y$, the oxide complex exhibited superconductivity starting at 98°K and a zero-resistance state at 94°K. In strong contrast to the La—Ba—Cu—O and La—Sr—Cu—O oxide systems with a K_2NiF_4 like phase structure, the Y—Ba—Cu—O oxide system was observed to have only a slight enhancement of its transition temperature by the application of pressure up to 19 Kbar. Examination of the Y—Ba—Cu—O oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal $YBa_2Cu_3O_{6+\partial}$ (black) and orthorhombic Y_2BaCuO_5 (green). The black and green phases comprised at lease 95% by volume of the initial Y—Ba—Cu—O oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase $YBa_2Cu_3O_{6+\partial}$ samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% ac diamagnetic shift. The molar oxygen content of the black phase is greater than twice that of the molar content of copper by an exact amount as yet undetermined, as indicated by the ∂ symbol in the phase formula.

The high temperature superconducting black phase, on a single phase basis, corresponds to the formula $[L_{1-x}M_x]_aA_bO_y$ wherein "L" is yttrium, "M" is barium, "A" is copper, "a" is 1, "b" is 1, "y" is 2 to 4 and "x" is 0.667. Further tetragonal oxide species were prepared according to the formula as above stated, but where "L" is lanthanum, neodymium, samarium, europium, gadolinium, erbium or lutetium. For convenience the oxide complexes so prepared are hereafter referred to as LaBCO, NdBCO, SmBCO, GdBCO, ErBCO, and LuBCO, respectively. All such oxide species were found to be superconducting with an onset temperature T_{co} between 90 and 95°K and a zero-resistance state T_{c1} between 70 and 94°K. This shows that different trivalent "L"-atoms do not dramatically affect the superconductivity property which is an intrinsic property in this class of compounds. The high temperature superconductivity observed in this class of compounds is believed to be associated with the CuO_2—Ba—CuO_2—Ba—CuO_2 plane assembly sandwiched between the "L"-layers. The significance of the inter-plane coupling within the layer-assembly is especially evident from the enhanced superconducting transition from ~30°K in the K_2NiF_4 like structure of a La—Ba—Cu—O or La—Sr—Cu—O type oxide (of Examples I–VIII) to ~90°K in the $LBa_2Cu_3O_{6+\partial}$ structure as

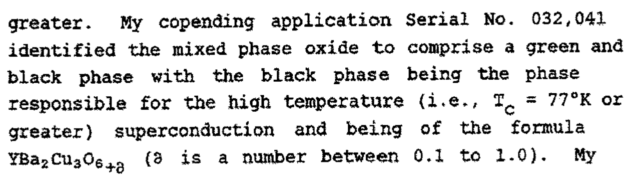


Examination of the Y—Ba—Cu—O oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal $YBa_2Cu_3O_{6+\partial}$ (black) and orthorhombic Y_2BaCuO_5 (green). The black and green phases comprised at lease 95% by volume of the initial Y—Ba—Cu—O oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase $YBa_2Cu_3O_{6+\partial}$ samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% ac diamagnetic shift. The molar oxygen content of the black phase is greater than twice that of the molar content of copper by an exact amount as yet undetermined, as indicated by the ∂ symbol in the phase formula.

The high temperature superconducting black phase, on a single phase basis, corresponds to the formula $[L_{1-x}M_x]_aA_bO_y$ wherein "L" is yttrium, "M" is barium, "A" is copper, "a" is 1, "b" is 1, "y" is 2 to 4 and "x" is 0.667. Further

Black Phase/Green Phase

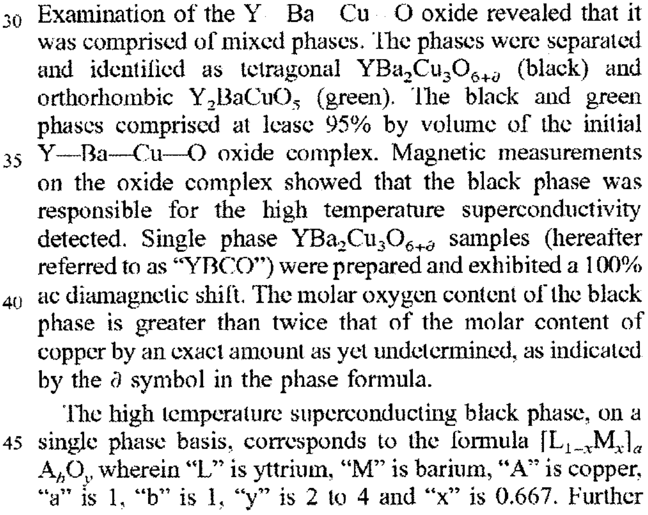
Excerpt from WO 89/08076 ('956 Application), p. 3, lines 32-37:



greater. My copending application Serial No. 032,041 identified the mixed phase oxide to comprise a green and black phase with the black phase being the phase responsible for the high temperature (i.e., T_C = 77°K or greater) superconduction and being of the formula $YBa_2Cu_3O_{6+\partial}$ (∂ is a number between 0.1 to 1.0). My

Black Phase / Green Phase

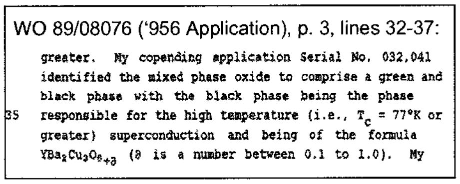
'866 patent col. 8, lines 30-47:



Examination of the Y Ba Cu O oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal $YBa_2Cu_3O_{6+\partial}$ (black) and orthorhombic Y_2BaCuO_5 (green). The black and green phases comprised at lease 95% by volume of the initial Y—Ba—Cu—O oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase $YBa_2Cu_3O_{6+\partial}$ samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% ac diamagnetic shift. The molar oxygen content of the black phase is greater than twice that of the molar content of copper by an exact amount as yet undetermined, as indicated by the ∂ symbol in the phase formula.

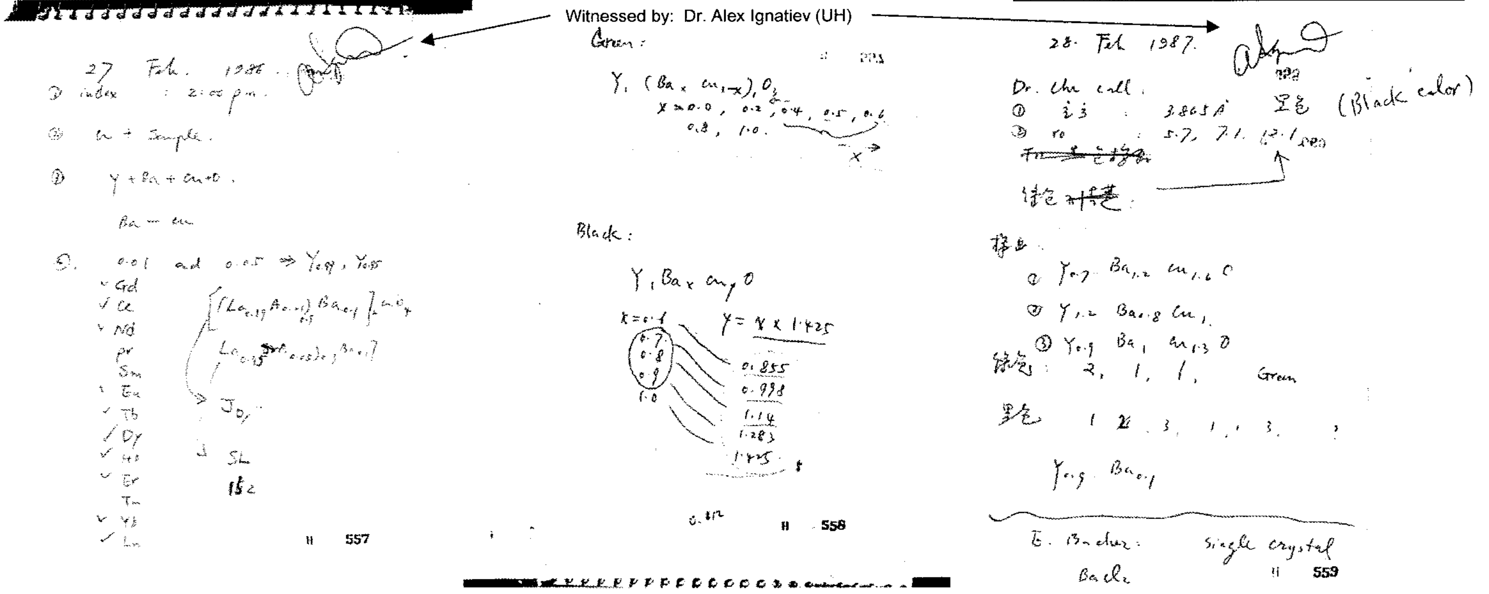
The high temperature superconducting black phase, on a single phase basis, corresponds to the formula $[L_{1-x}M_x]_a A_b O_y$ wherein "L" is yttrium, "M" is barium, "A" is copper, "a" is 1, "b" is 1, "y" is 2 to 4 and "x" is 0.667. Further

WO 89/08076 ('956 Application), p. 3, lines 32-37:



greater. My copending application Serial No. 032,041 identified the mixed phase oxide to comprise a green and black phase with the black phase being the phase responsible for the high temperature (i.e., T_c = 77°K or greater) superconduction and being of the formula $YBa_2Cu_3O_{6+\partial}$ (∂ is a number between 0.1 to 1.0). My

Dr. Meng's independent research and experiments identified and separated the superconducting phase ("black phase") and the non-superconducting phase ("green phase"). *See, e.g.*, pp. H 557-59, Meng's lab notebook:



Witnessed by: Dr. Alex Ignatiev (UH)

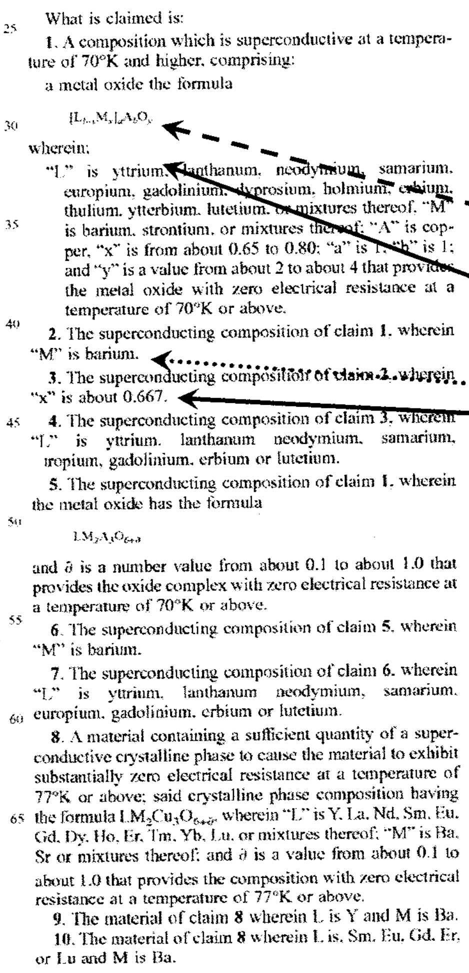
27 Feb. 1986
① index : 2:00 p.m.
② Cu + Sample.
③ Y + Ba + Cu + O.
Ba — Cu
④ 0.01 and 0.05 ⇒ $Y_{0.99}$, $Y_{0.95}$
✓ Gd
✓ Ce
✓ Nd
Pr
Sm
✓ Eu
✓ Tb
✓ Dy
✓ Ho
✓ Er
Tm
✓ Yb
✓ Lu
$[(La_{0.19}A_{0.01})_{0.5}Ba_{0.1}]_2CuO_y$
[illegible]
Dy
SL
[illegible]
H 557

Green:
$Y_1(Ba_xCu_{1-x})_1O_3$
x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0.
x →

Black:
$Y_1Ba_xCu_yO$
x = 0.6, 0.7, 0.8, 0.9, 1.0
y = x × 1.425
0.855
0.998
1.14
1.283
1.425
0.812
H 558

28 Feb 1987.
Dr. Chu call:
① 立方 : 3.865Å 黑色 (Black color)
② To : 5.7, 7.1, 12.1 [illegible]
~~[illegible]~~
结论 ~~[illegible]~~:
样品:
① $Y_{0.7}Ba_{1.2}Cu_{1.6}O$
② $Y_{1.2}Ba_{0.8}Cu_1$
③ $Y_{0.9}Ba_1Cu_{1.3}O$
绿色: 2, 1, 1, Green
黑色 1 2 3, 1, 1 3,
$Y_{0.9}Ba_{0.1}$
E. Bucher: single crystal
$BaCl_2$
H 559

CLAIMS - '866 patent col. 18-19:



What is claimed is:

1. A composition which is superconductive at a temperature of 70°K and higher, comprising:

a metal oxide the formula

$$[L_{1-x}M_x]_aA_bO_y$$

wherein:

"L" is yttrium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or mixtures thereof, "M" is barium, strontium, or mixtures thereof; "A" is copper, "x" is from about 0.65 to 0.80; "a" is 1, "b" is 1; and "y" is a value from about 2 to about 4 that provides the metal oxide with zero electrical resistance at a temperature of 70°K or above.

2. The superconducting composition of claim **1**, wherein "M" is barium.

3. The superconducting composition of claim **2**, wherein "x" is about 0.667.

4. The superconducting composition of claim **3**, wherein "L" is yttrium, lanthanum neodymium, samarium, europium, gadolinium, erbium or lutetium.

5. The superconducting composition of claim **1**, wherein the metal oxide has the formula

$$LM_2A_3O_{6+\partial}$$

and ∂ is a number value from about 0.1 to about 1.0 that provides the oxide complex with zero electrical resistance at a temperature of 70°K or above.

6. The superconducting composition of claim **5**, wherein "M" is barium.

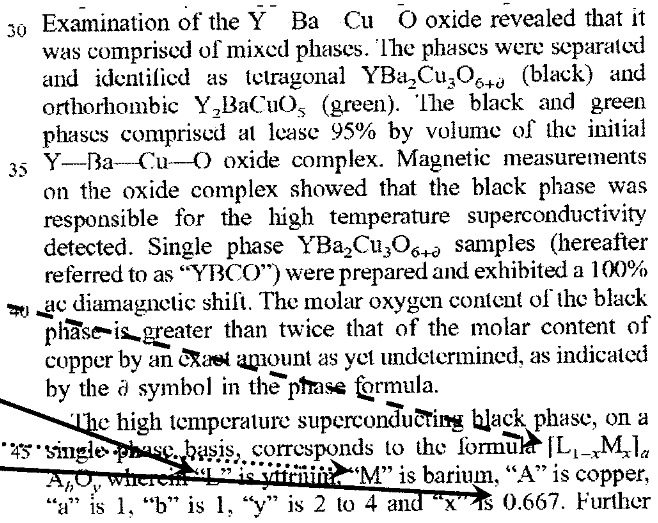
7. The superconducting composition of claim **6**, wherein "L" is yttrium, lanthanum neodymium, samarium, europium, gadolinium, erbium or lutetium.

8. A material containing a sufficient quantity of a superconductive crystalline phase to cause the material to exhibit substantially zero electrical resistance at a temperature of 77°K or above; said crystalline phase composition having the formula $LM_2Cu_3O_{6+\partial}$, wherein "L" is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, or mixtures thereof; "M" is Ba, Sr or mixtures thereof; and ∂ is a value from about 0.1 to about 1.0 that provides the composition with zero electrical resistance at a temperature of 77°K or above.

9. The material of claim **8** wherein L is Y and M is Ba.

10. The material of claim **8** wherein L is, Sm, Eu, Gd, Er, or Lu and M is Ba.

'866 patent col. 8, lines 30-47:



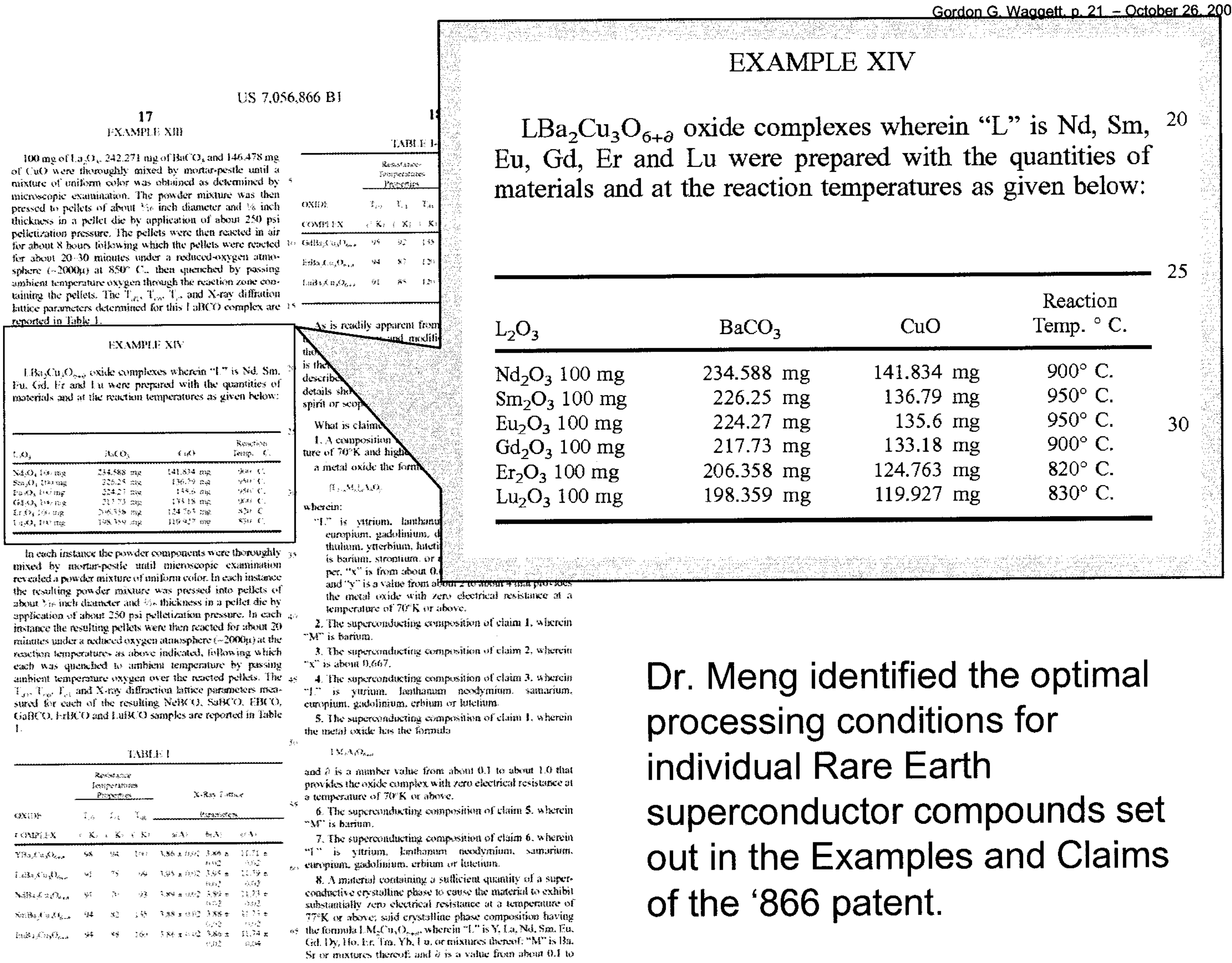
Examination of the Y—Ba—Cu—O oxide revealed that it was comprised of mixed phases. The phases were separated and identified as tetragonal $YBa_2Cu_3O_{6+\partial}$ (black) and orthorhombic Y_2BaCuO_5 (green). The black and green phases comprised at lease 95% by volume of the initial Y—Ba—Cu—O oxide complex. Magnetic measurements on the oxide complex showed that the black phase was responsible for the high temperature superconductivity detected. Single phase $YBa_2Cu_3O_{6+\partial}$ samples (hereafter referred to as "YBCO") were prepared and exhibited a 100% ac diamagnetic shift. The molar oxygen content of the black phase is greater than twice that of the molar content of copper by an exact amount as yet undetermined, as indicated by the ∂ symbol in the phase formula.

The high temperature superconducting black phase, on a single phase basis, corresponds to the formula $[L_{1-x}M_x]_aA_bO_y$ wherein "L" is yttrium, "M" is barium, "A" is copper, "a" is 1, "b" is 1, "y" is 2 to 4 and "x" is 0.667. Further

See also Examples I – VI, VIII, X-XI

See also Examples XII-XIV

Black Phase/Green Phase



US 7,056,866 B1

17

EXAMPLE XIII

100 mg of La_2O_3, 242.271 mg of $BaCO_3$ and 146.478 mg of CuO were thoroughly mixed by mortar-pestle until a mixture of uniform color was obtained as determined by microscopic examination. The powder mixture was then pressed to pellets of about 5/16 inch diameter and 1/8 inch thickness in a pellet die by application of about 250 psi pelletization pressure. The pellets were then reacted in air for about 8 hours following which the pellets were reacted for about 20-30 minutes under a reduced-oxygen atmosphere (~2000μ) at 850° C., then quenched by passing ambient temperature oxygen through the reaction zone containing the pellets. The T_{c0}, T_{cm}, T_c, and X-ray diffration lattice parameters determined for this LaBCO complex are reported in Table 1.

EXAMPLE XIV

$LBa_2Cu_3O_{6+\partial}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
Nd_2O_3 100 mg	234.588 mg	141.834 mg	900° C.
Sm_2O_3 100 mg	226.25 mg	136.79 mg	950° C.
Eu_2O_3 100 mg	224.27 mg	135.6 mg	950° C.
Gd_2O_3 100 mg	217.73 mg	133.18 mg	900° C.
Er_2O_3 100 mg	206.358 mg	124.763 mg	820° C.
Lu_2O_3 100 mg	198.359 mg	119.927 mg	830° C.

In each instance the powder components were thoroughly mixed by mortar-pestle until microscopic examination revealed a powder mixture of uniform color. In each instance the resulting powder mixture was pressed into pellets of about 5/16 inch diameter and 3/16 thickness in a pellet die by application of about 250 psi pelletization pressure. In each instance the resulting pellets were then reacted for about 20 minutes under a reduced oxygen atmosphere (~2000μ) at the reaction temperatures as above indicated, following which each was quenched to ambient temperature by passing ambient temperature oxygen over the reacted pellets. The T_{c0}, T_{cm}, T_{ct} and X-ray diffraction lattice parameters measured for each of the resulting NeBCO, SaBCO, EBCO, GaBCO, ErBCO and LuBCO samples are reported in Table 1.

TABLE I

As is readily apparent from

and modifi

the

is the

describe

details sho

spirit or scop

What is claim

1. A composition

ture of 70° K and high

a metal oxide the form

$(L_{1-x}M_x)_aA_bO_y$

wherein:

"L" is yttrium, lanthanu
europium, gadolinium, d
thulium, ytterbium, luteti
is barium, strontium, or
per, "x" is from about 0.
and "y" is a value from ab
the metal oxide with zero electrical resistance at a temperature of 70° K or above.

2. The superconducting composition of claim 1, wherein "M" is barium.

3. The superconducting composition of claim 2, wherein "x" is about 0.667.

4. The superconducting composition of claim 3, wherein "L" is yttrium, lanthanum neodymium, samarium, europium, gadolinium, erbium or lutetium.

5. The superconducting composition of claim 1, wherein the metal oxide has the formula

$LM_2A_3O_{6+\partial}$

and ∂ is a number value from about 0.1 to about 1.0 that provides the oxide complex with zero electrical resistance at a temperature of 70° K or above.

6. The superconducting composition of claim 5, wherein "M" is barium.

7. The superconducting composition of claim 6, wherein "L" is yttrium, lanthanum neodymium, samarium, europium, gadolinium, erbium or lutetium.

8. A material containing a sufficient quantity of a superconductive crystalline phase to cause the material to exhibit substantially zero electrical resistance at a temperature of 77° K or above; said crystalline phase composition having the formula $LM_2Cu_3O_{6+\partial}$, wherein "L" is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, or mixtures thereof; "M" is Ba, Sr or mixtures thereof; and ∂ is a value from about 0.1 to

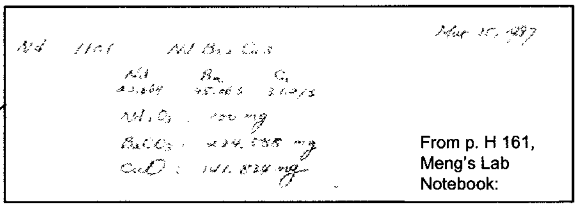
Dr. Meng identified the optimal processing conditions for individual Rare Earth superconductor compounds set out in the Examples and Claims of the '866 patent.

'866 Patent, Col. 17, lines 25-34:

EXAMPLE XIV

$LBa_2Cu_3O_{6+\delta}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
Nd_2O_3 100 mg	234.588 mg	141.834 mg	900° C.
Sm_2O_3 100 mg	226.25 mg	136.79 mg	950° C.
Eu_2O_3 100 mg	224.27 mg	135.6 mg	950° C.
Gd_2O_3 100 mg	217.73 mg	133.18 mg	900° C.
Er_2O_3 100 mg	206.358 mg	124.763 mg	820° C.
Lu_2O_3 100 mg	198.359 mg	119.927 mg	830° C.



Nd 1101 Nd Ba_2Cu_3

Mar 15, 1987

Nd Ba Cu

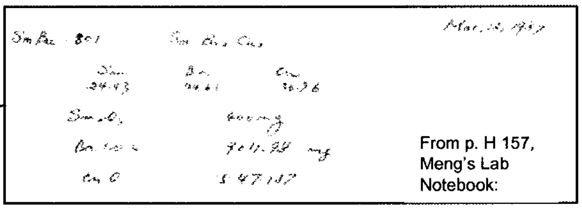
[illegible] [illegible] [illegible]

Nd_2O_3 : 100 mg

$BaCO_3$: 234.588 mg

CuO : 141.834 mg

From p. H 161, Meng's Lab Notebook:



Sm Ba 801 Sm Ba_2Cu_3

Mar. 15, 1987

Sm Ba Cu

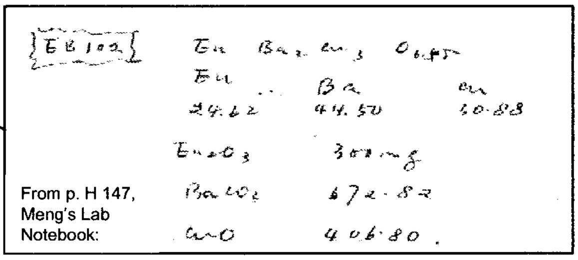
24.43 44.61 30.96

Sm_2O_3 400 mg

$BaCO_3$ 904.98 mg

CuO 547.147

From p. H 157, Meng's Lab Notebook:



EB 102

Eu $Ba_2Cu_3O_{6.85}$

Eu Ba Cu

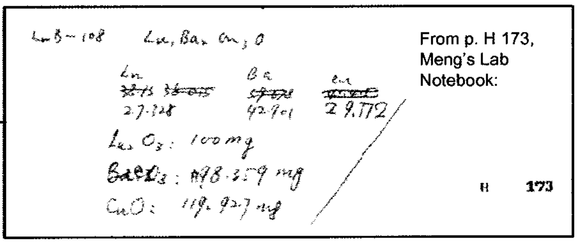
24.62 44.50 30.88

Eu_2O_3 300 mg

$BaCO_3$ 672.82

CuO 406.80 .

From p. H 147, Meng's Lab Notebook:



LuB-108 $Lu_1Ba_2Cu_3O$

Lu Ba Cu

~~[illegible]~~ ~~[illegible]~~ ~~[illegible]~~

27.128 42.901 29.772

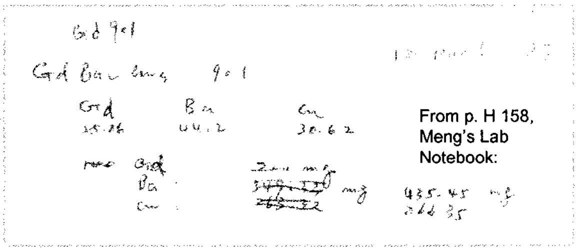
Lu_2O_3 : 100 mg

$BaCO_3$: 198.359 mg

CuO : 119.927 mg

From p. H 173, Meng's Lab Notebook:

H 173



Gd 901

Gd Ba_2Cu_3 901

Gd Ba Cu

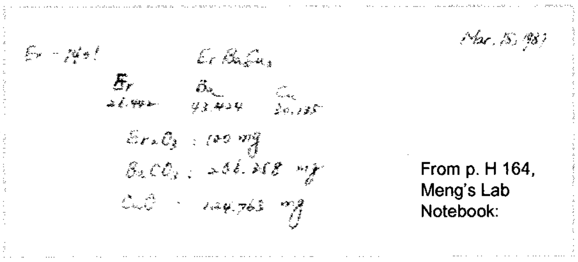
25.16 44.2 30.62

Gd 200 mg

Ba ~~[illegible]~~ mg 435.45 mg

Cu ~~[illegible]~~ 266.35

From p. H 158, Meng's Lab Notebook:



Er-1401 Er Ba_2Cu_3

Mar. 15, 1987

Er Ba Cu

26.442 43.424 30.135

Er_2O_3 : 100 mg

$BaCO_3$: 206.358 mg

CuO : 124.763 mg

From p. H 164, Meng's Lab Notebook:

Dr. Meng's Rare Earth Superconductor Work

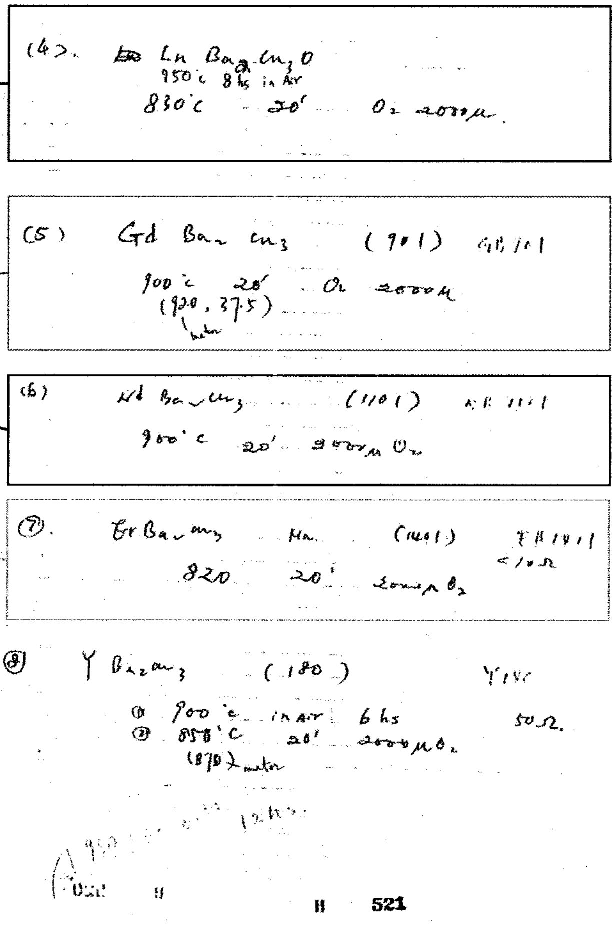
'866 Patent, Col. 17, lines 25-34:

EXAMPLE XIV

$LBa_2Cu_3O_{6+\delta}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
Nd_2O_3 100 mg	234.588 mg	141.834 mg	900° C.
Sm_2O_3 100 mg	226.25 mg	136.79 mg	950° C.
Eu_2O_3 100 mg	224.27 mg	135.6 mg	950° C.
Gd_2O_3 100 mg	217.73 mg	133.18 mg	900° C.
Er_2O_3 100 mg	206.358 mg	124.763 mg	820° C.
Lu_2O_3 100 mg	198.359 mg	119.927 mg	830° C.

p. H 521, Meng's Lab Notebook:



(4). ~~Eu~~ Lu Ba_2Cu_3O
950°c 8 hs in Air
830°c 20' O_2 2000μ.

(5) Gd Ba_2 Cu_3 (901) [illegible]
900°c 20' O_2 2000μ
(920, 37.5)
meter

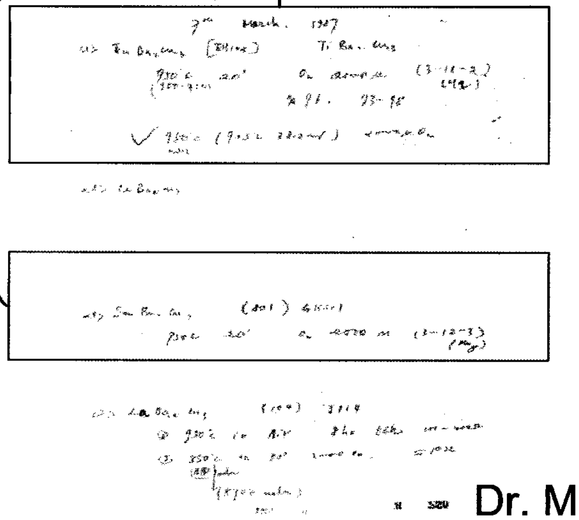
(6) Nd Ba_2Cu_3 (1101) NB 1101
900°c 20' 2000μ O_2

⑦. Er Ba_2Cu_3 Ha. (1401) EB 1401
< 10Ω
820 20' 2000μ O_2

⑧ Y Ba_2Cu_3 (180) [illegible]
① 900°c in air 6 hs 50Ω.
② 850°c 20' 2000μ O_2
(870) meter

521

p. H 520, Meng's Lab Notebook:



7th March. 1987
(1) Eu Ba_2Cu_3 [illegible] Ti Ba_2 Cu_3
950°c 20' O_2 2000μ (3-11-2)
[illegible]
✓ 950°c [illegible] 2000μ O_2

(2) La Ba_2Cu_3

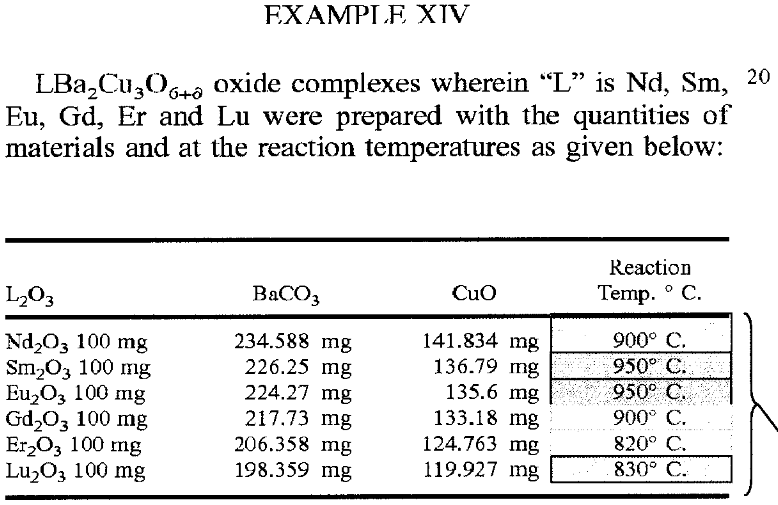
(3) Sm Ba_2 Cu_3 (801) [illegible]
950°c 20' O_2 2000μ (3-12-3)

(4) La Ba_2 Cu_3 (100) [illegible]
① 950°c in Air 8 hs [illegible]
② 850°c in O_2 2000μ [illegible]

520

Dr. Meng's Rare Earth Superconductor Work

'866 Patent, Col. 17, lines 25-34:

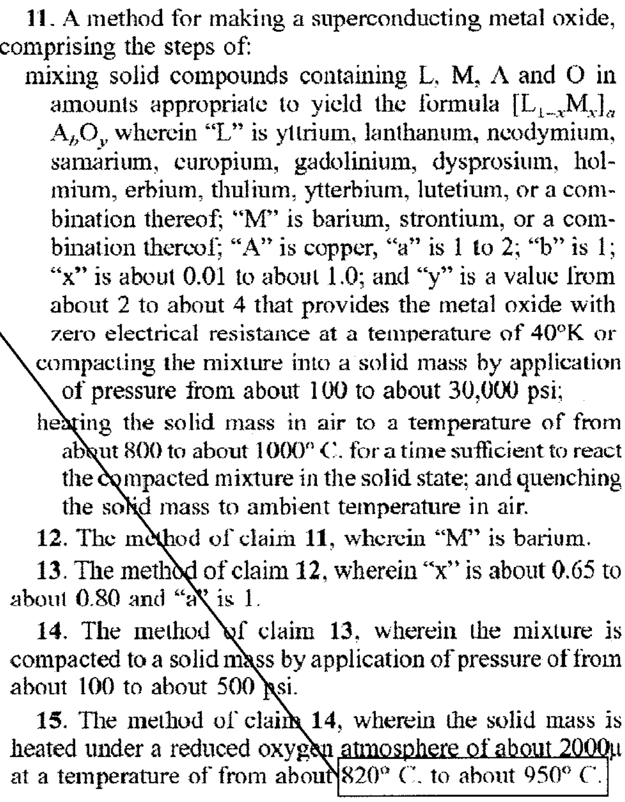


EXAMPLE XIV

$LBa_2Cu_3O_{6+\delta}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
Nd_2O_3 100 mg	234.588 mg	141.834 mg	900° C.
Sm_2O_3 100 mg	226.25 mg	136.79 mg	950° C.
Eu_2O_3 100 mg	224.27 mg	135.6 mg	950° C.
Gd_2O_3 100 mg	217.73 mg	133.18 mg	900° C.
Er_2O_3 100 mg	206.358 mg	124.763 mg	820° C.
Lu_2O_3 100 mg	198.359 mg	119.927 mg	830° C.

CLAIMS – '866 patent col. 19-20:



11. A method for making a superconducting metal oxide, comprising the steps of:

mixing solid compounds containing L, M, A and O in amounts appropriate to yield the formula $[L_{1-x}M_x]_a A_b O_y$ wherein "L" is yttrium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or a combination thereof; "M" is barium, strontium, or a combination thereof; "A" is copper, "a" is 1 to 2; "b" is 1; "x" is about 0.01 to about 1.0; and "y" is a value from about 2 to about 4 that provides the metal oxide with zero electrical resistance at a temperature of 40°K or

compacting the mixture into a solid mass by application of pressure from about 100 to about 30,000 psi;

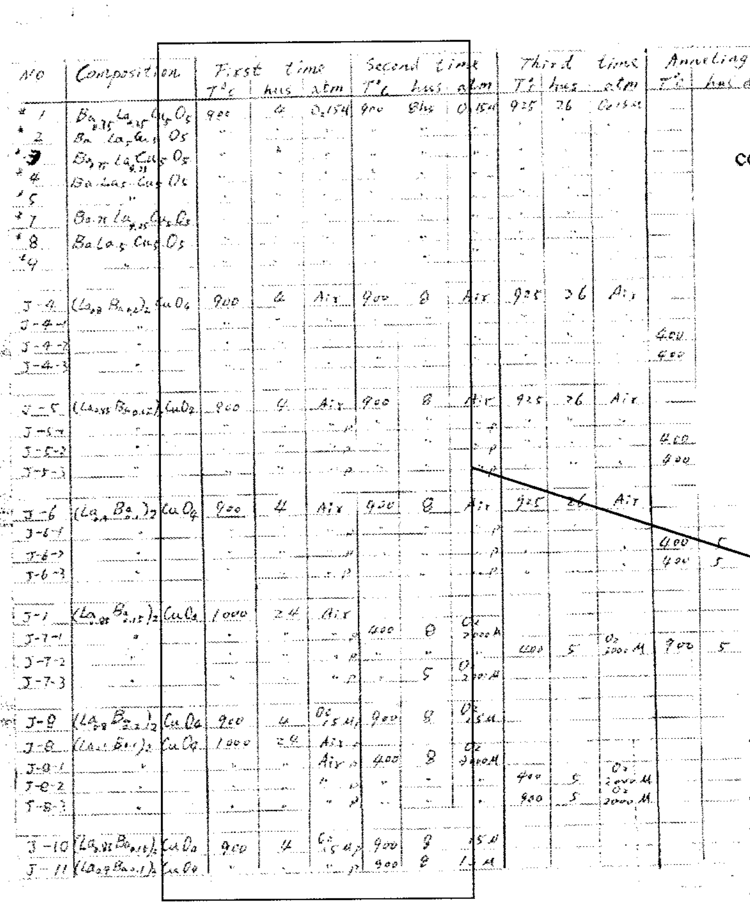
heating the solid mass in air to a temperature of from about 800 to about 1000° C. for a time sufficient to react the compacted mixture in the solid state; and quenching the solid mass to ambient temperature in air.

12. The method of claim **11**, wherein "M" is barium.

13. The method of claim **12**, wherein "x" is about 0.65 to about 0.80 and "a" is 1.

14. The method of claim **13**, wherein the mixture is compacted to a solid mass by application of pressure of from about 100 to about 500 psi.

15. The method of claim **14**, wherein the solid mass is heated under a reduced oxygen atmosphere of about 2000μ at a temperature of from about 820° C. to about 950° C.



Dec 1986

No	Composition	First time T°c	hrs	atm	Second time T°c	hrs	atm	Third time T°c	hrs	atm	Annealing-1 T°c	hrs	atm	Annealing-2 T°c	hrs	atm	Tc(i)	Tc(0)	R-T	Ratio	ρ	x
*1	$Ba_{0.75}La_{4.25}Cu_5O_5$	900	6	O_2 15M	900	8hs	O_2 15M	925	26	O_2 15M												
*2	$Ba\,La_5Cu_5O_5$																					
*3	$Ba_{.75}La_{4.25}Cu_5O_5$																					
*4	$Ba\,La_5Cu_5O_6$																					
*5																						
*7	$Ba_{.75}La_{4.25}Cu_5O_5$																					
*8	$Ba\,La_5Cu_5O_5$																					
*9																						
J-4	$(La_{0.9}Ba_{0.1})_2CuO_4$	900	4	Air	900	8	Air	925	26	Air												
J-4-1																						
J-4-2											400											
J-4-3											400											
J-5	$(La_{0.85}Ba_{0.15})_2CuO_4$	900	4	Air	900	8	Air	925	26	Air												
J-5-1																						
J-5-2											400											
J-5-3											400											
J-6	$(La_{0.9}Ba_{0.1})_2CuO_4$	900	4	Air	900	8	Air	925	26	Air												
J-6-1											400	5										
J-6-2											400	5										
J-6-3																						
J-7	$(La_{0.85}Ba_{0.15})_2CuO_4$	1000	24	Air																		
J-7-1					900	8	O_2 2000M	900	5	O_2 2000M	900	5										
J-7-2																						
J-7-3						5	O_2 2000M															
J-8	$(La_{0.9}Ba_{0.1})_2CuO_4$	900	4	O_2 15M	900	8	O_2 15M															
J-8	$(La_{0.9}Ba_{0.1})_2CuO_4$	1000	24	Air																		
J-8-1				Air	900	8	O_2 3000M															
J-8-2								900	5	O_2 2000M												
J-8-3								900	5	O_2 2000M												
J-10	$(La_{0.85}Ba_{0.15})_2CuO_4$	900	4	O_2 15M	900	8	15M															
J-11	$(La_{0.9}Ba_{0.1})_2CuO_4$				900	8	15M															

From p. H 471, Meng's Lab Notebook:

11. A method for making a superconducting metal oxide, comprising the steps of:

mixing solid compounds containing L, M, A and O in amounts appropriate to yield the formula $[L_{1-x}M_x]_a A_bO_y$ wherein "L" is yttrium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or a combination thereof; "M" is barium, strontium, or a combination thereof; "A" is copper, "a" is 1 to 2; "b" is 1; "x" is about 0.01 to about 1.0; and "y" is a value from about 2 to about 4 that provides the metal oxide with zero electrical resistance at a temperature of 40°K or above;

compacting the mixture into a solid mass by application of pressure from about 100 to about 30,000 psi;

heating the solid mass in air to a temperature of from about 800 to about 1000° C. for a time sufficient to react the compacted mixture in the solid state: and quenching the solid mass to ambient temperature in air.

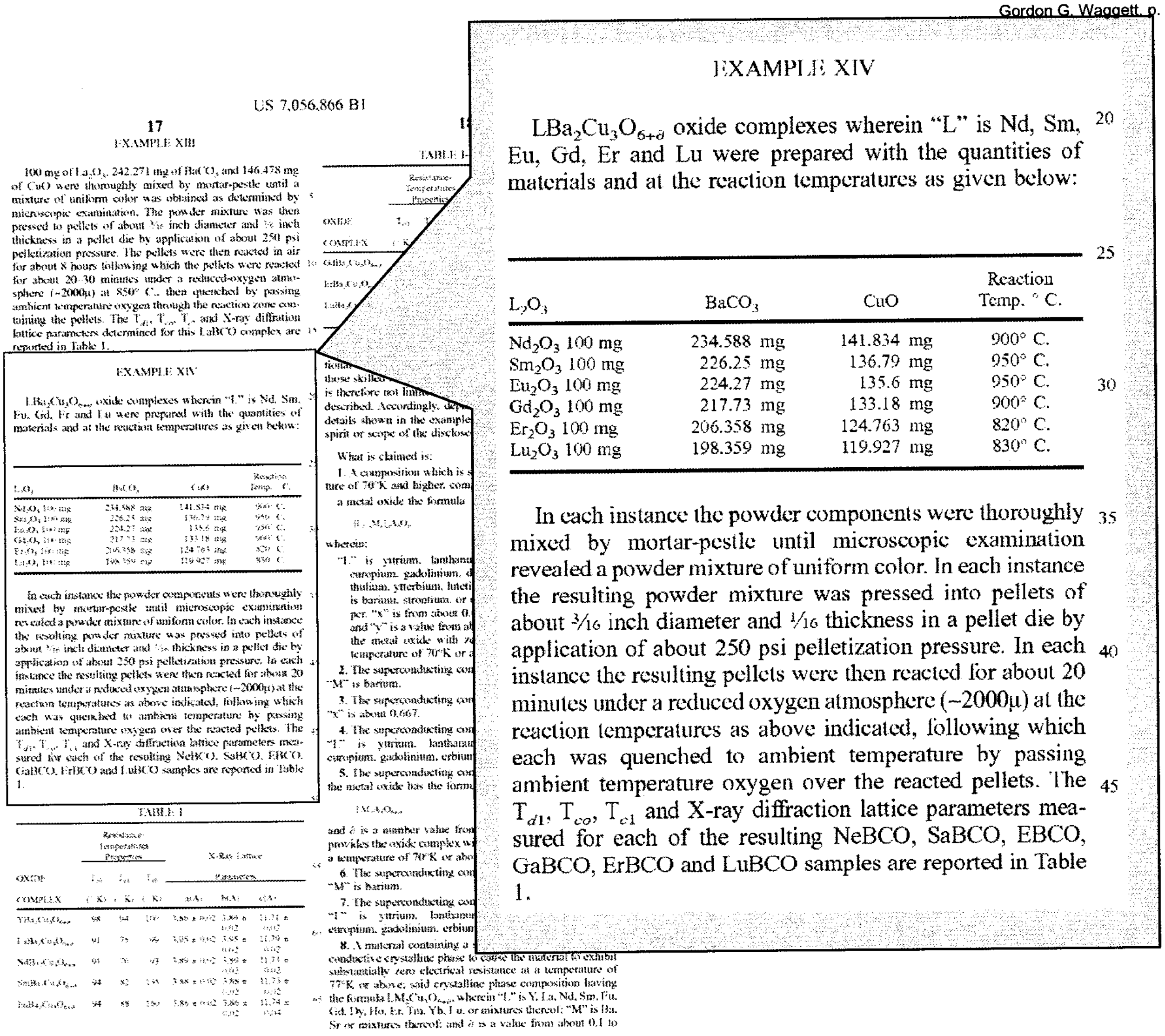
12. The method of claim **11**, wherein "M" is barium.

13. The method of claim **12**, wherein "x" is about 0.65 to about 0.80 and "a" is 1.

14. The method of claim **13**, wherein the mixture is compacted to a solid mass by application of pressure of from about 100 to about 500 psi.

15. The method of claim **14**, wherein the solid mass is heated under a reduced oxygen atmosphere of about 2000μ at a temperature of from about 820° C. to about 950° C.

CLAIMS - '866 patent col. 19-20:



US 7,056,866 B1

17

EXAMPLE XIII

100 mg of La_2O_3, 242.271 mg of $BaCO_3$ and 146.478 mg of CuO were thoroughly mixed by mortar-pestle until a mixture of uniform color was obtained as determined by microscopic examination. The powder mixture was then pressed to pellets of about 3⁄16 inch diameter and 1⁄16 inch thickness in a pellet die by application of about 250 psi pelletization pressure. The pellets were then reacted in air for about 8 hours following which the pellets were reacted for about 20-30 minutes under a reduced-oxygen atmosphere (~2000μ) at 850° C., then quenched by passing ambient temperature oxygen through the reaction zone containing the pellets. The T_{d1}, T_{co}, T_{c} and X-ray diffration lattice parameters determined for this LaBCO complex are reported in Table 1.

EXAMPLE XIV

$LBa_2Cu_3O_{6+\delta}$ oxide complexes wherein “L” is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
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Sm_2O_3 100 mg	226.25 mg	136.79 mg	950° C.
Eu_2O_3 100 mg	224.27 mg	135.6 mg	950° C.
Gd_2O_3 100 mg	217.73 mg	133.18 mg	900° C.
Er_2O_3 100 mg	206.358 mg	124.763 mg	820° C.
Lu_2O_3 100 mg	198.359 mg	119.927 mg	830° C.

In each instance the powder components were thoroughly mixed by mortar-pestle until microscopic examination revealed a powder mixture of uniform color. In each instance the resulting powder mixture was pressed into pellets of about 3⁄16 inch diameter and 1⁄16 thickness in a pellet die by application of about 250 psi pelletization pressure. In each instance the resulting pellets were then reacted for about 20 minutes under a reduced oxygen atmosphere (~2000μ) at the reaction temperatures as above indicated, following which each was quenched to ambient temperature by passing ambient temperature oxygen over the reacted pellets. The T_{d1}, T_{co}, T_{c1} and X-ray diffraction lattice parameters measured for each of the resulting NeBCO, SaBCO, EBCO, GaBCO, ErBCO and LuBCO samples are reported in Table 1.

TABLE 1

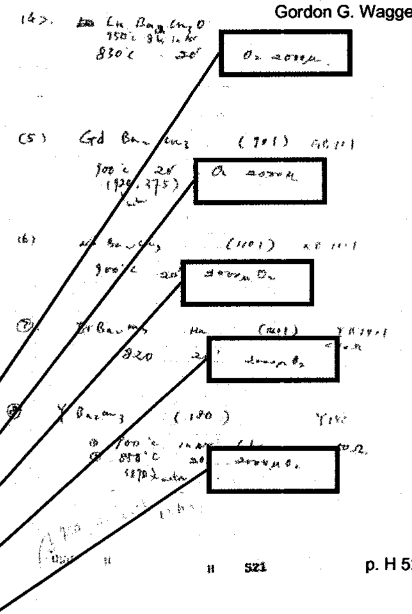
'866 Patent, Col. 17, lines 25-34:

EXAMPLE XIV

$LBa_2Cu_3O_{6+\partial}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
Nd_2O_3 100 mg	234.588 mg	141.834 mg	900° C.
Sm_2O_3 100 mg	226.25 mg	136.79 mg	950° C.
Eu_2O_3 100 mg	224.27 mg	135.6 mg	950° C.
Gd_2O_3 100 mg	217.73 mg	133.18 mg	900° C.
Er_2O_3 100 mg	206.358 mg	124.763 mg	820° C.
Lu_2O_3 100 mg	198.359 mg	119.927 mg	830° C.

In each instance the powder components were thoroughly mixed by mortar-pestle until microscopic examination revealed a powder mixture of uniform color. In each instance the resulting powder mixture was pressed into pellets of about 3⁄16 inch diameter and 1⁄16 thickness in a pellet die by application of about 250 psi pelletization pressure. In each instance the resulting pellets were then reacted for about 20 minutes under a reduced oxygen atmosphere (~2000μ) at the reaction temperatures as above indicated, following which each was quenched to ambient temperature by passing ambient temperature oxygen over the reacted pellets. The T_{d1}, T_{co}, T_{c1} and X-ray diffraction lattice parameters measured for each of the resulting NeBCO, SaBCO, EBCO, GaBCO, ErBCO and LuBCO samples are reported in Table 1.



(4>. Lu Ba2 Cu3 O
950°c 8½ hr
830°c 20'
O2 2000μ

(5) Gd Ba2 Cu3 (701) GdBCO
900°c 20'
(920, 375)
O2 2000μ

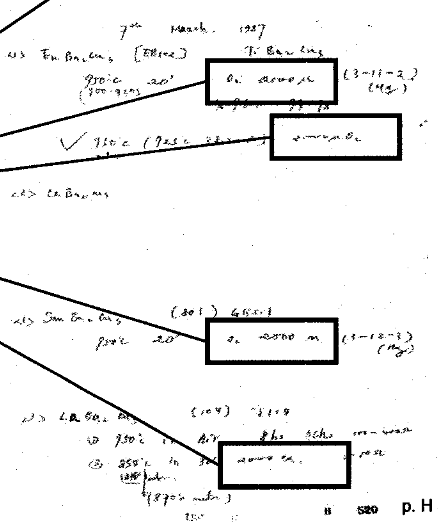
(6) Nd Ba2 Cu3 (1101) NdBCO
900°c 20'
2000μ O2

(7) Er Ba2 Cu3 (1101) ErBCO
820 20'
2000μ O2

(8) Y Ba2 Cu3 (100) YBCO
① 900°c
② 850°c 20'
2000μ O2

521

p. H 521, Meng's Lab Notebook:



7th March 1987

(1) Eu Ba2 Cu3 [EBCO]
950°c 20'
(900-925°)
O2 2000μ
(3-11-2)
(Mg)

✓ 950°c (925°c [illegible])
2000μ O2

(2) Eu Ba2 Cu3

(1) Sm Ba2 Cu3 (801) SBCO
950°c 20'
O2 2000μ
(3-12-3)
(Mg)

(2) La Ba2 Cu3 (104) LBCO
① 950°c in Air 8hr [illegible]
② 850°c in
2000μ O2
(870° [illegible])

520

p. H 520, Meng's Lab Notebook:

Gordon G. Waggett, p. 28 – October 26, 2006

'866 Patent, Col. 17, lines 25-34:

EXAMPLE XIV

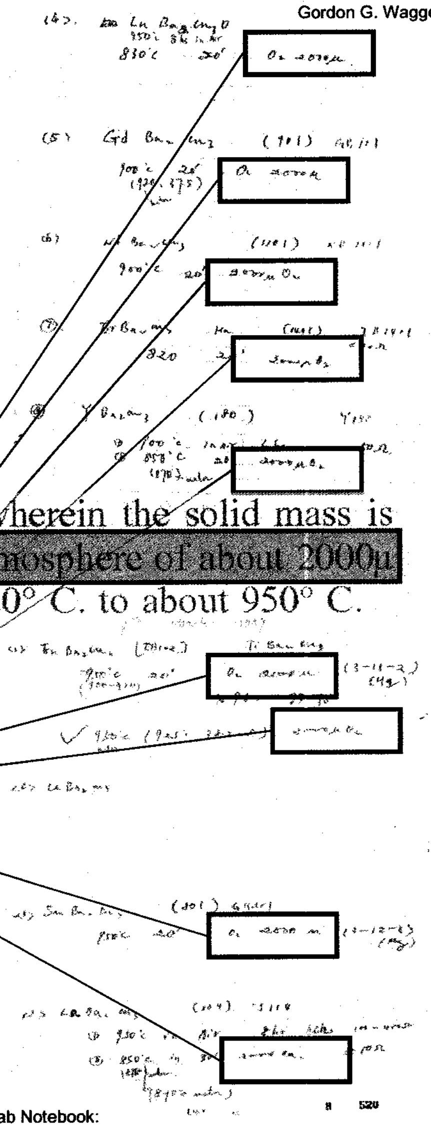
$LBa_2Cu_3O_{6+\partial}$ oxide complexes wherein "L" is Nd, Sm, Eu, Gd, Er and Lu were prepared with the quantities of materials and at the reaction temperatures as given below:

L_2O_3	$BaCO_3$	CuO	Reaction Temp. ° C.
Nd_2O_3 100 mg	234.588 mg	141.834 mg	900° C.
Sm_2O_3 100 mg			950° C.
Eu_2O_3 100 mg			950° C.
Gd_2O_3 100 mg			900° C.
Er_2O_3 100 mg	206.358 mg	[illegible]	[illegible]
Lu_2O_3 100 mg	198.359 mg	119.927 mg	[illegible]

'866 CLAIM 15

15. The method of claim 14, wherein the solid mass is heated under a reduced oxygen atmosphere of about 2000μ at a temperature of from about 820° C. to about 950° C.

In each instance the p[illegible] mixed by mortar-pestle until microscopic examination revealed a powder mixture of uniform color. In each instance the resulting powder mixture was pressed into pellets of about 3/16 inch diameter and 1/16 thickness in a pellet die by application of about 250 psi pelletization pressure. In each instance the resulting pellets were then reacted for about 20 minutes under a reduced oxygen atmosphere (~2000μ) at the reaction temperatures as above indicated, following which each was quenched to ambient temperature by passing ambient temperature oxygen over the reacted pellets. The T_{d1}, T_{co}, T_{c1} and X-ray diffraction lattice parameters measured for each of the resulting NeBCO, SaBCO, EBCO, GaBCO, ErBCO and LuBCO samples are reported in Table 1.

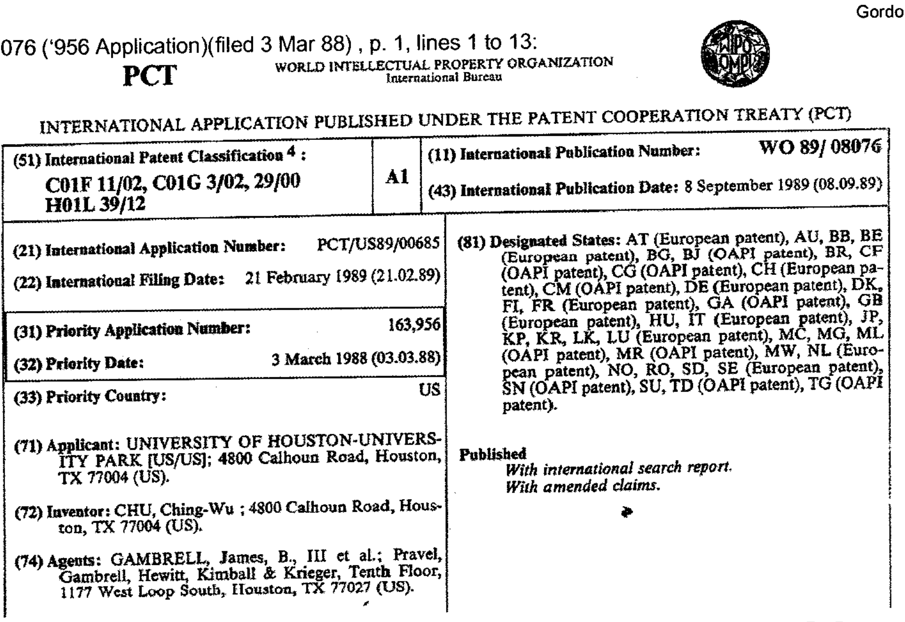


p. H 520, Meng's Lab Notebook:

‘956 continuation-in-part application filed on March 3, 1988

Similarly to the clear and convincing evidence above showing that Dr. Meng is a co-inventor of the ‘866 patent, Dr. Meng is likewise a co-inventor of the ‘956 continuation-in-part application filed on March 3, 1988. The following provides a brief look at the ‘956 specification and claims in view of exemplary excerpts from Dr. Meng’s laboratory notebook.

Excerpts from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 1, lines 1 to 13:



PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : **C01F 11/02, C01G 3/02, 29/00** **H01L 39/12**	**A1**	**(11) International Publication Number:** **WO 89/ 08076** **(43) International Publication Date:** 8 September 1989 (08.09.89)

(21) International Application Number: PCT/US89/00685

(22) International Filing Date: 21 February 1989 (21.02.89)

(31) Priority Application Number: 163,956

(32) Priority Date: 3 March 1988 (03.03.88)

(33) Priority Country: US

(71) Applicant: UNIVERSITY OF HOUSTON-UNIVERSITY PARK [US/US]; 4800 Calhoun Road, Houston, TX 77004 (US).

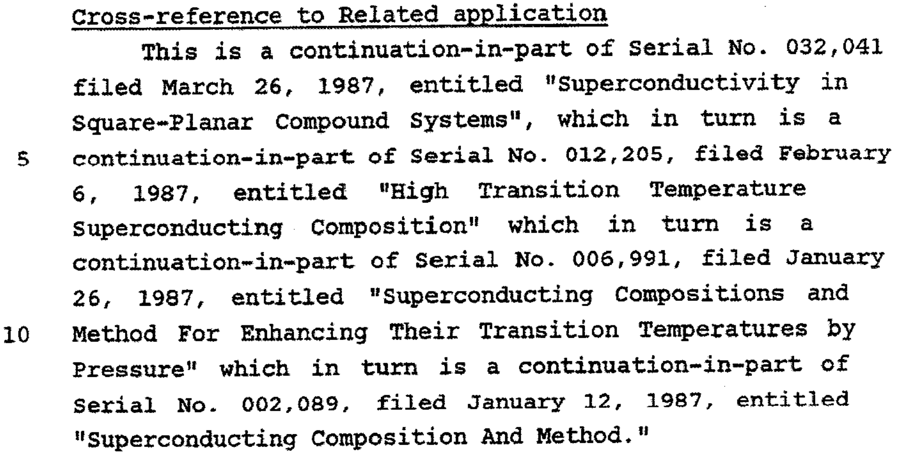
(72) Inventor: CHU, Ching-Wu ; 4800 Calhoun Road, Houston, TX 77004 (US).

(74) Agents: GAMBRELL, James, B., III et al.; Pravel, Gambrell, Hewitt, Kimball & Krieger, Tenth Floor, 1177 West Loop South, Houston, TX 77027 (US).

(81) Designated States: AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).

Published
With international search report.
With amended claims.

'956 continuation-in-part application filed on March 3, 1988

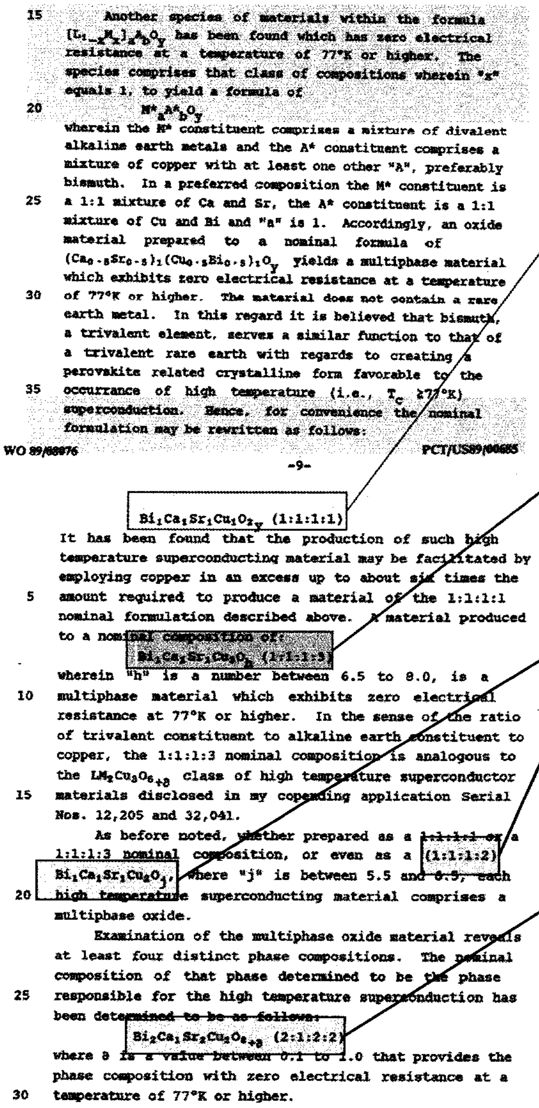


Cross-reference to Related application

This is a continuation-in-part of Serial No. 032,041 filed March 26, 1987, entitled "Superconductivity in Square-Planar Compound Systems", which in turn is a continuation-in-part of Serial No. 012,205, filed February 6, 1987, entitled "High Transition Temperature Superconducting Composition" which in turn is a continuation-in-part of Serial No. 006,991, filed January 26, 1987, entitled "Superconducting Compositions and Method For Enhancing Their Transition Temperatures by Pressure" which in turn is a continuation-in-part of Serial No. 002,089, filed January 12, 1987, entitled "Superconducting Composition And Method."

the '866 patent

Excerpts from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 8, line 15 to p. 9, line 30:



Another species of materials within the formula $[L_{1-x}M_x]_a A_b O_y$ has been found which has zero electrical resistance at a temperature of 77°K or higher. The species comprises that class of compositions wherein "x" equals 1, to yield a formula of

$M^*_a A^*_b O_y$

wherein the M* constituent comprises a mixture of divalent alkaline earth metals and the A* constituent comprises a mixture of copper with at least one other "A", preferably bismuth. In a preferred composition the M* constituent is a 1:1 mixture of Ca and Sr, the A* constituent is a 1:1 mixture of Cu and Bi and "a" is 1. Accordingly, an oxide material prepared to a nominal formula of $(Ca_{0.5}Sr_{0.5})_1(Cu_{0.5}Bi_{0.5})_1O_y$ yields a multiphase material which exhibits zero electrical resistance at a temperature of 77°K or higher. The material does not contain a rare earth metal. In this regard it is believed that bismuth, a trivalent element, serves a similar function to that of a trivalent rare earth with regards to creating a perovakite related crystalline form favorable to the occurrance of high temperature (i.e., $T_c \geq 77$°K) superconduction. Hence, for convenience the nominal formulation may be rewritten as follows:

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$Bi_1Ca_1Sr_1Cu_1O_{2y}$ (1:1:1:1)

It has been found that the production of such high temperature superconducting material may be facilitated by employing copper in an excess up to about six times the amount required to produce a material of the 1:1:1:1 nominal formulation described above. A material produced to a nominal composition of:

$Bi_1Ca_1Sr_1Cu_3O_h$ (1:1:1:3)

wherein "h" is a number between 6.5 to 8.0, is a multiphase material which exhibits zero electrical resistance at 77°K or higher. In the sense of the ratio of trivalent constituent to alkaline earth constituent to copper, the 1:1:1:3 nominal composition is analogous to the $LM_2Cu_3O_{6+\delta}$ class of high temperature superconductor materials disclosed in my copending application Serial Nos. 12,205 and 32,041.

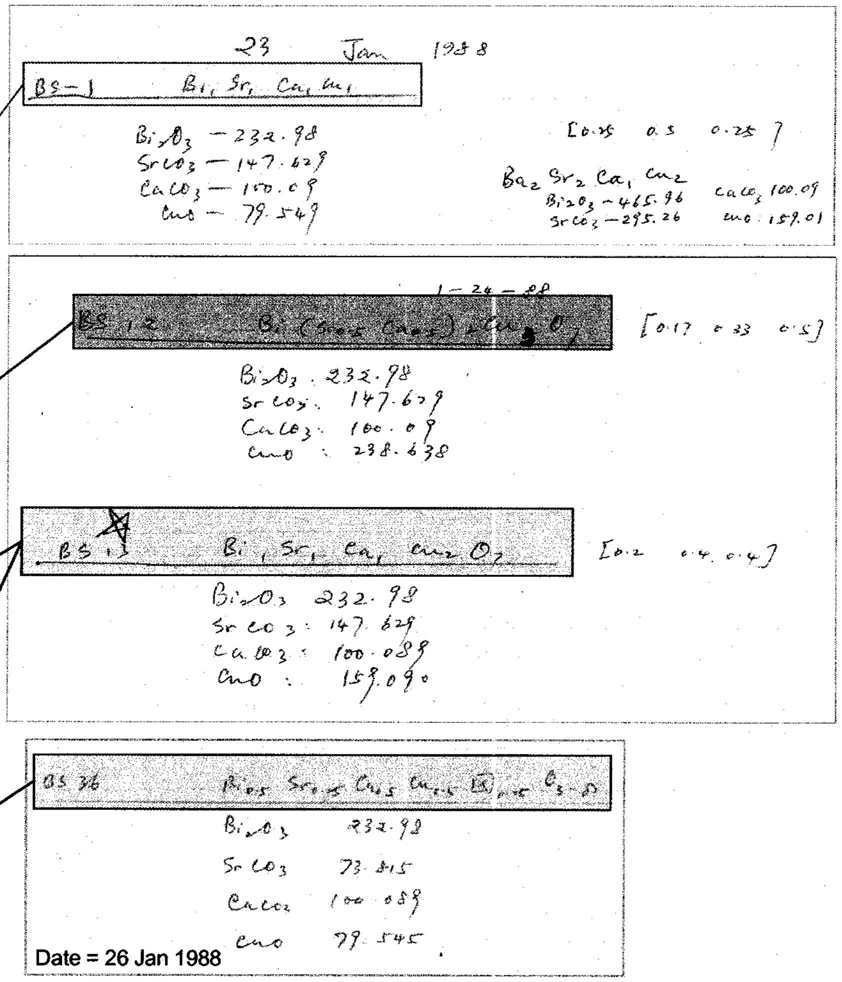
As before noted, whether prepared as a 1:1:1:1 or a 1:1:1:3 nominal composition, or even as a (1:1:1:2) $Bi_1Ca_1Sr_1Cu_2O_j$, where "j" is between 5.5 and 6.5, each high temperature superconducting material comprises a multiphase oxide.

Examination of the multiphase oxide material reveals at least four distinct phase compositions. The nominal composition of that phase determined to be the phase responsible for the high temperature superconduction has been determined to be as follows:

$Bi_2Ca_1Sr_2Cu_2O_{8+\delta}$ (2:1:2:2)

where δ is a value between 0.1 to 1.0 that provides the phase composition with zero electrical resistance at a temperature of 77°K or higher.

Example excerpts from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"



23 Jan 1988

BS-1 $Bi_1 Sr_1 Ca_1 Cu_1$

Bi_2O_3 – 232.98
$SrCO_3$ – 147.629
$CaCO_3$ – 150.09
CuO – 79.549

[0.25 0.5 0.25]

$Ba_2 Sr_2 Ca_1 Cu_2$
Bi_2O_3 – 465.96
$SrCO_3$ – 295.26
$CaCO_3$ 100.09
CuO : 159.01

1-24-88

BS 12 Bi $(Sr_{0.5} Ca_{0.5})_2 Cu_3 O_7$

[0.17 0.33 0.5]

Bi_2O_3 . 232.98
$SrCO_3$. 147.629
$CaCO_3$. 100.09
CuO : 238.638

BS 13 $Bi_1 Sr_1 Ca_1 Cu_2 O_7$

[0.2 0.4 0.4]

Bi_2O_3 232.98
$SrCO_3$: 147.629
$CaCO_3$: 100.089
CuO : 159.090

BS 36 $Bi_{0.5}$ $Sr_{0.5}$ $Ca_{1.5}$ $Cu_{1.5}$ [illegible] $O_{3.5}$

Bi_2O_3 232.98
$SrCO_3$ 73.815
$CaCO_3$ 100.089
CuO 79.545

Date = 26 Jan 1988

Excerpt from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 10, line 25 to p. 11, line 7:

For convenience the phase composition within a multiphase material prepared with a nominal composition Bi:Ca:Sr:Cu of 1:1:1:1; 1:1:1:2; or 1:1:1:3 may be represented as a metal oxide of the formula

$$T_dM^*_eCu_fO_g$$

wherein "T" is a trivalent transition metal such as Bi, Al, Ba, Tl, In, Sb or mixtures thereof; "M*" is a mixture of alkaline earth metals such as Sr and Ca, Ba and Sr, Ba and Ca, Sr and Mg, and Ca and Mg in a ratio of the alkaline earth metal of larger atomic radius (M^L) to the alkaline earth metal of smaller atomic radius (M^S) of from about 1:1 to about 1:3; "d" is a number from about 1 to about 3; "e" is a number from about 1 to about 6; "f" is a

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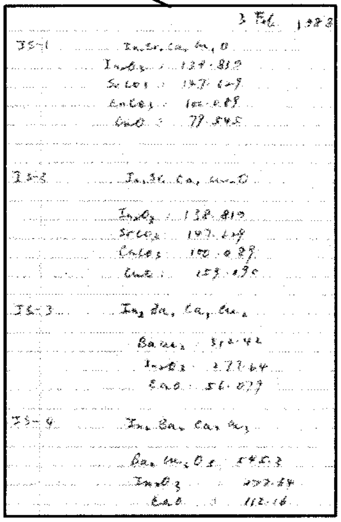
number from about 1 to about 6; "g" is a number between from about (3d + 2e + 2f)/2 to about (3d + 2e + 3f)/2 that provides the metal oxide with zero electrical resistance at a temperature of 77°K or higher. Preferably "T" is bismuth; "M*" is Ca and Sr at ratio of 1:2; "d" is 2; "e" is 3; "f" is 2 and "g" is a number between about 8 to about 9.



3 Feb 1988

IS-1 $In_2Sr_1Ca_1Cu_2O$

In_2O_3 : 138.819

$SrCO_3$: 147.629

$CaCO_3$: 100.089

CuO : 79.545

IS-2 $In_2Sr_1Ca_1Cu_2O$

In_2O_3 : 138.819

$SrCO_3$ 147.629

$CaCO_3$ 100.089

CuO : 159.090

IS-3 $In_2Ba_1Ca_1Cu_2$

$BaCuO_2$: 312.42

In_2O_3 : 277.64

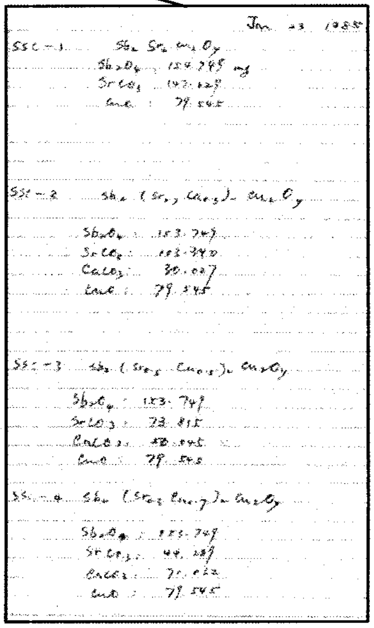
CaO : 56.079

IS-4 $In_2Ba_2Ca_2Cu_3$

$Ba_2Cu_3O_5$: 545.3

In_2O_3 : 277.64

CaO : 112.16



Jan 23 1988

SSC-1 $Sb_2Sr_2Cu_2O_y$

Sb_2O_4 : 153.749 mg

$SrCO_3$: 147.629

CuO : 79.545

SSC-2 $Sb_2(Sr_{0.7}Ca_{0.3})_2Cu_2O_y$

Sb_2O_4 : 153.749

$SrCO_3$: 103.340

$CaCO_3$: 30.027

CuO : 79.545

SSC-3 $Sb_2(Sr_{0.5}Ca_{0.5})_2Cu_2O_y$

Sb_2O_4 : 153.749

$SrCO_3$: 73.815

$CaCO_3$: 50.045

CuO : 79.545

SSC-4 $Sb_2(Sr_{0.3}Ca_{0.7})_2Cu_2O_y$

Sb_2O_4 : 153.749

$SrCO_3$: 44.289

$CaCO_3$: 70.062

CuO : 79.545

Example excerpts from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"

Excerpts from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 8, line 15 to p. 9, line 30:

Another species of materials within the formula $[L_{1-x}M_x]_aA_bO_y$ has been found which has zero electrical resistance at a temperature of 77°K or higher. The species comprises that class of compositions wherein "x" equals 1, to yield a formula of

$$M^*_aA^*_bO_y$$

wherein the M* constituent comprises a mixture of divalent alkaline earth metals and the A* constituent comprises a mixture of copper with at least one other "A", preferably bismuth. In a preferred composition the M* constituent is a 1:1 mixture of Ca and Sr, the A* constituent is a 1:1 mixture of Cu and Bi and "a" is 1. Accordingly, an oxide material prepared to a nominal formula of $(Ca_{0.5}Sr_{0.5})_1(Cu_{0.5}Bi_{0.5})_1O_y$ yields a multiphase material which exhibits zero electrical resistance at a temperature of 77°K or higher. The material does not contain a rare earth metal. In this regard it is believed that bismuth, a trivalent element, serves a similar function to that of a trivalent rare earth with regards to creating a perovakite related crystalline form favorable to the occurrance of high temperature (i.e., $T_c \geq 77$°K) superconduction. Hence, for convenience the nominal formulation may be rewritten as follows:

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$Bi_1Ca_1Sr_1Cu_1O_{2y}$ (1:1:1:1)

It has been found that the production of such high temperature superconducting material may be facilitated by employing copper in an excess up to about six times the amount required to produce a material of the 1:1:1:1 nominal formulation described above. A material produced to a nominal composition of:

$Bi_1Ca_1Sr_1Cu_3O_h$ (1:1:1:3)

wherein "h" is a number between 6.5 to 8.0, is a multiphase material which exhibits zero electrical resistance at 77°K or higher. In the sense of the ratio of trivalent constituent to alkaline earth constituent to copper, the 1:1:1:3 nominal composition is analogous to the $LM_2Cu_3O_{6+\partial}$ class of high temperature superconductor materials disclosed in my copending application Serial Nos. 12,205 and 32,041.

As before noted, whether prepared as a 1:1:1:1 or a 1:1:1:3 nominal composition, or even as a (1:1:1:2) $Bi_1Ca_1Sr_1Cu_2O_j$, where "j" is between 5.5 and 6.5, each high temperature superconducting material comprises a multiphase oxide.

Examination of the multiphase oxide material reveals at least four distinct phase compositions. The nominal composition of that phase determined to be the phase responsible for the high temperature superconduction has been determined to be as follows:

$Bi_2Ca_1Sr_2Cu_2O_{8+\partial}$ (2:1:2:2)

where ∂ is a value between 0.1 to 1.0 that provides the phase composition with zero electrical resistance at a temperature of 77°K or higher.

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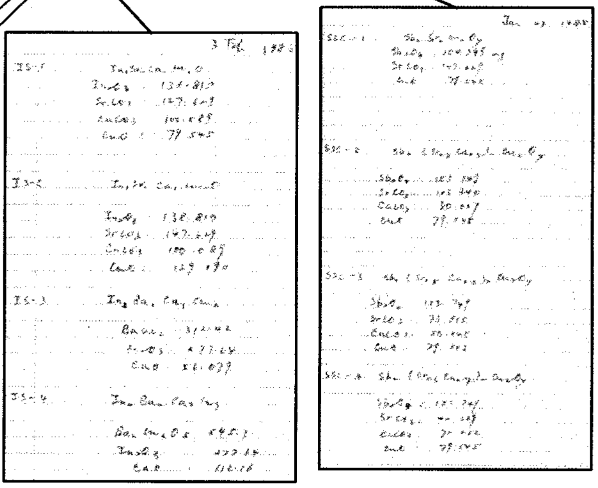
AMENDED CLAIMS

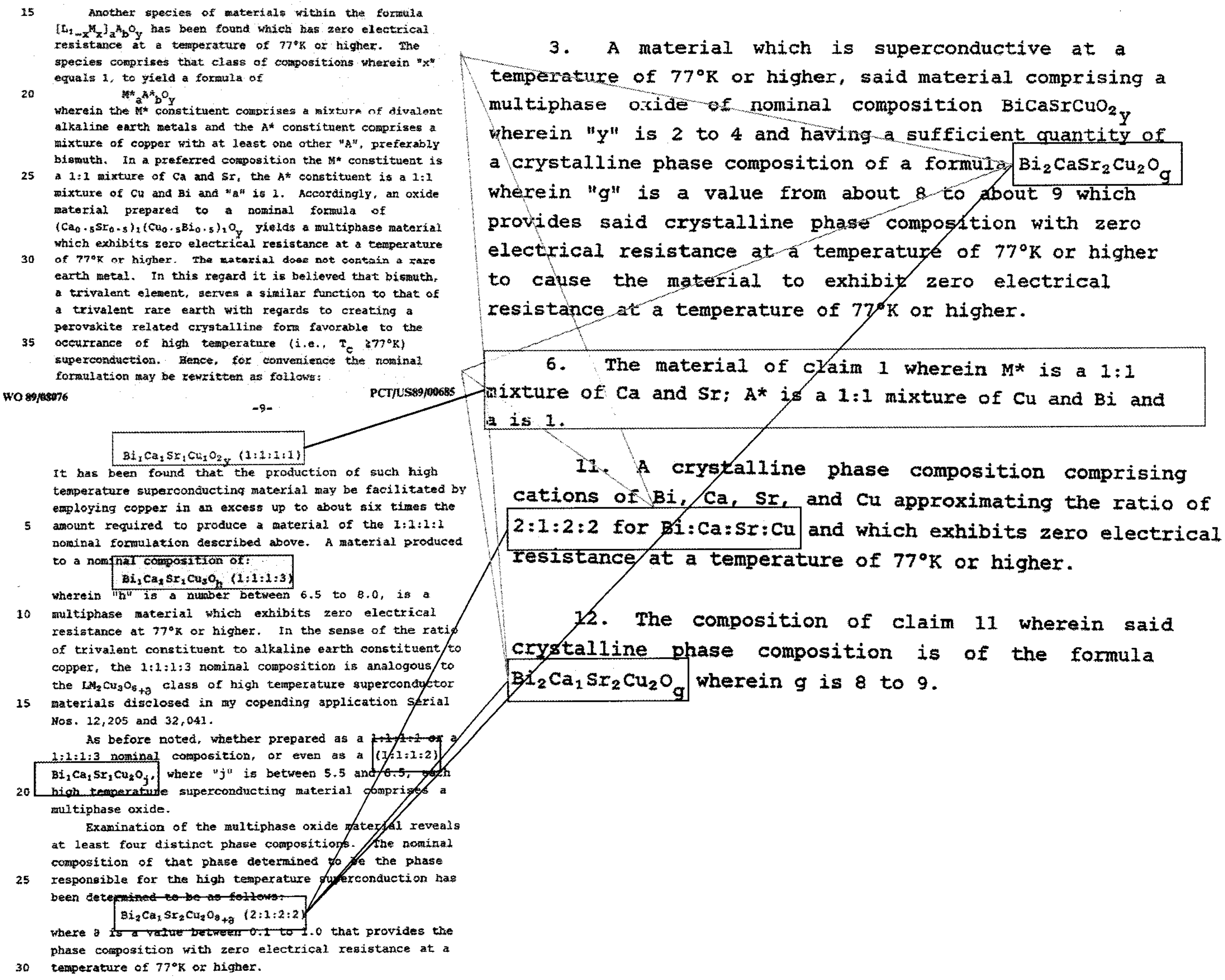
[received by the International Bureau on 07 August 1989 (07.08.89)
original claims 1 - 5 replaced by new claims 1-5 , claims 6-15 added (3 pages)]

1. A material which is superconductive at a temperature of 77°K or higher, said material comprising a multiphase oxide of nominal composition $M^*_aA^*_bO_y$ wherein M* is a mixture of divalent alkaline earth metals selected from the group consisting of Ba, Sr, Ca and Mg wherein the ratio of the alkaline earth metal of larger atomic radius to the alkaline earth metal of smaller atomic radius is from about 1:1 to about 3:1; A* is a mixture of Cu and a trivalent metal selected from the group consisting of Bi, Al, Ga, In, Tl and Sb wherein the molar ratio of Cu to said trivalent metal is from about 1:1 to about 3:1; "a" is 1 to 2; "b" is 1; and "y" is 2 to 4.



Example excerpts from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"

Excerpts from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 8, line 15 to p. 9, line 21:



Another species of materials within the formula $[L_{1-x}M_x]_aA_bO_y$ has been found which has zero electrical resistance at a temperature of 77°K or higher. The species comprises that class of compositions wherein "x" equals 1, to yield a formula of

$$M^*_aA^*_bO_y$$

wherein the M* constituent comprises a mixture of divalent alkaline earth metals and the A* constituent comprises a mixture of copper with at least one other "A", preferably bismuth. In a preferred composition the M* constituent is a 1:1 mixture of Ca and Sr, the A* constituent is a 1:1 mixture of Cu and Bi and "a" is 1. Accordingly, an oxide material prepared to a nominal formula of $(Ca_{0.5}Sr_{0.5})_1(Cu_{0.5}Bi_{0.5})_1O_y$ yields a multiphase material which exhibits zero electrical resistance at a temperature of 77°K or higher. The material does not contain a rare earth metal. In this regard it is believed that bismuth, a trivalent element, serves a similar function to that of a trivalent rare earth with regards to creating a perovskite related crystalline form favorable to the occurrance of high temperature (i.e., T_c ≥77°K) superconduction. Hence, for convenience the nominal formulation may be rewritten as follows:

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$$\boxed{Bi_1Ca_1Sr_1Cu_1O_{2y}\ (1:1:1:1)}$$

It has been found that the production of such high temperature superconducting material may be facilitated by employing copper in an excess up to about six times the amount required to produce a material of the 1:1:1:1 nominal formulation described above. A material produced to a nominal composition of:

$$\boxed{Bi_1Ca_1Sr_1Cu_3O_h\ (1:1:1:3)}$$

wherein "h" is a number between 6.5 to 8.0, is a multiphase material which exhibits zero electrical resistance at 77°K or higher. In the sense of the ratio of trivalent constituent to alkaline earth constituent to copper, the 1:1:1:3 nominal composition is analogous to the $LM_2Cu_3O_{6+\partial}$ class of high temperature superconductor materials disclosed in my copending application Serial Nos. 12,205 and 32,041.

As before noted, whether prepared as a 1:1:1:1 or a 1:1:1:3 nominal composition, or even as a $\boxed{(1:1:1:2)}$ $\boxed{Bi_1Ca_1Sr_1Cu_2O_j}$, where "j" is between 5.5 and 6.5, each high temperature superconducting material comprises a multiphase oxide.

Examination of the multiphase oxide material reveals at least four distinct phase compositions. The nominal composition of that phase determined to be the phase responsible for the high temperature superconduction has been determined to be as follows:

$$\boxed{Bi_2Ca_1Sr_2Cu_2O_{8+\partial}\ (2:1:2:2)}$$

where ∂ is a value between 0.1 to 1.0 that provides the phase composition with zero electrical resistance at a temperature of 77°K or higher.

3. A material which is superconductive at a temperature of 77°K or higher, said material comprising a multiphase oxide of nominal composition $BiCaSrCuO_{2y}$ wherein "y" is 2 to 4 and having a sufficient quantity of a crystalline phase composition of a formula $\boxed{Bi_2CaSr_2Cu_2O_g}$ wherein "g" is a value from about 8 to about 9 which provides said crystalline phase composition with zero electrical resistance at a temperature of 77°K or higher to cause the material to exhibit zero electrical resistance at a temperature of 77°K or higher.

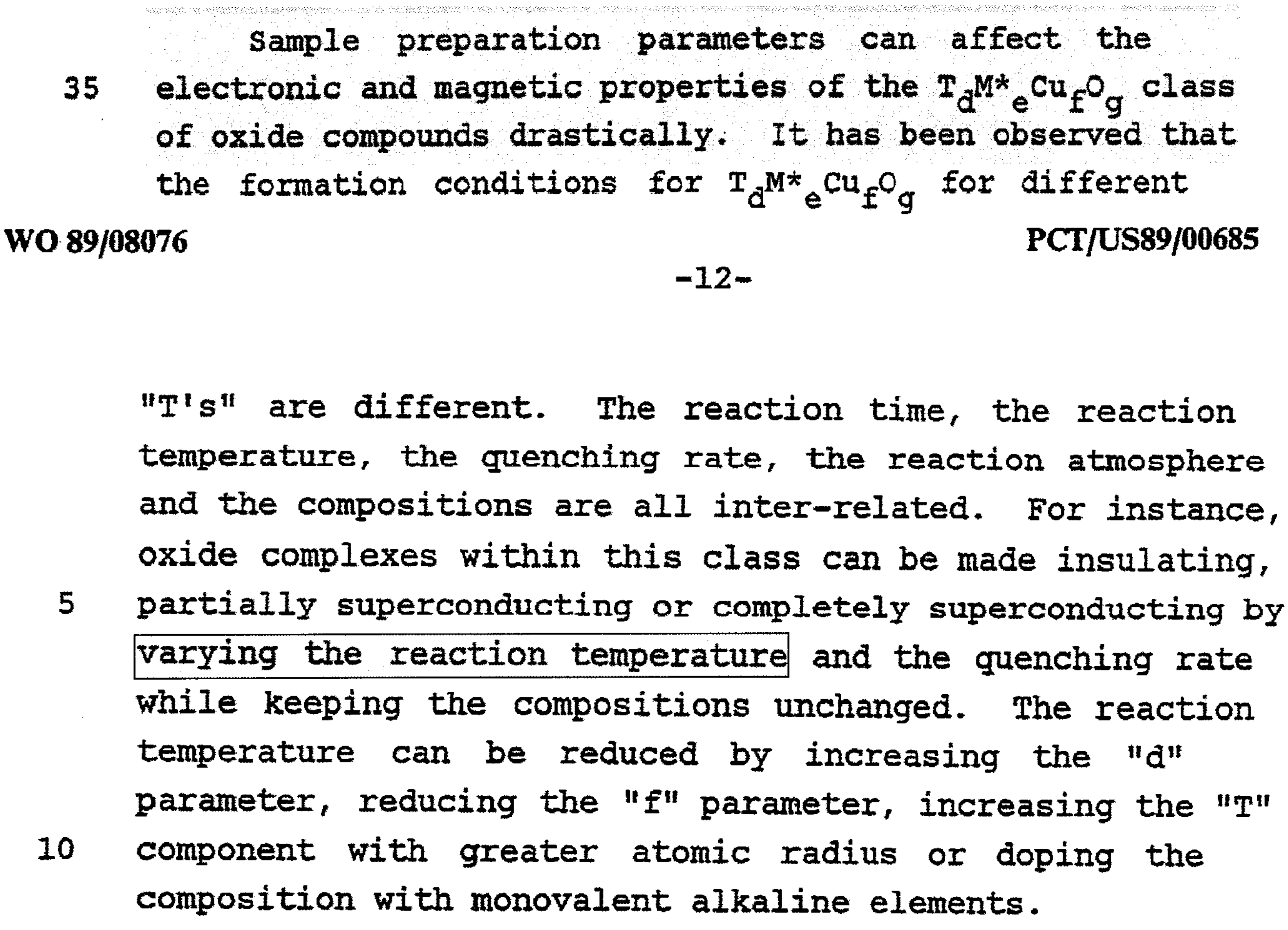
6. The material of claim 1 wherein M* is a 1:1 mixture of Ca and Sr; A* is a 1:1 mixture of Cu and Bi and a is 1.

11. A crystalline phase composition comprising cations of Bi, Ca, Sr, and Cu approximating the ratio of $\boxed{2:1:2:2 \text{ for } Bi:Ca:Sr:Cu}$ and which exhibits zero electrical resistance at a temperature of 77°K or higher.

12. The composition of claim 11 wherein said crystalline phase composition is of the formula $\boxed{Bi_2Ca_1Sr_2Cu_2O_g}$ wherein g is 8 to 9.

Dr. Meng was responsible for investigating and defining the sample preparation parameters made the subject of this '956 application.

Excerpt from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 11, lines 34 – p. 12 line 11:



Sample preparation parameters can affect the electronic and magnetic properties of the $T_dM^*_eCu_fO_g$ class of oxide compounds drastically. It has been observed that the formation conditions for $T_dM^*_eCu_fO_g$ for different

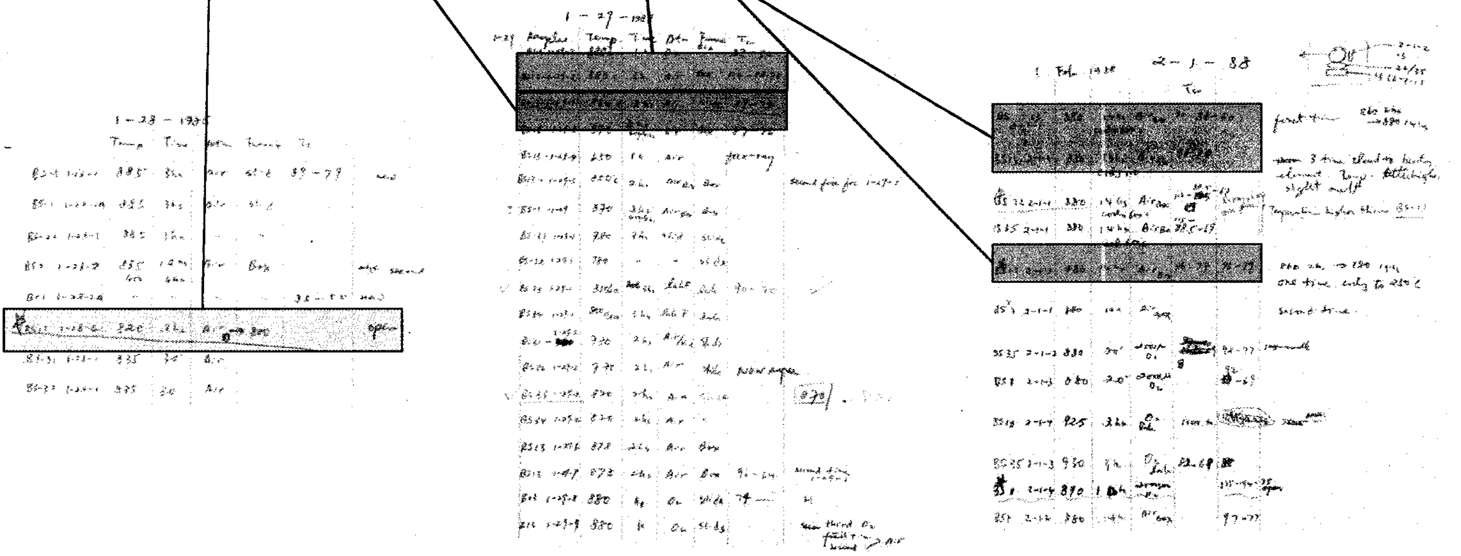
"T's" are different. The reaction time, the reaction temperature, the quenching rate, the reaction atmosphere and the compositions are all inter-related. For instance, oxide complexes within this class can be made insulating, partially superconducting or completely superconducting by varying the reaction temperature and the quenching rate while keeping the compositions unchanged. The reaction temperature can be reduced by increasing the "d" parameter, reducing the "f" parameter, increasing the "T" component with greater atomic radius or doping the composition with monovalent alkaline elements.

Excerpt from WO 89/08076 ('956 Application)(filed 3 Mar 88), p. 14, lines 30 - 35:

Three Bi-Ca-Sr-Cu-O (hereafter BCSCO) samples were synthesized by the described solid-state reaction techniques from appropriate amounts of Bi_2O_3, CuO, $SrCO_3$, and $CaCO_3$. The BCSCO samples were prepared according to a nominal composition of 1:1:1:1 for BCSCO-a; 1:1:1:2 for BCSCO-b, and 1:1:1:3 for BCSCO-c. The starting

Excerpt from WO 89/08076 (filed 3 Mar 88), p. 7, lines 10-12:

Fig. 8 illustrates resistance (R) vs. temperature (T) for BCSCO-b synthesized at different temperatures; a - 820°C, b - 864°C, c - 880°C. Curve d is for BCSCO-c.



Example excerpts from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"

Excerpt from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 10, line 25 to p. 11, line 33:

For convenience the phase composition within a multiphase material prepared with a nominal composition Bi:Ca:Sr:Cu of 1:1:1:1; 1:1:1:2; or 1:1:1:3 may be represented as a metal oxide of the formula

$$T_dM^*_eCu_fO_g$$

wherein "T" is a trivalent transition metal such as Bi, Al, Ba, Tl, In, Sb, or mixtures thereof; "M*" is a mixture of alkaline earth metals such as Sr and Ca, Ba and Sr, Ba and Ca, Sr and Mg, and Ca and Mg in a ratio of the alkaline earth metal of larger atomic radius (M^L) to the alkaline earth metal of smaller atomic radius (M^S) of from about 1:1 to about 1:3; "d" is a number from about 1 to about 3; "e" is a number from about 1 to about 6; "f" is a number from about 1 to about 6; "g" is a number between from about (3d + 2e + 2f)/2 to about (3d + 2e + 3f)/2 that provides the metal oxide with zero electrical resistance at a temperature of 77°K or higher. Preferably "T" is bismuth; "M*" is Ca and Sr at ratio of 1:2; "d" is 2; "e" is 3; "f" is 2 and "g" is a number between about 8 to about 9.

A method for making such $T_dM^*_eCu_fO_g$ containing superconductive composition oxide materials, includes the following steps, and for convenience is referred to as the compressed powder reaction method. Selected amounts of solid powdered compounds containing T, M^L, M^S, A, and O are thoroughly mixed preferably by selecting appropriate amounts of T_2O_3, M^LCO_3, M^SCO_3 (or M^LO and M^SO)and AO. The thoroughly mixed powder mixture is compressed into pellets which are thereafter reacted at a temperature between about 800°C and about 910°C, preferably about 850°C to ~~about 890°C, for a time suff~~icient to complete the solid state reaction. Thereafter the reacted pellets are rapidly quenched to room temperature. Mixing is preferably accomplished by an intensive mixer such as a jar mill or more preferably a ball mill. Pelletization of the oxide mixture is carried out at an applied pressure of from about 100 to about 30,000 psi and preferably at an applied pressure of from about 100 to about 500 psi, most preferably at about 500 psi. Reaction of the pelletized mixture may be conducted in air for about 5 minutes to about 24 hours, and most preferably in a reduced oxygen atmosphere of about 2000 μ for about 5 to about 30 minutes preferably for about 5 to about 15 minutes. Following the completion of the reaction step the reacted pellet composition is rapidly quenched to room temperature in air.

13. A superconducting oxide composition of nominal formula $T_dM^*_eCu_fO_g$ wherein "T" is Bi, Al, Ga, In, Tl or Sb; "M*" is a mixture of divalent alkaline earth metals selected from the group consisting of Ba, Sr, Ca and Mg wherein the ratio of the alkaline earth metal of larger atomic radius (M^L) to the alkaline earth metal of smaller atomic radius (M^S) is from about 1 to about 3; "d" is a number from about 1 to about 3; "e" is a number from about 1 to about 6; "f" is a number from about 1 to about 6; and "g" is a number from about 0.5(3d + 2e + 2f) to about 0.5(3d + 2e + 3f) that provides the oxide composition with zero electrical resistance at a temperature of 77°K or higher, wherein said composition is made by a process comprising the steps of:

compressing a mixture of solid powdered compounds comprising:

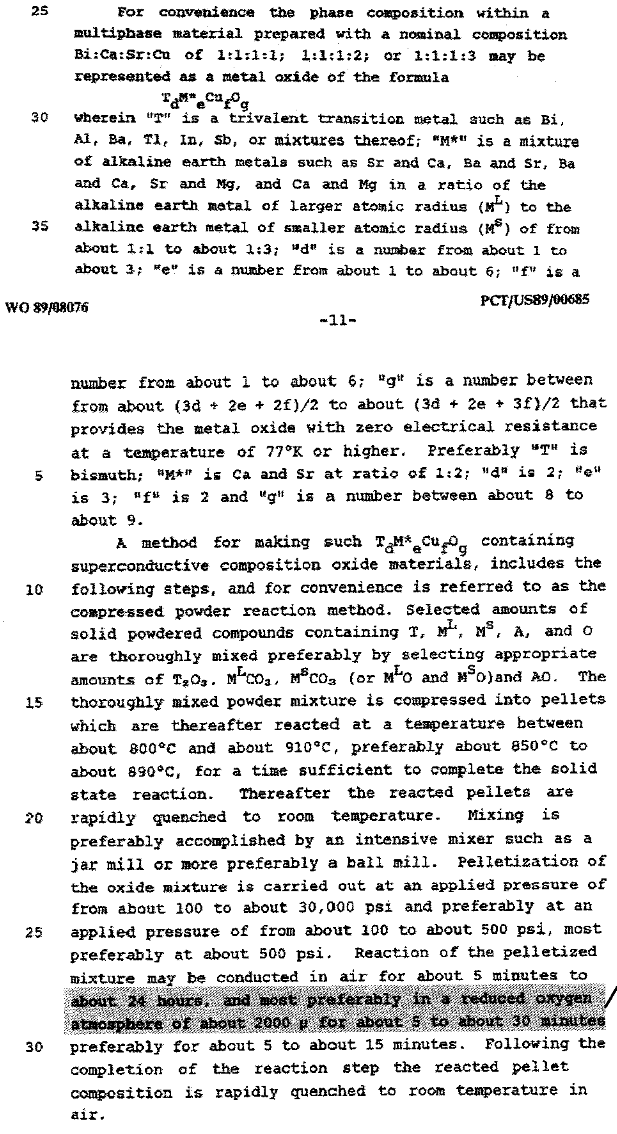
a) T_2O_3
b) M^LCO_3 or M^LO
c) M^SCO_3 or M^SO and
d) CuO

in proportions appropriate to yield said formula;

heating t~~he compressed powder mixtur~~e to a temperature of from about 800°C to about 910°C for a time sufficient to complete the solid state reaction; and

quenching said reacted compressed mixture to room temperature.

Excerpt from WO 89/08076 ('956 Application)(filed 3 Mar 88) , p. 10, line 25 to p. 11, line 33:



For convenience the phase composition within a multiphase material prepared with a nominal composition Bi:Ca:Sr:Cu of 1:1:1:1; 1:1:1:2; or 1:1:1:3 may be represented as a metal oxide of the formula

$$T_dM^*_eCu_fO_g$$

wherein "T" is a trivalent transition metal such as Bi, Al, Ba, Tl, In, Sb, or mixtures thereof; "M*" is a mixture of alkaline earth metals such as Sr and Ca, Ba and Sr, Ba and Ca, Sr and Mg, and Ca and Mg in a ratio of the alkaline earth metal of larger atomic radius (M^L) to the alkaline earth metal of smaller atomic radius (M^S) of from about 1:1 to about 1:3; "d" is a number from about 1 to about 3; "e" is a number from about 1 to about 6; "f" is a

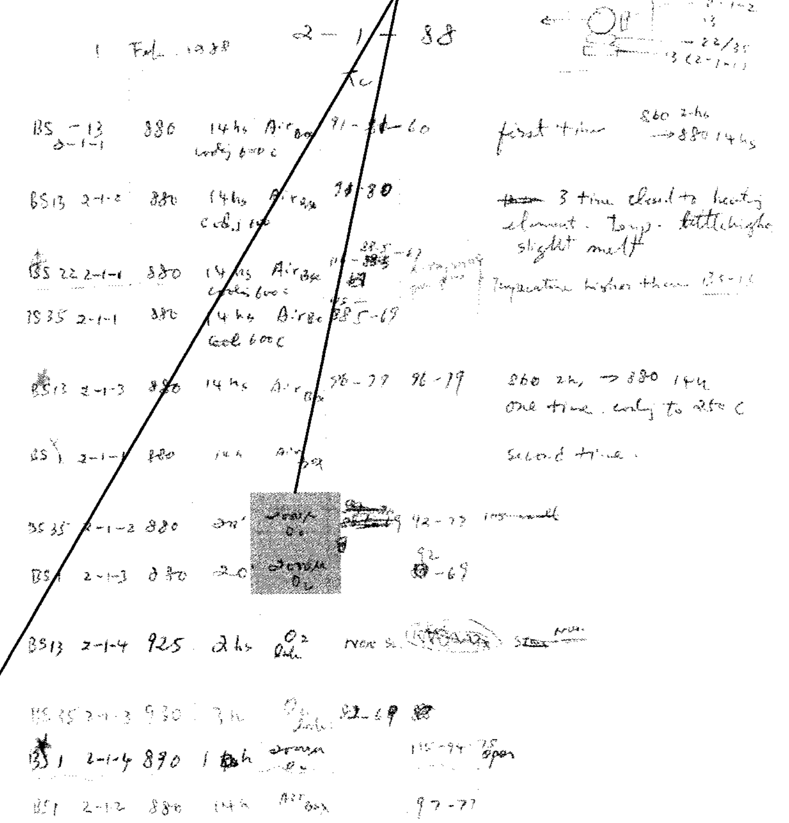
WO 89/08076 PCT/US89/00685

-11-

number from about 1 to about 6; "g" is a number between from about (3d + 2e + 2f)/2 to about (3d + 2e + 3f)/2 that provides the metal oxide with zero electrical resistance at a temperature of 77°K or higher. Preferably "T" is bismuth; "M*" is Ca and Sr at ratio of 1:2; "d" is 2; "e" is 3; "f" is 2 and "g" is a number between about 8 to about 9.

A method for making such $T_dM^*_eCu_fO_g$ containing superconductive composition oxide materials, includes the following steps, and for convenience is referred to as the compressed powder reaction method. Selected amounts of solid powdered compounds containing T, M^L, M^S, A, and O are thoroughly mixed preferably by selecting appropriate amounts of T_2O_3, M^LCO_3, M^SCO_3 (or M^LO and M^SO)and AO. The thoroughly mixed powder mixture is compressed into pellets which are thereafter reacted at a temperature between about 800°C and about 910°C, preferably about 850°C to about 890°C, for a time sufficient to complete the solid state reaction. Thereafter the reacted pellets are rapidly quenched to room temperature. Mixing is preferably accomplished by an intensive mixer such as a jar mill or more preferably a ball mill. Pelletization of the oxide mixture is carried out at an applied pressure of from about 100 to about 30,000 psi and preferably at an applied pressure of from about 100 to about 500 psi, most preferably at about 500 psi. Reaction of the pelletized mixture may be conducted in air for about 5 minutes to about 24 hours, and most preferably in a reduced oxygen atmosphere of about 2000 µ for about 5 to about 30 minutes preferably for about 5 to about 15 minutes. Following the completion of the reaction step the reacted pellet composition is rapidly quenched to room temperature in air.

15. The oxide composition of claim 13 wherein the compressed powder mixture is heated under a reduced oxygen atmosphere of approximately 2000µ.



1 Feb. 1988 2-1-88

Tc

BS-13 2-1-1 880 14 hs Air box cooling 600 C 91-80-60 first time 860 2 hs → 880 14 hs

BS13 2-1-2 880 14 hs Air box cooling 600 91-80 3 time closed to heating element. Temp. little higher slight melt

BS 22 2-1-1 880 14 hs Air box cooling 600 C 88.5-69 Temperature higher than BS-13

BS35 2-1-1 880 14 hs Air box cool 600 C 88.5-69

BS13 2-1-3 880 14 hs Air box 96-79 96-79 860 2h, → 880 14h one time, only to 250 C

BS1 2-1-1 880 14 h Air box Second time.

BS35 2-1-2 880 30' stream O2 92-77

BS1 2-1-3 880 20' stream O2 92-69

BS13 2-1-4 925 2 hs O2 bulk Non S.

BS35 2-1-3 930 3 h O2 bulk 82-69

BS1 2-1-4 890 1 h stream O2 115-94-75 open

BS1 2-1-2 880 14 h Air box 97-77

Example excerpt from Meng's Notebook Entitled: "Bi System (Bulk & Tape)"

CONCLUSION

Based on the foregoing exemplary clear and convincing evidence, Dr. Meng rightfully claims entitlement to be named as a co-inventor with Dr. Chu for the patents that were applied for by Dr. Chu during this time period relating to high temperature superconductors, such as, U.S. Patent No. 7,056,866, U.S. Patent Application Serial Nos. 07/300,063, and 163,956 and any other related U.S. or non-U.S. patents or patent applications.

As a coinventor, Dr. Meng is justly entitled to her fair share of revenue received by UH (both past and future) for these patents/applications under the terms of established UH intellectual property policies in place at all relevant times. Dr. Meng is aware that certain revenue-generating transactions (be they assignments or licenses) have occurred in the past respecting these patents and patent applications and hereby requests an accounting to her for her fair share of such proceeds. Dr. Meng also has a reputational interest in being recognized as a coinventor.

Valence Instabilities
P. Wachter and H. Boppart (eds.)

CHEMICAL PRESSURE EFFECTS IN Sc-SUBSTITUTED YbCuAl

W.C.M.Mattens, J.Aarts, A.C.Moleman, I.Rachman and F.R. de Boer

Natuurkundig Laboratorium der Universiteit van Amsterdam,
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Implications of Sc-substitution for nearly trivalent Yb in YbCuAl will be discussed. Magnetic properties, thermal expansion and specific heat of compounds with Sc-concentrations upto 20 percent will be presented. A possible occurrence of spin-fluctuations growing with increasing Sc-concentration is suggested.

INTRODUCTION

In a number of experiments over the past few years it has been established that dilution of intermediate valence (IV) compounds with non-magnetic atoms only produces a proportional reduction of the bulk properties of the IV state |1,2|. In other words, valence fluctuations at different ions seem to be incoherent and might be described as a single ion effect. Since, therefore, dilution does not disturb any coherency, the same experimental technique might be used to study the effect of chemical pressure upon the IV state. A very suitable system for this purpose is YbCuAl. It is intermediate valent and dilution with Y has been studied extensively |1|. Furthermore, Sc substitution may provide the sought-for chemical pressure effects since Sc is chemically identical to the rare earths, but has a significantly smaller ionic radius than trivalent Yb. Although the compound ScCuAl does not exist, we have found in the present work that single phase $Yb_{1-x}Sc_xCuAl$ samples can be produced up to x = 0.22.

EXPERIMENTAL RESULTS

A detailed description of the sample preparation procedure can be found in ref. |3|. In the $Yb_{1-x}Sc_xCuAl$ system compounds with x = 0.00, 0.05, 0.075, 0.10, 0.15, 0.20 and 0.22 have been prepared. The compounds crystallize in the hexagonal Fe_2P-type structure, in which every Yb atom has the same local environment. The room temperature lattice parameters are given in fig.1.

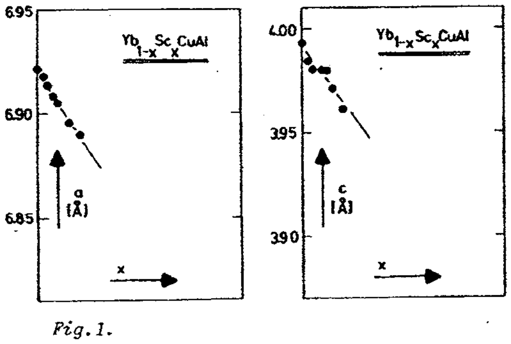

Fig.1.

Thermal expansion data by X-ray diffraction at low temperatures for various Sc-concentrations and also for pure YbCuAl are given in fig.2. The Sc-substituted compounds reveal a behaviour, similar to what earlier has been found for pure YbCuAl |4|: a smaller but clear anomaly is observed, shifting towards lower temperatures upon increasing Sc-substitution. In YCuAl, a non-magnetic dummy, a normal thermal expansion

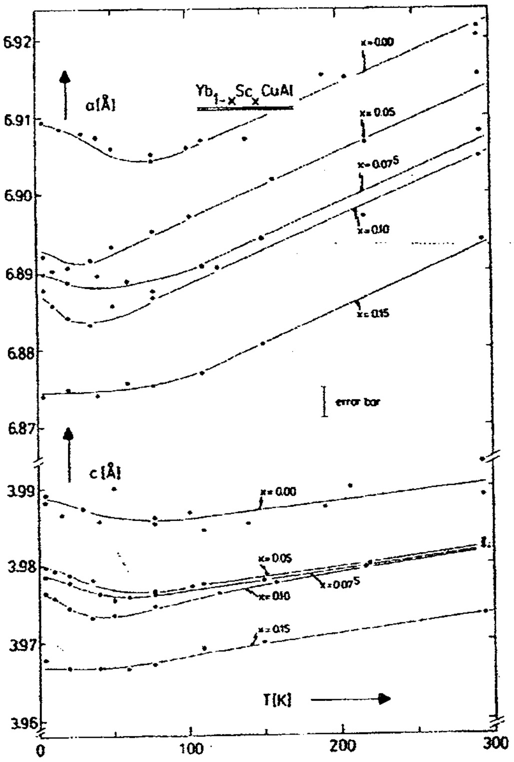

Fig.2.

has been observed. At room temperature we found the same slope as for YbCuAl, while below liquid nitrogen temperature the lattice parameters become temperature independent.

In fig.3 as-measured susceptibility curves are given. The susceptibilities given in fig.4 have been corrected for impurity contributions (of the order of about 1% trivalent Yb). It can be seen that the characteristic temperature T_{max}, the temperature of the well known susceptibility maximum, shifts towards lower temperatures and the low-temperature susceptibility increases gradually. At high temperatures (up to 1000 K) we find Curie-Weiss behaviour with an effective moment of 4.30 ± 0.05 μ_B/Yb atom and a paramagnetic Curie temperature of 33 ± 5K for all Sc-concentrations, the same as for pure YbCuAl and Y- and Gd-substituted YbCuAl |1|.

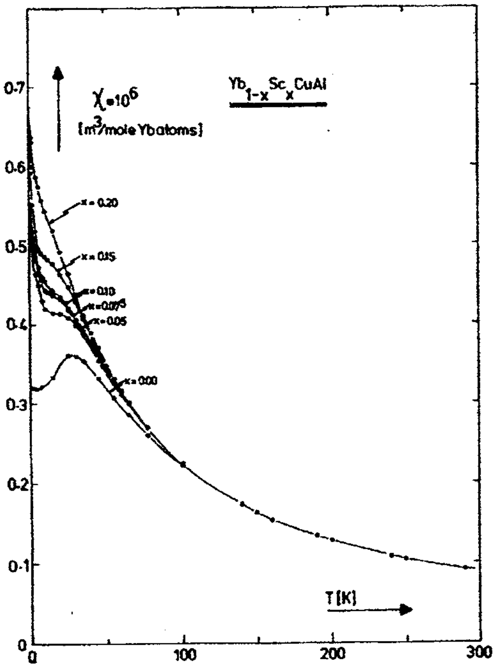

Fig. 3.

The magnetic isotherms at liquid helium temperatures up to 35 tesla are given in fig.5. In fig.6 we again present the magnetization, now corrected for the impurity contributions, which is saturated at 5 T. For x = 0.05 the magnetization is still similar to that of pure YbCuAl. For the higher Sc-concentrations, however, the characteristic shape (upward curvature in the high-field part) vanishes and at the highest Sc-concentrations the curves show a gradually saturating behaviour. If we identify the slope of the low-field part of the magnetization with the initial susceptibility, we find good agreement with the low-temperature susceptibility values presented in fig.4, which justifies the applied correction procedure.

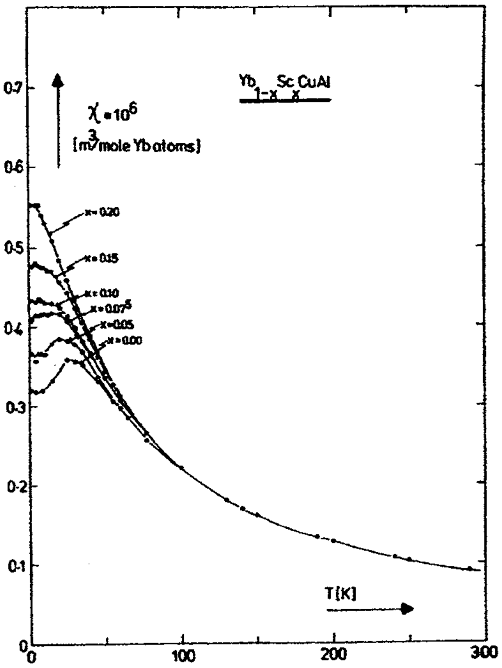

Fig.4.

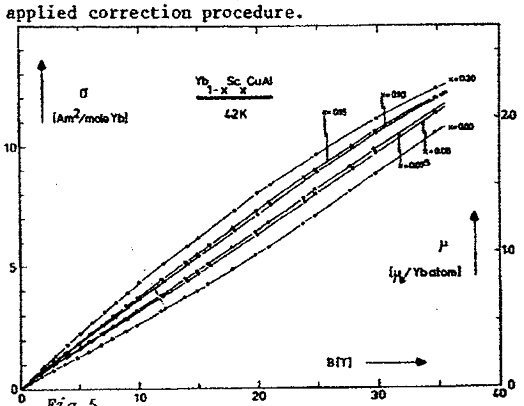

Fig.5.

The heat capacity for different Sc-concentrations is given in fig.7. It can be seen that the properties have changed drastically with respect to those of YbCuAl. For the x = 0.10 compound the coefficient of the linear term, γ, can be estimated to be about 370 mJ/K² mole Yb atoms, compared to 255 mJ/K² mole Yb atoms for pure YbCuAl. This relative change is similar to that in the low-temperature susceptibility. For the higher Sc-concentrations γ cannot be determined in a simple way. Furthermore the heat capacities are found to be field-independent at least up to 5 T.

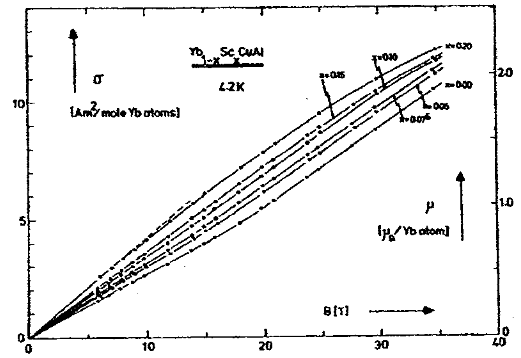

Fig. 6.

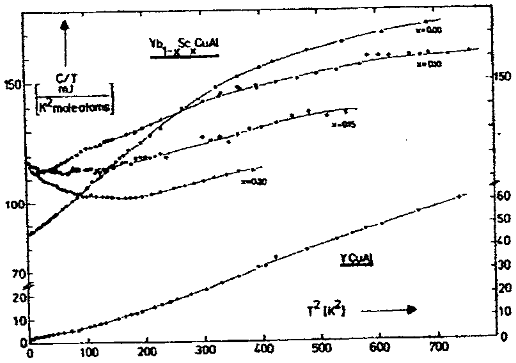

Fig. 7.

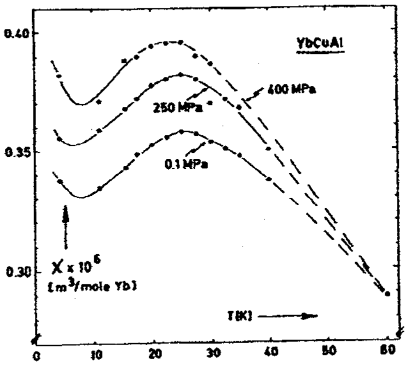

Fig. 8.

DISCUSSION

The most direct indication of pressure effects due to Sc-substitution would be lattice parameters deviating from Vegard's law. In this case it is not possible to establish this due to the absence of compounds with $x > 0.22$ (see fig.1). On the other hand we can compare the observed magnetic properties with the results of measurements of the magnetic susceptibility of pure YbCuAl when external pressure is applied. In fig.8 these measurements are given. The results show that T_{max} shifts towards lower temperatures when pressure is applied, while the value of the constant low-temperature susceptibility increases. From the susceptibility curves in fig.3 we can conclude that substitution of Sc has a similar effect as application of external pressure. One may object against the use of the impurity-correction procedure in the case of Sc-substituded compounds. It may be that here, due to shift of the maximum towards lower temperatures, the low-temperature susceptibility is no longer temperature independent below 8 K. However, since the χT vs T plots are still linear up to this temperature, it can be assumed that the susceptibility is fairly constant.

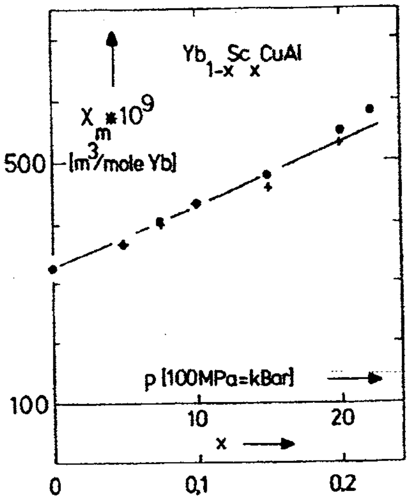

Fig. 9.

It has been found (fig.8) that the low-temperature susceptibility of pure YbCuAl increases with 3% per 100 MPa (1 kBar) [4]. Assuming that this value is independent of pressure, which is probably a very crude approximation, we can make an estimate of the pressures involved with Sc-substitution in YbCuAl. The results of such a procedure are given in fig.9. The low-temperature susceptibility depends essentially linearly upon the Sc-concentration. We can compare the pressures in fig.9 with the pressure required to accomplish a complete valence transition from divalent to trivalent Yb metal. This pressure can be estimated by identifying the transformation energy of 38 kJ/mole [4,5] with the $\int p dV$ term in the free energy. The volume of divalent Yb is 24.9 cm^3/mole. For trivalent Yb metal the molar volume can be approximated by taking the average of the values for Tm(18.1 cm^3/mole) and Lu(17.8 cm^3/mole); with a thus derived value for ΔV of 6.9 cm^3/mole we estimate a pressure of the order of 10 GPa (100 kBar) necessary to achieve the valence transition in pure Yb. Before discussing, however, the consequences of the pressure effect upon magnetization and specific heat, it is worthwhile to mention that substitu-

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tion of a smaller atom does not always lead to this effect. Majewski et al. [7] have investigated the magnetic properties of various compounds in the (Yb,Sc)Al_3 system. In contrast to what one would expect upon substitution of the smaller Sc-atom, the effect is that $YbAl_3$ becomes less magnetic with increasing Sc-concentration, which implies a shift towards more divalent character. This can be understood when it is remembered that the magnetic behaviour depends upon the valence state which, in its turn, is connected with the volume: a smaller volume is associated with the trivalent magnetic state, a larger volume with the divalent non-magnetic state. Therefore, in dilution experiments the sign of the deviation of the lattice parameter from Vegard's law is indicative for the magnetic behaviour. From ref. [7] it is known that the deviation in (Yb,Sc)Al_3 is positive (fig.10), which is likely to favour the non-magnetic state. At first sight one would say that the magnetic behaviour of mixed-valent Yb in YbCuAl is only gradually changing upon Sc-substitution. On the other hand, the specific heat behaviour is influenced rather drastically. The appearance of a growing upturn below 10 K with increasing Sc-concentration, which is hardly influenced by a magnetic field of about 5 T, betrayes that somehow the system is on the onset of critical behaviour. A more detailed comparison with for instance compounds like UCo_2 and UAl_2 [8,9] reveals a very similar behaviour. In these actinide compounds too, a peak in the specific heat is observed, which does not change when a magnetic field is applied. Therefore the upturn can not be ascribed to local magnetic moments. The specific heat of UAl_2 and UCo_2 has been analysed succesfully in terms of spin-fluctuation theory [10,11], which adds a $T^3 \ln T$ term to the linear and cubic contributions. In the case of Sc-substituted YbCuAl a detailed, quantitative analysis of the results in the framework of spin-fluctuation theory is hampered by the fact that, besides a spin-fluctuation part, still an appreciable mixed-valent part is contributing to the specific heat. This is underlined by the thermal expansion behaviour: the volume anomaly, characteristic for mixed-valency, remains qualitatively present.

When it comes to the magnetic properties of the $Yb_{1-x}Sc_xCuAl$ compounds in the light of spin-fluctuation behaviour, it is clear that they fit into this framework. Two slopes in the high-field magnetic isotherms, corresponding with the values of the magnetic susceptibility at zero temperature and at a higher characteristic temperature, are also observed in systems like UAl_2 and UCo_2 [8,9]. However, in pure YbCuAl the occurrence of spin-fluctuations should be excluded on the basis of the absence of an upturn in the specific heat.

In conclusion we find that pressure, induced by alloying with Sc, gradually drives the mixed-valent Yb in YbCuAl into a region where critical behaviour appears next to mixed valency. The spin-fluctuation contribution to the physical properties increases with pressure.

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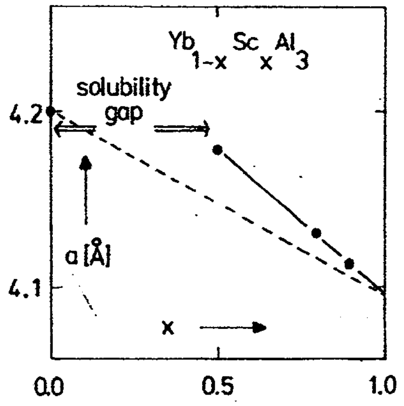

Fig.10. (Data for this plot have been taken from table 1, ref.7).

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MIXED VALENCE IN CeNi$_5$; EFFECTS OF DILUTION AND CHEMICAL PRESSURE

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(Received 8 June 1983 by B. Mühlschlegel)

X-ray L_{III} absorption measurements were employed to determine the (mixed) valence of the system $R_{0.9}Ce_{0.1}Ni_5$, where R = La, Pr, Gd, Er or Lu. The valences obtained spanned only the narrow range 3.13–3.16 in going from La to Lu, compared to 3.15 for the stoichiometric compound CeNi$_5$. These results establish the extreme insensitivity of the mixed valence of CeNi$_5$ to dilution effects, and, hence, that it is a local site phenomenon. Moreover, the valence is relatively insensitive to chemical pressure-induced lattice constant changes as alrge as 3 or 4%.

MIXED VALENT cerium-based metallic systems exhibit behavior which is irreconcilable within the Anderson lattice (or promotional) model, which describes the mixed valent state in terms of an admixture of $4f^nc^m$ and $4f^{n-1}c^{m+1}$ states, where c refers to the conduction electrons [1]. In particular, the valence, as determined by core level photoemission or X-ray absorption, is considerably smaller than implied by either the volume or the magnetic susceptibility [1–3]. Because of the relatively large spatial extent of the cerium $4f$ wave function, hybridization effects are expected to play an important role [4], in contrast to Sm-, Eu-, Tm- and Yb-based systems, all of which are well described by the promotional model [1].

In the presence of strong hybridization effects, one might expect dilution of the Ce ions in mixed valent Ce compounds to alter dramatically the degree of the $4f$ instability, and, hence, the valence; particularly, if such hybridization effects were to lead to itinerant bands with f-character. The study reported herein was designed to probe such dilution effects without changing the size of the unit cell or producing significant changes in the electronic band structure. The system CeNi$_5$ was chosen because it is moderately strongly mixed valent among Ce-based systems; and, the relatively small atomic number of Ni compared to that of Ce allowed the determination of the valence from X-ray L_{III} absorption experiments to be made at relatively small Ce-concentrations (i.e., down to $x = 0.1$ in the formula unit $R_{1-x}Ce_xNi_5$).

X-ray absorption measurements, particularly of the L_{III} edge, provide a convenient and direct method of determining the mixed valence of rare earth compounds. In the presence of a $4f$ hole, the L_{III} edge, corresponding to an excitation of the $2p$ core hole, is shifted by approximately 10 eV to higher binding energy. The ratio of the intensities of the two edges, corresponding to the final states $2p^*4f^1(5d6s)^4$ and $2p^*f^0(5d6s)^5$, where $2p^*$ refers to a $2p$-hole, is a direct measure of the ratio of the f^1 and f^0 components in the ground state [1]. There have been several conjectures that this simple picture may be spoiled by final state shake-up or shake-down effects [5]. Howver, it has been recently argued [6], based upon a study of L_{III} edges in a number of Ce-based intermetallics, along with their La- and Pr-based isomorphs, that such final state effects, being small, do not alter appreciably the apparent valence determined from the ratio of the two L_{III} edges. Hillebrecht and Fuggle [7] have reached similar conclusions concerning the use of core level photoemission for determining the (mixed) valence in metallic Ce-based systems.

The following compositions were chosen for the study: LaNi$_5$, CeNi$_5$ and $R_{0.9}Ce_{0.1}Ni_5$ (R = La, Pr, Gd, Er or Lu). The samples were prepared by arc-melting the constituents in an inert atmosphere. The five pseudobinaries were annealed at 800°C for 3 days to ensure homogeneity. X-ray powder diffraction studies confirmed that all compositions formed the hexagonal CaZn$_5$ structure; and no extraneous phases could be detected. The samples for the X-ray absorption study were prepared by powdering the material and then hermetically sealing it in a suitable tape sandwich whose thickness fell in a region for which the shape of the Ce–L_{III} edge was established experimentally to be thickness-independent. The L_{III} edge studies were performed in transmission at the Cornell University synchrotron facility (CHESS) using X-rays emitted by the storage ring (CESR) operating at 5.3 GeV. A CHESS-built monochromator using two Si (111) crystals offset by 8 cm and mounted 11 m from the source gave a resolution of about 1 eV at the Ce–L_{III} edge.

The results of the X-ray absorption studies are shown in Fig. 1. It is immediately apparent that there is very little change in the CE–L_{III} double edge

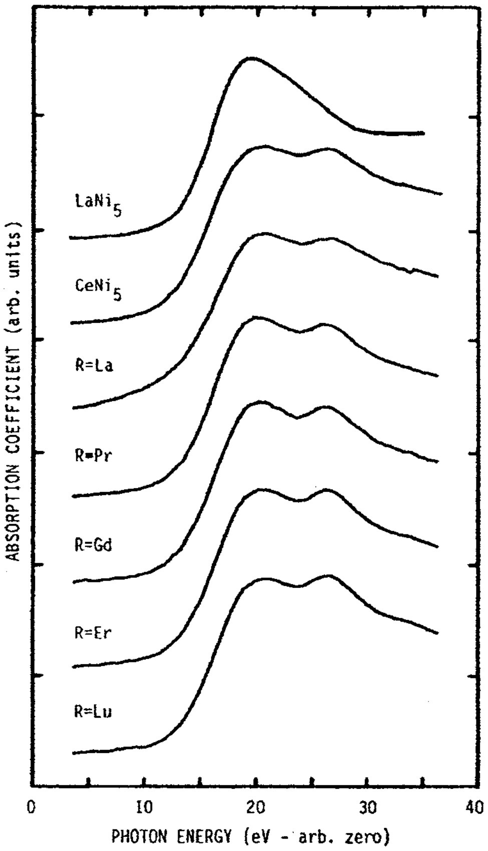

Fig. 1. La L_{III} absorption edge for LaNi$_5$ and Ce L_{III} edges for CeNi$_5$ and $R_{0.9}$Ce$_{0.1}$Ni$_5$ (R = La, Pr, Gd, Er or Lu) at 300 K. Only relative energies are shown on abscissa. The primary edge (lower energy edge in the case of Ce) occurs at about 5483 eV in LaNi$_5$ and about 5724 eV in the Ce compounds.

signature between CeNi$_5$ and the dilute Ce-pseudo-binaries; however, there is a slight increase in the relative strength of the high energy (f^0) edge as the series is traversed from La$_{0.9}$Ce$_{0.1}$Ni$_5$ to Lu$_{0.9}$Ce$_{0.1}$Ni$_5$. In order to extract the ratio of the two edge intensities, and hence the (mixed) valence, the following method was employed. A Gaussian with linearly decreasing tail on the high energy side, imposed on a background with a step discontinuity at the peak maixmum, was found to fit the LaNi$_5$ quite well. This function was then fit to each of the two edges in the Ce-based systems. The background step and slope, and the width of the Gaussian were constrained to be the same for the low energy edge throughout the series; however, these parameters were allowed to vary for the second edge. The contribution of each edge was determined by integrating the fitting function from 8 eV below to 8 eV above the maximum. The integration was truncated above the edge since small errors in determining the high energy tail would spoil the peak intensity determination if the integration were extended to high energy.

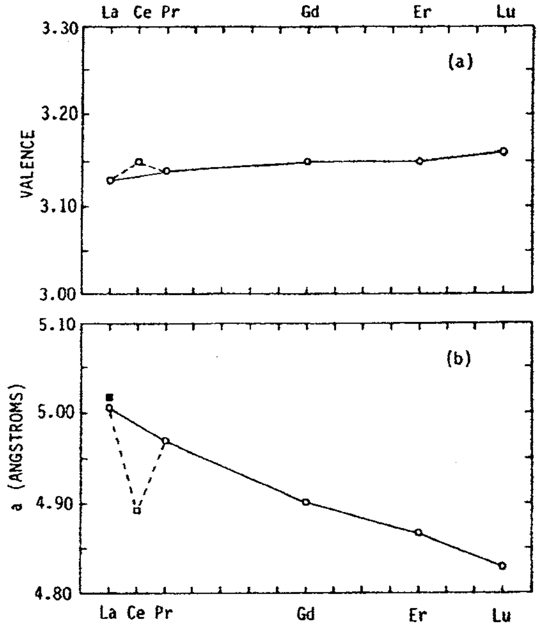

Fig. 2. (a) Valence determined from L_{III} edges; square: CeNi$_5$: circles: $R_{0.9}$Ce$_{0.1}$Ni$_5$ (R = La, Pr, Gd, Er or Lu). (b) Lattice constant in a-direction; solid square: LaNi$_5$; circles: $R_{0.9}$Ce$_{0.1}$Ni$_5$.

The (mixed) valence of the Ce-ions, given by $3 + B/(A + B)$, where A and B are the intensities of the low (f^1) and high (f^0) energy edges respectively is shown in Fig. 2(a) for the various systems studied. The Ce-valence determined in the above manner is expected to be internally consistent among the various samples studied; however, the absolute value is sensitive to the fitting procedure, as evidenced by variations in the reported values of the valence of mixed valent compounds from different laboratories, determined from spectra which are visually indistinguishable. It is of interest to compare our value (3.15) for CeNi$_5$ to that obtained in other laboratories from 3d-core level photoemission (3.15–3.20 [2]; 3.12–3.16 [8]) and L_{III} absorption (3.32) [3]. It should be kept in mind that L_{III} absorption is a bulk technique; whereas 3d-photoemission samples only a few atomic layers at the surface. However, a comparison of 3d-photoemission spectra of Ce-intermetallics with 4d-photoemission spectra [8], and also X-ray absorption spectra [2, 9, 10], suggest that the valence is shifted not appreciably if at all, at the surface.

In Fig. 2(b) are shown the lattice constants a of LaNi$_5$, CeNi$_5$ and the five pseudo-binaries, as determined by X-ray powder diffraction. The c-axis lattice constant varies only weakly through the series. Compared to CeNi$_5$, the La and Pr samples represent negative lattice pressure on the Ce-ions; whereas, Er and Lu represent positive pressure. The Gd sample, which has approximately the same lattice constant as $CeNi_5$, provides a matrix in which dilution effects can be examined in the absence of chemical pressure effects. The fact that the valence of $Ce_{0.1}Gd_{0.9}Ni_5$ is essentially identical to that of $CeNi_5$ implies that the mixed valence in $CeNi_5$ is a local site phenomenon.

The extremely weak dependence of valence on chemical pressure seen in Fig. 2 distinguishes $CeNi_5$ from elemental f.c.c. cerium, where lattice pressure dramatically affects the $4f$-instability [11, 12]. Several studies similar in purpose to the one reported here have been made on pseudo-binaries based on $CePd_3$. Dilution of Ce by La (up to 30% La) in $CePd_3$ produces an *expansion* of the lattice, an apparent *decrease* in the $4f$ stability as evidenced by a decrease in the magnetic susceptibility [13], yet no detectable change in the valence as determined from Ce–L_{III} edge spectra [14]. The dilution of Ce by Y in $CePd_3$ produces a *contraction* of the lattice and a concomitant *decrease* in the $4f$ stability as evidenced in the magnetic susceptibility [13, 15]. On the other hand, the dilution of Ce by Th produces a *contraction* of the lattice, but an apparent *increase* in the $4f$ stability as evidenced by a decrease in the (mixed) valence, as determined from Ce–L_{III} edge spectra [14]. The present study differs from the ones discussed above in that both negative and positive lattice pressures, relative to $CeNi_5$, were achieved by using additives expected to alter in no significant way the nature of the chemical bonding or the electronic band structure. Yttrium and thorium are chemically different than the lanthanides since their atomic outer electron configurations are $(4d^1 5s^2)$ and $(6d^2 7s^2)$ respectively. Moreover, since Th is tetravalent, its addition to $CePd_3$ is expected to produce band-filling of the Pd-derived d-bands. It is suggested by the results of valence band photoemission studies of $CePd_3$ and $CeRh_3$ [16], that such band-filling should have the effect of markedly decreasing the transition metal-derived d-density-of-states in the region near E_F. The study of La-substituted $CePd_3$, which is presumed free of the aforementioned chemical effects, is limited only to 30–40% La in the Ce-phase, because of a first-order volume instability which occurs at higher La concentration [14].

Several theoretical ideas have been advanced in an attempt to reconcile the anomalous behavior of mixed valent Ce-based systems; in particular, the failure of the promotional model to connect the observed (mixed) valence to the observed volume and magnetic susceptibility. Allen and Martin [17] propose a Kondo lattice approach, where the volume and susceptibility can be smaller than suggested by the valence, because of a volume collapse driven by the Kondo effect, with a concomitant increase in the Kondo temperature, and, hence, the spin fluctuation rate. Fujimori [18] introduces a new mixing term involving the interaction between the $4f$ electrons and the ligand states of the nearest neighbor atoms. This produces a new component in the ground state, viz., a spin-singlet, totally symmetric $4f^1$–L^{-1} excitonic state, where L^{-1} denotes a nearest neighbor ligand-hole state. This component of the ground state favors a reduced volume and reduced susceptibility, but would register as an f^1 signature in core level photoemission or Ce–L_{III} edge spectra. Yet a third approach, also in its infancy, is one by Schlüter and Varma [19], which explores the possibility of a bimodal radial distribution of f-charge on the Ce-site.

The above theoretical directions suggest the need for additional experiments of the genre of the one presented here. In all three approaches, it is possible conceptually to change the volume and the degree of the $4f$ instability, as registered in the magnetic susceptibility or inelastic neutron scattering, without changing appreciably the (mixed) valence, as determined by high energy spectroscopic probes. In the Fujimori approach the $4f$ instability depends strongly on the nearest neighbor-derived density of ligand states; whereas, in the Allen–Martin approach it depends strongly on the overlap between the $4f$-electron and the $5d$-electron. Hence, in the design of experiments, particularly those involving chemical additives, it is important to control and distinguish between the latter effects.

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Effet d'une pression chimique locale sur la structure cristalline de $CaFe_2O_4$

par

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RÉSUMÉ. – On étudie l'effet de la substitution des ions Ca^{2+} du ferrite monocalcique orthorhombique $CaFe_2O_4$ par des cations de taille plus petite.

Cette substitution est partielle si le cation substituant est Mg^{2+}, Mn^{2+}, Co^{2+} ou Ni^{2+}. Elle conduit à $Ca_{(1-x)}M_xFe_2O_4$ ($x \leqq 0,25$) dont la structure n'est pas de type $CaFe_2O_4$ mais de type $Ca_4Fe_9O_{17}$ de symétrie monoclinique. La structure de la phase substituée est en expansion par rapport à celle du ferrite initial et la coordination cationique globale diminue.

Ce résultat, paradoxal en apparence, est discuté en terme de pression chimique locale sur les polyèdres de coordination.

ABSTRACT. – The authors study the effect of substituting the Ca^{2+} ions by various smaller cations in monocalcium ferrite $CaFe_2O_4$ which crystallizes in the orthorhombic symmetry.

If the substituting cation is Mg^{2+}, Mn^{2+}, Co^{2+} or Ni^{2+}, the substitution is incomplete. It leads to $Ca_{(1-x)}M_xFe_2O_4$ ($x \leqq 0.25$) the structure of which is not the $CaFe_2O_4$ type but the $Ca_4Fe_9O_{17}$ type with monoclinic symmetry. The substituted ferrites have a more expanded structure than the initial one and the overall cation coordination number decreases.

This apparently paradoxic result is discussed in terms of the local chemical pressure on the coordination polyedra.

INTRODUCTION

Le ferrite monocalcique $CaFe_2O_4$ cristallise dans le système orthorhombique, *Pnam*, avec les paramètres suivants [1, 2] :

$$a = 9{,}230\ \text{Å}, \quad b = 10{,}705\ \text{Å}, \quad c = 3{,}024\ \text{Å}, \quad V = 299\ \text{Å}^3$$

$$Z = 4, \quad V_{\text{formulaire}}\ \#\ 75\ \text{Å}^3, \quad \rho = 4{,}8\ \text{g.cm}^{-3}.$$

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Dans cette structure tous l
4*c* de Wyckoff (fig. 1).

Les six atomes d'oxygène p
à base triangulaire : ⟨Ca–O
ensuite deux oxygènes à 2,53

Les atomes de fer trivalent
ques déformés où :

⟨Fe(I)–O⟩ = 2,

La distorsion peut être esti

$\frac{1}{6}\Sigma$

dist [Fe(I)] = 1,8.

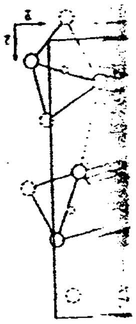

Fig. 1. – Structure

Le spectre Mössbauer en
deux doublets de même in
$\delta = 0{,}37$ mms^{-1}, d'éclatemen

$\Delta_{Fe(I)} = 0{,}30$ m

Nous allons comparer Ca
cristallise dans la structure s

$a = 8{,}698$ Å, $u =$

e sur la structure
)$_4$

NAZEBI,

u C.N.R.S. n° 158,

ance)

Ca^{2+} du ferrite monocalcique

Mg^{2+}, Mn^{2+}, Co^{2+} ou Ni^{2+}.
est pas de type $CaFe_2O_4$ mais
de la phase substituée est en
n cationique globale diminue.
pression chimique locale sur

g the Ca^{2+} ions by various
tallizes in the orthorhombic

e substitution is incomplete.
is not the $CaFe_2O_4$ type but
d ferrites have a more expan-
nation number decreases.
he local chemical pressure on

le système orthorhom-

V = 299 Å^3
.8 g.cm^{-3}.
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Dans cette structure tous les atomes sont en symétrie ponctuelle *m*, site 4*c* de Wyckoff (fig. 1).

Les six atomes d'oxygène premiers voisins du calcium forment un prisme à base triangulaire : $\langle Ca-O \rangle = 2{,}42$ Å. Comme seconds voisins viennent ensuite deux oxygènes à 2,53 et 2,58 Å (tableau I).

Les atomes de fer trivalent, Fe(I) et Fe(II), occupent deux sites octaédriques déformés où :

$$\langle Fe(I)-O \rangle = 2{,}05\text{ Å}, \qquad \langle Fe(II)-O \rangle = 2{,}03\text{ Å}.$$

La distorsion peut être estimée par la valeur

$$\frac{1}{6}\Sigma_i\left(\frac{d_i-\bar{d}}{\bar{d}}\right)^2 = \text{dist.}$$

$$\text{dist}[Fe(I)] = 1{,}8.10^{-4}, \qquad \text{dist}[Fe(II)] = 5.10^{-4}.$$

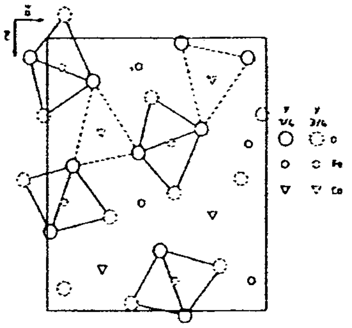

Fig. 1. – Structure de $CaFe_2O_4$: projection sur le plan (010).

Le spectre Mössbauer enregistré à 295 K [3] est une superposition de deux doublets de même intensité, de même déplacement isomérique : $\delta = 0{,}37$ mms^{-1}, d'éclatements quadrupolaires différents :

$$\Delta_{Fe(I)} = 0{,}30\text{ mms}^{-1}, \qquad \Delta_{Fe(II)} = 0{,}72\text{ mms}^{-1}.$$

Nous allons comparer $CaFe_2O_4$ au ferrite de cadmium $CdFe_2O_4$ qui cristallise dans la structure spinelle directe avec pour paramètres [4] :

$$a = 8{,}698\text{ Å}, \qquad u = 0{,}390 \pm 0{,}003, \qquad V_{\text{formulaire}} \# 82\text{ Å}^3.$$

En prenant 0,393 comme valeur la plus probable de *u* (mesure de Sawicki), on calcule :

$$\mathrm{Cd-O} = 2{,}15\,\text{Å},$$

$$\mathrm{Fe-O} = 2{,}03\,\text{Å}.$$

F. Menil [5] donne $\delta_{Fe} = 0{,}37\ \mathrm{mms^{-1}}$ comme déplacement isomérique des ions Fe^{3+} en site octaédrique.

Dans ces deux ferrites, le fer ayant la même coordinence et le même déplacement isomérique, on peut affirmer que la liaison Fe–O a le même degré d'ionicité.

Cd^{2+} ($4d^{10}$) est légèrement plus petit que Ca^{2+} ($3s^2\,3p^6$) [dans la même coordinence VI : $RCd^{2+}_{VI} = 0{,}95\,\text{Å}$, $RCa^{2+}_{VI} = 1{,}00\,\text{Å}$ (6)]. Cette faible différence suffit cependant à provoquer un changement radical de structure qui globalement se traduit par une diminution de la coordinence :

$$\underset{\mathrm{VI}}{\mathrm{Ca}}\,\underset{\mathrm{VI}}{\mathrm{Fe_2}}\mathrm{O_4} \rightarrow \underset{\mathrm{IV}}{\mathrm{Cd}}\underset{\mathrm{VI}}{\mathrm{Fe_2}}\mathrm{O_4},$$

et par une expansion structurale ($V_{f\,CaFe_2O_4} = 75\,\text{Å}^3 \rightarrow V_{f\,CdFe_2O_4} = 82\,\text{Å}^3$).

TABLEAU I

Distances métal-oxygène (Å), *dans* $CaFe_2O_4$

Fe(I)	2 × O	2,07	Fe(II)	2 × O	2,09	Ca	2 × O	2,51
	2 × O	2,07		2 × O	1,98		2 × O	2,38
	1 × O	2,03		1 × O	2,04		2 × O	2,37
	1 × O	2,00		1 × O	2,02			
$\bar{d} = 2{,}051$			$\bar{d} = 2{,}033$			$\bar{d} = 2{,}420$		
dist. = $1{,}8 \times 10^{-4}$			dist. = 5×10^{-4}			Ca	1 × O	2,53
							1 × O	2,58
							1 × O	3,41

TABLEAU II

Distances calcium-oxygène (Å), *dan*
$Ca_4Fe_9O_1$

Ca(I)	1 × O	2,278	Ca(II)	1 × O	2,322
	1 × O	2,284		1 × O	2,339
	1 × O	2,288		1 × O	2,349
	1 × O	2,431		1 × O	2,472
	1 × O	2,436		1 × O	2,493
	1 × O	2,463		1 × O	2,488
$\bar{d} = 2{,}363$			$\bar{d} = 2{,}410$		
Ca(I)	1 × O	2,826	Ca(II)	1 × O	2,506

La même corrélation : diminution de la coordinence-expansion structurale s'observe quand, sur $CaFe_2O_4$, on réalise la double substitution (Ca^{2+}-Fe^{3+}) par le couple (Tm^{3+}-Fe^{2+}) de taille moyenne voisine :

$$RCa^{2+}_{VI} + RFe^{3+}_{VI} = RTm^{3+}_{VI} + RFe^{2+}_{VI} \ \# \ 1{,}65\,\text{Å}\ [6].$$

On aboutit au composé $TmFe_2O_4$ qui cristallise dans le système rhomboédrique, $R\,\bar{3}\,m$, avec pour paramètres, exprimés en repère hexagonal [7] :

$$a = 3{,}472\,\text{Å}, \qquad c = 25{,}01\,\text{Å}, \qquad Z = 3,$$

V_{form}

Le thullium est en site octaéd
de Wyckoff, les six distances Tm
Le fer, bivalent et trivalent
bipyramidale à base triangulaire
Donc, sans changer globaleme
à $TmFe_2O_4$ se produit avec expa
nution globale de la coordinence

$$\underset{\mathrm{VI}}{\mathrm{Ca}}\,\underset{\mathrm{VI}}{\mathrm{Fe_2}}\mathrm{O}$$

Remarquons ici que l'expansi
est dû à la présence de cations e
Toujours en partant de CaFe
conséquences sur la structure d'
du site prismatique du calcium.
de la substitution de Ca^{2+}
($M^{2+} = Mg^{2+}$, Mn^{2+}, Co^{2+}, N
mes $CaFe_2O_4$-MFe_2O_4 pour de

ÉTUDE

Synthèse de $CaFe_2O_4$

Le ferrite monocalcique est obtenu par
de $CaCO_3$ et Fe_2O_3 pendant 24 heures

Synthèse de MFe_2O_4

Les ferrites MFe_2O_4 sont obtenus pa
de mélanges Fe_2O_3-MO, pendant 24 he

Recuits des mélanges $(1-x)$ *CaF*

Ils sont réalisés en ampoules scellées
radiocristallographique des produits a
recuit est suivi d'une trempe à l'eau.
Pour $0 < x < 0{,}07$, le système
type « $Ca_4Fe_9O_{17}$ » et de CaFe

obable de *u* (mesure de

lacement isomérique des

coordinence et le même
liaison Fe–O a le même

(3s^2 3p^6) [dans la même
Å (6)]. Cette faible diffé-
ment radical de structure
la coordinence :

→ $V_{f\,CaFe_2O_4} = 82$ Å³).

Tableau II

tances calcium-oxygène (Å), dan
$Ca_4Fe_9O_{17}$

I	1×0	2,278	Ca(II)	1×0	2,322
	×0	2,284		1×0	2,339
	×0	2,288		1×0	2,349
	×0	2,431		1×0	2,472
	1×0	2,436		1×0	2,493
	1×0	2,463		1×0	2,488
	$\bar{d}=2{,}363$			$\bar{d}=2{,}410$	
(I)	1×0	2,826	Ca(II)	1×0	2,506

nence-expansion structu-
la double substitution
moyenne voisine :

1,65 Å [6].

dans le système rhom-
en repère hexagonal [7] :

Z = 3,

$$V_{formulaire} \# 87\,Å^3.$$

Le thullium est en site octaédrique, de symétrie ponctuelle $\bar{3}m$, site 3*a* de Wyckoff, les six distances Tm–O = 2,25 Å.

Le fer, bivalent et trivalent, occupe le site 6*c* (3*m*), de coordinence bipyramidale à base triangulaire.

Donc, sans changer globalement la taille des cations, le passage $CaFe_2O_4$ à $TmFe_2O_4$ se produit avec expansion structurale (de 75 à 87 Å³) et diminution globale de la coordinence :

$$\underset{\text{VI}\ \ \text{VI}}{CaFe_2O_4} \rightarrow \underset{\text{VI}\ \ \text{V}}{TmFe_2O_4}.$$

Remarquons ici que l'expansion est particulièrement marquée, fait qui est dû à la présence de cations en coordinence V.

Toujours en partant de $CaFe_2O_4$, nous avons cherché à déterminer les conséquences sur la structure d'une modification des contraintes au niveau du site prismatique du calcium. Pour ce faire, nous avons étudié l'influence de la substitution de Ca^{2+} par un ion divalent M^{2+} plus petit ($M^{2+} = Mg^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}), ce qui revient à caractériser les systèmes $CaFe_2O_4$-MFe_2O_4 pour des rapports molaires $\frac{M}{Ca} \leqq 0{,}33$.

ÉTUDE EXPÉRIMENTALE

Synthèse de $CaFe_2O_4$

Le ferrite monocalcique est obtenu par un recuit à 1 190°C à l'air, d'un mélange équimolaire de $CaCO_3$ et Fe_2O_3 pendant 24 heures

Synthèse de MFe_2O_4

Les ferrites MFe_2O_4 sont obtenus par recuits en ampoules scellées sous vide, à 1 000°C, de mélanges Fe_2O_3-MO, pendant 24 heures

Recuits des mélanges $(1-x)\,CaFe_2O_4 - x\,MFe_2O_4$ $(x \leqq 0{,}25)$

Ils sont réalisés en ampoules scellées sous vide à 1 190°C, pendant 24 heures. L'analyse radiocristallographique des produits a donné le même résultat quel que soit M. Chaque recuit est suivi d'une trempe à l'eau.

Pour $0 < x < 0{,}07$, le système est constitué d'un composé de structure type « $Ca_4Fe_9O_{17}$ » et de $CaFe_2O_4$ en excès; pour $0{,}07 \leqq x \leqq 0{,}2$, la phase type « $Ca_4Fe_9O_{17}$ » est pure, tandis que pour $x>0{,}2$ apparaît en plus une structure type spinelle de magnétite dopée à la chaux.

L'analyse détaillée des clichés de diffraction aux rayons X de la phase pure ne permet pas de déceler de variations significatives des distances réticulaires avec la valeur de x et la nature de M. Le diffractogramme correspond à celui de « $Ca_4Fe_9O_{17}$ », indexé en maille monoclinique C 2 de paramètres :

$$a=10{,}441\ \text{Å},\quad b=6{,}025\ \text{Å},\quad c=11{,}384\ \text{Å},\quad \beta=98°80,$$
$$V=708\ \text{Å}^3,\quad Z=2,\quad \rho_{mes}=4{,}42\ \text{g.cm}^{-3}.$$

La structure de ce ferrite, décrite par B. Malaman *et al.* [8] se caractérise par des coordinences VI ou VII du calcium (tableau II), mais aussi par un plan de bipyramides trigonales de fer, associé à des tétraèdres FeO_4 et des octaèdres FeO_6, ce qui lui confère sa nature expansée (fig. 2).

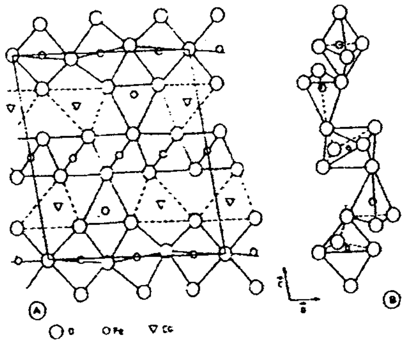

Fig. 2. — Structure de « $Ca_4Fe_9O_{17}$ » : *a* : Projection schématique sur le plan (010). *b* : Succession des polyèdres de coordination du fer.

Nous avons effectué une mesure de la masse volumique, par picnométrie à la décaline, de $Ca_{0.93}Co_{0.07}Fe_2O_4$ et obtenu $4{,}47\ \text{g.cm}^{-3}$, donc en concordance avec celle observée pour « $Ca_4Fe_9O_{17}$ ». Cette valeur conduit à $Ca_{8,1}Co_{0.6}Fe_{17.5}O_{35}$ comme contenu de maille soit un volume formulaire $(Ca, Co)_1Fe_2O_4 \# 82\ \text{Å}^3$.

Pour l'autre limite : $Ca_{0.8}Co_{0.2}Fe_2O_4$ on aboutit à $Ca_7Co_{1,7}Fe_{17,5}O_{35}$ comme contenu de maille.

Ainsi passant de $CaFe_2O_4$ à $Ca_{0.93}M_{0.07}Fe_2O_4$, on observe une augmentation de volume formulaire de l'ordre de 9 % soit une forte expansion structurale.

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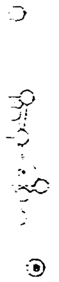

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Nous avons montré par ailleurs [9] que la réaction entre $CaFe_2O_4$ et MO ($M = Mg$, Co, Ni, Zn), à 1 120°C, conduit uniquement à un mélange de ferrite bicalcique et de spinelle.

Donc la réaction $(1-x)CaFe_2O_4 + xMFe_2O_4$ s'effectue grâce à une substitution du calcium seul et selon un mécanisme qui implique initialement des contraintes au niveau du site prismatique de ce calcium. Comme M^{2+} est plus petit que Ca^{2+}, on qualifiera cet effet de pression chimique locale puisque le polyèdre de coordination se contracte.

DISCUSSION ET CONCLUSION

Il est généralement établi que l'effet d'une pression chimique locale résultant de la substitution d'un cation donné par un cation plus petit provoque la contraction de son polyèdre de coordination, avec ou sans modification de la coordinence. Dans ce dernier cas, l'incidence de cette contrainte se traduit d'abord par la formation d'une solution solide dont les paramètres cristallographiques obéissent souvent à la loi de Vegard. Un tel comportement n'est pas systématique quand il y a modification de la coordinence.

Nos travaux sur la substitution de l'ion Ca^{2+} par un ion plus petit dans le ferrite monocalcique confirment la contraction du polyèdre de coordination de Ca^{2+} qui, dans ce cas, provoque un changement de structure. Celui-ci se traduit par une diminution de la somme des coordinences des cations présents (coordinence cationique globale) et par une augmentation du volume formulaire (expansion structurale).

Ces deux points sont en opposition avec ce qui est observé sous l'effet d'une pression physique externe qui s'accompagne en général d'un accroissement de la coordinence et corrélativement d'une densification.

Notre résultat peut donc sembler *a priori* paradoxal. En fait, il peut s'expliquer de la manière suivante :

La pression chimique s'exerce d'abord au niveau du polyèdre de coordination de Ca^{2+} qui passe de prismatique à tétraédrique ou octaédrique. Pour la substitution

$$(1-x)CaFe_2O_4 + xMFe_2O_4 \rightarrow Ca_{(1-x)}M_xFe_2O_4,$$

les tableaux I et II montrent que la distance moyenne Ca–O comptée sur les six atomes d'oxygène premiers voisins diminue, ce qui induit une modification de certains polyèdres de coordination du fer qui passe de la coordinence octaédrique aux coordinences tétraédrique, hexaédrique et octaédrique.

La tension locale au niveau du calcium est donc absorbée par le fer qui peut, au même degré d'oxydation, s'accommoder de plusieurs coordinences. Globalement, la structure devient moins compacte car l'empilement des polyèdres est plus lâche. Comme en première approximation, ces oxydes mixtes se décrivent avec le modèle ionique, il est certain que cette pression chimique accentue le caractère covalent des liaisons métal-oxygène et c'est pour cette raison que la coordinence cationique globale diminue.

En conclusion, la seule définition d'une pression chimique ne permet pas de prévoir le sens d'évolution des compacités des structures d'oxydes mixtes, elle peut augmenter si la coordinence cationique globale ne change pas ou diminuer si elle diminue.

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HIGH-TEMPERATURE SUPERCONDUCTIVITY IN THE $BaPb_{1-x}Bi_xO_3$ SYSTEM

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(*Received* 10 *February* 1975 *by J. Tauc*)

Phases of the type $BaPb_{1-x}Bi_xO_3$ have been prepared for the first time. These phases all have perovskite related structures, and superconductivity was observed over the range $x \cong 0.05$–0.3. The highest critical temperature is 13 K which is exceptionally high for an oxide and is much higher than that previously observed for any superconductor not containing a transition element. Semiconducting behavior is observed from $x = 1$ to about 0.35.

$BaPbO_3$ has been reported[1] with a perovskite-type structure. An orthorhombic cell of $a = 6.024$ Å $b = 6.065$ Å, and $c = 8.506$ Å has been given by Shannon and Bierstedt.[2] Despite the fact that this is a normal valence compound, $BaPbO_3$ has metallic properties.[2] Presumably, $BaPbO_3$ as well as PbO_2 are best described as semimetals.

$BaBiO_3$ has also been reported[3] with a perovskite related structure; however, no cell dimensions or physical properties have been given. We have grown bronze colored crystals of $BaBiO_3$ hydrothermally. Crystallographic studies indicate a primitive orthorhombic cell with $a = 4.343$ Å, $b = 4.358$ Å, and $c = 4.333$ Å. This cell contains only one formula unit of $BaBiO_3$, and it is possible that the true cell is larger as in the case of $BaPbO_3$ where $z = 4$. However, neither Guinier nor single crystal X-ray techniques showed any evidence of a larger cell. Four-probe electrical resistivity data were obtained from 4.2–970 K. Semiconducting behavior is indicated over this entire range with a room temperature resistivity of about 10 Ω-cm and an activation energy of about 0.2 eV. Since $BaBi^{4+}O_3$ would presumably be a metal, we can probably assume the situation to be $Ba_2Bi^{3+}Bi^{5+}O_6$.

Compositions of the type $BaPb_{1-x}Bi_xO_3$ were prepared by heating appropriate mixtures of oxides, carbonates or nitrates in air at 800–1000°C. A complete solid solution between $BaPbO_3$ and $BaBiO_3$ apparently exists. The pseudocubic cell edge ($\sqrt[3]{V/z}$) vs x is plotted in Fig. 1. The phase appear black up to $x \cong 0.3$, but the color is bronze-like for higher values of x. Electrical resistivity measurements on pellets indicate semiconducting behavior for all the bronze-colored phases and metallic properties for all the black phases.

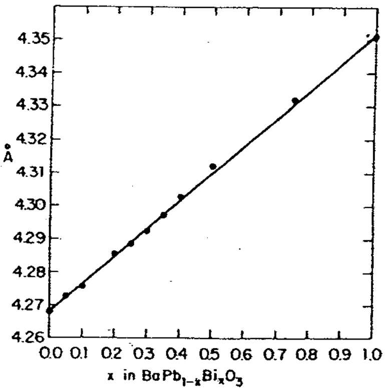

FIG. 1. a vs x in the $BaPb_{1-x}Bi_xO_3$ system where $a = \sqrt[3]{V/z}$.

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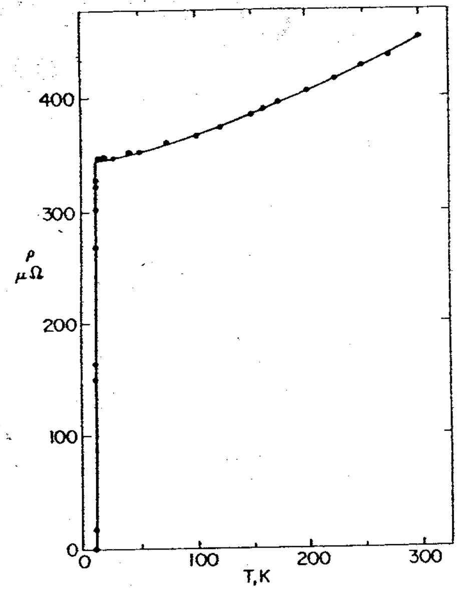

FIG. 2. Electrical resistivity vs temperature for a crystal of $BaPb_{0.8}Bi_{0.2}O_3$.

Superconductivity has been observed in the $BaPb_{1-x}Bi_xO_3$ system from $x = 0.05$–0.3. Meissner Effect measurements indicate that the critical temperature increases from about 9 K at $x = 0.05$ to a maximum of about 13 K at $x = 0.3$. A sample with $x = 0.35$ was not superconducting at 4.2 K. The superconducting transitions were not always sharp as found by the Meissner Effect measurement; thus, the critical temperatures reported represent the onset of superconductivity. Compositions of the type $Ba_{1-y}A_yPb_{1-x}Bi_xO_3$ where A is an alkali cation and y is 0.1–0.2 give similar critical temperatures, but the transitions are sharper. The reason for the broad transitions in some cases is not certain, but they may be related to nonrandom distributions of Pb and Bi.

Four-probe electrical resistivity data for a $BaPb_{0.8}Bi_{0.2}O_3$ crystal are shown in Fig. 2. The temperature dependence is metallic-like from 298–11 K.

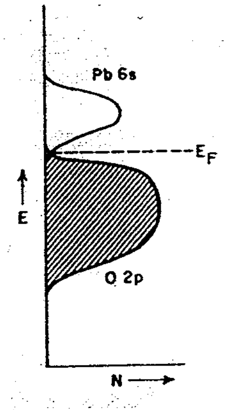

FIG. 3. Schematic energy level diagram for $BaPbO_3$.

However, at 11 K the resistivity drops abruptly to less than 10^{-6} Ω-cm. A pellet of $BaPb_{0.75}Bi_{0.25}O_3$ also clearly showed a loss of electrical resistivity at about the same temperature; thus, grain boundaries do not have detrimental effects on the superconductivity of this material.

A schematic energy level diagram for $BaPbO_3$ is shown in Fig. 3. The lead–oxygen bonding is highly covalent. Therefore, the oxygen $2p$ band has considerable lead character and the lead $6s$ band has considerable oxygen character. Electrons may directly enter the $6s$ band as x increases in the $BaPb_{1-x}Bi_xO_3$ system. However, the $6s$ band may also narrow and tend to split as x increases. The narrowing could cause an increase in the density of states at the Fermi level and consequently an increase in the superconducting critical temperature. The $6s$ band would split at about $x = 0.35$, and semiconducting properties are observed at higher values of x. Although this model is qualitatively satisfying, the assumptions of a rigid band may be very misleading. It is not at all certain that the Bi 6s state will mix completely into the Pb $6s$ band. The situation is very different than in the tungsten bronzes (A_xWO_3) where the states are not directly changed as x increases.

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HYDROSTATIC PRESSURE EFFECT ON T_c OF $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$

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(*Received* 31 *October* 1975 *by A.G. Chynoweth*)

The superconducting transition temperature of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ has been found to be suppressed smoothly by the application of hydrostatic pressure at a rate of $-(2.9 \pm 0.2) \times 10^{-5}\,\text{kbar}^{-1}$ up to 15 kbar. The implications of these results are discussed.

BOTH $BaPbO_3$[1] and $BaBiO_3$[2] exhibit perovskite-type structure but with slightly different symmetries.[3] They were recently found[3] to form a solid solution, $BaPb_{1-x}Bi_xO_3$, with Pb- and Bi-atoms occupying the octahedral sites. Wide range of electrical resistance behavior was also found[3] in this solution. The system is metallic for $x < 0.3$ while semiconducting otherwise. Superconductivity was observed in the composition range of $0.05 \leqslant x \leqslant 0.3$ with an onset transition temperature T_c increasing from ~ 9 K at $x = 0.05$ to ~ 13 K at $x = 0.3$ near the metal–semiconductor phase boundary. Samples with $x = 0$ and 0.35 are not superconducting down to 4.2 K. A T_c of 13 K in $BaPb_{1-x}Bi_xO_3$ system is the highest yet observed in compounds not containing any transition elements. The drastic variation of T_c with x was explained[3] in terms of the narrowing of the s-conduction band, consisting of the Pb- and Bi-6s states, as x increases. The semiconducting nature of the compounds with $x > 0.3$ was then attributed to the splitting of the 6s-conduction band and consequently the creation of a gap near the critical concentration.

The results of the present investigation show that: (1) d-electrons may have participated in the occurance of superconductivity in the $BaPb_{1-x}Bi_xO_3$ system, (2) the broad superconducting transition of the system seems likely to be caused by the concentration inhomogeneity near the metal–semiconductor phase boundary, and (3) the superconductivity in the system is a bulk effect.

Superconducting $BaPb_{1-x}Bi_xO_3$ compounds always show a broad transition.[3] However it has been demonstrated[3] that the substitution of 10–20% of the Ba in the compound by an alkaline element will sharpen the superconducting transition with little change in the onset of the transition temperature. Therefore high pressure study was carried out only on two powder samples of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$. The procedure for sample preparation was previously described elsewhere.[3] The Pb–Bi composition of the samples examined was near the critical concentration where T_c is maximum and the concentration induced metal–semiconductor transition occurs. The superconducting transition was detected by a standard ac inductance bridge operating at 10 Hz. The temperature was determined by a Ge-thermometer. The hydrostatic pressure environment was provided by a self-clamp technique.[4] A fluid mixture of 1 : 1 n-pentane and isoamyl alcohol was used as the pressure medium. The reproducibility of T_c after immersing the sample in the pressure medium for a week indicated the high chemical stability of the sample in the pressure medium. The pressure at low temperature was measured by a Pb-manometer surrounded by the powder sample. The superconducting signal of one of the samples at atmospheric pressure was plotted in Fig. 1 as a function of temperature. The transition was still broad even with the K-substitution. The onset of the transition shown as a small maximum in the a.c. susceptibility curve was (11.73 ± 0.02) K, which is about 1 K lower than the maximum superconducting onset temperature previously reported[3] for the system. This can be caused by one or more of the following reasons: the slightly smaller x of the present samples, the possible difference in temperature calibrations and the different measuring techniques employed. The bulk of the transition occurs between 11 and 7 K as shown in Fig. 1. At 5.1 K, 95% of the sample was estimated to be superconducting. Further

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* Research supported in part by the National Science Foundation under Grant No. DMR 7302660 and Research Corporation.

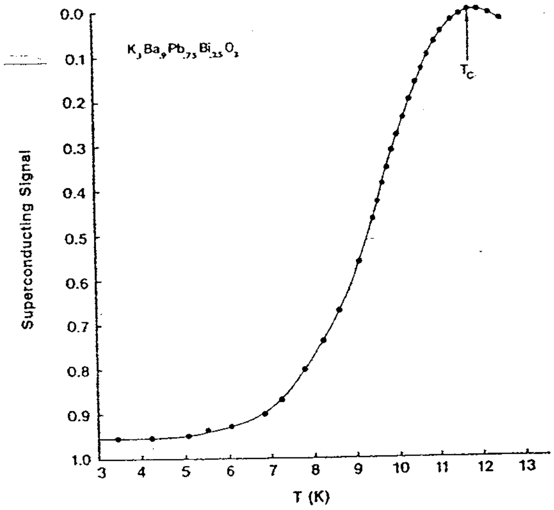

Fig. 1. Temperature dependence of the super conducting transition curve of a powder sample of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ as determined by an a.c. inductive method. The arrow defined the onset of the transition.

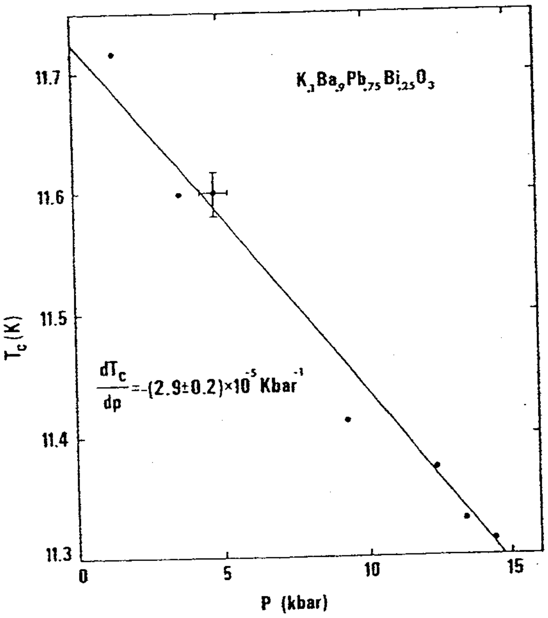

Fig. 2. Hydrostatic pressure effect on the onset temperature of the superconducting transition of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$.

reduction in temperature did not increase the superconducting signal size. Because of the broad transition, hydrostatic pressure effect was determined only on the onset of the superconducting transition temperature T_c. The results were shown in Fig. 2. T_c decreases smoothly with pressure up to ~ 15 kbar at a rate of $-(2.9 \pm 0.2) \times 10^{-5}$ kbar^{-1}. The vertical bar represents the uncertainity in defining T_c. The same results were obtained for the other sample.

It has been demonstrated[5] that the volume effect on T_c can be expressed as $d \ln (T_c/\theta)/dV \equiv \phi \ln (\theta/T_c)$, where θ is the Debye temperature, V the volume and ϕ a material dependent constant. For nontransition metal (or *sp*) superconductors, $\phi \sim 2.5$, while for the transition metal (or *d*) superconductors, $\phi < 2.5$ and can become negative. The lack of knowledge on θ and the compressibility of $BaPb_{1-x}Bi_xO_3$ system prevents us from making use of this procedure to assess the different roles played by electrons in different bands. However an alternative approach was adopted. By examining all available data[5–7] on the relative pressure effect of T_c, i.e. $d \ln T_c/dP$, we found[8] that generally values of $d \ln T_c/dP$ fall into two groups with $d \ln T_c/dP < -8 \times 10^{-6}$ bar^{-1} for the *sp* superconductors, but $> -2 \times 10^{-6}$ bar^{-1} for superconductors with *d*-electrons in their conduction band, and the value is not sensitive to impurity except for cases where a pressure or impurity-induced Fermi surface topology change takes place. Since $d \ln T_c/dP$ for $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ is -1.7×10^{-6} bar^{-1}, it is suggested that electrons from the *d*-band may contribute significantly to the high T_c of the system due to the *5d–2p* and/or *5d–6s* hybridizations and the system may show a large critical field.

The abrupt disappearance of superconductivity following the T_c-peak strongly suggests a drastic change in the electron energy spectrum of $BaPb_{1-x}Bi_xO_3$ as x becomes larger than ~ 0.3, inspite of the fact[3] that no no apparent anomaly was detected at $x \sim 0.3$ in the size of the pseudocubic cell of the system. This makes it all the more tempting to propose that the metal–semiconductor transition is electronic in nature. Such an electronic instability can be due to the large density of state which varies drastically with concentration or the particular shape of the Fermi surface of the system near the critical concentration. This would result in the splitting of the conduction band and the creation of an energy gap associated with the semiconducting phase, as previously suggested.[3] The broad superconducting transition of the system can then be easily attributed to a concentration inhomogeniety (or fluctuation) near the metal–semiconductor phase boundary, instead of any internal strain due to the possible presence of a small two phase region near the critical concentration in view of the small pressure effect on T_c observed. Experiments to provide further evidence are in progress.

Finally, we would like to point out that all known high T_c oxide systems ($BaPb_{1-x}Bi_xO_3$,[3] $Li_{1+x}Ti_{2-x}O_4$,[9] A_xWO_3,[10] with A as an alkaline or alkaline earth atom) have the following in common: (1) superconductivity

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occurs only over a limited range of x, and the superconducting phase usually is sandwiched between a conducting and a semiconducting phase, (2) T_c increases rapidly as x approaches the semiconducting phase boundary and disappears abruptly beyond the phase boundary, and (3) they all have atoms occupying the octahedral sites with six oxygen nearest neighbors. Further study is under way way to look for possible pressure or temperature induced electronic transition in $BaPb_{1-x}Bi_xO_3$ and to understand the causes responsible for the peculiar superconducting behavior in these high T_c oxide systems.

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The Structure of La_2CuO_4 and $LaSrVO_4$*

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We have examined the structure of La_2CuO_4 at room temperature and found it to be an orthorhombic distortion of the K_2NiF_4 structure ($a = 5.363$ Å, $b = 5.409$ Å, $c = 13.17$ Å). Refinement of position parameters, based on powder X-ray diffraction data, shows the copper to have two long Cu–O distances (2.40 Å) and four short distances (1.90 Å). The orthorhombic unit cell becomes tetragonal at 260°C without any significant change in Cu–O distances. The magnetic susceptibility of La_2CuO_4 is less than 10^{-6} emu/g from room temperature to 4.2 K and in fields to 17 kOe. We have prepared $LaSrVO_4$ by reaction of component oxides in vacuum at 1000°C. The new compound has a tetragonal K_2NiF_4 structure with $a = 3.869$ Å and $c = 12.652$ Å. Optimization of position parameters gave two longer V–O distances (2.09 Å) and four shorter (1.94 Å).

Compounds with the general formula A_2BX_4 generally have the tetragonal K_2NiF_4 structure when the radius of the A cation is $1.0 < r_A < 1.9$ Å, the radius of the B cation is $0.5 < r_B < 1.2$ Å and X is an anion such as oxygen, fluorine or chlorine. The larger A cation has nine-fold coordination and the smaller B cation has octahedral coordination (Fig. 1). This structure can be described as containing alternate layering of perovskite (ABX_3) and rock-salt (AX) units with the nine-coordinated A cation having a surrounding that is the average of what it would be in perovskite and rock salt. This A_2BX_4 composition is one end member of a series of structurally related compounds with the general formula $AX(ABX_3)_n$ where $n = 1, 2, 3$ and ∞. As n increases, the rock salt layer is separated by a larger number of perovskite units until there are three. There are no known examples for n between 3 and ∞ (the perovskite end member).

Materials with the K_2NiF_4 structure exhibit a wide range of magnetic (*1*) and electrical properties. The investigation of these properties has given insight into the important and structurally related compounds with the perovskite structure.

As part of our broad program to investigate the properties of interesting and potentially useful transition-metal compounds, we have examined various aspects of materials with K_2NiF_4-related structures (*2*). In this paper, we report on the structure of La_2CuO_4, the effect of temperature on the structures of La_2CuO_4 and Pr_2CuO_4, and the preparation and structure of $LaSrVO_4$.

A_2CuO_4 (A = La, Pr)

Many workers (*3–7*) have reported on the preparation and characterization of Ln_2CuO_4 (Ln = La–Gd). These compounds, with the exception of La_2CuO_4, have the tetragonal K_2NiF_4 structure. The structure of La_2CuO_4 has been described as "more complex" (*3–5*) or "different" (*6*) than Ln_2CuO_4 (Ln = Pr–Gd).

We prepared La_2CuO_4 by the solid-state reaction of dried La_2O_3 and CuO. The well ground mixtures of components were fired at 1000–1200°C in air for a few days with frequent regrinding. This procedure was sufficient to yield single phase La_2CuO_4 as determined by X-ray diffraction. This same technique was used to prepare Pr_2CuO_4. After examination of the complete powder pattern for La_2CuO_4, we were able to index all diffraction peaks using an orthorhombic unit cell that is closely related to

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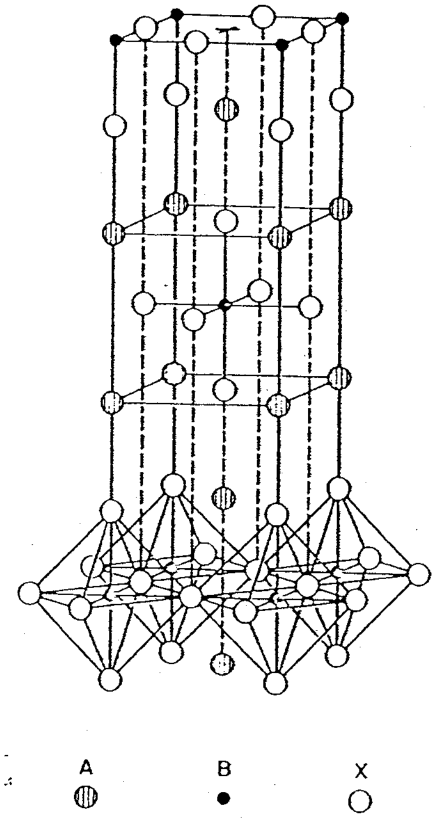

FIG. 1. The tetragonal K_2NiF_4 structure.

that of tetragonal K_2NiF_4 through the relationship:

$$a_0 \simeq \sqrt{2}\, a_T,\; b_0 \simeq \sqrt{2}\, b_T,\; c_0 \approx c_T.$$

Refinement of lattice parameters was accomplished with a computer program developed in our laboratory which minimizes the differences in observed and calculated 2θ values. Using 20 line positions as read from a slow-scanned (1/4°/min) diffractometer pattern, we obtained for La_2CuO_4

$$a = 5.363(5)\,\text{Å} \quad b = 5.409(5)\,\text{Å} \quad c = 13.17(1)\,\text{Å}$$

A similar distortion of the K_2NiF_4 structure has been found for La_2CoO_4 (*8*) and β-Na_2UO_4 (*9–11*).

In order to confirm the structure of La_2CuO_4 and determine interatomic distances, we refined the position parameters and temperature factors by minimizing the differences between our observed X-ray intensities and those calculated on the basis of an orthorhombic distortion of the tetragonal K_2NiF_4 structure. Integrated intensities for La_2CuO_4 were obtained on a General Electric XRD-5 diffractometer by accumulating both time and counts while scanning through a peak at 1/4°/min and subtracting total background as determined from a smooth plot of minimum background data. Where two or more peaks overlapped, they were grouped and assigned a single intensity value. Calculation of intensities was made assuming space group *Fmmm* and placing the atoms as given in Table I. The scattering factors for La^{3+}, Cu^{2+} (*12*) and O^{2-} (*13*) were corrected for the real and imaginary part of the anomalous dispersion term (*14*). The theoretical polarization term for a LiF-crystal diffracted-beam monochromator was also applied to our data. The two variable position parameters (z_{La} and z_{O1}) and the atomic temperature factors were refined by minimization of

$$R = 100 \times \sum |I_{obsd} - I_{calcd}| / \sum I_{obsd}$$

using a program developed in our laboratory. During the refinement based on twenty four intensities between 24° and 100° (2θ), the value of the atomic temperature factors for O1 (B_{O1}) rose to an unusually high value of 4.0.

The results of our final refinement (with $R = 2.4$) are listed in Table I and a comparison of observed and calculated intensities is given in Table II. Fixing the value of B_{O1} and B_{O2} at 1.5 changed R to 2.8 but did not change any of the variables beyond their stated error limits. Even

TABLE I

CRYSTALLOGRAPHIC DATA FOR La_2CuO_4

Unit cell dimensions:	$a = 5.363(5)^a$ Å, $b = 5.409(5)$ Å, $c = 13.17(1)$ Å
Space group:	*Fmmm* (No. 69)
Cell contents:	four La_2CuO_4; face-centered translations applied to:
La in (8*i*)	$0, 0, z; 0, 0, \bar{z}$
Cu in (4*a*)	$0, 0, 0$
O1 in (8*i*)	$0, 0, z; 0, 0, \bar{z}$
O2 in (8*e*)	$1/4, 1/4, 0; 1/4, 1/4, 1/2$
Refined parameters:	$z_{La} = 0.362(1)$, $z_{O1} = 0.182(3)$ $B_{La} = 0.7(1)$ Å^2, $B_{Cu} = 0.6(1)$ Å^2, $B_{O1} = 4(1)$ Å^2, $B_{O2} = 1.5(5)$ Å^2

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[a] Value in parentheses is estimated error in last place of number.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED X-RAY DIFFRACTION DATA FOR ORTHORHOMBIC La_2CuO_4

d_{obsd}	$d_{calc}{}^a$	$h\,k\,l$	I_{calc}	I_{obsd}	d_{obsd}	d_{calc}	$h\,k\,l$	I_{calc}	I_{obsd}
6.592	6.585	0 0 2	3.7	3.0^b	—	1.314	4 0 2	0.1	0.0^b
3.660	3.658	1 1 1	24.4	24.3	1.265	1.265	1 3 7	5.1	11.7
3.293	3.293	0 0 4	12.9	13.2	—	1.264	3 3 1	1.5	
2.876	2.877	1 1 3	100.0	100.0	1.260	1.260	3 1 7	5.1	
2.704	2.705	0 2 0	34.0	66.7	1.251	1.251	0 4 4	1.8	11.1
2.680	2.682	2 0 0	33.2		1.245	1.245	2 2 8	8.9	
2.504	2.502	0 2 2	0.7	0.8^b		1.242	4 0 4	1.8	
2.486	2.483	2 0 2	0.7	0.8^b	1.219	1.219	3 3 3	8.1	7.5
2.194	2.195	0 0 6	10.6	9.8	1.207	1.207	2 4 0	5.3	10.1
2.167	2.166	1 1 5	23.3	23.3	1.201	1.201	4 2 0	5.2	
2.090	2.090	0 2 4	15.4	30.6	—	1.188	2 4 2	0.0	2.7
2.079	2.079	2 0 4	15.2		—	1.184	0 2 10	1.1	
1.904	1.904	2 2 0	33.8	34.2	1.81	1.182	2 0 10	1.1	
1.829	1.829	2 2 2	0.5	0.4^b	—	1.182	4 2 2	0.0	
1.704	1.704	0 2 6	5.2	32.1	1.151	1.151	0 4 6	2.0	17.4
1.698	1.699	2 0 6	5.1		1.146	1.144	4 0 6	2.0	
1.695	1.695	1 3 1	3.4			1.144	3 3 5	2.4	
1.686	1.687	1 1 7	12.4		1.141	1.142	1 1 11	9.9	
1.683	1.683	3 1 1	3.3		1.133	1.134	2 4 4	4.1	8.7
1.648	1.648	2 2 4	8.3	13.6	1.128	1.128	4 2 4	4.0	
1.645	1.646	0 0 8	5.6		—	1.112	1 3 9	0.1	0.2^b
1.593	1.593	1 3 3	19.0	3.72	—	1.108	3 1 9	0.1	
1.583	1.583	3 1 3	18.7		—	1.098	0 0 12	0.1	0.0^b
1.438	1.438	2 2 6	9.3	20.1	1.082	1.083	2 2 10	1.1	1.5^b
1.434	1.434	1 3 5	5.5		1.058	1.058	2 4 6	2.1	10.0^b
1.426	1.427	3 1 5	5.4		—	1.057	1 5 1	1.0	
1.407	1.406	0 2 8	4.7	8.5	1.053	1.054	4 2 6	2.1	
1.402	1.403	2 0 8	4.6		1.052	1.052	3 3 7	3.1	
—	1.366	1 1 9	0.2	0.0^b	1.049	1.049	5 1 1	0.9	
1.352	1.352	0 4 0	5.0	4.3	1.045	1.045	0 4 8	2.6	3.0^b
1.340	1.341	4 0 0	4.8	5.0	1.039	1.040	4 0 8	2.6	3.0^b
—	1.325	0 4 2	0.1	0.0^b	1.031	1.031	1 5 3	5.1	5.0
—	1.317	0 0 10	0.4	0.0^b	1.023	1.023	5 1 3	5.0	5.8

[a] $a = 5.636$ Å, $b = 5.409$ Å, $c = 13.17$ Å.

[b] Estimated and not used in refinement.

though we have very good agreement between observed and calculated intensities, the high value of B_{01} and the poor agreement for the [400], [040], [513], and [153] reflections indicate that the true structure of La_2CuO_4 probably has symmetry lower than that required by the space group *Fmmm*. Kovba (*11*) has recently reported as a result of single crystal studies that the structure of β-Na_2UO_4 has *Pbnb* symmetry instead of *Fmmm* as earlier reported (*9*, *10*) on the basis of powder patterns.

Though some question still remains concerning the exact structure of La_2CuO_4, the general nature of the structure is not in doubt. The most striking feature of structure is the two long Cu-O1 distances (2.40 Å) and the four short Cu-O2 distances (1.90 Å). The average Cu-O distance (2.07 Å) is in good agreement with that predicted (2.08 Å) when the "effective ionic radii" of Shannon and Prewitt (*15*) are used.

If we calculate c/a_T where $a_T = (a + b)/(2 \times \sqrt{2})$, we obtain a value of 3.46. For the tetragonal K_2NiF_4 structure, c/a is always found to be 3.30 ± 0.05 (*16*) except when there is a Jahn–Teller ion present. The unusually large c/a value for La_2CuO_4 is consistent with a Jahn-Teller configuration for $Cu^{2+}(d^9)$ and supports our finding of two longer and four shorter Cu-O distances.

In order to further show the structural relation of orthorhombic La_2CuO_4 to tetragonal K_2NiF_4, we have measured the lattice parameters of La_2CuO_4 as a function of temperature to 990°C using a Tempres high-temperature attachment on a General Electric XRD-5 diffractometer. The orthorhombic unit cell becomes less distorted with increasing temperature and transforms to tetragonal symmetry at 260°C. The lattice parameters for the tetragonal cell at 420°C are $a = 3.81(1)$ Å, $c = 13.24(5)$ Å; ($c/a = 3.47$). By following the position of the [006] and [200] reflections as the temperature is increased, the value of c/a was found to remain constant at 3.47 ± 0.01 up to 990°C where $a = 3.85(1)$ Å and $c = 13.37(5)$ Å. This would indicate that there is little change in going from the orthorhombic to the tetragonal unit cell. Using the pseudo-tetragonal a_T and c of the orthorhombic unit cell we are able to calculate a coefficient of linear thermal expansion (α) for La_2CuO_4 between room temperature and 990°C. The values we obtain, $\alpha_a = 12 \times 10^{-6}$ °C^{-1} and $\alpha_c = 16 \times 10^{-6}$ °C^{-1}, are in good agreement with those found for Sr_2TiO_4, $\alpha_a = 14.6 \times 10^{-6}$ °C^{-1} and $\alpha_c = 14.4 \times 10^{-6}$ °C^{-1} (*17*).

We have prepared Pr_2CuO_4 and confirm that its structure is K_2NiF_4 (*5*). Refinement of lattice parameter based on 20 line positions between 23° and 74° (2θ) gives $a = 3.966(8)$ Å, $c = 12.24(2)$ Å, and $c/a = 3.09$. This no doubt indicates that the Jahn–Teller ion Cu^{2+} has two shorter and four longer Cu–O distances. Knox (*18*) has found the same surroundings for Cu^{2+} in isostructural K_2CuF_4 ($c/a = 3.07$). These Cu–O distances are opposite to what is found for La_2CuO_4 and reflects a change from a $d^2_{x^2-y^2} - d^1_{z^2}$ (Pr_2CuO_4) to a $d^1_{x^2-y^2} - d^2_{z^2}$ (La_2CuO_4) configuration. We have followed the c/a ratio for Pr_2CuO_4 up to 900°C and find that it remains constant at 3.09 ± 0.01. At 900°C the tetragonal unit cell is $a = 4.00(1)$ Å and $c = 12.31(3)$ Å. The coefficients of linear expansion between room temperature and 900°C are $\alpha_a = 9.5 \times 10^{-6}$ °C^{-1} and $\alpha_c = 6.7 \times 10^{-6}$ °C^{-1}. These values are much smaller than those found for La_2CuO_4.

We have investigated the magnetic properties of La_2CuO_4 using a vibrating sample magnetometer. The magnetic susceptibility of our sample (0.2142 g) was below the sensitivity of our instrument (10^{-6} emu/g) from room temperature to 4.2°K and in fields to 17 kOe. Since Cu^{2+} has an odd number of d electrons, the absence of a normal magnetic moment probably indicates antiferromagnetism.

$LaSrBO_4$

An examination of the literature (*1*) of known materials with the K_2NiF_4 structure revealed that $LaSrVO_4$ and $LaSrTiO_4$ have not been reported as members of the series $LaSrBO_4$ where B^{3+} = Al, Cr, Mn, Fe, Co, Ni, Ga, Rh. All of the known compounds have been obtained by reaction of oxides and carbonates in air, N_2 or O_2. We have attempted the preparation of $LaSrVO_4$ and $LaSrTiO_4$ by the reaction of stoichiometric amounts of dry La_2O_3, freshly prepared SrO and V_2O_3, or Ti_2O_3. The reactants were intimately mixed, pelleted and fired in evacuated silica capsules at 1000°C for 24 hr. X-ray diffraction patterns of the reaction products in the case of the Ti compound revealed a mixed phase with no compound having the K_2NiF_4 structure. However, there was compound formation for $LaSrVO_4$ with only trace amounts of a second phase.

The X-ray pattern of $LaSrVO_4$ could be interpreted assuming the material has the tetragonal K_2NiF_4 structure. Refinement of the lattice parameters was based on 15 well-defined peaks whose positions were determined from a 1/4°/min scan over the 2θ interval 50°–125°. For $LaSrVO_4$, we obtained $a = 3.869(1)$ Å and $c = 12.652(3)$ Å. The c/a ratio is 3.27 and is similar to those found for most materials wth the K_2NiF_4 structure. To confirm our structure assignment, we have compared our observed intensities with those calculated for the K_2NiF_4

TABLE III

CRYSTALLOGRAPHIC DATA FOR $LaSrVO_4$

Unit cell dimensions:	$a = 3.869(1)^a$ Å, $c = 12.652(3)$ Å (Tetragonal)
Space group:	$I4/mmm$
Unit cell contents:	two $LaSrVO_4$; body-centered translation applied to:
A in ($4e$)	0, 0, z; 0, 0, $\bar{z}$ where A is equal amounts of La and Sr randomly placed.
V in ($2a$)	0, 0, 0
O1 in ($4e$)	0, 0, z; 0, 0, $\bar{z}$
O2 in ($4c$)	0, 1/2, 0; 1/2, 0, 0
Optimized parameters:	$z_A = 0.357(2)$, $z_{O1} = 0.165(5)$, $B_{cell} = 1.0(2)$ Å^2

[a] Value in parentheses is estimated error in last place of number.

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED X-RAY DIFFRACTION DATA FOR TETRAGONAL $LaSrVO_4$

d_{obsd}	d_{calc}[a]	$h\,k\,l$	I_{calc}	I_{obsd}
6.334	6.326	0 0 2	2.603	1.82
3.696	3.700	1 0 1	18.612	17.31
3.162	3.163	0 0 4	12.239	11.84
2.852	2.851	1 0 3	100.000	91.12
2.739	2.736	1 1 0	73.448	71.06
2.511	2.511	1 1 2	4.328	4.01
2.110	2.118	1 0 5	11.986	24.60
	2.109	0 0 6	14.841	
2.068	2.069	1 1 4	33.478	31.89
1.934	1.935	2 0 0	38.223	43.73
1.850	1.850	2 0 2	0.174	0.18
1.715	1.714	2 1 1	4.747	5.46
1.670	1.670	1 1 6	14.603	15.49
1.650	1.650	2 0 4	7.217	8.20
1.638	1.638	1 0 7	9.191	10.93
1.600	1.601	2 1 3	34.529	38.27
1.582	1.582	0 0 8	3.438	7.29
1.428	1.428	2 1 5	5.482	17.31
1.426	1.426	2 0 6	13.096	
1.370	1.369	1 1 8	4.441	15.52
1.369	1.368	2 2 0	10.028	
—	1.337	2 2 2	0.026	0
1.322	1.321	1 0 9	0.983	0.91
1.283	1.283	3 0 1	0.930	1.09
1.265	1.265	0 0 10	0.745	1.09
1.256	1.256	2 2 4	2.807	2.74
1.250	1.250	2 1 7	7.217	8.20
1.234	1.233	3 0 3	6.752	7.81
1.224	1.224	2 0 8	5.097	16.40
	1.224	3 1 0	9.421	
—	1.201	3 1 2	0.315	0
1.148	1.149	3 0 5	1.163	10.01
	1.148	1 1 10	3.687	
	1.148	2 2 6	5.508	
1.141	1.141	3 1 4	7.036	7.29
1.102	1.103	1 0 11	5.904	6.92
1.091	1.091	2 1 9	1.050	1.09
1.069	1.069	3 2 1	1.097	1.27
1.059	1.059	2 0 10	1.727	7.29
1.058	1.058	3 1 6	5.597	
—	1.054	0 0 12	0.035	0
1.050	1.050	3 0 7	2.133	2.74
1.040	1.040	3 2 3	7.930	8.75
1.035	1.035	2 2 8	2.912	4.19
0.9881	0.9882	3 2 5	1.476	1.45
—	0.9841	1 1 12	0.000	0
0.9676	0.9680	3 1 8	3.217	6.38
	0.9675	4 0 0	3.142	
0.9579	0.9581	2 1 11	8.386	9.11
	0.9564	4 0 2	0.003	
0.9505	0.9506	3 0 9	0.393	0.55
0.9442	0.9441	1 0 13	0.447	0.36
0.9358	0.9361	4 1 1	0.844	0.73
0.9287	0.9290	2 2 10	1.388	1.09
0.9250	0.9260	2 0 12	0.089	1.1
	0.9252	4 0 4	1.344	
0.9229	0.9229	3 2 7	3.494	3.64
0.9160	0.9162	4 1 3	6.501	6.55
0.9121	0.9122	3 3 0	2.256	2.74
0.9039	0.9039	0 0 14	1.229	1.09
—	0.9028	3 3 2	0.069	0
0.8795	0.8800	4 1 5	1.327	6.74
	0.8797	3 1 10	4.385	
	0.8794	4 0 6	3.139	
0.8763	0.8764	3 3 4	2.148	2.19
0.8652	0.8653	4 2 0	6.013	5.46
0.8547	0.8549	3 0 11	4.160	7.1
	0.8546	1 1 14	3.849	
	0.8537	4 2 2	0.004	
0.8530	0.8531	3 2 9	0.809	0.73
0.8483	0.8484	2 1 13	0.957	0.73

[a] $a = 3.869$ Å, $c = 12.652$ Å

structure in space group *I4/mmm*. In a series of calculations, we have optimized the two positional parameters (z_A and z_{01}) and cell temperature factor (B). It was assumed that the La and Sr are randomly placed on the *A* site. The scattering factors for Sr^{2+}, La^{3+}, V^{3+} (*12*) and O^{2-} (*13*) were corrected for the real and imaginary parts of the anomalous dispersion term (*14*). The theoretical polarization term for a graphite crystal—diffracted beam monochromator was also applied to our data. A summary of the crystallographic data found for $LaSrVO_4$ is given in Table III. A comparison of observed and calculated intensities and *d* values is given in Table IV. The good agreement

$$(R = 100 \times \sum |I_0 - I_c| / \sum I_0 = 9.4)$$

between observed and calculated intensities confirms the assignment of the K_2NiF_4 structure to $LaSrVO_4$. Along the *c* axis of $LaSrVO_4$, a value of $z = 0.165$ gives two V-O1 distance of 2.09 Å while in the *a–b* plane, there are four

V–O2 distances of 1.94 Å. The average V–O distance in the elongated octahedron is 1.99 Å which agree exactly with that predicted from the effective ionic radii of Shannon and Prewitt (*15*).

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Superconducting and Normal State Properties of $Li_{1+x}Ti_{2-x}O_4$ Spinel Compounds. I. Preparation, Crystallography, Superconducting Properties, Electrical Resistivity, Dielectric Behavior, and Magnetic Susceptibility

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$LiTi_2O_4$ is one end member of the homogeneity range of the spinel phase $Li_{1+x}Ti_{2-x}O_4$ ($0 \leq x \leq 1/3$) and is superconducting at temperatures up to 13.7 K. Various measurements were carried out in order to characterize the superconducting and normal state properties of $LiTi_2O_4$ and of other compositions within the homogeneity range of the spinel phase. These measurements establish $LiTi_2O_4$ as a d-band superconductor and show that T_c decreases to <1.5 K for $x \gtrsim 0.1$. This disappearance of superconductivity with increasing x was found to be correlated with anomalous changes in the lattice parameter with composition, and, from electrical resistivity measurements, is tentatively attributed to the occurrence of a composition-induced metal–semiconductor transition at $x \approx 0.1$. The metallic character of $LiTi_2O_4$ and the composition dependence of the observed electrical properties are shown to follow from crystallographic considerations.

1. INTRODUCTION

Superconductivity in oxide compounds has been known for about a decade, and began with a report in 1964 of superconductivity in reduced $SrTiO_3$ ($T_c = .03$ K).[1] However, the presently known number (23) of superconducting oxide compounds is still very small in comparison to the ~1000

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known superconducting intermetallic compounds. Apart from TiO[2-6] and NbO,[2,6,7] all of these superconducting oxide compounds are ternary compounds. The importance of ternary compounds in the search for new high-temperature superconductors has recently been stressed.[8,9]

A brief preliminary report has been given concerning the superconductivity in one such ternary compound, $LiTi_2O_4$, which becomes superconducting at temperatures up to about 13.7 K.[10] This compound is one end member of the homogeneity range of the spinel phase in the Li–Ti–O ternary system: $Li_{1+x}Ti_{2-x}O_4$ $(0 \leq x \leq 1/3)$.[10,11] The other end member is a colorless electrical insulator. $LiTi_2O_4$ has a high T_c compared with most other oxide superconductors and is the only oxide superconductor having the spinel structure. The reason that no other oxide spinel compounds have been found to be superconducting is related to the occurrence of metallic properties among members of this structure class. Of the several hundred known oxide spinel compounds, few are known to exhibit a metallic electronic ground state at low temperatures. One of these few is LiV_2O_4,[12] and this compound is not superconducting above 1.5 K.[13] The reason for lack of superconductivity in LiV_2O_4 is apparent from a consideration of the magnetic susceptibility data[14] for this compound: The susceptibility follows a Curie–Weiss law, and the Curie constant yields an effective moment of 1.93 μ_B per V cation, slightly greater than the value of 1.73 μ_B expected for a spin-only d^1 cation. Superconductivity in LiV_2O_4 is therefore precluded by the apparent large concentration of local moments inherent in this material. In contrast to LiV_2O_4, it will be shown here that although the susceptibility of $LiTi_2O_4$ is also relatively large, it is nearly temperature independent.

The unusual characteristics of $LiTi_2O_4$ noted above prompted a detailed investigation[15] into its superconducting and normal state properties. In addition, measurement of these properties was extended to other compositions within the homogeneity range of the spinel phase, and the results of these investigations are presented here and in the following paper.

2. SAMPLE PREPARATION

The assignment of the observed high-temperature superconductivity in the Li–Ti–O ternary system to the spinel phase[10] was initially hampered by the fact that the x-ray patterns of several of the phases in this ternary system are nearly identical in line positions and are similar in line intensities. Therefore, a careful consideration of the phase relations, crystal structures, and lattice parameters of the various phases was required. This information was also necessary in determining the best method of synthesis for the spinel phase and in searching for other superconducting phases[13] in the Li–Ti–O system. Since the previously published data are scattered and are nowhere

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tabulated in one place, a summary of these data are included with several peripheral results of the present investigation in the appendix. There, it is shown that the spinel phase is not stable above about 1000°C and that an orthorhombic Ramsdellite phase exists for spinel phase compositions at higher temperatures. A low-temperature method of synthesis of the spinel phase is described below which was found to yield single-phase spinel samples with reproducible crystallographic properties.

Spinel phase samples were synthesized from Li_2CO_3, $TiO_{1.5}$, and TiO_2. The Li_2CO_3 of stated purity 99.999% was obtained from Apache Chemicals. The TiO_2 was either obtained from Apache Chemicals (99.9% purity), or was synthesized by reaction of $TiCl_4$ (Alfa Inorganics, 99.95% pure) with high-purity O_2 and H_2O at 500–1000°C. The Li_2CO_3 and TiO_2 were dried before use under a stream of high-purity oxygen at temperatures of 600 and 1000°C, respectively. The $TiO_{1.5}$ was either obtained from Alfa Inorganics or was synthesized by melting Ti metal (Materials Research Corp. MARZ Grade, 99.97% pure) with TiO_2 in an arc furnace under a high-purity argon atmosphere.

The sample synthesis was carried out using the reaction

$$\frac{1+x}{2}Li_2CO_3+(1-3x)TiO_{1.5}+(1+2x)TiO_2\rightarrow Li_{1+x}Ti_{2-x}O_4+\frac{1+x}{2}CO_2$$

The procedure was as follows:

1. Appropriate quantities of predried Li_2CO_3 and TiO_2 were thoroughly ground together for 30–60 min using an agate mortar and pestle in a dry argon atmosphere. The ground powder was loaded into a pellet die and then pressed at 10,000 psi into a pellet. After weighing, the pellet was fired at 740–750°C in a pure oxygen atmosphere for 20–60 min to effect reaction between the Li_2CO_3 and TiO_2. The fired pellet was then reweighed to ensure that the CO_2 in Li_2CO_3 was released. The weight loss due to release of CO_2 was always within 0.3% of the theoretical value. For the compound $Li_{4/3}Ti_{5/3}O_4$ ($x = 1/3$), no $TiO_{1.5}$ was required. However, this compound had to be reground and refired several times before single-phase spinel was obtained.

2. For the compositions with $x \neq 1/3$, the required amount of $TiO_{1.5}$ was then ground with the prefired pellet of step 1 under dry argon atmosphere for 30–60 min. A pellet of this ground powder was pressed at 40,000–80,000 psi, sealed into a prefused quartz tube under He gas, and fired at 750–800°C for 12–24 h. For this firing schedule, no reaction between the sample and quartz tube was observed.

All measurements to be described were carried out soon after the samples were synthesized, since it was observed that the electrical and superconducting properties of the samples deteriorated after being stored for periods of about one month or more. This behavior was not accompanied by observable crystallographic changes; the reason for the deterioration may be related to the sintered nature of the samples.

3. MEASUREMENT TECHNIQUES

X-ray powder diffraction data were obtained with a General Electric XRD-6 diffractometer using Cu K_α radiation and equipped with a diffracted beam crystal monochromator. Lattice parameters were determined by extrapolation to a Bragg angle $2\theta = 180°$, using the extrapolation function $\cos^2\theta/\sin\theta$. The Cu K_α doublet was very well resolved at the higher Bragg angles for all samples investigated. Line intensities were determined by measuring the area under diffraction peaks on diffractometer tracings. When calculating line intensities, the atomic form factors were taken from Ref. 16.

Superconducting transition temperatures T_c were determined using standard ac inductance techniques at a frequency of 20 Hz. The volume fraction of superconducting material in a sample was determined by comparing a superconducting throw to that obtained from a known volume of lead. The transition temperatures were measured to an accuracy of better than 0.1 K, using a calibrated carbon resistor.

Electrical resistivity measurements were carried out below room temperature using standard four-probe ac or dc techniques. Absolute resistivity values were determined using the van der Pauw method[17] or by direct calculation from the measured sample dimensions. For low-resistance samples ($\leq 0.1\ \Omega$), an ac technique was employed. For samples showing high contact resistance or with a resistance greater than 0.1 Ω, dc techniques were used. In the latter cases, the current–voltage characteristics were checked at several temperatures to ensure that they were linear, and the currents were such that the power dissipated in the samples was always less than 1 μW. The electrical leads (0.002-in-diameter Pt wire) were attached to the samples with silver paint, and the bond of the silver paint to the samples was found to be satisfactory. All resistivity measurements reported here were carried out on samples in the form of sintered pellets. Temperatures were determined using calibrated Ge and Pt resistance thermometers.

The dielectric constant for sintered disks of $Li_{4/3}Ti_{5/3}O_4$ was determined at a frequency of 1 kHz. The ends of these disks were coated with silver paint, which was allowed to dry under a heat lamp. The capacitance of a sample prepared in this way was measured using the three-lead technique over the temperature range 2–295 K. A sample was suspended between two

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gold-plated pressure contacts, which were connected via miniature low-thermal-conductivity coax cables to the terminals of a General Radio 1650-A impedance bridge. The coax shields were grounded to the case of the bridge. The temperature was measured with a calibrated 1/10-W Allen-Bradley carbon resistor.

Static susceptibility measurements were carried out using the Faraday technique in the temperature range 0.4–295 K in a field of 7.8 kG. Details of the apparatus are described elsewhere.[18,19] The accuracy of the measurements reported here is 2% or 1×10^{-6} cm³/mole, whichever is larger. Magnetization versus field isotherms were determined by nulling the force on a sample at given values of applied field with a current flowing through a coil surrounding the sample. Alternatively, the isotherms were determined by measuring the force on a sample versus applied field.

4. CRYSTALLOGRAPHY

4.1. General Considerations

A unit cell of the face-centred-cubic (fcc) spinel structure of an oxide spinel with composition AB_2O_4 consists of an approximately cubic-close-packed array of 32 oxygen atoms, with one-eighth of the 64 tetrahedral holes per unit cell and one-half of the 32 octahedral holes per unit cell filled by the cations A and B. The resultant unit cell contains eight formula units of AB_2O_4. The distribution of cations in the octahedral and tetrahedral sites of a spinel is usually indicated by putting the cations occupying the octahedral sites in brackets: $A[B_2]O_4$ is denoted a "normal" spinel, and $B[AB]O_4$ an "inverse" spinel. Assuming a normal spinel configuration, the positions of the A, B, and O ions in the unit cell are as follows[20]:

Origin at $\bar{4}3m$
Equivalent positions $(0, 0, 0); (0, \tfrac{1}{2}, \tfrac{1}{2}); (\tfrac{1}{2}, 0, \tfrac{1}{2}); (\tfrac{1}{2}, \tfrac{1}{2}, 0);\ +$
8 A in (a):$(0, 0, 0); (\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4});$
16 B in (d):$(\tfrac{5}{8}, \tfrac{5}{8}, \tfrac{5}{8}); (\tfrac{5}{8}, \tfrac{7}{8}, \tfrac{7}{8}); (\tfrac{7}{8}, \tfrac{7}{8}, \tfrac{5}{8}); (\tfrac{7}{8}, \tfrac{5}{8}, \tfrac{7}{8});$
32 O in (e):$(u, u, u); u, \bar{u}, \bar{u}); (\tfrac{1}{4}-u, \tfrac{1}{4}-u, \tfrac{1}{4}-u); (\tfrac{1}{4}-u, \tfrac{1}{4}+u, \tfrac{1}{4}+u);$
$(\bar{u}, \bar{u}, u); (\bar{u}, u, \bar{u}); (\tfrac{1}{4}+u, \tfrac{1}{4}-u, \tfrac{1}{4}+u); (\tfrac{1}{4}+u, \tfrac{1}{4}+u, \tfrac{1}{4}-u);$

with $u\approx3/8$.

If the oxygen parameter u is identically equal to 3/8 and the cations are in the normal spinel configuration, then an ideal spinel structure results, in which the oxygen atoms form a perfect fcc sublattice. This ideal spinel structure is shown in Fig. 1a, where it is seen that each oxygen anion is coordinated on one side with an equilateral triangle of three B cations, and on the other side by one A cation. Each A cation is at the center of an oxygen

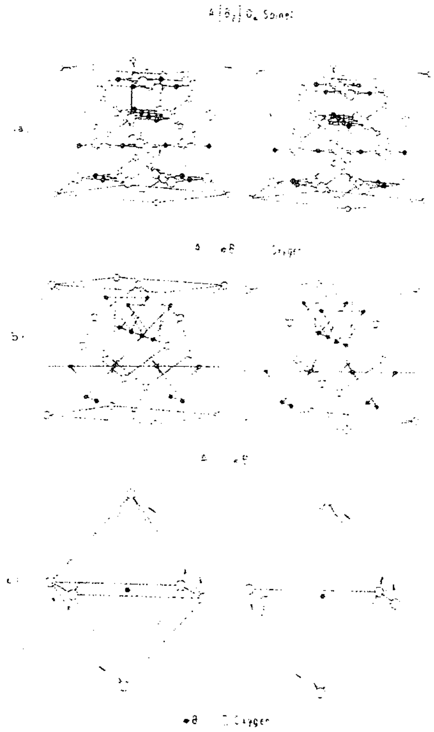
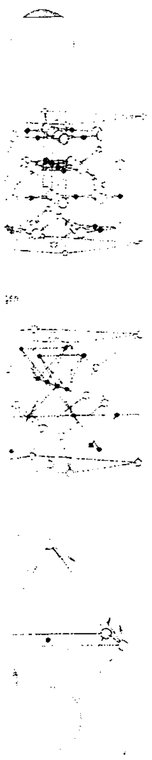


Fig. 1. Stereo pairs showing various aspects of the spinel structure. (a) Ideal spinel structure for an oxide spinel $A[B_2]O_4$. (b) $A[B_2]$ cation sublattice of the spinel structure. (c) Oxygen octahedron around a B cation. The arrows indicate the distortion of the octahedron for an oxygen parameter larger than the "ideal" value.

tetrahedron, and each B cation resides at the center of a perfect oxygen octahedron. The oxygen octahedra surrounding the B cations share edges with each other, and share corners with the oxygen tetrahedra surrounding the A cations. However, these tetrahedra do not make contact with each other.

The cation sublattice AB_2 is shown in Fig. 1b. The B cations form a network of tetrahedra connected at their corners. The A cations form a diamond-type lattice. An interesting aspect of the cation sublattice is that it is identical to the fcc C-15 ($MgCu_2$) structure. This latter structure class



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contains compounds with rather high superconducting transition temperature (e.g., 9.6 K for HfV_2).[21] However, only one compound AB_2 in the C-15 structure class is also known to form the cation sublattice in a spinel compound: $TiCo_2 \rightarrow Co[CoTi]O_4$, which is an inverse spinel as defined above.

For most spinel compounds, the value of the oxygen parameter u is found to deviate slightly in a positive direction from the ideal value of 0.375, resulting in a small displacement of the oxygen anions in a [111] direction away from the nearest A cation, toward the center of the equilateral triangle of B cations on the opposite side of the oxygen anions. This displacement does not distort the tetrahedral coordination around the A cations, but does result in a distortion of the oxygen octahedra around the B cations. This trigonal distortion is shown in Fig. 1c, where the direction and length of the arrows correspond to the change in an oxygen octahedron as the value of u increases from the ideal value of 0.375 to a value of 0.425 (3–10 times the distortion normally found).

Because the cation sublattice is independent of u, the cation–cation distances depend only on the lattice parameter a_0. However, the cation–oxygen distances are functions of both the lattice parameter a_0 and the oxygen parameter u. These distances are as follows:

Distances (with $u = 0.375 + \Delta$):

(a) Cation–oxygen distances

$$d_{\text{A-O}} = (3^{1/2}/8)a_0(1+8\Delta) = 0.2165a_0(1+8\Delta)$$

$$d_{\text{B-O}} = \tfrac{1}{4}a_0(1-8\Delta+24\Delta^2)^{1/2} \approx 0.25a_0(1-4\Delta)$$

(b) Cation–cation distances

$$d_{\text{A-A}} = (3^{1/2}/4)a_0 = 0.43301a_0$$

$$d_{\text{B-B}} = a_0/8^{1/2} = 0.35355a_0$$

$$d_{\text{A-B}} = (11^{1/2}/8)a_0 = 0.41458a_0$$

The determination of the oxygen parameter u is therefore of interest in establishing the cation–anion distances and the extent of oxygen octahedron distortion around the B cations.

4.2. Results

The lattice parameters a_0 for single-phase samples are plotted versus the composition parameter x in Fig. 2. The data of Deschanvres *et al.*[11] have been included for comparison. As the composition parameter x increases from 0, the lattice parameter decreases rapidly in the range $0 \le x \le 0.1$, then linearly and at a lower rate as x increases further to its maximum value of

1/3. The behavior for $0 \leq x \leq 0.1$ may be associated with anomalous changes in the superconducting and electrical properties occurring in this composition range (Sections 5 and 6).

In Fig. 2 it is seen that for $x \neq 1/3$, there is considerable disagreement between the lattice parameters determined in the present work and those of Deschanvres *et al.* It is possible that the latter data were obtained for samples which were oxidized more than the nominal composition would indicate, thereby giving a true spinel composition corresponding to a larger x value, and hence a lower lattice parameter. For the fully oxidized composition ($x = 1/3$), the lattice parameter determined here is identical to that found by Deschanvres *et al.* and by most other previous workers.[22-24]

For determining the distribution of cations among the tetrahedral and octahedral sites, the diffracted intensities of lines having even indices and satisfying the following conditions were used:

$$\left.\begin{matrix} h \neq 4n+2 \\ k \neq 4n+2 \\ l \neq 4n+2 \end{matrix}\right\} \quad \text{and} \quad \left.\begin{matrix} 4n \\ 4n \\ 4n \end{matrix}\right\} \quad and\; h+k+l=4n$$

For the lines satisfying these relations [e.g., (220), (422), (620)], the line intensities depend primarily upon the form factor of the cations occupying the tetrahedral sites: Statistically distributed cations occupying octahedral

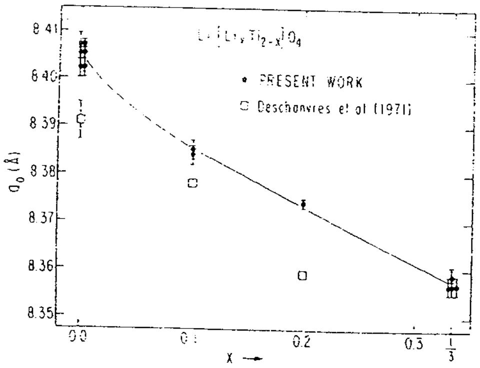

Fig. 2. Lattice parameter versus composition for $Li_{1+x}Ti_{2-x}O_4$. The data of Deschanvres *et al.*[11] have been included for comparison.

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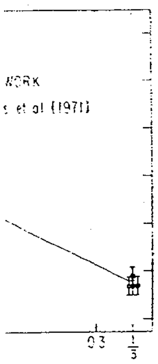

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sites make no contribution to the intensities of these lines; the contribution due to the oxygen anions is zero for the ideal oxygen parameter $u = 0.375$ and increases only slowly for $u \neq 0.375$. Since the atomic form factor for Ti is much greater than that for Li, the intensities of these lines are therefore very sensitive to the occupation of the tetrahedral sites by titanium cations. The observed intensities for these lines were found to be ~0, and a quantitative calculation showed that the tetrahedral sites are at least 95% occupied by lithium cations.

Since the tetrahedral sites are occupied solely by Li cations, the octahedral site occupation is determined by the composition, and the general site occupation is given by $Li[Li_xTi_{2-x}]O_4$ $(0 \leq x \leq 1/3)$. For $x \neq 0$, the observed line intensities are consistent with a statistical distribution for the Li and Ti cations on octahedral sites (see below). The two limiting compositions of the spinel homogeneity range correspond to the cation distribution $Li^{1+}[Ti^{3+}Ti^{4+}]O_4$ $(x = 0)$ and $Li^{1+}[Li^{1+}_{1/3}Ti^{4+}_{5/3}]O_4$ $(x = 1/3)$, where the formal valences of the cations have also been indicated. The homogeneity range is limited at $x = 0$ by the reluctance of Ti cations to occupy tetrahedral sites, and at $x = 1/3$ by the inability of Ti and Li to assume formal valences in the spinel structure greater than four and one, respectively. Attempts to synthesize samples with $x < 0$ resulted in multiphase samples containing $(Ti, Li)_2O_3$ or $(Ti, Li)O$ phases in addition to the spinel phase (see the phase diagram in the appendix).

The oxygen parameter u was determined for the two end members of the spinel homogeneity range by calculating the intensities for the particular pairs of strong, low-angle diffraction lines for which the intensity ratios were strong functions of u, and comparing these calculated ratios with those obtained experimentally. Figure 3 shows the theoretical calculations (solid curves) and the experimental points (filled circles). In the case of $Li[Li_{1/3}Ti_{5/3}]O_4$, the curves of Fig. 3 were computed assuming a statistical distribution for the cations in the octahedral sites. From the consistency of the experimentally predicted values of u for this compound, this assumption appears to be justified.

The values of the oxygen parameter obtained from Fig. 3 are in agreement with those found by Deschanvres *et al.*[11] These values were then used to calculate the line intensities for the full diffraction patterns. The results of these calculations are compared with the experimental data in Table I. The calculated and observed lattice d spacings have also been included in the table.

Using the lattice parameters and oxygen parameters found above, the interatomic distances in the Li–Ti–O spinel were computed and are listed in Table II, along with data on several other titanium–oxygen spinels for comparison.

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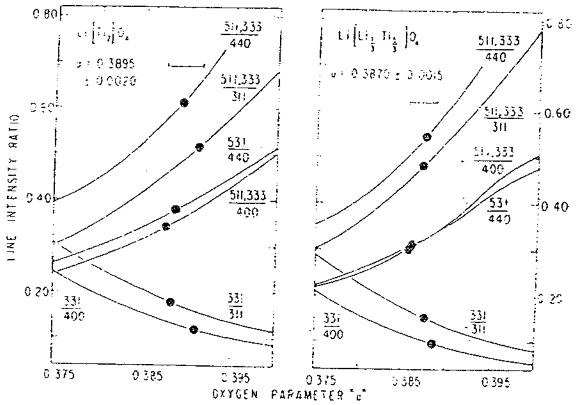

Fig. 3. Determination of the oxygen parameter for the spinel compounds $LiTi_2O_4$ and $Li_{4/3}Ti_{5/3}O_4$. The solid curves are calculated ratios of the intensities of various pairs of diffraction lines, plotted versus the oxygen parameter u. The experimentlally determined intensity ratios are indicated by filled circles.

5. SUPERCONDUCTING PROPERTIES

The superconducting transition temperature of spinel-phase samples $Li_{1+x}Ti_{2-x}O_4$ determined from ac susceptibility measurements are plotted vs. composition x and lattice parameter a_0 in Fig. 4. For compositions near $LiTi_2O_4$ ($x = 0$), the midpoints of the superconducting transitions are independent of composition, and for most samples are in the range 10–12 K. For three samples in the composition range $0.05 \leq x \leq 0.15$, the T_c onsets were 11–12 K, but the volume fraction of superconducting material in the samples was small (<40%), even at the lowest temperatures (1.5 K). T_c data for these samples have therefore not been included in Fig. 4. For $x > 0.15$, no superconductivity was observed in any sample. Heat capacity measurements have been carried out[15,29] which show that the superconducting transitions for $x \approx 0$ are indeed bulk transitions, and which substantiate the present findings concerning the composition dependence of the superconducting behavior.

Although most of the transition temperatures shown in Fig. 4 for $x \approx 0$ are in the range 10–12 K, for a few samples superconducting transitions were observed which showed onsets as high as 13.5–13.7 K. Despite much effort, the particular conditions necessary for the reproducible synthesis of samples with these higher transition temperatures have not yet been determined.

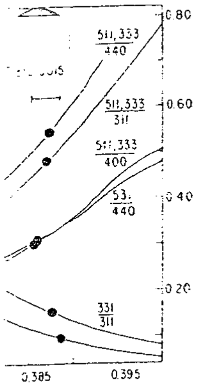

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TABLE I

Calculated and Observed X-Ray Intensities and Lattice *d* Spacings for $Li_{4/3}Ti_{5/3}O_4$ and $LiTi_2O_4$[a]

	$LiTi_2O_4$				$Li_{4/3}Ti_{5/3}O_4$			
hkl	d_{obs}, Å	d_{calc}, Å	I_{obs}	I_{calc}	d_{obs}, Å	d_{calc}, Å	I_{obs}	I_{calc}
111	4.85	4.85	>130	177	4.87	4.83	>124	149
220	—	2.972	0	1	2.945	2.955	1	1
311	2.531	2.534	70	75	2.518	2.520	67	67
222	2.420	2.426	9	10	2.409	2.413	3	3
400	2.096	2.101	106	100	2.090	2.089	104	100
331	1.926	1.928	12	12	1.9152	1.9172	10	11
422	—	1.716	0	0.	—	1.3928	0	0.
511, 333	1.615	1.618	36	36	1.6081	1.6083	32	32
440	1.484	1.486	59	59	1.4764	1.4773	59	60
531	1.419	1.421	22	23	1.4120	1.4126	18	19
442	—	1.401	0	0.	—	1.3928	0	0.
620	—	1.329	0	0.	—	1.3214	0	0.
533	1.2803	1.2818	8	8	1.2742	1.2744	7	7
622	1.2663	1.2671	9	8	1.2597	1.2599	5	4
444	1.2121	1.2132	14	14	1.2056	1.2062	12	14
711, 551	1.1760	1.1769	10	12	1.1698	1.1702	10	10
642	—	1.1232	0	0.	—	1.1168	0	0.
731, 553	1.0934	1.0942	12	11	1.0874	1.0880	10	10
800	1.0500	1.0506	8	8	1.0442	1.0446	7	8
733	—	1.0268	0	0.	—	1.0210	0	0.
644	—	1.0193	0	0.	—	1.0134	0	0.
822, 660	—	0.9905	0	0.	—	0.9849	0	0.
751, 555	0.9700	0.9705	8	10	0.9652	0.9650	9	9
662	0.9636	0.9641	4	5	0.9585	0.9586	3	3
840	0.9395	0.9397	18	22	0.9344	0.9343	16	23
911, 753	0.9222	0.9226	8	10	0.9174	0.9173	7	9
842	—	0.9171	0	0.	—	0.9118	0	0.
664	—	0.8960	0	0.	—	0.8909	0	0.
931	0.8809	0.8811	10	13	0.8759	0.8761	10	12
844	0.8577	0.8578	23	29	0.8529	0.8529	20	31
933, 771, 755	0.8446	0.8447	7	7	0.8397	0.8399	6	9
862, 10,2,0	—	0.8242	0	0.	—	0.8195	0	0.
951, 773	0.8124	0.8125	20	27	0.8080	0.8079	16	27
666, 10,2,2	0.8088	0.8088	14	15	0.8042	0.8042	8	10

[a] Cu *Kα* radiation. For $LiTi_2O_4$, $a_0 = 8.405$ Å and $u = 0.3895$. For $Li_{4/3}Ti_{5/3}O_4$, $a_0 = 8.357$ Å and $u = 0.3870$.

TABLE II

Interatomic Distances in $LiTi_2O_4$, $Li_{4/3}Ti_{5/3}O_4$, and Several Other Titanium–Oxygen Spinels[a]

$A[B_2]O_4$	Lattice parameter a_0, Å	Oxygen parameter, u	d_{A-O}, Å	d_{B-O}, Å	d_{B-B}, Å	Ref.
$Li[Ti_2]O_4$	8.405 (0.001)	0.3895 (0.0020)	2.031 (0.030)	1.981 (0.016)	2.9716 (0.0004)	Present work
$Li[Li_{1/3}Ti_{5/3}]O_4$	8.357 (0.002)	0.3870 (0.0015)	1.983 (0.022)	1.990 (0.012)	2.9546 (0.0007)	Present work
$Mg[Ti_2]O_4$	8.474 (0.002)	—	—	—	2.9960 (0.0007)	25
	8.505 (0.003)	—	—	—	3.0069 (0.0011)	13
$Mg[MgTi]O_4$	8.445 (0.001)	0.3875 (0.0005)	2.011 (0.008)	2.007 (0.004)	2.9857 (0.0004)	26, 27
$Co[CoTi]O_4$	8.445	0.381 (0.002)	1.916 (0.029)	2.061 (0.017)	2.9857	28

[a] Accuracies are placed in parentheses.

Mg[MgTi]O₄	8.445 (0.001)	0.3875 (0.0005)	2.011 (0.008)	2.007 (0.004)	2.9857 (0.0004)	
Co[CoTi]O₄	8.445	0.381 (0.002)	1.916 (0.029)	2.061 (0.017)	2.9857	28

[a] Accuracies are placed in parentheses.

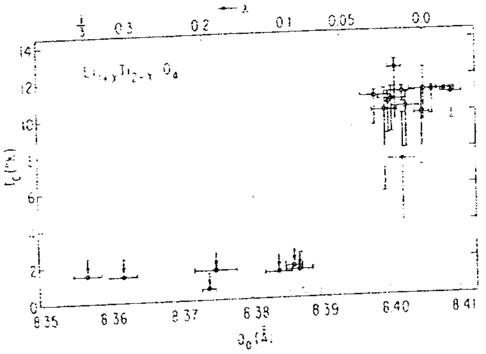


Fig. 4. Superconducting transition temperature versus composition x and lattice parameter a_0 for $Li_{1+x}Ti_{2-x}O_4$. The arrows indicate that no superconductivity was observed above the temperature indicated by the tip of the arrow. The vertical error bars for superconducting samples mark the temperatures at which 10% and 90% of the samples become superconducting, and the filled circles indicate the midpoints of the transitions.

6. ELECTRICAL PROPERTIES

Measurements of the temperature dependence and absolute value of the electrical resistivity were carried out for several compositions within the homogeneity range of the spinel phase $Li_{1+x}Ti_{2-x}O_4$. Samples with composition parameter $x = 0.0$, 0.1 (nominal composition $Li_{1.1}Ti_{1.9}O_{3.95}$), and 0.2 were measured. X-ray analysis indicated that these samples were single-phase spinel compounds, with lattice parameters shown in Fig. 2. Resistivities for two samples with nominal compositions outside the homogeneity range of the spinel phase ($x = -0.1, -0.2$) were also determined. These two samples contained small quantities of the $(Ti, Li)_2O_3$ and $(Ti, Li)O_x$ phases in addition to the spinel phase.

The samples with composition parameters $x = 0.2$ and $x = 0.1$ showed high resistivities, and the measurements for these samples were therefore carried out using dc techniques. For the other samples, ac techniques were employed.

The results of the resistivity measurements are collected in Fig. 5. For the single-phase spinel samples ($x = 0$, 0.1, and 0.2), the room-temperature resistivity increases by nearly three orders of magnitude as the composition changes from superconducting $LiTi_2O_4$ to $Li_{1.1}Ti_{1.9}O_4$. For the latter sample and for $Li_{1.2}Ti_{1.8}O_4$, the resistivity shows a rapid increase as the

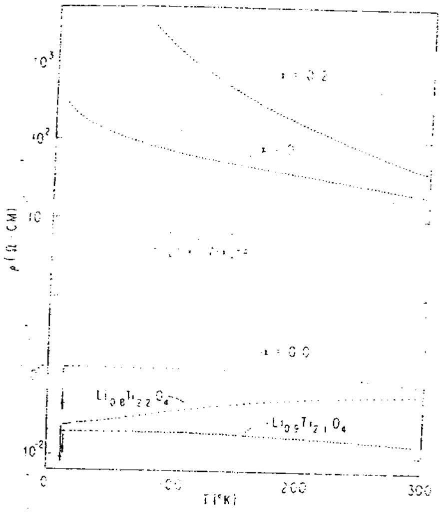
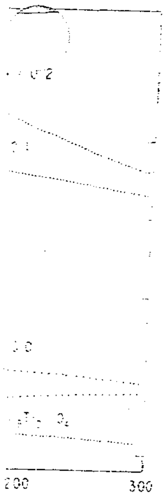


Fig. 5. Electrical resistivity versus temperature for several $Li_{1+x}Ti_{2-x}O_4$ samples.

temperature is lowered from 300 K, in contrast to that for $LiTi_2O_4$, which increases slightly in the temperature range 300 to 100 K, but is temperature independent below 100 K (apart from the superconducting transition). The resistivities determined for the two samples with compositions ($x = -0.1$, -0.2) beyond the $LiTi_2O_4$ end of the spinel phase homogeneity range have about the same absolute magnitude as that for $LiTi_2O_4$. Although resistivity data obtained on sintered oxides are often only of qualitative significance, the present measurements do suggest the occurrence of a metal–semiconductor transition as the composition of the spinel phase changes from $LiTi_2O_4$ to $Li_{1.1}Ti_{1.9}O_4$. Attempts to grow single crystals of $Li_{1+x}Ti_{2-x}O_4$ in order to verify this behavior have not as yet been successful.

7. DIELECTRIC PROPERTIES

Besides the $Li_{1+x}Ti_{2-x}O_4$ spinel system, there are other classes of compounds which undergo composition-induced metal–insulator (–semiconductor) transitions without change in crystal structure. One of these is the class of degenerate semiconductors in which metallic behavior is obtained by doping the parent semiconducting host with suitable dopants,



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and in which metallic properties are initiated through impurity band conduction. These materials are characterized by high static dielectric constants relative to the charge carrier effective masses, and several of them are superconducting.[1,30,31]

The electronic properties of this class of degenerate semiconductors are often treated within the framework of the theory of impurity states in semiconductors, in which the ground-state orbit radius a_H for a hydrogen-like donor impurity is[32]

$$a_H = [\varepsilon/(m^*/m)](0.53\ \text{Å}) \tag{1}$$

where ε is the static macroscopic dielectric constant of the host, m^* is the effective mass of the current carriers, and m is the rest mass of the electron. It has been shown[33] that a semiconductor to metal transition occurs when the donor concentration N attains a value N_{min} given by

$$N_{min}^{1/3} a_H \simeq 0.3 \tag{2}$$

It should be noted that this theory describing electron delocalization and impurity band formation is only valid if the donor orbit radius defined in Eq. (1) is much larger than an interatomic distance.

Dielectric constant measurements were carried out for the electrically insulating spinel composition $Li_{4/3}Ti_{5/3}O_4$ in order to ascertain whether the formation of a degenerate Fermi gas in the $Li_{1+x}Ti_{2-x}O_4$ system as $x \to 0$ can be described within the framework of the theory cited above. The results of this measurement showed that the dielectric constant is independent of temperature for $2 \leq T \leq 295$ K, and no dielectric anomalies were observed. The dielectric constant of $Li_{4/3}Ti_{5/3}O_4$ was found to be 11 ± 1. Utilizing this value of the dielectric constant along with the effective mass of $9.4m$ found for the current carriers in $LiTi_2O_4$ from magnetic susceptibility measurements (see Section 8), a_H and N_{min} were computed from Eq. (1) and (2). The results of these calculations, along with similar calculations for several well-known degenerate semiconductor hosts, are shown in Table III. From the table, the calculated radius of a donor orbit in $Li_{4/3}Ti_{5/3}O_4$ is only about 0.6 Å, which is much smaller than an interatomic distance, and is in contrast to the values obtained for the known degenerate semiconductor hosts shown there. Therefore, the theory cited above is not applicable to the metal–insulator transition in the $Li_{1+x}Ti_{2-x}O_4$ system, and the metallic ground state for spinel-phase compositions approaching $LiTi_2O_4$ does not occur through the formation of a distinct impurity band. The electronic properties of $Li_{1+x}Ti_{2-x}O_4$ are discussed further in Section 9.

TABLE III

Dielectric Properties of $Li_{4/3}Ti_{5/3}O_4$ and of Several Degenerate Semiconductor Hosts

Material	m^*/m	ε	a_H, Å	N_{min}, cm^{-3}
Ge	0.2^{40}	15.8^{32}	42	4×10^{17}
Si	0.3^{40}	11.7^{32}	21	3×10^{18}
SnTe	$\sim1.5^{63}$	$1200^{64,a}$	420	4×10^{14}
$SrTiO_3$	$5^{35,65,66}$	300^{67}	32	8×10^{17}
$Li_{4/3}Ti_{5/3}O_4$	9.4^{b}	11^{b}	0.6^{c}	1×10^{23c}

[a] At 100 K.
[b] Present work.
[c] For comparison only; see text.

8. MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility measurements were carried out on several samples at room temperature and/or in the temperature range 0.4–295 K. The susceptibilities for three different single-phase samples of $LiTi_2O_4$ were determined, along with data for samples of composition $Li_{1.1}Ti_{1.9}O_{3.95}$, $Li_{1.2}Ti_{1.8}O_4$, and $Li_{4/3}Ti_{5/3}O_4$. The three $LiTi_2O_4$ samples were previously determined by ac susceptibility measurements to be superconducting, with transition temperatures in the range 10–12 K. The $Li_{1.1}Ti_{1.9}O_{3.95}$ sample also showed about 1% volume superconductivity below ~11 K, and the susceptibility measurement for this sample was therefore limited to higher temperatures. The $Li_{1.2}Ti_{1.8}O_4$ sample showed no trace of superconductivity above 0.44 K.

Most of the samples showed small nonlinearities in the *M* vs. *H* characteristics at fields below about 1 kG, attributed to ferromagnetic impurities. The concentration of these impurities was estimated from the zero-field intercept of the extrapolated high-field linear portion of the *M* vs. *H* plots, and was found for various samples to be equivalent to 1–30 ppm of ferromagnetic iron impurities (saturation moment 2.2 μ_B). The susceptibility data presented below were determined from the slope of the linear portion of the *M* vs. *H* curves.

The results of the susceptibility measurements are shown in Fig. 6, where the measured molar susceptibilities (Fig. 6a) and inverse molar susceptibilities (Fig. 6b) are plotted vs. temperature. Near room temperature, the susceptibilities are only weakly temperature dependent, with the magnitude of the susceptibility decreasing monotonically with increasing values of the composition parameter *x*. At the lowest temperatures, however, the susceptibilities increase rapidly.

The analysis of the data is complicated by possible contributions due to paramagnetic impurities in addition to the intrinsic contribution due to the al Degenerate Semiconductor Hosts

a_H, Å	N_{min}, cm^{-3}
42	4×10^{17}
21	3×10^{18}
420	4×10^{14}
32	8×10^{17}
0.6^c	1×10^{23c}

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were carried out on several
temperature range 0.4–295 K.
-phase samples of $LiTi_2O_4$ were
of composition $Li_{1.1}Ti_{1.9}O_{3.95}$,
Ti_2O_4 samples were previously
ts to be superconducting, with
K. The $Li_{1.1}Ti_{1.9}O_{3.95}$ sample
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was therefore limited to higher
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ributed to ferromagnetic
was estimated from the
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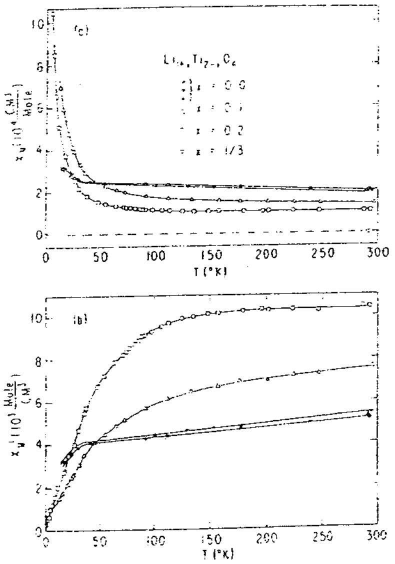

Fig. 6. Temperature dependence of the molar susceptibilities (Fig. 6a) and inverse molar susceptibilities (Fig. 6b) for several samples of $Li_{1+x}Ti_{2-x}O_4$.

samples. From the low-temperature region of the χ_M^{-1} vs. *T* plots (Fig. 6b), the susceptibilities appear to approach a Curie–Weiss law. Therefore, the temperature dependences of the susceptibilities shown in Fig. 6 are analyzed in terms of the following equation:

$$\chi_M(T) = [C/(T+\theta)] + F(T)$$

where the first term is attributed to paramagnetic impurities and the second term describes the susceptibilities of the impurity-free compounds. The values of θ indicated by the data of the low-temperature region of Fig. 6b are at most a few K, so at higher temperatures, the impurity terms are well approximated by C/T. Therefore, above a few K, the above equation takes the approximate form

$$T\chi_M(T) = C + TF(T)$$

Assuming that $F(T)$ is nearly temperature independent at low temperatures, the Curie constants were obtained from the intercepts of $T\chi_M$ vs. *T* plots

(Fig. 7a). The deviation of the data from straight-line behavior at the higher temperatures is attributed to the temperature dependence of $F(T)$. In Fig. 7b, the temperature-dependent molar susceptibilities have been replotted, after subtracting out the Curie-like impurity term, and the data of this figure therefore represent the intrinsic susceptibilities of the compounds.

Assuming the Curie constants to result from the presence of spin-1/2 moments, with a g factor of 2, the impurity concentration can be calculated from the relation

$$n(\text{moles impurity/mole } \mathrm{Li}_{1+x}\mathrm{Ti}_{2-x}\mathrm{O}_4) = C/0.375$$

From the Curie constants determined in Fig. 7a, the concentration of impurities is in the range 0.35 mole % for $\mathrm{LiTi_2O_4}$ to 1.63 mole % for $\mathrm{Li_{1.1}Ti_{1.9}O_4}$. These impurity concentrations are much larger than the concentration of foreign magnetic impurities expected to be in the samples. It is therefore likely that the impurity susceptibilities arise from the presence of local Ti^{3+} moments in the samples. The lowest number of these local

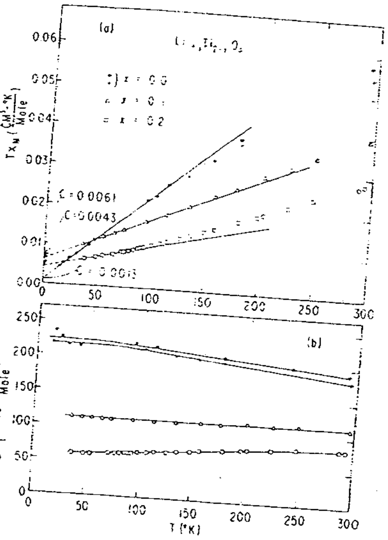

Fig. 7. (a) Determination of the Curie constants due to paramagnetic impurities in $\mathrm{Li}_{1+x}\mathrm{Ti}_{2-x}\mathrm{O}_4$ samples from $T\chi_M$ versus T plots. (b) Molar susceptibilities versus temperature for $\mathrm{Li}_{1+x}\mathrm{Ti}_{2-x}\mathrm{O}_4$ after correction for the impurity Curie terms.

ght-line behavior at the higher
e ndence of $F(T)$. In Fig.
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erm, and the data of this figure
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rom the presence of spin-1/2
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$$ {}_x O_4) = C/0.375 $$

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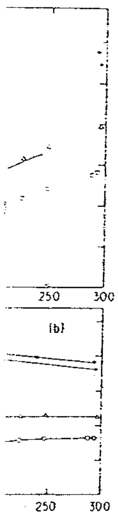

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$i_{1+x}Ti_{2-x}O_4$
s. (b) Molar
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the impurity

moments occurs in the samples that are superconducting and metallic (LiTi$_2$O$_4$), even though all the samples were prepared in a similar fashion, using similar starting materials.

Because the Li$_{1.2}$Ti$_{1.8}$O$_4$ sample showed no trace of superconductivity, detailed low-temperature measurements were carried out to further characterize the nature of the local moments. In Fig. 8a, the inverse molar susceptibility for this sample is plotted for the temperature region below 4 K, after subtracting out the temperature-independent term found from Fig. 7b (60×10^{-6} cm^3/mole at $T < 40$ K). From Fig. 8a, the impurity contribution to the susceptibility of the sample in the region 0.4–4 K is given by a Curie-Weiss law $\chi_M = C/(T + \theta)$, with $\theta = 0.8$ K and $C = 0.0050$ cm^3 K/mole. Below 1.3 K, the impurity susceptibility begins to saturate in fields of 10 kG, so the susceptibility values for lower temperatures shown in Fig. 8a were determined from the linear portion of the M vs. H curves. This saturation is illustrated in Fig. 8b, in which M is plotted vs.

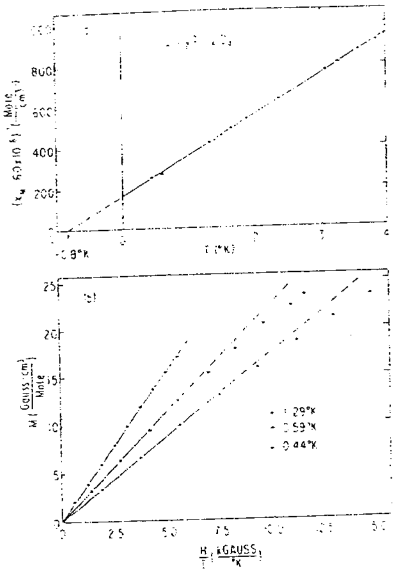

Fig. 8. (a) Inverse susceptibility of Li$_{1.2}$Ti$_{1.8}$O$_4$ (corrected for a small temperature-independent term) versus temperature for the temperature range below 4 K. (b) Magnetization of Li$_{1.2}$Ti$_{1.8}$O$_4$ plotted versus the ratio of field to temperature for the temperature range below 1.3 K.

TABLE IV

Magnetic Susceptibility Data for Several $Li_{1+x}Ti_{2-x}O_4$ Compounds

Composition	T, K	$10^6\chi_M$ cm^3/mole	C, cm^3 K/mole	$n_{impurity}$, mole %	$10^6(\chi_M - C/T)$, cm^3/mole
$Li_{4/3}Ti_{5/3}O_4$	294	−3	—	—	—
$Li_{4/3}Ti_{5/3}O_4$	294	0	—	—	—
$Li_{1.2}Ti_{1.8}O_4$	294	96	0.0043	1.15	82
	50	145			60
	4[a]	1130	0.0050	1.33	—
$Li_{1.1}Ti_{1.9}O_{3.95}$	294	133	0.0061	1.63	112
	50	232			112
$LiTi_2O_4$	294	190	—	—	—
$LiTi_2O_4$	294	196	0.0013	0.35	192
	50	244			222
$LiTi_2O_4$	294	185	0.0013	0.35	181
	50	236			216

[a] Below 4 K, $\chi_M \sim C/(T+0.8\text{ K})$.

H/T. Since the value of the Weiss temperature θ is nonzero, the data of Fig. 8b do not lie on a common curve, and no attempt was made to fit the data with Brillouin functions. Various of the above magnetic properties are listed in Table IV.

In order to interpret the intrinsic magnetic susceptibility for the $Li_{1+x}Ti_{2-x}O_4$ spinel compounds, the various contributions to the susceptibility must be considered. After accounting for the impurity terms, the data of Fig. 7b may still be the sum of several contributions. For metallic samples, the contributions are

$$\chi = \chi^{core} + \chi^{Pauli} + \chi^{Landau} + \chi^{orbital}$$

where the first term is the sum of the core diamagnetism and Van Vleck paramagnetism of the ion cores, and the last three terms are the Pauli paramagnetism, diamagnetic susceptibility, and orbital contribution, respectively, due to the conduction electrons.

The diamagnetic contribution due to the ion cores may be estimated from published tables. The table of Selwood[34] will be used here. For the electrical insulator $Li_{4/3}Ti_{5/3}O_4$, the diamagnetic susceptibility due to the ion cores is -58×10^{-6} cm^3/mole. However, Ti^{4+} has been observed to possess a temperature-independent Van Vleck susceptibility of $+33 \times$

IV
ral $Li_{1+x}Ti_{2-x}O_4$ Compounds

	C cm³ K/mole	n_{impurity}, mole %	$10^6(\chi_M - C/T)$, cm³/mole
	—	—	—
	—	—	—
	0.0043	1.15	82 60
	0.0050	1.33	—
	0.0061	1.63	112 112
	—	—	—
	0.0013	0.35	192 222
	0.0013	0.35	181 216

mperature θ is nonzero, the data of Fig.
d no attempt was made to fit the data
ve magnetic properties are listed

nsic magnetic susceptibility for the
various contributions to the suscepti-
unting for the impurity terms, the data
ral contributions. For metallic samples,

$$+\chi^{\text{Landau}}+\chi^{\text{orbital}}$$

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ue to the ion cores may be estimated
Selwood[34] will be used here. For the
diamagnetic susceptibility due to the
However, Ti^{4+} has been observed to
Van Vleck susceptibility of $+33\times$

10^{-6} cm³/mole Ti^{4+} when coordinated by oxygen octahedra,[35,36] as they are in the present case. Therefore, the Van Vleck susceptibility due to the Ti^{4+} cations in $Li_{4/3}Ti_{5/3}O_4$ is $+55\times10^{-6}$ cm³/mole. The calculated temperature-independent susceptibility due to the sum of the two terms is therefore $\chi^{\text{core}}_{\text{calc}} = -3\times10^{-6}$ cm³/mole. From Table IV, the measured room-temperature values for this composition are -3×10^{-6} and 0×10^{-6} cm³/mole (both values $\pm1\times10^{-6}$ cm³/mole), in good agreement with the calculated value. Therefore, the net correction to the molar susceptibilities due to χ^{core} is very small, and will be neglected here.

If conduction electron band effects are represented by an effective mass, χ^{Pauli} and χ^{Landau} take the form[37]

$$\chi^{\text{Pauli}} = (m^*/m)\chi^{\text{Pauli}}_{\text{free el.}} = \mu_B^2 N_{bs}(0) \tag{3}$$

$$\chi^{\text{Landau}} = -(m/3m^*)\chi^{\text{Pauli}}_{\text{free el.}} \tag{4}$$

where $\chi^{\text{Pauli}}_{\text{free el.}}$ is the Pauli paramagnetic susceptibility for a free-electron Fermi gas containing the same volume concentration of electrons as the sample under study, $N_{bs}(0)$ is the band structure density of electron energy states at the Fermi surface for both spin directions, m is the rest mass of the electron, m^* is the effective mass of the conduction electrons, and μ_B is the Bohr magneton. Thus, after correcting for the susceptibility of the ion cores and for the impurity contribution to the susceptibility, one has

$$\chi_M = [(m^*/m)-(m/3m^*)]\chi^{\text{Pauli}}_{\text{free el.}} \tag{5}$$

(Possible susceptibility enhancement effects and orbital susceptibility contributions are difficult to estimate and are neglected in the present treatment, but are discussed in more detail elsewhere.[29]) The expressions for $\chi^{\text{Pauli}}_{\text{free el.}}$ is

$$\chi^{\text{Pauli}}_{\text{free el.}}\,(\text{cm}^3/\text{mole}) = 2.207\times10^{-14}\,V_m(N/V)^{1/3} \tag{6}$$

where V_m is the molar volume and N/V is the electron concentration in cm^{-3}. For the spinel phase $Li_{1+x}Ti_{2-x}O_4$, the concentration of electrons outside closed shells is assumed to be

$$N/V = 8(1-3x)/a_0^3 \tag{7}$$

where a_0 is the lattice parameter in cm.

From Eqs. (5)–(7), the effective mass of the conduction electrons may now be determined, by solving the relation

$$(m^*/m)-(m/3m^*) = \chi_M/\chi^{\text{Pauli}}_{\text{free el.}} \tag{8}$$

From the value of m^*/m determined from Eq. (8), the band structure density of states for both spin directions $N_{bs}(0)$ can be determined from Eq.

TABLE V

Electronic Parameters Characterizing the Conduction Electrons in $LiTi_2O_4$. Derived from Magnetic Susceptibility Measurements

Property		Value
(a)	a_0, Å	8.402
(b)	N/V, cm^{-3}	1.349×10^{22}
(c)	V_m, cm^3/mole	44.67
(d)	$\chi^{Pauli}_{free\ el.}$, cm^3/mole	23.5×10^{-6}
(e)	χ_M, cm^3/mole ($T \leq 50$ K)	220×10^{-6}
(f)	m^*/m	9.4
(g)	$N_{bs}(0)$, states/eV-atom	0.97

[a] Lattice parameter.
[b] Conduction electron concentration.
[c] Molar volume.
[d] Calculated Pauli paramagnetism for free electrons.
[e] Measured susceptibility, corrected for impurity and ion core contributions.
[f] Conduction electron band structure effective mass.
[g] Density of electron energy states at the Fermi surface, for both electron spin directions.

(3). In convenient units, $N_{bs}(0)$ is given by

$$N_{bs}(0)\left(\frac{\text{states}}{\text{eV-atom}}\right) = \frac{1}{r}\frac{m^*}{m}\, 3.090 \times 10^4 \chi^{Pauli}_{free\ el.} \tag{9}$$

where r is the number of atoms per formula unit ($r = 7$ in the present case) and $\chi^{Pauli}_{free\ el.}$ is expressed in units of cm^3/mole from Eq. (6).

The above computations were carried out for the superconducting spinel composition $LiTi_2O_4$ and the results are listed in Table V.

9. SUMMARY AND DISCUSSION

A crystallographic study of the spinel phase in the Li–Ti–O ternary system showed that the composition and cation distribution for this phase are $Li[Li_xTi_{2-x}]O_4$ ($0 \leq x \leq 1/3$), with a statistical distribution of the Li and Ti cations on the octahedral sites for $x \neq 0$. For $x = 0$, only titanium cations occupy the octahedral sites, and the crystallographic equivalence of these cations has an important consequence[38]: a +3 or +4 valence cannot be assigned to particular Ti cations, even though the formal valence of these cations in this case is +3.5. By this symmetry property, $LiTi_2O_4$ must be metallic, as observed. However, for $x \neq 0$, the crystallographic equivalence of the octahedral-site Ti cations is destroyed by the presence of Li cations on

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ceptibility Measurements

Value
8.402
1.349×10^{22}
44.67
23.5×10^{-6}
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$$0 \qquad 10^4 \chi^{\text{Pauli}}_{\text{free el.}} \tag{9}$$

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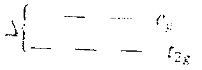
these sites, and symmetry arguments do not predict whether these compositions should be metallic or not. On the other hand, for $x = 1/3$ the valences of the Li and Ti cations attain their maximum values of +1 and +4, respectively, and $Li_{4/3}Ti_{5/3}O_4$ is an electrical insulator. Therefore, somewhere within the homogeneity range of the spinel phase, a metal–insulator (–semiconductor) transition must occur, and the composition dependence of the superconducting and normal state properties is intimately related to the nature of this transition and the composition at which it occurs.

A study of the variation of T_c with composition x for $Li_{1+x}Ti_{2-x}O_4$ showed that for compositions in the vicinity of $LiTi_2O_4$ ($x = 0$), the T_c was 10–12 K. As the composition parameter x increased from 0.05 to 0.15, the T_c abruptly decreased to <1.5 K with increasing x. From $x \approx 0.15$ to $x = 1/3$, no superconductivity was observed. However, in no case was there any evidence from the x-ray data for the formation of superstructures, structural distortion, or additional crystallographic phases for any of the compositions within the spinel homogeneity range. The disappearance of superconductivity at $x \approx 0.1$ was found to be coincident with a large increase in the room-temperature resistivity and with qualitative changes in its temperature dependence, suggesting that the occurrence of a composition-induced metal–semiconductor transition at about this composition is the factor responsible for the disappearance of superconductivity. This finding is tentative, however, since these resistivity data were obtained from sintered pellets in which grain boundary effects may be important.

Since the maximum possible number of free electrons increases from zero at $x = 1/3$ to about $1 \times 10^{22}\ \text{cm}^{-3}$ at $x = 0$, the resistivity data are consistent with the dielectric constant data, which indicated that a large concentration of electrons outside closed shells would have to be present in order that a degenerate electron gas could form in the Li–Ti–O spinel. The dielectric measurements also showed that the occurrence of metallic properties for the $Li_{1+x}Ti_{2-x}O_4$ compounds as $x \to 0$ is not initiated by impurity band conduction.

Magnetic susceptibility measurements showed that for all compositions studied within the homogeneity range of the spinel phase, the susceptibilities are nearly temperature independent over most of the temperature range below room temperature. This magnetic behavior was observed both for the superconducting compositions ($x \approx 0$) and for nonsuperconducting compositions ($x \gtrsim 0.1$), indicating that if a composition-induced metal–semiconductor transition does occur at $x \approx 0.1$, this transition is not accompanied by discrete localization of the electrons outside closed shells. In this connection, a study of other ternary titanium oxides has been made which indicated that nonmetallic oxides containing "Ti^{3+}" do not necessarily exhibit Curie–Weiss susceptibilities and need not order magnetically.[15]

A rapid deterioration of the metallic character as the composition changes from $LiTi_2O_4$ toward $Li_{4/3}Ti_{5/3}O_4$ is a likely consequence of both electronic and crystallographic considerations, as follows. The magnetic susceptibility measurements determined that the band effective mass of a conduction electron in $LiTi_2O_4$ is large, with a value of $\sim 9m_e$, indicating that the conduction electrons in this compound are of d character. Since the titanium cations are the only d cations present, the d bands probably arise from orbitals on these cations. In the crystallographic consideration of the spinel structure in Section 4, it was determined that for all compositions of the spinel, the titanium cations are situated in oxygen octahedra. The five-fold orbital degeneracy of a d^1 cation situated in such an oxygen octahedron is lifted, due to the crystal field of the coordinating oxygen atoms, in the following way (Ref. 39, p. 62):



That is, removing the original five-fold orbital degeneracy results in a low-energy threefold orbitally degenerate state (denoted as the t_{2g} orbitals) and a twofold orbitally degenerate state (e_g orbitals) separated by an energy Δ from the first set. For Ti^{3+} in such a cubic crystal field, the energy Δ is about 2.5 eV (Ref. 39, p. 227). In the spinel structure, the t_{2g} orbitals of one transition metal cation are directed at neighboring octahedral site cations.[41] Therefore, these would be the primary orbitals from which a conduction band is formed in $LiTi_2O_4$, and it is likely that the conduction electrons in $LiTi_2O_4$ reside primarily on the titanium octahedral site sublattice of the spinel structure. Further, a deviation in the composition of the spinel $Li_{1+x}Ti_{2-x}O_4$ from $x = 0$ was found in Section 4 to result in the substitution of a fraction $x/2$ of the titanium cations by lithium cations. Since the Li^0 state does not occur in oxide compounds, the presence of Li^{1+} in the octahedral sublattice of the Li–Ti–O spinel should inhibit electron conduction along this sublattice.

If the integrity of the titanium octahedral site sublattice is in fact the dominant factor in determining the metallic character of the $Li_{1+x}Ti_{2-x}O_4$ spinel compounds as deduced above, then substitution of other alkali or alkaline earth metals for Li on the tetrahedral sites should have much less effect upon the metallic character of $Li[Ti_2]O_4$ than a similar Li substitution for Ti cations on the octahedral sites. Preliminary experiments[13] indicate this to be true. Whereas in the present work it was found that substitution of Li for only 5% of the octahedral-site Ti cations destroys both the metallic character and the superconductivity in $Li[Ti_2]O_4$, a substitution of at least 20% of the tetrahedral-site Li cations by Mg results in retention of both the metallic character of $LiTi_2O_4$ and its related superconductivity.[13]

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a likely consequence of both
ns, as follows. The magnetic
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APPENDIX. PHASE RELATIONS AND CRYSTAL STRUCTURES IN THE Li–Ti–O TERNARY SYSTEM

The collected data on the phase relations in this ternary system at 800°C are shown in part in Fig. 9. In addition, the known temperature–composition phase diagram for the pseudo-binary system Li_2TiO_3–TiO_2 is shown on the left side of the figure. The lattice parameters and various other data for the various phases are given in Table VI. Several results of the present work (PW) are discussed below, along with a summary of literature data.

In the pseudo-binary system Li_2O–TiO_2, four colorless compounds are known to exist: Li_4TiO_4, Li_2TiO_3, $Li_4Ti_5O_{12}$, and $Li_2Ti_3O_7$. The Li_4TiO_4 (not shown in Fig. 9) is formed by reacting Li_2CO_3 with TiO_2 in the molar ratio 2:1 at 800–900°C in a gold foil boat for several hours.[42] Its crystal structure is orthorhombic.[42] and the compound is isostructural with the low-temperature form of Li_4GeO_4.[42,43] The titanium ions show very unusual tetrahedral oxygen coordination in this compound.[42] The compound is stable in this crystal structure at least up to 640–690°C, but a phase transition is seen by differential thermal analysis upon heating through this temperature range.[43] The crystal structure of the high-temperature phase was not determined.

Li_2TiO_3 is a very stable compound, which was first obtained by Kordes in 1934[44,45] from the reaction of TiO_2 with a melt of Li_2CO_3. The crystal structure of the compound he obtained was of the NaCl type, with a statistical distribution of the cations on the metal–atom sublattice. However, upon annealing above about 900°C, Li_2TiO_3 develops a superstructure,

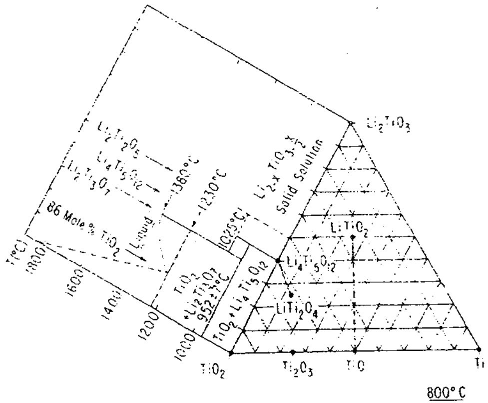

Fig. 9. Ternary phase diagram for the Li–Ti–O system in the region bounded by Ti, Li_2TiO_3, and TiO_2.

TABLE VI

Crystal Structures and Other Data for Phases in the Li–Ti–O Ternary System

Composition	Lattice parameters, Å			Comments	Ref.
	a	*b*	*c*		
Li_4TiO_4	7.91	6.15	7.41	Infrared studies	42, 43
	Disordered-cation and/or disordered-vacancy NaCl phases				
Li_2TiO_3	4.1355	—	—	$Z = 4/3$, $D_{20°C} = 3.418$, $D_{calc} = 3.421$	45
$LiTiO_2$	4.140	—	—	$Z = 2$, $D_{meas} = 3.80$	25, 50
	4.136	—	—	—	51
	4.142	—	—	—	13
TiO	4.157	—	—	1000°C synthesis	51
	4.1796	—	—	Hi-*T* synthesis	60
	4.180	—	—	Hi-*T* synthesis	6
	4.184	—	—	1300–1500°C, quenched	4
	4.180	—	—	>1250°C	53
	Ordered-cation and/or ordered-vacancy NaCl phases				
Li_2TiO_3	5.05	8.76, $\beta = 100.0°$	9.68	$D_{calc} = 3.46$	46
	5.041	8.806 $\beta = 100° 0.5'$	9.726	—	47
	8.27–8.28	—	—	Pseudo-cubic indexing	22, 48
$Li_2Ti_2O_5$	8.29–8.30	—	—	Pseudo-cubic indexing, $D_{meas} = 3.50$	PW[a]
TiO	12.54	—	—	980–1250°C	48
	5.855	9.340 $\gamma = 107°32'$	4.142	<990°C	53 54
	9.355	5.868 $\gamma = 107°32'$	4.135	<980°C	61
	Spinel phase				
$Li_4Ti_5O_{12}$ (low *T*)	8.359	—	—	—	23
	8.357	—	—	—	11, PW[a]
	8.36	—	—	—	24
	8.352	—	—	Decomposes at 1100°C	62
$LiTi_2O_4$ (low *T*)	8.405	—	—	—	10, PW[a]
	8.391	—	—	—	11
	Ramsdellite phase				
$Li_2Ti_3O_7$	5.011	9.549	2.948	$V_{cell} = 141.1$ Å^3	56
	9.77	—	8.79	Tetragonal	62
$LiTi_2O_4$ (high *T*)	5.033	9.626	2.944	$V_{cell} = 142.6$ Å^3	PW[a]

[a] PW = present work.

corresponding to ordering of the cations.[22,46–48] This superstructure formation is irreversible[22] and the cationic ordering reduces the symmetry of the ses in the Li–Ti–O Ternary System

	Comments	Ref.
:1	Infrared studies	42, 43
red-vacancy NaCl phases		
	$Z = 4/3$, $D_{20°C} = 3.418$, $D_{calc} = 3.421$	45
	$Z = 2$, $D_{meas} = 3.80$	25, 50
	—	51
	—	13
	1000°C synthesis	51
	Hi-T synthesis	60
	Hi-T synthesis	6
	1300–1500°C, quenched	4
	>1250°C	53
vacancy NaCl phases		
	$D_{calc} = 3.46$	46
5	—	47
	Pseudo-cubic indexing	22, 48
	Pseudo-cubic indexing,	PW[a]
	$D_{meas} = 3.50$	48
	-1250°C	53
	°C	54
	<980°C	61
	—	23
	—	11, PW[a]
	—	24
	Decomposes at 1100°C	62
	—	10, PW[a]
	—	11
se		
	$V_{cell} = 141.1$ Å^3	56
	Tetragonal	62
	$V_{cell} = 142.6$ Å^3	PW[a]

6-48 This superstructure forma-
ng reduces the symmetry of the lattice from cubic to monoclinic.[46,47] However, the strongest lines in the powder x-ray pattern can still be indexed on a pseudo-cubic basis (face-centred indexing) with a lattice parameter of 8.28 Å,[22,48] which corresponds to twice the lattice parameter of the cation-disordered Li_2TiO_3. The ordered form of Li_2TiO_3 has a homogeneity range that extends at least to the composition $Li_2Ti_2O_5$,[48,49] for which the pseudo-cubic lattice parameter has increased slightly to 8.29–8.30 Å (PW). From density measurements, it was deduced that the existence of the solid solution range is due to the formation of cation vacancies.[48,49]

A cation-disordered NaCl phase has also been found for the compositions $Ti_{1-x}Li_xO$ $(0 \leq x \leq 0.5)$.[25,50,51] It is not known whether this phase extends to $x > 0.5$. The lattice constants for this phase range from about 4.14 to 4.18 Å (see Table VI), and are therefore almost half of the lattice parameters of the spinel phase (see below). This phase has been produced by reaction of Li_2TiO_3 and TiO in appropriate ratios at 1000°C[51] or at 800°C (PW). $LiTiO_2$ can also be synthesized by reaction of Li_2O and Ti_2O_3 at 1000°C.[25,50] Subjecting $LiTiO_2$ to various annealing procedures did not result in the appearance of superstructure lines in the x-ray patterns,[25,50] indicating that the cations do not order, in contrast to Li_2TiO_3. The other end member of the solid solution range, TiO, on the other hand, is known to contain about 15% vacancies on each of the cation and anion sublattices.[52] These vacancies are disordered above 1250°C, but below this temperature the vacancies do order, producing a superstructure with a period of three times the high-temperature lattice constant.[53] Below about 980°C, the vacancies order in a different way, resulting in a reduction of the lattice symmetry from cubic to monoclinic.[54] The possible existence of these vacancies for compositions $Ti_{1-x}Li_xO$ has not been considered in the literature. In the Ti–O binary system, there also exists a large homogeneity range in the metal : oxygen ratio for the NaCl-type phase. At high temperatures, the TiO_x NaCl phase is stable between the limits $0.7 < x < 1.3$.[52] A similar large homogeneity range in the metal : oxygen ratio has been found[13] for $(Li, Ti)O_x$ at high temperatures. Data on this homogeneity range and other properties of the $(Li, Ti)O_x$ NaCl phase[13] will be published later.

The existence of a spinel phase in the Li–Ti–O system was first established by Bertaut and Durif.[23] On the line joining TiO_2 and Li_2TiO_3, the composition of the spinel is $Li_4Ti_5O_{12}$.[22] This compound has a lattice parameter of 8.357 Å (Refs. 11 and 23 and the present work), very similar to but slightly larger than the pseudo-cubic lattice parameters of the ordered Li_2TiO_3 phase. However, it is not nearly as stable as Li_2TiO_3, and melts incongruently at 1025°C.[55] For compositions along the line TiO_2–Li_2TiO_3, the homogeneity range of the spinel phase is very narrow. Synthesis of compositions on either side of the composition $Li_4Ti_5O_{12}$ below 950°C results in the appearance of second phases: TiO_2 (rutile) or the ordered Li_2TiO_3 phase, and the lattice constant of the spinel remains unchanged (PW). However, a homogeneity range does exist which extends into the region of reduced Ti^{4+} of the phase diagram.[10,11] This homogeneity range extends from $Li_4Ti_5O_{12}$ to $LiTi_2O_4$, for which the lattice parameter has increased to ~8.405 Å (Ref. 10 and the present work). The preparation, lattice parameters, and normal and superconducting state properties of the spinel phase are discussed in detail in the main body of this paper.

The difficulty of interpreting x-ray powder patterns containing mixtures of the phases Li_2TiO_3–$Li_2Ti_2O_5$, $Li_4Ti_5O_{12}$–$LiTi_2O_4$, and/or $LiTiO_2$–TiO therefore stems from the commensurate cubic or pseudo-cubic lattice parameters of these phases. The observed x-ray diffractometer patterns for these phases are shown schematically in Fig. 10: the similarities are immediately apparent.

The compound $Li_2Ti_3O_7$ was discovered by Jonker in 1956,[22] and is stable from 952°C to its melting point of about 1380°C.[55] Below 950°C, it decomposes very slowly into $Li_4Ti_5O_{12}$ and TiO_2 (rutile).[55] Its crystal structure was found to be related to the orthorhombic Ramsdellite structure,[56,57] which contains four metal atoms and eight oxygen atoms per unit cell. This structure has tunnels running in the direction of the *c* axis[57] which can accommodate lithium cations.[56] The titanium cations are positioned in

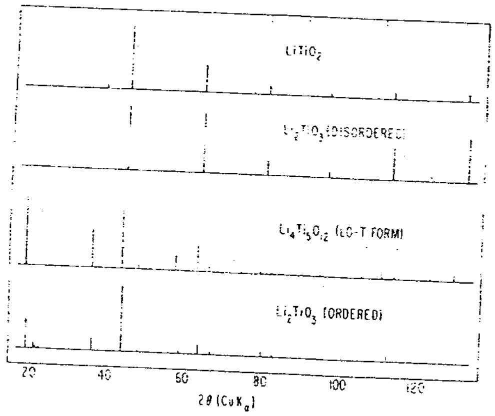

Fig. 10. Schematic illustration of the powder diffractometer tracings obtained for several compounds in the Li–Ti–O ternary system. The data for Li_2TiO_3 (disordered) were taken from Ref. 45.

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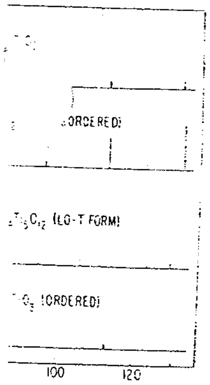

powder diffractometer
ounds in the Li–Ti–O
O_3 (disordered) were

distorted octahedra of oxygen anions. Since lithium cations can also substitute for the titanium cations, the general chemical formula for this phase is $Li_{x+y}Ti_{4-y}O_8$. The colorless composition $Li_2Ti_3O_7$ then corresponds to $x + y = 16/7$ and $y = 4/7$. The homogeneity range of this phase along the line Li_2TiO_3–TiO_2 has not been studied in detail, although a single-phase sample was also obtained for the composition $Li_2Ti_{2-5/6}O_{6-2/3}$.[58] Other studies (PW) indicate a homogeneity range extending into the region of the phase diagram containing reduced Ti^{3+} cations (compare with the spinel homogeneity range above). Samples with composition $LiTi_2O_4$ (spinel structure below ~950°C) were found after induction melting in a sealed Mo crucible to have single-phase Ramsdellite structure, but with a change in the lattice parameters as compared to $Li_2Ti_3O_7$, and an increase of about 1% in the unit cell volume (PW) (Table VI). In terms of the chemical formula for the Ramsdellite phase, the composition $LiTi_2O_4$ corresponds to the parameters $x = 2$ and $y = 0$. A Ramsdellite-phase sample at this composition was found to have a room-temperature resistivity of 60 Ω-cm, indicating nonmetallic character (PW). Attempts to synthesize Ramsdellite structure compounds at high temperature for metal : oxygen ratios greater than 3 : 4 resulted in multiphase samples containing the NaCl phase $(Ti, Li)O_x$ as the principal second phase (PW). None of the samples with the Ramsdellite structure were found to be superconducting above 1.5 K (PW).

The liquidus line shown in Fig. 9 was determined by Hummel and Tien.[59] A eutectic exists at 1230°C for a mole ratio of $TiO_2 : Li_2TiO_3$ of 86 : 14.

ACKNOWLEDGMENTS

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A Series of Oxygen-Defect Perovskites Containing Cu^{II} and Cu^{III}: The Oxides $La_{3-x}Ln_xBa_3\,[Cu^{II}_{5-2y}\,Cu^{III}_{1+2y}]\,O_{14+y}$

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A series of oxygen-defect perovskites, containing Cu^{II} and Cu^{III}, $La_3Ba_3[Cu^{II}_{5-2y}Cu^{III}_{1+2y}]O_{14+y}$, has been synthesized at 1000°C, for $0.05 \le y \le 0.43$. The substitution of lanthanum for yttrium and lanthanides has been studied. These oxides are tetragonal: $a = a_p 2^{1/2}$ and $c = 3a_p$. The structural study of $La_3Ba_3Cu_6O_{14.10}$ shows that oxygen vacancies are ordered, involving for copper three sorts of coordination: square, pyramidal (4 + 1), and distorted octahedral (4 + 2). The distribution of Cu^{III}, as well as the lanthanide ions on the different sites, is discussed.

Introduction

The number of oxygen-defect perovskites ABO_{3-x} known at the present time is limited. This is probably related to the nature of the B atoms forming the octahedral framework: the anion deficiency should be stabilized if the B atom is going to be able to present, in addition to the octahedral coordination, an environment derived from the latter but characterized by a smaller number of coordination. In this respect, copper is a potential candidate due to its ability to take octahedral, square planar, or pyramidal coordination. Moreover, the oxygen nonstoichiometry in the copper oxides can be influenced by the possibility of formation of trivalent copper, depending on the experimental conditions. Ternary oxides $A_mCu_nO_t$ containing Cu^{III} can indeed be prepared under 1 atm oxygen pressure (*1–4*) or under high oxygen pressure (*5, 6*) according to the nature of the A element. Some A elements like barium allow the formation of Cu^{III} in air (*7, 8*). The present paper deals with a series of defect perovskites $La_{3-x}Ln_xBa_3Cu_6O_{14+y}$ which have been synthesized in air and in which copper takes two oxidation states: +2 and +3.

Synthesis and Characterization

The Oxides $La_3Ba_3Cu_6O_{14+y}$

La_2O_3 and CuO oxides and $BaCO_3$ were mixed and heated in air, in platinum crucibles, first for 12 hr at 900°C, then for 24 hr at 1000°C, and finally quenched at room temperature. From the different compositions which were investigated a pure compound was isolated with the atomic ratios: La/Ba = (La + Ba)/Cu = 1. The observed weight loss was smaller than that deduced from the departure of CO_2. The partial oxidation of Cu(II) to Cu(III) was thus considered, leading to the formula La_3Ba_3

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$[\mathrm{Cu}^{II}_{5-2y}\,\mathrm{Cu}^{III}_{1+2y}]\,\mathrm{O}_{14+y}$. The y value obtained from the weight loss during the synthesis, $y = 0.10$, was in agreement with this hypothesis. This was confirmed by the microthermogravimetric study of the reduction of the quenched product under hydrogen.

The variation of y as a function of temperature and especially oxygen pressure was then examined. Annealing the quenched compound in air gave a maximum value of y (0.37) at 400°C. The quenched compound ($y = 0.10$) was then annealed at this temperature under different oxygen pressures, ranging from 5.10^{-3} to 1 atm. The y value and thus the Cu(III) amount, deduced from microthermogravimetric measurements, increased regularly with the oxygen pressure, as shown in Table I.

All these oxides were obtained in the form of a black powder, whose X-ray patterns show strong reflections similar to those of the stoichiometric perovskites. They have been indexed in a tetragonal cell whose parameters are related to that of the cubic perovskite a_p, in the following way: $a = b = a_p \cdot 2^{1/2}$; $c = 3a_p$. These parameters do not vary appreciably with the oxygen amount: $a = 5.5253(4)$ Å and $c = 11.721(1)$ Å for the air-quenched sample ($y = 0.10$), while $a = 5.5291(8)$ Å and $c = 11.729(2)$ Å for the sample annealed under 1 atm oxygen ($y = 0.43$).

The Oxides $La_{3-x}Ln_xBa_3Cu_6O_{14+y}$ (Ln = Y, Pr, Nd, Sm, Eu, Gd, Er, Yb)

These compounds were prepared in the same way as the oxide $La_3Ba_3Cu_6O_{14.10}$, quenching the sample from 1000°C to room temperature in air. In the case of yttrium and europium, the oxides were heated for periods greater than 24 hr, in order to obtain better crystallization. The possibility of substitution of lanthanum for another lanthanide or for yttrium decreases regularly with the size of Ln^{3+} (Fig. 1): a total substitution ($x = 3$) was obtained for praseodymium, while less than 50% of lanthanum could be replaced by ytterbium. The evolution of the oxygen amount y, was not investigated in an exhaustive manner. It can be stated that for the same experimental conditions as those used for $La_3Ba_3Cu_6O_{14.10}$, the variation of the Cu^{III} amount remains weak. It seems, however, that y decreases with the size of the Ln^{3+} ion: the y values observed for the three richest compounds in Ln^{3+}, Ln = Pr, Nd, and Sm are respectively 0.10, 0.04, and 0.01.

All these oxides are black and are isostructural of $La_3Ba_3Cu_6O_{14.10}$ the c/a ratio remains equal to $3/2^{1/2}$ independently of the composition. The corresponding a_p parameter decreases regularly with the size of Ln^{3+} in agreement with the lanthanidic contraction (Fig. 2).

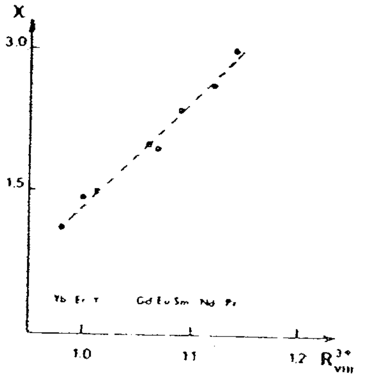

FIG. 1. Substitution of La^{3+} for Ln^{3+} in $La_{3-x}Ln_xBa_3Cu_6O_{14+y}$: evolution of x as a function of the ionic radii of Ln^{3+} (*13*).

TABLE I

THE OXIDES $La_3Ba_3Cu_6O_{14+y}$: EVOLUTION OF y AS A FUNCTION OF OXYGEN PRESSURE[a]

P_{O_2} (atm)	5.10^{-3}	10^{-2}	2.10^{-2}	5.10^{-2}	0.1	0.2	1
y	0.05	0.19	0.25	0.31	0.34	0.37	0.43

[a] After annealing the quenched oxide ($y = 0.10$) at 400°C.

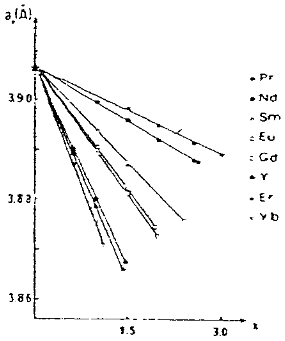

FIG. 2. Evolution of the a_p parameter of the oxides $\mathrm{La}_{3-x}Ln_x\mathrm{Ba}_3\mathrm{Cu}_6\mathrm{O}_{14+y}$.

Structural Study of the Oxide $\mathrm{La_3Ba_3Cu_6O_{14.10}}$

No single crystal could be obtained due to the decomposition of the compounds at temperatures greater than 1000°C. The structure of this oxide was thus studied from its X-ray powder pattern registered with a Philips goniometer for the Cu$K\alpha$ radiation. The intensities of the peaks corresponding to 74 reflections were measured. The observed density ($d_{\mathrm{exp}} = 6.70$) corresponds to one group $\mathrm{La_3Ba_3Cu_6O_{14.10}}$ per cell ($d_{\mathrm{calc}} = 6.67$). The existence of the 1 0 0 reflection, though weak, involves the absence of reflection conditions. From the eight possible space groups, we have chosen the most symmetrical space group, $P\,4/mmm$, in order to limit the number of variable parameters. Because of the similarity of this phase to the perovskite, the metallic atoms were placed in analogous positions: the barium and lanthanum ions were statistically distributed in $4(i)$ $(0\ \frac{1}{2}\ z;\ z = \frac{1}{6})$ and $2(f)$ $(0\ \frac{1}{2}\ \frac{1}{2})$, while the copper atoms were placed in $1(a)$ $(0\ 0\ 0)$, $1(c)$ $(\frac{1}{2}\ \frac{1}{2}\ 0)$, $2(g)$ $(0\ 0\ z;\ z = \frac{1}{3})$, and $2(h)$ $(\frac{1}{2}\ \frac{1}{2}\ z;\ z = \frac{1}{3})$. The great anionic deficiency with respect to the stoichiometric perovskites set the problem of the distribution of the 14.1 oxygen atoms over the 18 possible sites of the structure. Starting from the ideal formula $\mathrm{La_3Ba_3Cu_6O_{14}}$, we have assumed that the structure was built up from $\mathrm{CuO_2}$ sheets parallel to (001) as in $\mathrm{La}_{2-x}A_{1+x}\mathrm{Cu_2O}_{6-x/2}$ (9) involving, for copper at least, the square planar coordination. Twelve oxygen atoms $\mathrm{O_1}$ and $\mathrm{O_2}$ were thus respectively distributed on $4(j)$ $(x\ x\ 0;\ x = \frac{1}{4})$ and $8(r)$ $(x\ x\ z;\ x = \frac{1}{4}$ and $z = \frac{1}{3})$. For the two remaining oxygen atoms $\mathrm{O_3}$, located between the $\mathrm{CuO_2}$ layers at about the same level as the barium and the lanthanum atoms, different distributions over four sets of sites—$1(b)$ $(0\ 0\ \frac{1}{2})$; $1(d)$ $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$; $2(h)$ $(\frac{1}{2}\ \frac{1}{2}\ z;\ z = \frac{1}{6}$; $2(g)$ $(0\ 0\ z;\ z = \frac{1}{6})$—were considered. After successive refinement of the atomic coordinates of the metallic atoms, of the oxygen atoms $\mathrm{O_1}$ and $\mathrm{O_2}$, and of the isotropic thermal parameters it was found that the $\mathrm{O_3}$ atoms were located principally in $2(h)$. The minimum discrepancy factor $R = \Sigma|I_{\mathrm{obs}} - I_{\mathrm{calc}}|/\Sigma I_{\mathrm{obs}}$, $R = 0.039$, was obtained for the thermal and positional parameters given in Table II. Table III shows the agreement between the calculated and observed intensities.

Description of the Structure and Discussion

This structure can be described from that of perovskite by formation of ordered oxygen vacancies in the "A–O" planes. The result is that the plane stacking sequence

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS OF $\mathrm{Ba_3La_3Cu_6O_{14.1}}$

Atom	Site	x	y	z	B (Å^2)
A_1	$4(i)$	0	½	0.1798(3)	0.43(4)
A_2	$2(f)$	0	½	½	0.35(7)
$\mathrm{Cu_1}$	$1(a)$	0	0	0	0.1(3)
$\mathrm{Cu_2}$	$1(c)$	½	½	0	0.2(3)
$\mathrm{Cu_3}$	$2(g)$	0	0	0.348(2)	0.8(2)
$\mathrm{Cu_4}$	$2(h)$	½	½	0.346(2)	0.9(2)
$\mathrm{O_1}$	$4(j)$	¼	¼	0	0.1(1)
$\mathrm{O_2}$	$8(r)$	¼	¼	0.358(2)	1.8(5)
$\mathrm{O_3}$	$2(h)$	½	½	0.147(5)	0.1(1)

TABLE III

X-RAY DIFFRACTION DATA OF $La_3Ba_3Cu_6O_{14.10}$

hkl	d_{obs}	d_{calc}	I_{obs}	I_{calc}
001	11.67	11.72	0.6	1.0
100	—	5.525	vw	0.3
003	3.907	3.907	12.9	1.9
110				10.3
111	3.705	3.706	0.6	0.3
112	3.249	3.251	1.1	0.9
113	2.7630	2.7626	100	71.3
200				28.1
202	—	2.4988	0.3	0.3
005	2.3432	2.3442	4.5	1.2
114				2.3
203	2.2553	2.2556	12.9	12.7
115	2.0097	2.0101	0.8	0.1
204				0.3
006	1.9536	1.9535	27.1	7.7
220				19.4
205	1.7875	1.7874	0.5	0.4
116	1.7473	1.7472	6.0	2.0
223				1.4
310				2.3
007	1.6734	1.6744	0.5	0.5
312				0.3
206	1.5948	1.5949	33.8	9.6
313				25.0
117	1.5383	1.5390	0.5	0.5
225	1.5012	1.5006	2.1	0.9
314				0.9
207	—	1.4319	0.6	0.7
226	1.3814	1.3813	14.7	8.5
400				5.2
118	—	1.3718		0.9
009	1.3025	1.3023	3.1	0.1
316				1.7
403				0.7
330				0.5
227	—	1.2712	1.0	0.6
332				0.1
119	1.2358	1.2354	13.6	3.6
333				4.9
420				4.5
317	—	1.2089	0.4	0.5
405	—	1.1900	0.2	0.4
334				0.2
209	1.1782	1.1780	3.0	0.8
423				2.5
406	1.1276	1.1278	5.1	4.0
1110	—	1.1227		0.9
318				0.9
229	—	1.0836	1.7	0.4
336				0.5
510				0.6
2010	—	1.0790		0.3
0011	—	1.0655	0.2	0.2
407				0.3
512				0.1
319	1.0443	1.0441	15.5	4.3
426				4.8
513				5.9
2011	—	0.9941	0.9	0.3
427				0.5
0012	—	0.9767	3.7	0.4
440				1.8
3110	—	0.9734		1.3
338				0.3
1112	—	0.9475	2.3	0.3
409				0.3
516				1.0
443				0.5
530				0.6
428	—	0.9445		0.1
2012	0.9210	0.9208	9.0	1.3
339				1.9
533				5.2
600				1.2

$|AO - CuO_2|_\infty$ along a in the cubic perovskite is replaced by the sequence $|Cu_2O_4 - A_2O\square - Cu_2O_4 - A_2\square_2 - Cu_2O_4 - A_2O\square|_\infty$ along c in $La_3Ba_3Cu_6O_{14.10}$ (Fig. 3). Three sorts of coordination are thus observed for copper in this structure: square planar for Cu_1 and Cu_3, pyramidal (4 + 1) for Cu_4, and distorted octahedral (4 + 2) for Cu_2 (Table IV).

Whatever the nature of the copper coordination may be, we always observed for this atom a basal plane characterized by four Cu–O distances close to 1.95–1.96 Å. The great distance (2.33 Å) observed for Cu_4 is close to that obtained for copper with a similar coordination in $La_{2-x}A_{1+x}Cu_2O_{6-x/2}$ (9) (2.26–2.36 Å). On the other hand, Cu_2 has four long Cu-O distances in the (x 0 y) plane and two short distances along c, contrary to the usually

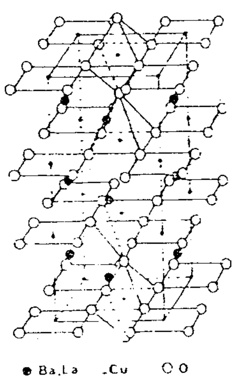

FIG. 3. Structure of $La_3Ba_3Cu_6O_{14.10}$.

observed Jahn–Teller distortion. Such an environment has, however, already been observed in K_2CuF_4 (*10*) Pr_2CuO_4 (*11*). The very short Cu_2–O distances (1.72 Å), smaller than those observed for copper in 4 + 1 coordination in $BaCuO_2$ (1.80 Å) (*12*) made us think that the oxidation state of this element may be +3, in agreement with the very short distances observed in $LaSrCuO_4$ (*6*). This environment suggests for Cu^{III} a $d^2_{x^2-y^2} - d^0_{z^2}$ configuration (*11*).

The distribution of lanthanum and barium over the A_1 and A_2 sites could not be studied due to the similar values of the scattering factors of La^{3+} and Ba^{2+} which are isoelectronic. The A_1–O distances are much greater than the A_2–O distances: these let us deduce that the barium atoms are located only on the A_1 sites. In order to verify this hypothesis, the yttrium compound $La_2YBa_3Cu_6O_{14+y}$ was examined, the scattering factor of yttrium being smaller than that of lanthanum or barium. The intensities ratio of the 1 1 2 and 2 0 3 reflections of this compound was thus compared to that of $La_3Ba_3Cu_6O_{14.10}$. The I_{112}/I_{203} ratio varies appreciably indeed with the electronic distribution on the A_1 and A_2 sites, since the contributions of the A_1 sites to the structure factors F_{112} and F_{203} have opposite signs, while the contributions of A_2 sites have the same sign. The experimental value $(I_{112}/I_{203})_Y = 0.20$ observed for the $La_2YBa_3Cu_6O_{14+y}$, much greater than that of $La_3Ba_3Cu_6O_{14.1}$, $(I_{112}/I_{203}) = 0.085$, shows that the smallest ion, yttrium, is located on the A_2 site, leading to the probable distribution: (3Ba + 1La) on A_1 and (1La + 1Y), on A_2, in agreement with our hypothesis.

The very large oxygen deviation from stoichiometry is an important feature of these compounds. The ordered distribution of the oxygen vacancies with regard to the ideal perovskite must be emphasized; it is worth noting that the distribution of the O_3 atoms on the 1(*b*) and 1(*d*) sites appreciably increases the *R* factor. In the same manner, a statistical distribution of these atoms over the 2(*g*) and 2(*h*) sites, which would involve the disappearance of the superstructure in the (0 0 1) plane, is not possible. A partial occupation of the 2(*g*) sites cannot, however, be eliminated. The 0.1 supplementary oxygen atoms, which have not been considered for these calculations, could be located, if we consider Cu^{3+} ions with an octahedral coordination, either on the 2(*g*) or on the 1(*d*) sites. The second hypothesis agrees with the fact that the introduction of one supplementary oxygen atom induces the presence of two Cu^{3+} ions. However, calculations made on a richer oxygen compound do not allow us to choose between these sites. The presence of copper in these compounds, simulta-

TABLE IV

INTERATOMIC DISTANCES OF $La_3Ba_3Cu_6O_{14.10}$

M–O	Distance (Å)	*M*–O	Distance (Å)
A_1–O_1	2.874(3) × 4	Cu_2–O_1	1.954(0) × 4
A_1–O_2	2.860(17) × 4	Cu_2–O_3	1.723(59) × 1
A_1–O_3	2.790(8) × 2	Cu_3–O_2	1.957(2) × 4
A_2–O_2	2.567(15) × 8	Cu_4–O_1	1.959(2) × 4
Cu_1–O_1	1.954(0) × 4	Cu_4–O_3	2.333(63) × 1

neously with two oxidation states, Cu(II) and Cu(III), suggests interesting electrical properties, which will be investigated as a function of oxygen amounts.

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[11] **4,357,426**

[45] **Nov. 2, 1982**

[54] HUMIDITY SENSITIVE CERAMICS

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[52] **U.S. Cl.** **501/135**; 501/136; 501/137; 501/138; 501/139; 501/152; 252/520; 252/521

[58] **Field of Search** 501/135-139, 501/152; 252/520, 521

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[57] **ABSTRACT**

A humidity sensitive ceramics comprises a sintered body consisting essentially of a semiconductive compound oxide with a perovskite structure and a compound oxide, said semiconductive compound oxide having a composition expressed by the general formula (I):

$$A_{1-x}A'_xBO_{3-\delta} \ldots \quad (I)$$

wherein A is at least one element selected from the group consisting of rare earth elements with atomic numbers 57 to 71, yttrium and hafnium, A' is at least one element selected from the group consisting of alkaline-earth metals, B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30, x is a mole fraction and takes a value of the following range, $0 \leqq x \leqq 1$, and δ is a non-stoichiometric parameter, said compound oxide having a composition expressed by the general formula (II):

$$AMO_3 \ldots \quad (II)$$

wherein A is at least one element selected from the group consisting of alkaline earth elements, Zn, Cd, Fe, Co, Ni, Mn and Pb, M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn.

1 Claim, 4 Drawing Figures

Fig. 1

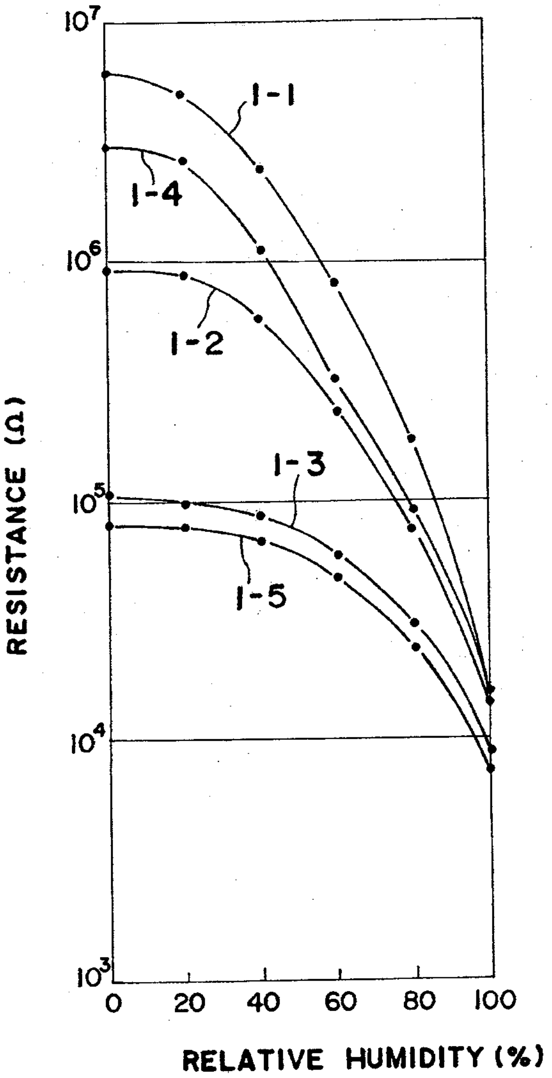

10^7
10^6
10^5
10^4
10^3
RESISTANCE (Ω)
0
20
40
60
80
100
RELATIVE HUMIDITY (%)
1-1
1-4
1-2
1-3
1-5

Fig. 2

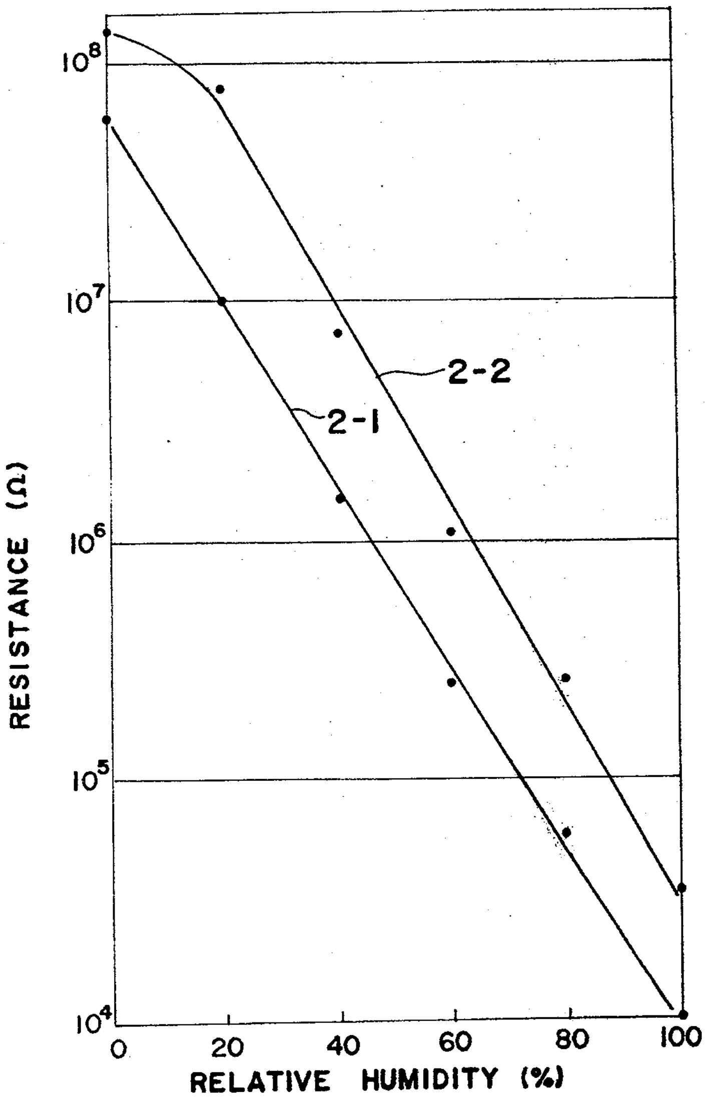

RESISTANCE (Ω)
10⁸
10⁷
10⁶
10⁵
10⁴
0
20
40
60
80
100
RELATIVE HUMIDITY (%)
2-1
2-2

Fig. 3

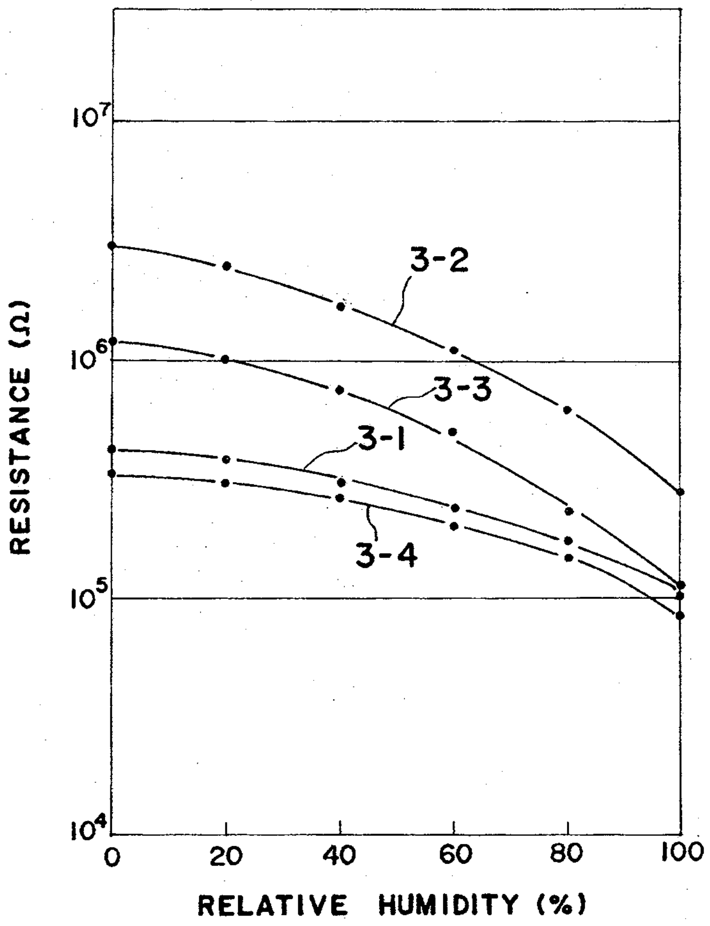
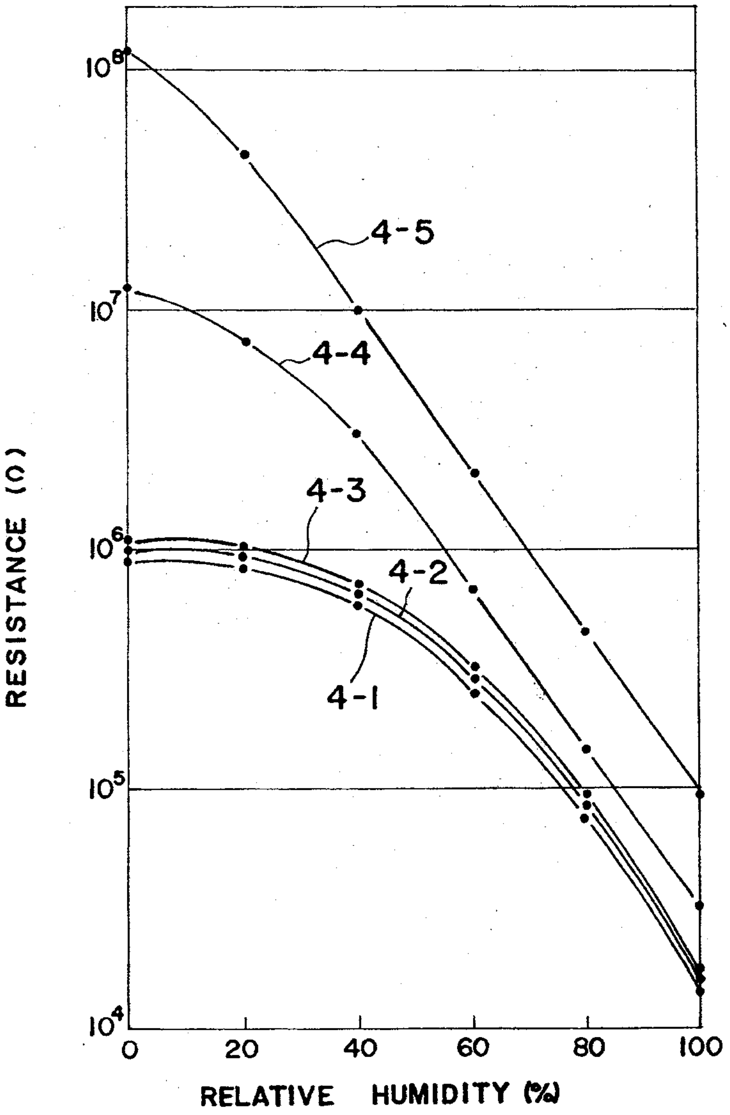

RESISTANCE (Ω)
10^7
10^6
10^5
10^4
3-2
3-3
3-1
3-4
0
20
40
60
80
100
RELATIVE HUMIDITY (%)

Fig. 4


RESISTANCE (Ω)
10^8
10^7
10^6
10^5
10^4
0
20
40
60
80
100
RELATIVE HUMIDITY (%)
4-5
4-4
4-3
4-2
4-1

HUMIDITY SENSITIVE CERAMICS

FIELD OF THE INVENTION

This invention relates to humidity sensitive ceramics which possess the change of resistivity with change in humidity.

BACKGROUND OF THE INVENTION

As a humidity sensor or a moisture detecting element that makes use of the change of resistivity of a humidity sensitive material with change in humidity, there have been used those comprising lithium chloride, or these comprising ceramics of the system such as TiO_2-SnO_2, TiO_2-V_2O_5, $MgCr_2O_4$ or ZnO-Li_2O-V_2O_5. Among them, the humidity sensors comprising the above ceramics, or humidity sensitive ceramic sensors possess excellent stability in characteristics as compared with the sensors of lithium chloride. The ceramic sensors possess poor aging in the humidity detecting function as well as the sensors of lithium chloride. For example, when the ceramic sensors of the prior art are allowed to stand 3 months in an atmosphere of 40% relative humidity, the resistance thereof change by some 40% from the value of initial resistance. However, their function can be recovered to the previous level by heating since the ceramics used as a material for humidity sensors do not change in quality even if heated to high temperatures. For this reason, the ceramic sensors are combined with heating element for practical purposes to recover its humidity detecting function by intermittent heating. However, this lead to increase of the consumption of electric power.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a humidity sensitive ceramics with good aging in the humidity detecting function.

Another object of the present invention is to provide humidity sensitive ceramics which makes it possible to produce humidity sensors with a desired resistance change rate by the variation of compositioned proportions of the components, and the resistance of which is lowered with increase of the humidity.

According to the present invention, there is provided a humidity sensitive ceramics comprising a sintered body consisting essentially of a semiconductive compound oxide with a perovskite structure and a compound oxide. The semiconductive compound oxide has a composition expressed by the general formula(I):

$$A_{1-x}A'_xBO_{3-\delta} \ldots \qquad (I)$$

wherein A is at least one element selected from the group consisting of rare earth elements with atomic numbers 57 to 71, yttrium and hafnium, A' is at least one element selected from the group consisting of alkaline-earth metals, B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30, x is a mole fraction and takes a value in the following range, $0 \leqq x \leqq 1$, and δ is a nonstoichiometric parameter. The compound oxide has a composition expressed by the general formula(II):

$$AMO_3 \ldots \qquad (II)$$

wherein A is at least one element selected from the group consisting of alkaline-earth elements, Zn, Cd, Fe, Co, Ni, Mn and Pb, M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn.

In the preferred embodiment, the semiconductive compound oxide having the perovskite structure expressed by the general formula(I): $A_{1-x}A'_xBO_{3-\delta}$, wherein A is at least one element selected from the group consisting of rare-earth elements with atomic numbers 57 to 71 inclusive, yttrium and hafnium, A' is at least one element selected from the group consisting of alkaline-earth metal, and B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30 inclusive, may have a composition expressed by the formula: $La_{1-x}Sr_xCo_{1-y}Ni_yO_3$ wherein $0 \leqq x \leqq 1$ and $0 \leqq y \leqq 1$.

In further preferred embodiment, the semiconductive compound oxide expressed by the general formula(I) has a composition expressed by the formula: $Nd_{1-x-x'}Sr_xBa_{x'}CoO_3$ wherein $0 \leqq x \leqq 1$, $0 \leqq x' \leqq 1$, $0 \leqq x+x' \leqq 1$.

In another preferred embodiment, the semiconductive compound oxide expressed by the general formula(I) has a composition expressed by the formula: $Y_{1-x}Sr_xCoO_3$, wherein $0 \leqq x \leqq 1$.

In still another preferred embodiment, the semiconductive compound oxide expressed by the general formula(I) has a composition expressed by the formula: $La_{1-x}Sr_xMnO_3$ wherein $0 \leqq x \leqq 1$.

In the above general formula(I), A and A' may take a coexistence state, and are also allowed to be exsisted independently each other. Thus, x in the formula may take any value within the range of 0 to 1 inclusive.

In the general formula(I), $A_{1-x}A'_xBO_{3-\delta}$, oxygen defects which changes the composition into a semiconducting state are expressed by using δ as a nonstoichiometric parameter. The oxygen defect state of the composition can be obtained by sintering the composition in a reducing or oxydizing atmosphere.

In the preferred embodiments, the compound oxide expressed by the general formula(II): AMO_3, wherein A is at least one element selected from the group consisting of alkaline-earth metals, Zn, Cd, Fe, Co, Ni, Mn and Pb, and M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn, has a composition $SrTiO_3$, $BaTiO_3$, $CaSnO_3$, or $Sr_{1-y}Ca_yTiO_3$ (where $0 \leqq y \leqq 1$).

The semiconductive compound oxide with the perovskite structure expressed by the general formula(I) and the compound oxide expressed by the general formula(II) may be mixed in any ratio to produce ceramics with a desired initial resistance and a change rate of resistance with the change in humidity. The semiconductive compound oxide and the compound oxide are generally mixed in the ratio within the range of 1:100 to 100:1, preferably, within the range of 1:50 to 1:1. Because, if humidity sensitive ceramics are composed of the compound oxide AMO_3 alone, i.e., if no semiconductive compound oxide with the perovskite structure is present in the ceramics, they possess extremely high resistance, thus making it impossible to put them into practical use. Further, if ceramics are composed of the semiconductive compound oxide with the perovskite structure alone, i.e., if no compound oxide expressed by the general formula(II) is present in the ceramics, they possess considerably small change rate of resistance with change in humidity, thus making it impossible to use them as a material for humidity sensitive sensors.

The humidity sensitive ceramics according to the present invention may be produced in a manner conventionally employed for known ceramic materials. For example, the humidity sensitive ceramics of the present invention may be produced in the following manner:

The raw materials in forms of oxides and/or carbonates are weighed out, mixed, calcined, powdered and granulated with a suitable amount of binder, and the resultant mixture is formed into suitable shapes. The shaped bodies are sintered at a temperature within the range of 800° to 1400° C. to produce humidity sensitive ceramics. The resultant sintered ceramic bodies may be provided with electrodes to produce humidity sensors. The sintered body may be in the shape of disc, rod bar, pellet, or cylindrical. The electrodes for detecting the change of resistivity of ceramics may be formed in any shape, for example, such as opposed, plate electrodes, comb-shaped electrodes, or porous electrodes.

In order to obtain good humidity detecting characteristic, the sintered ceramic body has preferably porosity within the range of 20 to 50%.

In the foregoing, the nonstoichiometric amount of oxygen (δ) in the semiconductive compound oxide with the perovskite structure is not specified but represented in the form of O_3 as well as in Examples.

The humidity sensitive ceramics according to the present invention are considerably small in aging even if they are exposed to repeated change of humidity surroundings for a long time, thus making it possible to produce humidity sensors without combining them with heating elements. In addition, the humidity sensitive ceramics with a desired change rate of resistance with change in humidity can be produced at will by variation of compositional ratio of the semiconductive compound oxide and the compound oxide expressed by the general formula AMO_3, thus making it possible to produce humidity sensitive sensors with various humidity detecting characteristics.

The invention will be further apparent from the following description with reference to examples and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 to 4 are graphs showing resistance vs. relative humidity characteristics of humidity sensors comprising humidity sensitive ceramics according to the present invention.

EXAMPLE 1

As raw materials, there are provided powder of La_2O_3, $SrCO_3$, Co_2O_3 and TiO_2. These raw materials are mixed to obtain mixtures respectively corresponding to a composition $La_{0.8}Sr_{0.2}CoO_3$ or a composition $SrTiO_3$. The resultant mixtures are then calcined at 1100° C., crushed and ground to powder. The resultant presintered powder of $La_{0.8}Sr_{0.2}CoO_3$ and that of $SrTiO_3$ are mixed in various ratios shown in Table 1, granulated by using 10 wt% of binder, and then shaped into disks with a 10 mm diameter and a 0.6 mm thick. The disks are fired in air at 1250° C. to obtain sinterd bodies of ceramics which are humidity sensitive ceramics. A set of porous electrodes of various electrically conductive materials shown in Table 1 are applied to the opposite disk surfaces of the sintered bodies, and a pair of lead wires are connected to the respective electrodes to provide humidity sensors. The porous electrodes may be formed by printing an electrically conductive paste on the opposite disk surfaces of each sintered body, and then stoving the same in air.

For each thus prepared humidity sensor, the resistance at various relative humidities are measured to know the change of restistance with change in humidity. The results are shown in FIG. 1.

TABLE 1

Specimen No.	Composition (weight %)		Electrode Material
	$La_{0.8}Sr_{0.2}CoO_3$	$SrTiO_3$	
1-1	5	95	Au
1-2	10	90	Au
1-3	15	85	Au
1-4	15	85	RuO_2
1-5	20	80	Au

In order to investigate the aging characteristic, the sensors of the specimen No. 1-2 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in Table 1B together with the initial values.

TABLE 1B

Relative Humidity	Initial value	After 3 months	After 6 months
40%	540 KΩ	560 KΩ	550 KΩ
80%	80 KΩ	80 KΩ	83 KΩ

EXAMPLE 2

Using La_2O_3, $SrCO_3$, Co_2O_3, TiO_2, $CaCO_3$, ZrO_2 and MgO as raw materials, there are prepared powder of a presintered semiconductive compound oxide, $La_{0.8}Sr_{0.2}CoO_3$, and powder of presintered compound oxides, $CaZrO_3$ and $MgTiO_3$, which are then mixed in the proportions shown in Table 2. The respective resultant mixtures are granulated, shaped and fired in the same manner as in Example 1 to obtain ceramic sintered bodies. A set of porous electrodes are applied to the opposite disk surfaces of each ceramic sintered body by printing a gold paste and then stoving the same in air. A pair of lead wires are electrically connected to the porous gold electrodes.

For the thus prepared humidity sensors, the resistance at various relative humidities are measured to know the change of resistance with change in humidity. The results are shown in FIG. 2.

TABLE 2

Specimen No.	Composition (weight %)	
	$La_{0.8}Sr_{0.2}CoO_3$	AMO_3
2-1	25	$MgTiO_3$: 75
2-2	30	$CaZrO_3$: 70

In order to investigate the aging characteristic, the sensors of the specimen No. 2-2 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in Table 2B together with the initial values.

TABLE 2B

Relative Humidity	Initial value	After 3 months	After 6 months
40%	8 MΩ	8.3 MΩ	8.6 MΩ
80%	280 KΩ	290 KΩ	300 KΩ

EXAMPLE 3

Using La_2O_3, $SrCO_3$, Co_2O_3, BaO, TiO_2, $CaCO_3$ and SnO_2 as raw materials, there are prepared mixtures corresponding to a semiconductive compound oxide, $La_{0.8}Sr_{0.2}CoO_3$, and compound oxides, $BaTiO_3$ and $CaSnO_3$. The mixtures are calcined at 1100° C., crushed and powdered.

The resultant powder of $La_{0.8}Sr_{0.2}CoO_3$, that of $BaTiO_3$ and that of $CaSnO_3$ are mixed in the proportions shown in Table 3, together with 10% by weight of a binder, granulated and then shaped into disks with a 10 mm diameter and a 0.5 mm thick. The disks are fired at 1300° C. in air to obtain sintered ceramic bodies. A set of porous gold electrodes are added to the opposite disk surfaces of the sintered bodies in the same manner as in Example 2, and a pair of lead wires are electrically connected to the electrodes.

For the thus prepared humidity sensors, the resistance at various relative humidities are measured to know the change of resistance with change in relative humidity. The results are shown in FIG. 3.

TABLE 3

Specimen	Composition (weight %)	
No.	$La_{0.8}Sr_{0.2}CoO_3$	AMO_3
3-1	5.0	$BaTiO_3$: 95.0
3-2	7.5	$CaSnO_3$: 92.5
3-3	17.5	$CaSnO_3$: 82.5
3-4	27.5	$CaSnO_3$: 72.5

In order to investigate the aging characteristic, the sensors of the specimen No. 3-1 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in TABLE 3B together with the initial values.

TABLE 3B

Relative Humidity	Initial value	After 3 months	After 6 months
40%	340 KΩ	345 KΩ	350 KΩ
80%	180 KΩ	182 KΩ	183 KΩ

EXAMPLE 4

Raw materials are mixed and calcined at 1100° C. to provide presintered bodies of semiconductive compound oxides and compound oxides respectively having the compositions shown in Table 4. The presintered bodies are crushed, powdered and mixed in the proportions shown in Table 4. The mixed powder is added 10% by weight of binder, granulated and shaped into disks with a 10 mm diameter and a 0.5 mm thick. The disks are then fired at 1250° C. in air to provide sintered ceramic bodies. Porous gold electrodes are applied to the opposite disk surfaces of the sintered bodies in the same manner as in Example 2 and lead wires are connected to the electrodes.

For the thus prepared humidity sensors, the resistance at various relative humidities are measured to know the change of resistance of the sensors with change in humidity. The results are shown in FIG. 4.

TABLE 4

Specimen	Composition (weight %)	
No.	$A_{1-x}A'_xBO_3$	AMO_3
4-1	$La_{0.8}Sr_{0.2}Co_{0.9}Ni_{0.1}O_3$: 10	$Sr_{0.95}Ca_{0.05}TiO_3$: 90
4-2	$Nd_{0.6}Sr_{0.4}CoO_3$: 10	$SrTiO_3$: 90
4-3	$Nd_{.08}Sr_{0.1}Ba_{0.1}CoO_3$: 10	$SrTiO_3$: 90
4-4	$Y_{0.5}Sr_{0.5}CoO_3$: 10	$SrTiO_3$: 90
4-5	$La_{0.7}Sr_{0.3}MnO_3$: 10	$SrTiO_3$: 90

In order to investigate the aging characteristic, the sensors of the specimen No. 4-1 are kept in an atmosphere of 40% or 80% relative humidity, and their resistance are measured after the lapse of 3 and 6 months. Results are shown in TABLE 4B together with the initial values.

TABLE 4B

Relative Humidity	Initial value	After 3 months	After 6 months
40%	560 KΩ	550 KΩ	580 KΩ
80%	78 KΩ	79 KΩ	79 KΩ

As can be seen from the above examples, the present invention makes it possible to produce humidity sensitive ceramics with a desired change rate of resistance with change in humidity, by variation of the components and that of a compositional ratio of the semiconductive compound oxide to the compound oxide. In addition, the ceramics of the present invention is small in aging even if changes of humidity surroundings are repeated. Thus, the humidity sensitive ceramics of the present invention is useful as a material for humidity sensors, and the humidity sensors comprising the ceramics of the invention can be put into practical use without combining it with a heating element.

What we claim is:

1. A humidity sensitive ceramics comprising a sintered body consisting essentially of a semiconductive compound oxide with a perovskite structure and a compound oxide, said semiconductive compound oxide having a composition expressed by the general formula(I):

$$A_{1-x}A'_xBO_{3-\delta}\cdots \qquad (I)$$

wherein A is at least one element selected from the group consisting of rare earth elements with atomic numbers 57 to 71, yttrium and hafnium, A' is at least one element selected from the group consisting of alkaline-earth metals, B is at least one element selected from the group consisting of transition elements with atomic numbers 23 to 30, x is a mole fraction and takes a value of the following range, $0 \leqq x \leqq 1$, and δ is a non-stoichiometric parameter, said compound oxide having a composition expressed by the general formula(II):

$$AMO_3\ldots \qquad (II)$$

wherein A is at least one element selected from the group consisting of alkaline earth elements, Zn, Cd, Fe, Co, Ni, Mn and Pb, M is at least one element selected from the group consisting of Ti, Zr, Hf and Sn.

* * * * *

Observation of a reentrant superconducting resistive transition in granular $BaPb_{0.75}Bi_{0.25}O_3$ superconductor

85

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A normal-superconducting-normal transition has been observed resistively in the granular $BaPb_{0.75}Bi_{0.25}O_3$ compound, while the compound remains diamagnetic to the lowest temperature investigated. This has been attributed to the decoupling of the superconducting grains at low temperature caused by the reduction of charge carriers in the grain barriers, in good agreement with the theory.

Granular superconductors exhibit a wide range of electrical transport behavior which has made the study of this material a subject of great interest in the last few years, concerning the questions of electron-localization and electron-electron correlation. Prospects have subsequently been raised such as the possible existence, in this material, of reentrant superconductivity[1,2] in which the material undergoes a superconducting to normal transition on cooling and of a superconducting insulator[3] where superconductivity prevails in a localized electron system. In a granular superconductor, the superconducting grains are coated with an insulating layer or imbedded in an insulating matrix. When the separation between the superconducting grains is small and the Josephson coupling energy[4] is stronger than the Coulomb charging energy between the grains, the material becomes superconducting resistively at low temperature through Josephson tunneling between grains. Since the effective Josephson coupling and thus the critical current I_c of a granular superconductor is inversely proportional to the normal tunneling resistance,[5,6] to vary the normal tunneling resistance under proper conditions will be one of the most effective ways to control I_c. The increase of normal tunneling resistance of such a barrier at low temperature can result in a decoupling between the superconducting grains and thus the disruption of the superconducting current. A normal-superconducting-normal resistive transition may therefore be achievable.

The presence of semiconducting barriers in the perovskite-type compounds $BaPb_{1-x}Bi_xO_3$ has long been implied by the difficulty[7] in obtaining a bulk $BaPb_{1-x}Bi_xO_3$ superconductor. A sample of this kind may be considered as an array of series or parallel-series Josephson junctions.[8] Without questioning the occurrence of the high-temperature superconductivity in these compounds which is currently still under intense investigation, we have measured the resistance (R), the ac magnetic susceptibility (χ), and the current-voltage (I-V) characteristics of the sintered $BaPb_{0.75}Bi_{0.25}O_3$ compound as a function of temperature (T) at various magnetic field (H). Indeed, a normal-superconducting-normal resistive transition and a maximum I_c have been observed in this compound on cooling. Meanwhile, the χ results fail to show the return of the superconducting state to the normal state down to 1.2 K, the lowest temperature of the present study. The observations, therefore, demonstrate, for the first time, the existence of a reentrant superconducting resistive transition associated with the specific character of the tunneling barriers in a granular superconductor, instead with a ferromagnetic ordering. The nonmonotonic variation of I_c with T observed is in good agreement with the recent theoretical calculations[6] on the Josephson effect in a superconductor-semiconductor-superconductor junction.

The $BaPb_{0.75}Bi_{0.25}O_3$ compound was formed by first reacting a compacted mixture of appropriate amounts of $BaCO_3$, PbO_2, and Bi_2O_3 in an oxygen atmosphere at 800 °C for 24 h. The compacted disks of 4-mm diam × 6-mm thickness so obtained were then pulverized, compressed, and heated several times under the above conditions. Samples with dimensions of $\sim 1.5 \times 1.5 \times 6\ mm^3$ were sawed off the disks for the present study. Four Pt electrodes were attached to each sample with In ultrasonic solder, or silver paste for R measurements. Independent of the material used to mount the electrodes, the contact resistance of our samples always fell between 10 and 20 Ω at 300 K and between 20 and 40 Ω at 4.2 K. This poses a limit to our voltage resolution at about $\pm 0.5\ \mu V$. The four lead dc resistance technique and a standard ac inductance bridge operated at 26 Hz were employed for the R and χ measurements, respectively. The temperature above 20 K was determined by a chromel-alumel thermocouple and below by a Ge thermometer.

Within a resolution of $\sim 5\%$, the powder x-ray diffraction patterns of our $BaPb_{0.75}Bi_{0.25}O_3$ samples display only a single perovskite structure with the lattice parameters $a = 6.08 \pm 0.01$ Å and $c = 8.59 \pm 0.02$ Å. However, the scanning electron microscope results show $a \sim 20\%$ precipitation in a uniform matrix. The precipitation is in the form of spheres of diameters 1000–5000 Å evenly distributed in the matrix. Preliminary energy dispersive analysis of x ray indicates that the precipitation has a slightly higher Bi content but slightly lower Ba content than the matrix, while both materials have the same O and Pb contents. This is consistent with our powder x-ray data in view of the small variations of lattice parameters and structure with x in $BaPb_{1-x}Bi_xO_3$. Detailed analyses of the sample and the identification of the origin of superconductivity are underway and will be published later.

The typical T dependence of R, measured with different currents I's at different H's is shown in Fig. 1. The value of R at 300 K is 7 Ω corresponding to a resistivity of 1.05 Ω cm. R increases with decreasing T before the sample becomes superconducting at T_{c1}, as observed previously.[7] However, the sample returns to the normal state at a lower temperature T_{c2}. At 1.2 K, R reaches a value more than 100 times that above T_{c1}. Increase of I or H suppresses T_{c1}, enhances T_{c2}, and thus reduces the superconducting region. When I or H exceeds the critical value, the superconducting region is totally destroyed, leaving the sample behaving like a semiconductor. The superconducting state so observed resistively is also evident from the appearance of a supercurrent I_c shown in Fig. 2. I_c is always suppressed by H as expected but exhibits a maximum at ~6 K. The zero field I_c determined by both the dc and pulse methods is summarized as a function of T in Fig. 3. Independent of the method used, I_c peaks at ~6 K, demonstrating the effect is not caused by heating. The diffference between the values of the I_c's from different techniques is attributed to the flux motion. When either T or H is above its respective critical value, I_c is completely suppressed and a simple Ohmic I-V behavior results. On the other hand, accompanying with the above observations, χ shows only a simple superconducting transition near T_{c1} without any sign of reentrance as displayed in Fig. 1. Comparison of this superconducting χ signal with that of a Pb sets an upper limit of ~30% on the sample volume that is superconducting, qualitatively consistent with the scanning electron microscope results. Figure 4 displays the variation of V and χ with $I > I_c$. It is clear that the sample remains superconducting magnetically although it is already in the normal state resistively when $I_c < I < I_{cb}$, where I_{cb} represents the critical current of the "bulk" material as shown in the same figure. Heating effect above a few mA is evident from the difference between curves 2 and 2′ in Fig. 4.

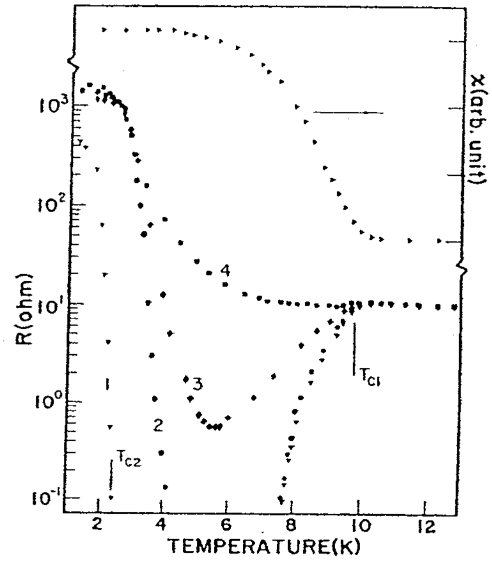

FIG. 1. T dependence of R and χ measured with different I's at different H's: (1) 11 μA, 0.5 G; (2) 72 μA, 0.5 G; (3) 94 μA, 2.0 G; (4) 72 μA, 216 G.

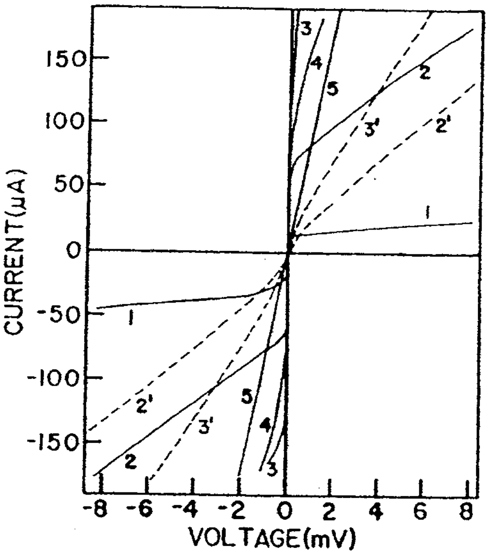

FIG. 2. I-V characteristics at different T's and H's: (1) 2.74 K, 0.5 G; (2) 4.30 K, 0.5 G; (2′) 4.30 K, 180 G; (3) 5.20 K, 0.5 G; (3′) 5.20 K, 100 G; (4) 6.90 K, 0.5 G; (5) 11.52 K > T_{c1}.

The results in Figs. 1 and 2 clearly demonstrate that a superconducting current path exists only for $T_{c2} < T < T_{c1}$ in our $BaPb_{0.75}Bi_{0.25}O_3$ samples, although the "bulk" (< 30%) of the sample remains superconducting below T_{c2}. The path becomes semiconducting when the superconducting path is interrupted below T_{c2}. This is further supported by the observation of a nonmonotonic variation of I_c with T shown in Fig. 3. The I-V characteristics in Fig. 4 show a Giaever type of tunneling when $I < I_{cb}$ and the existence of strongly T-

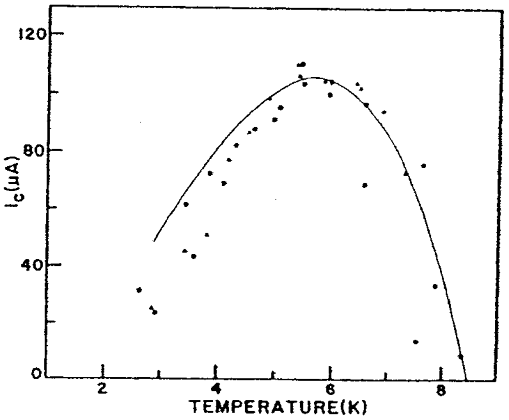

FIG. 3. T dependence of I_c: ■—determined by dc method; ▲—by 2.0-ms I pulse; ●—by 0.3-ms I pulse. The solid curve represents Eq. (1), with $I_{c0}=16.9\times10^2$ μA and $\gamma=0.823$.

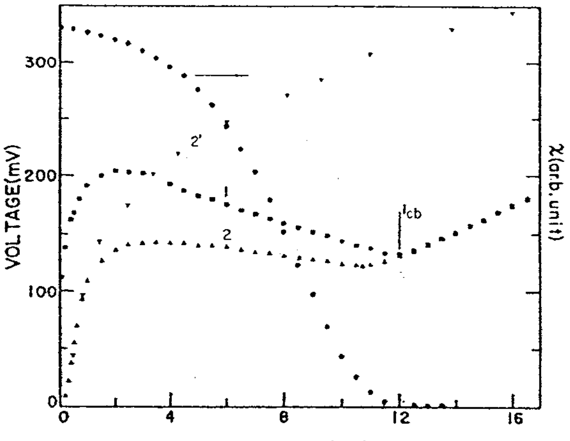

FIG. 4. I dependence of V and χ at different T's for $I > I_c$: (1) and (2) were determined by a dc method at 1.2 and 4.2 K, respectively, (2') by 0.3-ms pulse method at 4.2 K, and χ was measured at 4.2 K when a dc current was flowing through the sample.

dependent resistive layers between the superconducting grains. The large apparent gap of >100 mV stems from the many tunneling junctions in series. The observed reentrant superconductivity can then be understood in the following way: as T is reduced, superconductivity first appears in the material grains separated by semiconducting layers. Below T_{c1}, phase matching between grains is established through Josephson coupling, resulting in the appearance of a supercurrent. This is evident from the slightly lower onset T_c determined resistively than that determined magnetically. However, below T_{c2}, decoupling between the superconducting grains occurs when the Josephson energy reaches a certain critical value with respect to the Coulomb charging energy.[2] It should be noted that reentrant superconductivity in a dirty or thin-film homogeneous superconductor has been predicted[9] and just observed[10] in homogeneous Al thin films at a high magnetic field. In contrast to our observations, the superconducting state in these thin films is considered to be a gapless bulk state and the reentrance to result from the competition between the spin paramagnetic effect and the orbital depairing effect.

Recently, it has been shown[6] that for a superconductor-semiconductor-superconductor junction with a degenerate temperature of the semiconductor comparable to the junction temperature,

$$I_c = I_{c0}(T/T_c)^{5/2}(\Delta/T_c)^2[(\Delta/T_c)^2+(\pi T/T_c)^2]^{-1} \times\exp[-\gamma(T/T_c)^{1/2}] \ , \qquad (1)$$

where I_{c0} and γ are constants depending on the material characteristics of the superconductor and insulator of the junction, and Δ is the superconducting gap. The competition between the factor $T^{5/2}$ and the rest of the equation gives rise to a maximum I_c. Using $2\Delta(0)/T_c \sim 3.5$ and the $\Delta(T)$ from the BCS calculation, an $I_c - T$ curve was obtained and shown in Fig. 3 by choosing $I_{c0} = 16.9\times 10^2$ μA and $\gamma = 0.823$. The agreement is good in view of the scattering of the data. Although the BCS-Δ has been shown to be slightly and consistently overestimated[8] for this compound for $T/T_c \gtrsim 0.75$, such a Δ correction is expected to vary I_{c0} and γ only slightly. The physical significance of the values of I_{c0} and γ so obtained are being examined together with the detailed characteristics of the compound. Although the theory was developed for a simple tunneling junction with a single T_c, the agreement between the theory and experiment, where many junctions with a distribution of T_c exist, is expected: As far as I_c is concerned, an array of tunneling junctions may be replaced by an equivalent junction whose T_c is dictated by the lowest T_c of the original junctions when in series or the highest T_c when in parallel, provided proper phase interference is taken into consideration.

In conclusion, we have observed a reentrant superconducting transition resistively in the sintered $BaPb_{0.75}Bi_{0.25}O_3$ samples. On the contrary, the samples remain superconducting magnetically down to the lowest temperature of the present study. Therefore the observation has been attributed to the decoupling between superconducting grains at low temperature, in good agreement with recent theoretical predictions. Preliminary data also indicate that the observation of a reentrant superconducting resistive transition in a granular superconductor depends not only on the physical characteristics of the barriers but also crucially on the distribution of the superconducting grains. However, reentrant superconductivity of this kind should be common in other granular superconducting systems[11] with proper barrier characteristics. The present observations should provide important insight to the study of this class of material in general.

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United States Patent [19]
Beyerlein et al.

[11] **Patent Number:** **4,482,644**
[45] **Date of Patent:** **Nov. 13, 1984**

[54] OXYGEN-DEFICIENT, BARIUM-CONTAINING PEROVSKITES

[75] Inventors: **Robert A. Beyerlein**, Westfield; **Allan J. Jacobson**, Princeton; **Kenneth R. Poeppelmeier**, Flemington, all of N.J.

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[21] Appl. No.: **485,708**

[22] Filed: **Apr. 18, 1983**

[51] **Int. Cl.**^{3} **B01J 23/02**; B01J 23/10; B01J 23/18

[52] **U.S. Cl.** **502/303**; 502/302; 502/304; 502/328; 502/340; 502/341; 502/343; 502/525

[58] **Field of Search** 502/302, 303, 304, 328, 502/340, 341, 343, 525; 423/593

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Primary Examiner—W. J. Shine
Attorney, Agent, or Firm—Janet E. Hasak; Henry E. Naylor

[57] ABSTRACT

A class of oxygen-deficient, barium-containing compounds having a perovskite-type structure may be prepared which are of the formula:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

if M is a trivalent cation, or

$$Ba_3M_aM'_{3-a}O_{[7.5-(a/2)+y]}$$

if M is a divalent cation, wherein M is Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanides of atomic number 58 or greater, Ni, Fe, Cu,Al, Ga, In, Zn, Cd, Hg, Bi, Tl or a mixture thereof, M' is Sb or Bi, a is equal to or greater than O but less than or equal to 1, and if M is trivalent, y is equal to or greater than 0 but less than 1, and if M is divalent, y is equal to or greater than O but less than (3+a)/2.

Preferably, the compounds herein are of the formula:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

where M is La or Sc, a is equal to or greater than O but less than or equal to 1 and y is equal to or greater than O but less than 1.

This class of compounds are readily reoxidized and therefore are useful in oxidative dehydrogenation reactions.

20 Claims, 2 Drawing Figures

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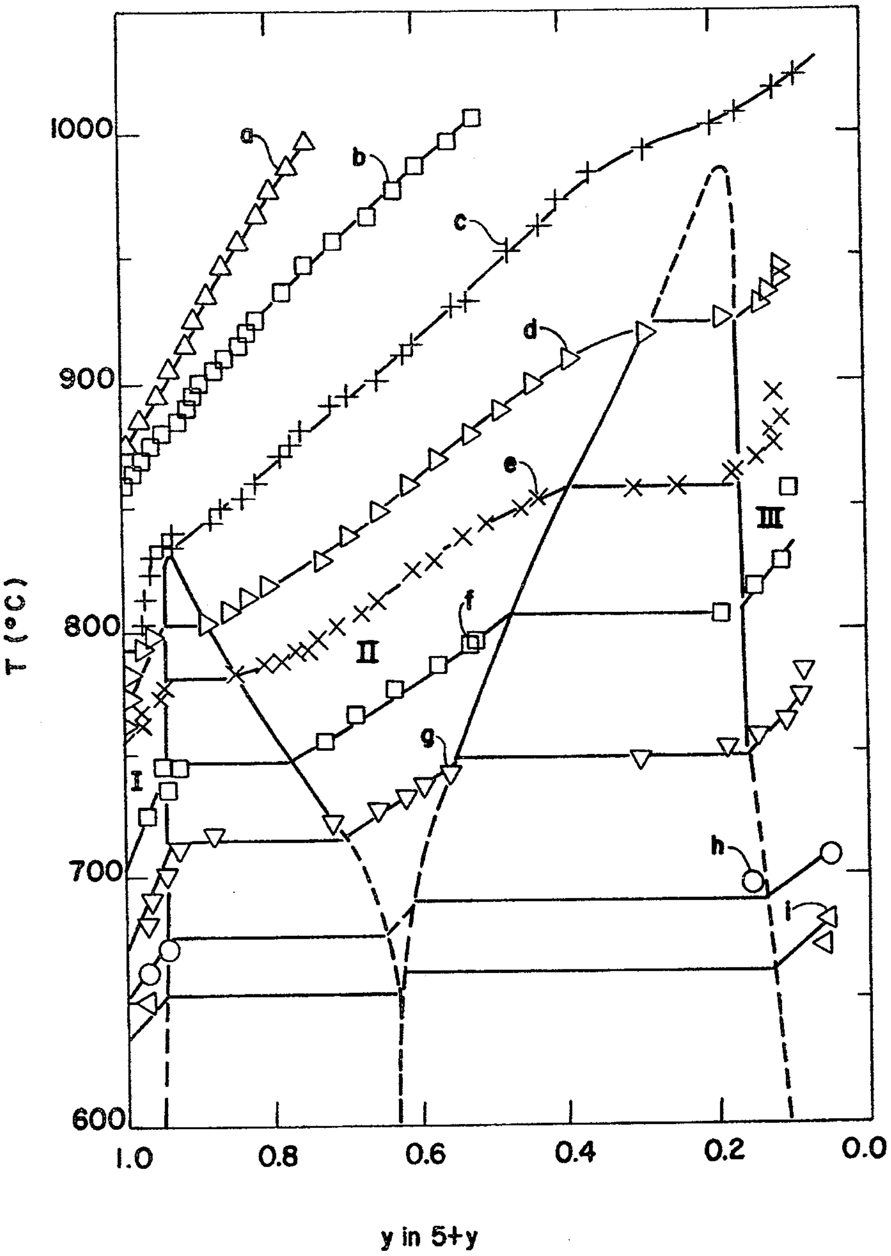
T (°C)
1000
900
800
700
600
1.0
0.8
0.6
0.4
0.2
0.0
y in 5+y
a
b
c
d
e
f
g
h
i
I
II
III

FIG. 1

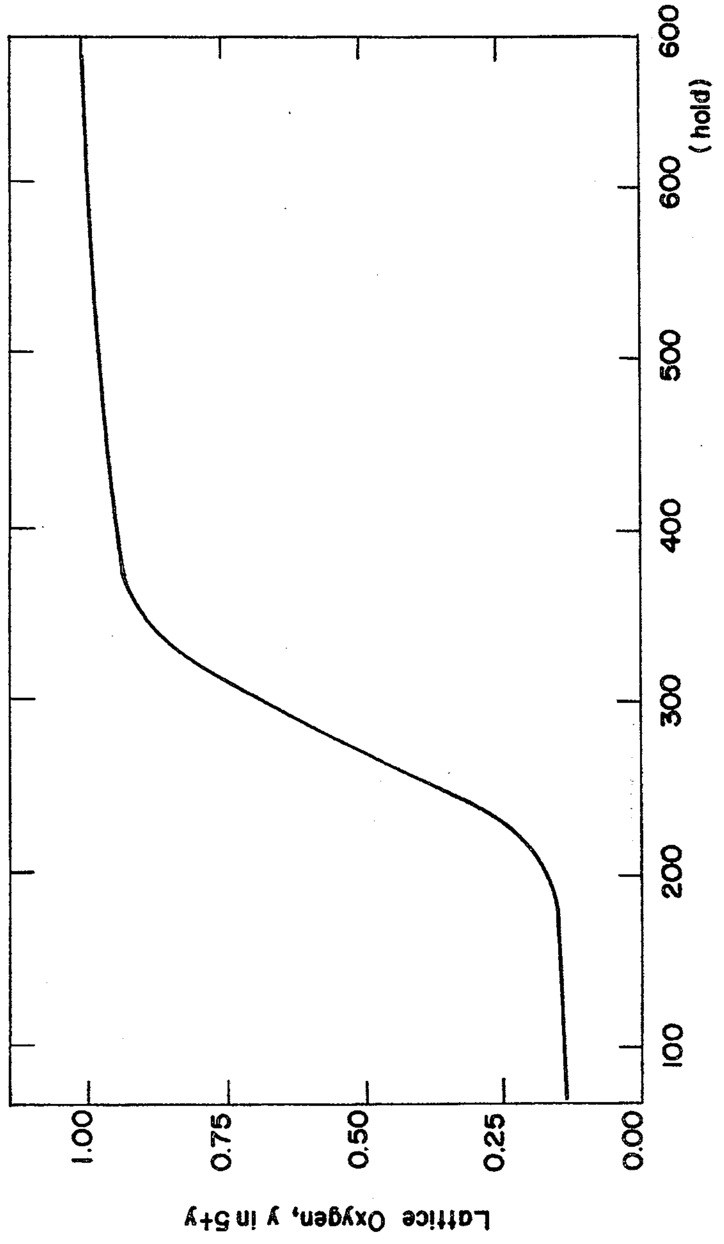
Lattice Oxygen, y in 5+y
1.00
0.75
0.50
0.25
0.00
T (°C)
100
200
300
400
500
600
600 (hold)

FIG. 2

OXYGEN-DEFICIENT, BARIUM-CONTAINING PEROVSKITES

BACKGROUND OF THE INVENTION

This invention is related to a class of novel oxygen-deficient, barium-containing compounds having a perovskite-type structure and to a process for the preparation thereof. Preferably, the compounds also contain bismuth.

DESCRIPTION OF RELATED DISCLOSURES

During a typical petroleum refining operation large quantities of low molecular weight paraffins and olefins are produced. Unlike paraffins which may be sold at relatively low cost for fuels, olefins have undesirable combustion properties which hamper their potential use as fuels. Thus, much research effort has been directed toward upgrading the olefins, either for use as fuel or as chemical intermediates in the chemicals industry. For those olefins containing three to four carbon atoms, much research effort has been directed toward reaction products such as dimers and aromatic products having greater potential value, with bismuth oxide representing a conventional oxidation catalyst particularly for producing dimers.

Oxidative conversions of unsaturated hydrocarbons have recently been conducted using various catalyst combinations. A recently published comprehensive review article on oxidative dehydrogenation of olefins is E. A. Mamedov, *Russ. Chem. Reviews,* 50, 291 (1981), which lists numerous references disclosing use of catalysts containing bismuth oxide in combination with other elements to convert olefins to dienes and aromatic products in the presence or absence of molecular oxygen.

U.S. Pat. No. 4,110,258 to Lauder discloses perovskites of the form $BaBO_3$ which may include Bi or mixtures of Bi and La on the B site but require 1 to 20% of the B site to be occupied by a Pt group metal for use as exhaust gas clean-up catalysts in the conversion of NO_x, CO and hydrocarbons to N_2, CO_2 and H_2O. U.S. Pat. No. 3,730,957 to Bozik et al. discloses use of bismuth-containing catalysts for use in oxidative dehydrodimerization.

SUMMARY OF THE INVENTION

There is provided herein a novel class of oxygen-deficient, barium-containing compounds having a perovskite-type structure of the formula:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

if M is a trivalent cation, or

$$Ba_3M_aM'_{3-a}O_{[7.5-(a/2)+y]}$$

if M is a divalent cation, wherein M is selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanides of atomic number 58 or greater, Ni, Fe, Cu, Al, Ga, In Zn, Cd, Hg, Bi, Tl and a mixture thereof, M' is selected from the group consisting of Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and if M is a trivalent cation, y is equal to or greater than 0 but less than 1, and if M is a divalent cation, y is equal to or greater than 0 but less than (3+a)/2. Preferably, M' is Bi and a is 0, or if a is greater than 0, M is Sc or La. Most preferably, the compounds herein are oxygen-deficient, barium- and bismuth-containing compounds having a perovskite-type structure of the formula:

$$Ba_2M_aBi_{2-a}O_{5+y}$$

where M is La or Sc, a is defined above and y is equal to or greater than 0 but less than 1. If a in the above formula is greater than 0 and M is La, y is preferably less than or equal to 0.1.

The above class of compounds may be prepared by heating the fully oxidized precursor compound (wherein in the above formulae y is about but no greater than 1 if M is trivalent and y is about but no greater than (3+a)/2 is M is divalent) in the presence of an effective amount of oxygen at a temperature of at least about 600° C., depending on the particular precursor compound and the amount of oxygen present, for a sufficient period of time to produce the oxygen-deficient compound (where y is less than 1 if M is trivalent and y is less than (3+a)/2 if M is divalent).

The class of oxygen-deficient compounds herein are readily reoxidized and therefore may be used in oxidative dehydrogenation reactions or in similar processes requiring solid oxidizing agents. In particular, the compounds herein (and their fully oxidized precursors) may be used as catalysts in selectively producing aromatic products or dimers fom acyclic olefins, preferably propylene or isobutylene, as described in U.S. Patent Application Ser. Nos. 485,706 and 485,707, respectively filed of even date with this application, both now abandoned with applicants K. Poeppelmeier and J. Longo, the disclosures of which applications are incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents a phase diagram for synthesis of $Ba_2Bi_2O_{5+y}$ which is a plot of the temperature used for the synthesis versus the extent of oxygen deficiency in $Ba_2Bi_2O_{5+y}$ (the value of y) for nine given partial pressures of oxygen.

FIG. 2 represents a thermogravimetric record of $Ba_2La_{0.5}Bi_{1.5}O_{5+y}$, where y is about 0.14, reoxidized to $Ba_2La_{0.5}Bi_{1.5}O_6$ in the presence of oxygen to 600° C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The class of oxygen-deficient compounds herein have the perovskite-type structure as described in A. F. Wells, *Structural Inorganic Chemistry,* 4th ed., Ch. 4 (Clarendon Press, 1975).

The compounds herein have a composition of one of the formulae:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

if M is trivalent, or

$$Ba_3M_aM'_{3-a}O_{[7.5-(a/2)+y]}$$

if M is divalent, wherein M is selected from Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanides of atomic number 58 or greater, Ni, Fe, Cu, Al, Ga, In, Zn, Cd, Hg, Bi or Tl, M' is either Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and, if M is a trivalent cation, y is equal to or greater than 0 but less than 1, and, if M is a divalent cation, y is equal to or greater than 0 but less than (3+a)/2. The precise value of y is the amount necessary to satisfy the valence of M'. The lanthanides of atomic number of at least 58 consist of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tkm, Yb and Lu. Preferably, M′ is Bi and a is 0 or M′ is Bi, a is greater than 0, and M is La or Sc. Examples of suitable compounds for this purpose include $Ba_3MgBi_2O_{7+y}$, $Ba_3CaBi_2O_{7+y}$, $Ba_3SrBi_2O_{7+y}$, $Ba_3BaBi_2O_{7+y}$, Ba_2ScBiO_{5+y}, Ba_2YBiO_{5+y}, Ba_2LaBiO_{5+y}, $Ba_2La_{0.5}Bi_{1.5}O_{5+y}$, Ba_2CeBiO_{5+y}, Ba_2PrBiO_{5+y}, Ba_2NdBiO_{5+y}, Ba_2DyBiO_{5+y}, Ba_2AlBiO_{5+y}, $Ba_2GaKBiO_{5+y}$, Ba_2InBiO_{5+y}, Ba_2TlBiO_{5+y}, $Ba_{2l\,BiBI}O_{5+y}$, $Ba_3NiBI_2O_{7+y}$, Ba_2FeBiO_{5+y}, $Ba_3CuBi_2O_{7+y}$, $Ba_3ZnBi_2O_{7+y}$, $Ba_3CdBi_2O_{7+y}$, $Ba_3HgBi_2O_{7+y}$, and the like.

In the above formulae, the word "divalent" signifies that the metal M is contained in the oxide in an oxidation state of +2, and the word "trivalent" signifies that the metal M is contained in the oxide in an oxidation state of +3.

It is noted that the compositions of this invention having the above general formulae may comprise more than one phase having the overall composition described above. One preferred class of compounds herein are those of the formula:

$$Ba_2La_aBi_{2-a}O_{5+y}$$

where a is from 0 to 1 and y is equal to or greater than 0 but less than 1. These preferred compounds, many of which have been characterized by x-ray diffraction, generally comprise one phase. If the compounds of this preferred class do not contain lanthanum (i.e., a is 0), y preferably ranges from about 0 to about 0.6 and more preferably is about 0.6 or about 0 (i.e., ranges from 0 to 0.2). If the compound contains lanthanum (i.e., a is greater than 0), y preferably is less than or equal to 0.1, and more preferably y is 0 and a is 0.5.

The fully oxidized precursor compounds to be used as starting materials in preparing the novel compositions of this invention are of the formula:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

if M is trivalent, or

$$Ba_3M_aM'_{3-a}O_{[7.5-(a/2)+y]}$$

if M is divalent, wherein M, M′, and a are defined above, y is about 1 but not greater than 1 if M is trivalent, and y is about (3+a)/2 but not greater than (3+a)/2 if M is divalent. These precursors may be prepared by any convenient means known to those skilled in the art. A typical procedure involves preparing a physical mixture by grinding stoichiometric amounts of barium carbonate or nitrate with salts or oxides of the other two metal components, heating the mixture to about 350°-450° C., preferably to about 400° C., cooling and regrinding the resultant mixture in air, and heating the ground, cooled mixture to about 700° to 1000° C. for about three to seventy hours, depending on other conditions, in a furnace. Product formation is monitored via X-ray diffraction measurements. The products have structures related to the perovskite structure with pseudo-cubic unit cells of about 4.3 Å, depending slightly on the ionic radii of M.

For the investigations and experiments herein disclosed for preparing the preferred class of bismuth-containing or bismuth- and lanthanum-containing precursors, a mixture may be formed containing barium nitrate and bismuth nitrate pentahydrate and, if a is greater than 0, also containing lanthanum oxide. In this technique the nitrates (and oxide, if applicable) in the appropriate amounts are oxidatively decomposed in air at about 400° C. for 2-3 hours in a Lindberg furnace followed by successive regrinding and refiring to 800° C. for a period of 3 to 70 hours until no unreacted nitrate can be detected in either the x-ray powder diffraction patterns or the infrared spectra of the oxygenated precursor compound product.

For the lanthanum-containing materials with a greater than zero, a smooth and essentally linear increase in lattice parameter with increasing lanthanum content is observed. Thus, as a is increased from zero to one, the lattice parameter of the fully oxidized precursor compounds increases smoothly from $a_o=8.71(1)$Å ($a=0$, $Ba_2Bi_2O_6$) to $a_o=8.77(1)$ Å ($a=1$, Ba_2LaBiO_6). Because the two end members, $Ba_2Bi_2O_6$ and Ba_2LaBiO_6, are known to have $y=1$ in the above formulae as discussed by G. Thornton and A. J. Jacobson, *Acta. Cryst.* B34, 351-354 (1978) and V. R. Scholder, et al., *Zeitschrift fur Anorganische und Allgemeine Chemie,* 319, 375-386 (1963), it follows that each of the oxidized precursor compounds with values of a intermediate between zero and one have $y=1$, and their compositions may be written as $Ba_2La_aBi_{2-a}O_6$.

Once the precursor compound is obtained it is heated in a suitable reactor, preferably a Linberg tube furnace, in the presence of an amount of oxygen effective for a particular temperature to obtain an oxygen-deficient compound. The amount of oxygen which is effective will depend mainly on the type of precursor compound employed, the temperature at which the precursor is being heated, and the length of time for which the precursor is heated. Typically the heating will take place under a flow of a mixture of oxygen gas and an inert gas such as helium or argon at a flow rate of about 100 to 500 cm³/minute. Higher or lower flow rates may be employed depending mainly on the amount of precursor sample and the size of the reactor tube.

The temperature at which the precursor compound is heated is likewise dependent on many factors such as the type or precursor compound and the amount of oxygen present. At minimum, the temperature should be about 600° C., but preferably the temperature is higher, and more preferably is 600° to 1000° C. The time for heating will similarly depend on several factors such as the precursor, temperature and oxygen partial pressure. When the class of compounds is $Ba_2M_aBi_{2-a}O_{5+y}$ where M is trivalent, the interrelationships among the amount of oxygen, the temperature and the time employed can be expressed as follows, as demonstrated by the preferred class of compounds where M is lathanum: When the temperature is decreased, a lower oxygen pressure is required to obtain the product. As the value of a in the compound is increased, the temperature must be increased and/or the oxygen partial pressure must be decreased and the time for heating must be increased to obtain the reduced product. Even when these parameters are adjusted, however, if a in the formulae is increased beyond about 0.7 the product obtained on cooling will generally not be a single-phase material but rather will comprise two phases which may be a mixture of the fully oxidized material ($y=1$) and the fully reduced material ($y=0$). If the precursor compound is such that a is 0.5, when the compound is heated at about 600° to 1000° C. the oxygen partial pressure will be between about 0.001 and 0.000002 atm, depending on the temperature. The preferred temperature range of heating for $a=0.5$ is 800° to 1000° C. and most preferred is 950° to 1000° C. When a temperature of 1000° C. is employed for $a=0.5$ the oxygen partial pressure must be about 0.001 atm to obtain the product, whereas if the temperature is 950° C., the oxygen partial pressure is about 0.0001 atm and the time is at least 8 hours, preferably 10 to 12 hours. When a is increased to about 0.65 or greater, the preferred temperature is 900° to 1000° C. and the preferred oxygen partial pressure is from 0.001 to 0.000002 atm, and the reaction must be carried out for a longer period of time.

The composition range for the class of bismuth-containing compounds of the formula $Ba_2Bi_2O_{5+y}$ (where a in the general formula is 0) and the conditions for the synthesis of these compounds are summarized in the phase diagram depicted in FIG. 1. In this figure the temperature of heating is plotted against the y value in $Ba_2Bi_2O_{5+y}$ for nine fixed oxygen partial pressures in the range from 0.0001 to 1.00 atm. Each of the nine families of points, designated a through i, represents measurements at a fixed oxygen partial pressure. Thus, for plot a, represented by upright triangles (pointing upward), the oxygen partial pressure was 1.0 atm; for plot b, represented by squares, the oxygen partial pressure was 0.35 atm; for plot c, represented by plus signs, the oxygen partial pressure was 0.10 atm; for plot d, represented by triangles pointing to the right, the oxygen partial pressure was 0.03 atm; for plot e, represented by cross signs, the oxygen partial pressure was 0.010 atm; for plot f, represented by squares, the oxygen partial pressure was 0.0032 atm; for plot g, represented by triangles pointing downward, the oxygen partial pressure was 0.0010 atm; for plot h, represented by circles, the oxygen partial pressure was 0.00032 atm; and for plot i, represented by triangles pointing to the left, the oxygen partial pressure was 0.00010 atm. The lines connecting the points in the plots are drawn to aid the eye. Phase boundaries are dashed in regions where there is some uncertainty.

This diagram (FIG. 1) shows that for a fixed oxygen partial pressure of 0.0032 atm, three single-phase regions (designated I to III), each with variable oxygen stoichiometry, are encountered as the temperature is raised from 725° to 850° C. In phase region I where y is from 1.0 to 0.94, there is a narrow range of variable stoichiometry. In the single-phase regions II and III the oxygen stoichiometry ranges are: y from0.77 to 0.47 and y from 0.16 to 0.10, respectively.

The oxygen-deficient compounds herein can be easily reoxidized in the presence of oxygen or air. This reoxidation is very rapid in air at temperatures as low as 300° C. The thermogravimetric record of $Ba_2La_{0.5}Bi_{1.5}O_{5+y}$ (where y is about 0.14) in oxygen given in FIG. 2 shows that oxidation begins at temperatures above 200° C. and is very rapid at 300° C.

Tables I-VIII list all of the observed x-ray diffraction data for several compounds from the preferred class of compounds ($Ba_2La_aBi_{2-a}O_{5+y}$) over the angular range $10° < 2\theta < 83°$. For the oxidized precursors, the x-ray diffraction patterns can be roughly indexed on the basis of a pseudocubic lattice parameter $a_o=2a_c$. Here a_c is the simple cubic distance characteristic of the Bi-O-Bi, Bi-O-La, or La-O-La arrays and varies from $a_c=4.355(5)$ Å for $Ba_2Bi_2O_6$ with $a=0$ to $a_c=4.385(5)$ Å for the lanthanum-containing material with $a=1$. With the exception of certain of the materials for which $a=0$, all of the oxygen-deficient materials can be indexed on the basis of similar distortions of the simple cubic distance a_c. The cell volume expands as oxygen is lost from the lattice so that for the lanthanum-containing oxygen-deficient materials with $a>0$ and $y=0$, $a_c \simeq 4.50$ Å and the pseudocubic lattice parameter $a_o=2a_c$. For the material containing no lanthanum with $a=0$ and $y=0.1$, there is a pronounced tetragonal distortion so that $(a_t+b_t)/2 \simeq 2\ a_c$ where $a_c \simeq 4.44$ Å and a_t and b_t are the new tetragonal lattice parameters.

The invention is further explicated by the examples which follow. In all examples, the parts and percentages are by weight and the temperatures are in degrees Celsius unless otherwise noted.

EXAMPLE 1

Preparation of $Ba_2Bi_2O_{5.0}$

$Ba_2Bi_2O_6$ was prepared by heating a mixture of 12.000 g $Ba(NO_3)_2$ and 22.269 g $Bi(NO_3)_3.5H_2O$ in air at 400° C. for 2 hours followed by regrinding and refiring at 800° C. for 1 hr., and finally regrinding and refiring at 800° C. for 1 day. About 2 g of this material was heated to 800° C. in a Lindberg tube furnace in an oxygen-argon mixture containing 100 ppm oxygen (0.0001 atm oxygen) flowing at 300 cm³/min. The furnace was maintained at 800° C. for 2.5 hours after which the heating was discontinued and the sample was cooled in the same gas mixture. The sample was magenta in color when removed from the furnace at ambient temperature. It was necessary to store the sample in a moisture-free, inert gas atmosphere to maintain its integrity. An x-ray powder diffraction pattern of this single-phase material was recorded with a diffractometer using CuK_α radiation and the data is recorded in Table I. The pseudo-cubic lattice parameter of this perovskite-related structure is $a_o=8.89(2)$Å. Thermogravimetric oxidation in pure oxygen to 600° C. of the sample revealed its oxide stoichiometry as $Ba_2Bi_2O_{5.0\pm0.02}$.

TABLE I

X-Ray Powder Diffraction Data For $Ba_2Bi_2O_{5.0}$

peak no.	hkl[a]	$d_{observed}$ (Å)	Intensity[b]
1		5.41	w−
2	111	5.12	w−
3		4.70	w+
4		4.37	w+
5		3.92	w
6		3.54	w
7		3.46	w−
8		3.29	w
9	220	3.15	s++
10		3.11	m+
11		2.75	w
12		2.61	w−
13		2.50	w−
14	400	2.258	w
15		2.226	m+
16		2.213	m+
17		2.190	w+
18		2.04	w−
19		1.89	w−
20	422	1.818	s
21		1.813	s+
22	440	1.570	m
23		1.554	w
24	620	1.407	m−
25		1.400	w+
26	444	1.283	w

TABLE I-continued

X-Ray Powder Diffraction Data For $Ba_2Bi_2O_{5.0}$			
peak no.	hkl[a]	$d_{observed}$ (Å)	Intensity[b]
27	642	1.189	m

[a] Indexing was done on basis of a pseudocubic cell with a_o = 8.89 Å.
[b] w = weak, m = medium, s = strong

EXAMPLE 2

Preparation of $Ba_2Bi_2O_{5.1}$ (tetragonal form)

$Ba_2Bi_2O_6$ was prepared as described in Example 1. About 2 g of this material was heated for three hours at 765° C. in a stream of argon and oxygen containing 1000 ppm oxygen (0.001 atm oxygen) and thereafter cooling the product in a stream of oxygen and argon containing 100 ppm oxygen (0.0001 atm). The resulting material, black in color, displayed an x-ray diffraction pattern showing a single-phase perovskite-like structure with a pronounced tetragonal distortion with a_{tetr}=8.784(5)Å and c_{tetr}=8.977(5)Å, as indicated in Table II. Thermogravimetric reoxidation of this material in oxygen to 600° C. showed an oxygen stoichiometry of $Ba_2Bi_2O_{5.10}$±0.04. The product of this reoxidation was $Ba_2Bi_2O_6$.

TABLE II

x-Ray Powder Diffraction Pattern for $Ba_2Bi_2O_{5.1}$, tetragonal form				
Peak No.	hkl	d-value (observed) (Å)	d-value[a] (calc.) (Å)	Intensity[b]
1a	111	5.121	5.108	w
1b		5.051	5.108	w
2	200	4.367	4.392	m
3	102	4.042	3.997	w
4a,	20 3/2	3.500	3.541	w
b	"	3.536	"	"
5	21 3/2	3.279	3.284	w−
6	202	3.139	3.139	s++
7	220	3.104	3.106	s+
8	103	2.821	2.832	w
9	311	2.646	2.654	w−
10	004	2.244	2.244	m
11	400	2.197	2.196	s
12	303	2.090	2.093	w−
13	331	2.014	2.017	w−
14	420	1.960	1.964	w
15	412	1.930	1.925	w−
16	421	1.915	1.919	w−
17	224	1.819	1.819	m+
18	422	1.799	1.799	s+
19	511	1.692	1.692	w−
20	404	1.570	1.570	m−
21	440	1.552	1.553	w+
22	433	1.515	1.515	w−−
"	503	"	"	"
23	601	1.444	1.444	w−
"	610	"	"	"
24	206	1.416	1.416	w+
25	602, 405	1.390	1.390	m−
"	620	"	"	"
26	444	1.277	1.277	w+
27	426	1.191	1.190	w+
28a	624	1.181	1.181	w+
28b	642	1.177	1.176	w+

[a] calculated d-values were determined using $a_t = b_t$ = 8.784 Å, c_t = 8.977 Å
[b] w = weak, m = medium, s = strong

EXAMPLE 3

Prepartion of $Ba_2Bi_2O_{5.1}$ (low symmetry form)

A 2 g sample of $Ba_2Bi_2O_{5.1}$ prepared as described in Example 2 was heated for three hours at 770° C. in a stream of argon and oxygen containing 1000 ppm oxygen (0.001 atm oxygen). Thereafter, the product was cooled in a stream of pure argon. The resulting material was bright yellow and showed an x-ray diffraction pattern which could not be indexed on the basis of a pseudocubic perovskite. The observed d-values for this "low symmetry" $Ba_2Bi_2O_{5.1}$ given in Table III show that this material contains no BaO or Bi_2O_3. Thermogravimetric reoxidation of this material in oxygen showed an oxygen stoichiometry of $Ba_2Bi_2O_{5.06}$±0.04. The product of this reoxidation was $Ba_2Bi_2O_6$.

EXAMPLE 4

Preparation of $Ba_2Bi_2O_{5.6}$

A 2 g sample of $Ba_2Bi_2O_6$ prepared as described in Example 1 was heated for 58 hours at 715° C. in a stream of oxygen and argon containing 1000 ppm O_2 (0.001 atm O_2). The sample was cooled in the same atmosphere. The resulting material was dark brown and showed a perovskite-related x-ray diffraction pattern. The observed d-values and intensities are given in Table IV. The weak line at 3.15 Å is at the position of the strongest line of $Ba_2Bi_2O_{5.1}$ of Example 2 and may indicate the presence of a trace amount of this phase. Thermogravimetric reoxidaton in oxygen to 600° C. showed an oxygen stoichiometry of $Ba_2Bi_2O_{5.62}$±0.04. The product of this reoxidation was $Ba_2Bi_2O_6$.

TABLE III

x-Ray Powder Diffraction Pattern for $Ba_2Bi_2O_{5.1}$, low symmetry form					
Peak No.	d-value (observed) (Å)	Intensity[a]	Peak No.	d-value (observed) (Å)	Intensity[a]
1	7.25	w	21	2.304	w−−
2	5.249	m−	22	2.260	w+
3	4.189	w	23	2.179	w
4	3.797	w+	24	2.074	s− (2 peaks)
5	3.627	w−	25	2.049	w−
6	3.363	w−−	26	2.013	w+
7	3.267	s	27	1.944	w−
8	3.202	s++	28	1.908	w−
9	3.154	w−	29	1.896	w+
10	3.057	s+	30	1.826	w+
11	2.990	s	31	1.810	m−
12	2.940	w−−	32	1.783	m−
13	2.842	w+	33	1.768	m−
14	2.741	w	34	1.733	w−
15	2.707	s	35	1.704	w−
16	2.626	w	36	1.675	w+
17	2.515	w−	37	1.666	w
18	2.384	m	38	1.638	m−
19	2.352	w	39	1.603	w++
20	2.323	w	40	1.574	w−

[a] w = weak, m = medium, s = strong

TABLE IV

x-Ray Powder Diffraction Data for $Ba_2Bi_2O_{5.6}$					
Peak No.	d-value (observed) (Å)	Intensity[a]	Peak No.	d-value (observed) (Å)	Intensity[a]
1	7.47	w−	21	1.824	w
2	4.54	w−	22	1.795	w
3	4.34	w+	23	1.778	m
4	4.21	w	24	1.772	m+
5	3.58	w−	25	1.718	w+
6	3.48	w	26	1.674	w
7	3.148	w	27	1.651	w−
8	3.063	s++	28	1.546	w+
9a	2.940	w	29	1.536	m−
9b	2.919	w+	30	1.510	w−
10	2.658	w	31	1.453	w
11	2.629	w	32	1.427	w
12	2.398	w	33a	1.382	w+

TABLE IV-continued

x-Ray Powder Diffraction Data for $Ba_2Bi_2O_{5.6}$

Peak No.	d-value (observed) (Å)	Intensity[a]	Peak No.	d-value (observed) (Å)	Intensity[a]
13	2.275	w+	33b	1.378	m−
14	2.216	w−	33c	1.375	m−
15	2.176	m	33d	1.372	w+
16	2.108	w+	34	1.317	w−
17	2.002	w−	35a	1.260	w
18	1.941	w+	35b	1.258	w
19	1.914	w−	36	1.254	w
20	1.854	w−	37	1.207	w−
			38	1.161	m

[a] w = weak, m = medium, s = strong

EXAMPLE 5

Preparation of $Ba_2La_{0.5}Bi_{1.5}Bi_{1.5}O_{5+y}$

A mixture of 12,000 g of $Ba(NO_3)_2$, 16.701 g of $Bi(NO_3)_3.5H_2O$, and 1.870 g of La_2O_3 was heated in air to 400° C. for two hours. The sample was reground and fired at 800° C. in air for 1 hour followed by regrinding and refiring at 800° C. for 60 to 70 hours. The resulting material was determined by X-ray diffraction to be a pseudocubic perovskite material which could be roughly indexed using a lattice parameter $a_o=8.74(1)$ Å. Comparison with the lattice parameters for $Ba_2Bi_2O_6$ and Ba_2LaBiO_6 shows that the correct oxygen composition for this material is specified by $Ba_2La_{0.5}Bi_{1.5}O_6$.

About 2 g of this composition was placed in an alumina boat in a Lindberg tube furnace under a gas stream of oxygen and argon containing 100 ppm oxygen (0.0001 atm partial pressure oxygen) flowing at 300 cm^3/min. Separate thermogravimetric measurements showed that this material began to lose oxygen at 730° C. under these conditions and reached an approximate composition of $Ba_2La_{0.5}Bi_{1.5}O_{5.0}$ after being heated at 950° C. for 12 to 24 hours. The reduced material obtained after heating for 14 hours at 950° C. under the conditions described above in this example was bright yellow. Thermogravimetric reoxidation of this material in pure oxygen to 600° C. showed that the oxygen stoichiometry of the reduced material was $Ba_2La_{0.5}Bi_{1.5}O_{5.05}$. X-ray diffraction analysis indicated that the product of this reoxidation was the starting material previously identified as $Ba_2La_{0.5}Bi_{1.5}O_6$.

The X-ray diffraction pattern of the oxygen-deficient material, indicated in Table V, shows its structure to be a pseudocubic perovskite with a_0 (reduced)=8.94 (1) Å. Additional investigations revealed that the diffraction pattern for the intermediate compositions where x is between 0 and 1 showed a two-phase mixture of $Ba_2La_{0.5}Bi_{1.5}O_6$ and $Ba_2La_{0.5}Bi_{1.5}O_5$.

TABLE V

X-ray Powder Diffraction Data for $Ba_2La_{0.5}Bi_{1.5}O_{5.05}$

Peak No.	hkl[a]	$d_{observed}$ (Å)	Intensity[b]
1	111	5.13	w−
2		4.89	w
3		4.72	w+
4	210	3.99	w
5		3.87	w
6		3.43	w
7		3.31	w
8	220	3.16	s+
9	300, 221	2.98	w−
10	310	2.82	w
11	400	2.246	s−
12		2.233	
13		2.139	w
14	330, 411	2.099	w
15		2.077	w
16	422	1.829	s−
17		1.825	
18	440	1.584	m
19		1.576	
20	620	1.421	m
21		1.414	
22	444	1.291	w+
23	642	1.197	m

[a] Indexing was done on the basis of a cubic cell with $a_o = 8.94(1)$ Å

[b] w = weak, m = medium, s = strong

EXAMPLE 6

Preparation of $Ba_2La_{0.8}Bi_{1.2}O_{5+y}$

A mixture of 3.0 g $Ba(NO_3)_2$, 3.340 g $Bi(NO_3)_3.5H_2O$ and 0.748 g La_2O_3 was heated and ground as described in Example 5 above. The product was found to be a pseudocubic perovskite material with a lattice parameter consistent with the composition $Ba_2La_{0.8}Bi_{1.2}O_6$. Thermogravimetric measurements in 0.0001 atm partial pressure oxygen showed that this material began to lose oxygen at 850° C. These investigations further showed that, at a temperature of 950° C., $y \simeq 0.74$ upon achieving equilibrium after about 20 hours. The material obtained was found to be rust colored.

EXAMPLE 7

Preparation of $Ba_2La_{0.75}Bi_{1.25}O_{5+y}$

A mixture of 6.0 g $Ba(NO_3)_2$, 6.959 g $Bi(NO_3)_3.5H_2O$ and 1.403 g La_2O_3 was heated as described in Example 5 to give a pseudo-cubic perovskite with $a_o=8.75(1)$ Å. Again comparison with the lattice parameters for $Ba_2Bi_2O_6$ ($a_o=8.71$ Å) and Ba_2BiLaO_6 ($a_o=8.77$ Å) shows that the correct oxygen composition for this fully oxidized material is specified by $Ba_2La_{0.75}Bi_{1.25}O_6$. This composition was heated as described in Example 5 to a temperature of 950° C. in 0.0001 atm oxygen partial pressure for 16 hours. The x-ray diffraction pattern for the material, represented in Table VI, indicated that the material was composed of approximately two-thirds of $Ba_2La_{0.75}Bi_{1.25}O_6$ (pseudocubic perovskite lines at higher angles corresponding to this product at $a_o=8.75(1)$ Å) and one-third of $Ba_2La_{0.75}Bi_{1.25}O_5$ (pseudocubic perovskite lines at lower angles corresponding to this product at $a_o=8.95(1)$ Å).

TABLE VI

X-Ray Powder Diffraction Data for $Ba_2La_{0.75}Bi_{1.25}O_{5+y}$

	$d_{observed}$ (Å)		
hkl[a]	y = 1	y = 0	Intensity[b]
111	5.07		w
		4.89	w−
		4.71	w−
200	4.39		w+
220	3.097	3.161	s++
311	2.64		w
400	2.192	2.235	m+

TABLE VI-continued

X-Ray Powder Diffraction Data for $Ba_2La_{0.75}Bi_{1.25}O_{5+y}$

hkl[a]	$d_{observed}$ (Å)		Intensity[b]
	y = 1	y = 0	
420	1.961		w
422	1.788	1.828	s
333, 511	1.687		w
440	1.551	1.583	m
620	1.387	1.415	m
444	1.265	1.292	w+
642	1.172	1.197	m

[a] Indexing was done on a cubic cell with $a_o = 8.75(1)$ Å for y = 1 (oxidized) and $a_o = 8.95(1)$ Å for y = 0 (reduced) phases, respectively.

[b] w = weak, m = medium, s = strong

EXAMPLE 8

Preparation of Ba_2LaBiO_{5+y}

A mixture of 13.068 g $Ba(NO_3)_2$, 12.125 g $Bi(NO_3)_3.5H_2O$ and 4.073 g La_2O_3 was heated as described in Example 5 to yield a pseudo-cubic perovskite with $a_o = 8.77(1)$ Å and with composition Ba_2LaBiO_6. This composition was found to be stable to reduction at a temperature of 950° C. and 0.0001 atm partial pressure oxygen. On reducing the oxygen pressure to 0.000002 atm (a purified argon stream), heating of the Ba_2LaBIO_6 for 2.5 days at 900° C. resulted in an orange-rust colored material whose stoichiometry was shown by thermogravimetric oxidation to be $Ba_2BiLaO_{5.84}$. The X-ray diffraction pattern of the material, indicated in Table VII, showed dominantly Ba_2LaBiO_6 plus an additional pseudocubic perovskite material which could be indexed using $a_o = 8.98(3)$ Å. The latter minor phase was assumed to be Ba_2LaBiO_5.

TABLE VII

X-Ray Powder Diffraction Data for Ba_2LaBiO_{5+y}

hkl[a]	$d_{observed}$ (Å)		Intensity[b]
	y = 1	y = 0	
111	5.07		m−
200	4.39		m−
220	3.100	3.17	s++
311	2.644		w
400	2.194	2.25	s
420	1.961		w
422	1.789	1.83	s+
440	1.550	1.59	m+
620	1.387		m+
444	1.265		w+
642	1.172		m+

[a] Indexing was done using a cubic cell with $a_o = 8.77(1)$ Å for y = 1 (oxidized) and $a_o = 8.98(3)$ Å for y = 0 (reduced) phases, respectively.

[b] w = weak, m = medium, s = strong

EXAMPLE 9

Preparation of $Ba_2La_{0.67}Bi_{1.33}O_5$

A mixture of 10.454 g of $Ba(NO_3)_2$, 2.183 g of La_2O_3 and 12.9 g of $Bi(NO_3)_3.5H_2O$ was heated as described in Example 5 to yield a pseudo-cubic perovskite with $a_o = 8.75(1)$ Å. Comparison with the lattice parameters for $Ba_2Bi_2O_6$ ($a_o = 8.71$ Å) and Ba_2LaBiO_6 ($a_o = 8.77$ Å) shows that the correct oxygen composition for this fully oxidized material is specified by $Ba_2La_{0.67}Bi_{1.33}O_6$. Thermogravimetric analysis of a 0.1 g sample of this composition showed that this material began to lose oxygen at a temperature of about 800° C. when exposed to an oxygen pressure of 0.001 atm and that upon increasing the temperature to 1000° C. and reducing the oxygen pressure to 0.000002 atm (purified argon stream), the material was reduced to a composition $Ba_2La_{0.67}Bi_{1.33}O_5$ after a period of 12 to 24 hours. The x-ray diffraction spectrum of the resulting material, which was yellow in color, was that of a single phase pseudo-cubic perovskite material with a lattice parameter $a_o = 8.96(1)$ Å as is indicated in Table VIII.

TABLE VIII

X-Ray Powder Diffraction Data For $Ba_2La_{0.67}Bi_{1.33}O_5$

Peak No.	hkl[a]	$d_{observed}$ (Å)	Intensity[b]
1		4.72	w
2	220	3.16	s+
3	400	2.238	m+
4	422	1.829	s−
5	440	1.584	m
6	620	1.416	m
7	444	1.294	w+
8	642	1.198	m

[a] Indexing was done on the basis of a cubic cell with $a_o = 8.96(1)$ Å.

[b] w = weak, m = medium, s = strong

All of the oxygen-deficient, bismuth-containing materials of Examples 1–9, which represent the preferred class of compounds herein, were found to be extremely hygroscopic and showed significant hydration in a matter of minutes under ambient conditions. The x-ray patterns are for the anhydrous materials, although there are indications that some hydration occurred during the measurement. It appears that substitution of lanthanum for a portion of the bismuth in $Ba_2Bi_2O_6$ suppressed the intermediate phase (Region II) in the phase diagram of FIG. 1. Long-term thermogravimetric studies indicated that the $Ba_2La_aBi_{2-a}O_{5+y}$ materials constitute single phases under conditions of their synthesis at high temperature and low oxygen partial pressure. Phase separation occurred on cooling. Each of the lanthanum-containing compounds showed about a 7% increase in cell volume from the oxidized (y=1) to the reduced (y=0) phase comparable to the approximately 5% volume expansion when $BaBiO_3$ was reduced to $BaBiO_{2.55}$. The fact that these materials are readily reoxidized in air or oxygen at relatively low temperatures (see FIG. 2) and that $Ba_2La_{0.8}Bi_{1.25}O_{5+y}$ was observed as a reaction product upon reduction by propylene at 475°–500° C. indicates that the class of compounds herein described are useful in oxidative dehydrogenation reactions.

EXAMPLE 10

Preparation of Ba_2ScBiO_{5+y}

This example illustrates the preparation of a scandium-containing oxygen-deficient perovskite.

A mixture of 15.680 g of $Ba(NO_3)_2$, 2.069 g of Sc_2O_3 and 14.549 g of $Bi(NO_3)_3.5H_2O$ was heated in air to 400° C. for 1 hour, followed by regrinding and refiring at 400° C. for an additional hour followed by several regrindings and refirings at 800° C. in air for a total of 170 hours. Thermogravimetric analysis of a 0.1 g sample of the resulting oxidized material showed that this material began to lose oxygen at a temperature of 500° C. when exposed to an oxygen pressure of 0.0001 atm. Upon increasing the temperature to 925° C. and holding at that temperature for a period of 1 hour, the material was reduced to the extent that the value of y in the composition Ba_2ScBiO_{5+y} was decreased from its initial value by 0.50±0.04. Following cooling, the resulting oxygen-deficient material was reoxidized by heating in oxygen to 600° C., with reoxidation being very rapid as the temperature was increased above 300° C.

EXAMPLE 11

Preparation of $Ba_2Sc_{0.5}Bi_{1.5}O_{5+y}$

This example illustrates the preparation of a scandium-containing oxygen-deficient perovskite for which the value of a in $Ba_2Sc_aBi_{2-a}O_{5+y}$ *is intermediate between* 0 and 1.

A mixture of 10.454 g of $Ba(NO_3)_2$, 0.690 g of Sc_2O_3, and 14.550 g of $Bi(NO_3)_3.5H_2O$ was heated as described in Example 10. Thermogravimetric analysis of a 0.1 g sample of the resulting fully oxidized material showed that this material began to lose oxygen at a temperature of 500° C. when exposed to an oxygen pressure of 0.0001 atm. Upon increasing the temperature to 925° C. and holding at 925° C. for a period of 1 hour, the material was reduced to the extent that the value of y in the composition $Ba_2Sc_{0.5}Bi_{1.5}O_{5+y}$ was decreased from its initial value by 0.88±0.04. Following cooling, the resulting oxygen-deficient material was reoxidized by heating in oxygen to 600° C., with reoxidation being very rapid as the temperature was increased above 300° C.

Examples 12-15 below, which illustrate the use of the reoxidizable compositions herein and/or their fully oxidized precursors as oxidizing agents, constitute the examples of U.S. patent application Ser. Nos. 485,706 and 485,707, respectively, filed of even date with this application, both now abandoned both having the applicants K. Poeppelmeier and J. Longo. Wherever the word "moles" is used in the tables, it will be understood to mean moles per mole bismuth.

EXAMPLE 12

Catalyst mixtures were prepared either by mixing two moles of barium oxide with one mole of the post-transition metal oxide and one mole of the trivalent metal oxide, or by mixing three moles of barium oxide with two moles of the post-transition metal oxide and one mole of the divalent metal oxide catalyst, as indicated in Table IX. The mixtures were ground, heated to 400° C. in air, and then cooled and ground in air, and reheated to 800° C. in air or oxygen for 6 hours. This last step effectively increases the amount of oxygen (y) available for reaction when contacted with a hydrocarbon to its maximum amount. Formation of catalyst was detected by X-ray diffraction analysis.

Each catalyst so prepared, in an amount of 3 grams, was supported on a glass frit in the isothermal zone of a 20 mm outer diameter glass reactor. The reactor was heated in a conventional resistance-heated furnace.

A feedstream consisting of about 5% isobutylene and 95% helium was introduced through each reactor at a rate of 30 cc per minute after heating the reactor and its contents to a temperature of 475° C. in helium. During the first two to three hours of reaction, samples of the reaction mixture were injected at 15 minute intervals using a gas sampling valve into a gas chromatograph and the identity and quantity of each product were determined. The molar amounts of 2,5-dimethyl-1,5-hexadiene dimer and aromatic products per mole bismuth were calculated from the integrations of the chromatographic peaks so as to determine the total yield of all hydrocarbon products for each catalyst and the relative yield of para-xylene for each catalyst.

The types and yields of products as well as the relative yields of aromatic product for each catalyst are indicated in Table IX. The molar yields of each product are all expressed in units of moles per mole bismuth and are all normalized to the molar yield of p-xylene using Ba_2ScBiO_{5+y} as catalyst. (In the formulae, for catalysts containing O_{7+y}, y has a maximum value of 2, whereas for the catalysts containing O_{5+y}, y has a maximum value of 1.)

After sampling the reaction mixture for subsequent analysis (about 2-3 hours of reaction) each catalyst was regenerated by stopping the flow of feedstream and injecting oxygen gas into the reaction chamber for about 60 minutes. The feedstream was then reinitiated for subsequent conversion of isobutylene to products.

The results show that no broad generalization can be made as to which groups of the Periodic Table can be utilized effectively for production of para-xylene. It can be seen, however, that trivalent metal cations are preferred over divalent cations in the majority of catalysts for increasing the relative yield of aromatic product. For those materials which exhibit a good relative yield of para-xylene (e.g., greater than 70%), Ba_2ScBiO_{5+y} is by far the best catalyst under the conditions employed herein in terms of total yield of product.

TABLE IX

Group of Periodic Table	Metal Oxide Catalyst	Yield of para-Xylene[a] (A)	Yield of 2,5-Dimethyl-1,5-hexadiene Dimer[a] (B)	Yield of Other Products[a,b] (C)	Relative Yield[c] $\frac{A}{A+B+C}$	Total Yield[d]
IIA	$Ba_3MgBi_2O_{7+y}$	0.05	0.32	trace	13	0.37
	$Ba_3BaBi_2O_{7+y}$	0.01	0.13	N.D.	7	0.14
IIIB	Ba_2ScBiO_{5+y}	1.00	0.01	trace	99	1.01
	Ba_2YBiO_{5+y}	0.55	0.06	trace	90	0.61
	Ba_2LaBiO_{5+y}	0.43	0.12	trace	78	0.55
Lanthanide	Ba_2PrBiO_{5+y}	0.03	0.30	N.D.	9	0.33
	Ba_2NdBiO_{5+y}	0.54	0.12	trace	82	0.66
	Ba_2DyBiO_{5+y}	0.39	0.10	trace	80	0.49
IIIA	Ba_2AlBiO_{5+y}	0.03	0.30	N.D.	9	0.33
	Ba_2GaBiO_{5+y}	0.32	0.22	trace	59	0.54
	Ba_2InBiO_{5+y}	0.69	0.06	less than 0.05	92	0.75
	Ba_2TlBiO_{5+y}	0.65	0.40	less than 0.05	62	1.05

TABLE IX-continued

Group of Periodic Table	Metal Oxide Catalyst	Yield of para-Xylene[a] (A)	Yield of 2,5-Dimethyl-1,5-hexadiene Dimer[a] (B)	Yield of Other Products[a,b] (C)	Relative Yield[c] $\frac{A}{A+B+C}$	Total Yield[d]
—	α-Bi_2O_3*	0.23	0.34	0.09	35	0.66

*Comparative examples.

[a] This number is normalized to the moles of p-xylene produced using Ba_2ScBiO_{5+y} as catalyst, which was arbitrarily assigned a value of 1.00.

[b] Other products detected (excluding combustion products, e.g. CO and CO_2) were benzene, toluene, 2,5-dimethyl-2,4-hexadiene, and two undetermined products (ethylbenzene and o, m-xylene were not detected).

[c] This number (mole fraction) represents the yield of para-xylene divided by the sum of the yields of para-xylene, 2,5-dimethyl-1,5-hexadiene dimer, and other products, multiplied by 100%.

[d] This number represents the sum of the yields of para-xylene, 2,5-dimethyl-1,5-hexadiene dimer, and other hydrocarbon products.

N.D. = not detectable

EXAMPLE 13

The procedure of Example 12 was repeated except that propylene gas was substituted for isobutylene gas. The catalysts employed and the results obtained are indicated in Table X. All nomenclature used in the table follows from Example 12.

For those catalysts which exhibit a good relative yield of benzene (e.g., greater than 50%), the results show that Ba_2ScBiO_{5+y} is the best catalyst in terms of total yield of products.

TABLE X

Group of Periodic Table	Metal Oxide Catalyst	Yield of Benzene[a] (A)	Yield of 1,5-Hexadiene Dimer[a] (B)	Yield of Other Products[a,b] (C)	Relative Yield[c] $\left(\frac{A}{A+B+C}\right)$	Total Yield[d]
IIA	$Ba_3MgBi_2O_{7+y}$	0.21	0.12	N.D.	64	0.33
	$Ba_3BaBi_2O_{7+y}$	0.14	0.11	N.D.	56	0.25
IIIB	Ba_2ScBiO_{5+y}	1.00	0.02	trace	98	1.02
	Ba_2YBiO_{5+y}	0.18	0.01	trace	95	0.19
	Ba_2LaBiO_{5+y}	0.18	0.02	trace	90	0.20
Lanthanide	Ba_2PrBiO_{5+y}	0.42	0.18	trace	70	0.60
	Ba_2NdBiO_{5+y}	0.06	0.01	N.D.	86	0.07
	Ba_2DyBiO_{5+y}	0.10	0.02	trace	83	0.12
IIIA	Ba_2AlBiO_{5+y}	0.03	0.01	N.D.	75	0.04
	Ba_2GaBiO_{5+y}	0.17	0.13	trace	57	0.30
	Ba_2InBiO_{5+y}	0.65	0.18	N.D.	78	0.83
	Ba_2TlBiO_{5+y}	0.60	0.60	N.D.	50	1.20

[a] This number is normalized to the moles of benzene produced using Ba_2ScBiO_{5+y} as catalyst, which was arbitrarily assigned a value of 1.00.

[b] Other products detected (excluding combustion products, e.g. CO and CO_2) were 2,4-hexadiene isomers (mixture).

[c] This number (mole fraction) represents the yield of benzene divided by the sum of the yields of benzene, 1,5-hexadiene dimer, and other products, multiplied by 100%.

[d] This number represents the sum of the yields of benzene, 1,5-hexadiene dimer, and other hydrocarbon products.

N.D. = not detectable

EXAMPLE 14

Catalyst mixtures were prepared either by mixing two moles of barium oxide with one mole of the post-transition metal oxide and one mole of the trivalent metal oxide, or by mixing three moles of barium oxide with two moles of the post-transition metal oxide and one mole of the divalent metal oxide catalyst, as indicated in Table XI. The mixtures were ground, heated to 400° C. in air, and then cooled and ground in air, and reheated to 800° C. in air or oxygen for 6 hours. This last step effectively increases the amount of oxygen (y) available for reaction when contacted with a hydrocarbon to its maximum amount. Formation of catalyst was detected by X-ray diffraction analysis.

Each catalyst so prepared, in an amount of 3 grams, was supported on a glass frit in the isothermal zone of a 20 mm outer diameter glass reactor. The reactor was heated in a conventional resistance-heated furnace.

A feedstream consisting of about 5% isobutylene and 95% helium was introduced through each reactor at a rate of 30 cc per minute after heating the reactor and its contents to a temperature of 475° C. in helium. During the first two to three hours of reaction, samples of the reaction mixture were injected at 15 minute intervals using a gas sampling valve into a gas chromatograph and the identity and quantity of each product were determined. The molar amounts of 1,5-dimethyl-1,5-hexadiene dimer and other products per mole bismuth were calculated from the integrations of the chromatographic peaks so as to determine the total yield of all hydrocarbon products for each catalyst and the relative yield of dimer for each catalyst.

The types and yields of products as well as the relative yields of aromatic product for each catalyst are indicated in Table XI. The molar yields of each product are all expressed in units of moles per mole bismuth and are all normalized to the molar yield of p-xylene using Ba_2ScBiO_{5+y} as catalyst. (In the formulae, for catalysts containing O_{7+y}, y has a maximum value of 2, whereas for the catalysts containing O_{5+y}, y has a maximum value of 1).

After sampling the reaction mixture for subsequent analysis (about 2-3 hours of reaction) each catalyst was regenerated by stopping the flow of feedstream and injecting oxygen gas into the reaction chamber for about 60 minutes. The feedstream was then reinitiated for subsequent conversion of isobutylene to products.

For those catalysts which exhibit a good relative yield of 2,5-dimethyl-1,5-hexadiene dimer (e.g., at least 50%), the results show that Ba_2BiBiO_{5+y} is clearly the best of all catalysts tested in terms of total yield of products.

TABLE XI

Group of Periodic Table	Metal Oxide Catalyst	Yield of 2,5-Dimethyl-1,5-hexadiene Dimer[a] (A)	Yield of para-Xylene[a] (B)	Yield of Other Products[a,b] (C)	Relative Yield of 2,5-Dimethyl-1,5-hexadiene Dimer[c] $\left(\frac{A}{A+B+C}\right)$	Total Yield[d]
IIA	$Ba_3MgBi_2O_{7+y}$	0.32	0.05	trace	87	0.37
	$Ba_3CaBi_2O_{7+y}$	0.34	0.17	trace	67	0.51
	$Ba_3SrBi_2O_{7+y}$	0.13	0.01	N.D.	93	0.14
	$Ba_3BaBi_2O_{7+y}$	0.13	0.01	N.D.	93	0.14
IIIB	Ba_2ScBiO_{5+y}	0.01	1.00	trace	1	1.01
Lanthanide	Ba_2CeBiO_{5+y}	0.30	0.04	N.D.	88	0.34
	Ba_2PrBiO_{5+y}	0.30	0.03	N.D.	91	0.33
	Ba_2NdBiO_{5+y}	0.12	0.54	trace	18	0.66
VIII	$Ba_3NiBi_2O_{7+y}$	0.20	0.02	trace	91	0.22
	Ba_2FeBiO_{5+y}	0.21	0.15	trace	58	0.36
IB	$Ba_3CuBi_2O_{7+y}$	0.11	N.D.	N.D.	100	0.11
IIB	$Ba_3ZnBi_2O_{7+y}$	0.29	0.01	N.D.	97	0.30
	$Ba_3CdBi_2O_{7+y}$	0.35	0.04	trace	90	0.39
	$Ba_3HgBi_2O_{7+y}$	0.37	0.03	N.D.	93	0.40
IIIA	Ba_2AlBiO_{5+y}	0.30	0.03	N.D.	91	0.33
	Ba_2InBiO_{5+y}	0.06	0.69	less than 0.05	8	0.75
	Ba_2TlBiO_{5+y}	0.40	0.65	less than 0.05	38	1.05
VA	Ba_2BiBiO_{5+y}	0.85	0.01	N.D.	99	0.86
—	α-Bi_2O_3	0.34	0.23	0.09	52	0.66

*Comparative examples.

[a] This number is normalized to the moles of p-xylene obtained using Ba_2ScBiO_{5+y} as catalyst, which was arbitrarily assigned a value of 1.00.

[b] Other products detected (excluding combustion products, e.g., CO and CO_2) were benzene, toluene, 2,5-dimethyl-2,4-hexadiene, and two undetermined products (ethylbenzene and o,m-xylene were not detected).

[c] This number (mole fraction) represents the yield of 2,5-dimethyl-1,5-hexadiene dimer divided by the sum of the yields of 2,5-dimethyl-1,5-hexadiene dimer, para-xylene, and other products, multiplied by 100%.

[d] This number represents the sum of the yields of 2,5-dimethyl-1,5-hexadiene dimer, para-xylene, and other hydrocarbon products.

N.D. = not detectable.

EXAMPLE 15

The procedure of Example 14 was repeated except that propylene gas was substituted for isobutylene gas.

TABLE XII

Group of Periodic Table	Metal Oxide Catalyst	Yield of 1,5-hexadiene Dimer[a] (A)	Yield of Benzene[a] (B)	Yield of Other Products[a,b] (C)	Relative Yield of 1,5-Hexadiene Dimer[c] $\left(\frac{A}{A+B+C}\right)$	Total Yield[d]
IIA	$Ba_3MgBi_2O_{7+y}$	0.12	0.21	N.D.	36	0.33
	$Ba_3CaBi_2O_{7+y}$	0.06	trace	N.D.	100	0.06
	$Ba_3SrBi_2O_{7+y}$	0.11	0.05	N.D.	69	0.16
	$Ba_3BaBi_2O_{7+y}$	0.11	0.14	N.D.	44	0.25
IIIB	Ba_2ScBiO_{5+y}	0.02	1.00	trace	2	1.02
Lanthanide	Ba_2CeBiO_{5+y}	0.23	0.12	N.D.	66	0.35
	Ba_2PrBiO_{5+y}	0.18	0.42	trace	30	0.60
	Ba_2NdBiO_{5+y}	0.01	0.06	N.D.	14	0.07
VIII	$Ba_3NiBi_2O_{7+y}$	0.15	0.03	N.D.	83	0.18
	Ba_2FeBiO_{5+y}	0.22	0.08	N.D.	73	0.30
IB	Ba_3CuBiO_{7+y}	0.05	trace	N.D.	100	0.05
IIB	$Ba_3ZnBi_2O_{7+y}$	0.09	trace	N.D.	100	0.09
	$Ba_3HgBi_2O_{7+y}$	0.12	0.05	N.D.	71	0.17
	$Ba_3CdBi_2O_{7+y}$	0.08	trace	N.D.	100	0.08
IIIA	Ba_2AlBiO_{5+y}	0.01	0.03	N.D.	25	0.04
	Ba_2InBiO_{5+y}	0.18	0.65	N.D.	22	0.83
	Ba_2TlBiO_{5+y}	0.60	0.60	N.D.	50	1.20
VA	Ba_2BiBiO_{5+y}	0.11	trace	N.D.	100	0.11

[a] This number is normalized to the moles of benzene obtained using $Ba_2ScBiOhd\ 5+y$ as catalyst, which was arbitrarily assigned a value of 1.00.

[b] The other products (excluding combustion products, e.g., CO and CO_2) detected were 2,4-hexadiene isomer (mixture).

[c] This number (mole fraction) represents the yield of total 1,5-hexadiene dimer divided by the sum of the yields of 1,5-hexadiene dimer, benzene, and other products, multiplied by 100%.

[d] This number represents the sum of the yields of total 1,5-hexadiene dimer, benzene, and other hydrocarbon products.

N.D. = not detectable.

The catalysts employed and the results obtained are indicated in Table XII. All nomenclature used in the table follows from Example 14.

The results show that Ba_2BiBiO_{5+y} is a superior catalyst in terms of relative yield of dimer.

In summary, the present invention is seen to provide a class of oxygen-deficient, barium-containing compounds having a perovskite-type structure which are readily reoxidized and therefore can be used as continuously regenerable catalysts in oxidative dehydrogenation or in similar processes requiring solid oxidizing agents.

What is claimed is:

1. An oxygen-deficient, barium-containing compound having a perovskite-type structure of the formula:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

if M is a trivalent cation, or

$$Ba_3M_aM'_{3-a}O_{[7.5-(a/2)+y]}$$

if M is a divalent cation, wherein M is selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, the lanthanides of atomic number 58 or greater, Ni, Fe, Cu, Al, Ga, In, Zn, Cd, Hg, Bi, Tl and a mixture thereof, M' is selected from the group consisting of Sb or Bi, a is equal to or greater than 0 but less than or equal to 1, and if M is a trivalent cation, y is equal to or greater than 0 but less than 1, and if M is a divalent cation, y is equal to or greater than 0 but less than (3+a)/2.

2. An oxygen-deficient, bismuth-containing compound having a perovskite-type structure of the formula:

$$Ba_2M_aBi_{2-a}O_{5+y}$$

wherein M is La or Sc, a is equal to or greater than 0 but less than or equal to 1 and y is equal to or greater than 0 but less than 1.

3. A compound according to claim **1** of the formula:

$$Ba_2Bi_2O_{5+y}$$

wherein y is equal to or greater than 0 but less than 1.

4. A compound according to claim **3** wherein y is from 0 to 0.6.

5. A compound according to claim **3** wherein y is about 0 or about 0.6.

6. A compound according to claim **2** of the formula:

$$Ba_2La_aBi_{2-a}O_{5+y}$$

wherein a is greater than 0 but no greater than 1.

7. A compound according to claim **6** wherein y is less than or equal to 0.1.

8. A compound according to claim **6** wherein a is 0.5 and y is 0.

9. A process for preparing the oxygen-deficient, barium-containing compound of claim **1** which comprises heating a precursor compound of the formula:

$$Ba_2M_aM'_{2-a}O_{5+y}$$

if M is a trivalent cation, or

$$Ba_3M_aM'_{3-a}O_{[7.5-(a/2)+y]}$$

if M is a divalent cation, wherein M, M', and a are defined in claim **1**, y is about 1 but not greater than 1 if M is trivalent, and y is about (3+a)/2 but not greater than (3+a)/2 if M is divalent, in the presence of an effective amount of oxygen at a temperature of at least about 600° C., depending on the particular precursor compound and the amount of oxygen present, for a sufficient period of time to produce the oxygen-deficient compound.

10. A process according to claim **9** wherein M is Sc or La and M' is Bi.

11. A process according to claim **9** wherein the precursor compound is of the formula:

$$Ba_2M_aBi_{2-a}O_6$$

where M is La or Sc.

12. A process according to claim **11** wherein a is 0 and the precursor compound is prepared from a mixture of barium carbonate or nitrate with a salt or oxide of bismuth.

13. A process according to claim **11** wherein a is greater than 0 and the precursor compound is prepared from a mixture of barium carbonate or nitrate with a salt or oxide of bismuth and a salt or oxide of M.

14. A process according to claim **9** wherein the precursor compound is heated at from about 600° to 1000° C., depending on the particular precursor compound and the amount of oxygen present.

15. A process according to claim **11** wherein the precursor compound is heated at from about 800° to 1000° C., depending on the particular precursor compound and the amount of oxygen present.

16. A process according to claim **11** wherein the amount of oxygen present is sufficient to yield an oxygen partial pressure of between about 0.001 and 0.000002 atm.

17. A process according to claim **14** wherein the amount of oxygen present is sufficient to yield an oxygen partial pressure of between about 0.001 and 0.000002 atm.

18. A process for preparing an oxygen-deficient, bismuth-containing compound having a perovskite-type structure of the formula:

$$Ba_2La_{0.5}Bi_{1.5}O_{5+y}$$

wherein y is equal to or greater than 0 but less than 1, which process comprises (a) heating a mixture of $Ba(NO_3)_2$, $Bi(NO_3)_3.5H_2O$ and La_2O_3 in air to 800° C. in relative proportions so as to produce a precursor compound of the formula:

$$Ba_2La_{0.5}Bi_{1.5}O_6;$$

and (b) heating the precursor compound at an oxygen partial pressure of between about 0.001 and 0.0001 atm and at a temperature of 950° to 1000° C., depending on the oxygen partial pressure, for a sufficient period of time to produce the oxygen-deficient compound.

19. A process according to claim **18** wherein y is 0.

20. A process according to claim **19** wherein the precursor compound is heated at 950° C. at an oxygen partial pressure of 0.0001 atm for at least 8 hours.

* * * * *

United States Patent [19]
Beyerlein et al.

[11] **Patent Number: 4,503,166**
[45] **Date of Patent: Mar. 5, 1985**

[54] CATION-REORDERED, BISMUTH-CONTAINING PEROVSKITES

[75] Inventors: **Robert A. Beyerlein**, Westfield; **Kenneth R. Poeppelmeier**, Flemington; **Allan J. Jacobson**, Princeton, all of N.J.

[73] Assignee: **Exxon Research & Engineering Co.**, Florham Park, N.J.

[21] Appl. No.: **601,076**

[22] Filed: **Apr. 16, 1984**

[51] **Int. Cl.**^{3} **B01J 23/02**
[52] **U.S. Cl.** **502/303**; 502/525
[58] **Field of Search** 585/415, 417, 418, 520, 585/530, 533; 502/303, 525

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Primary Examiner—Delbert E. Gantz
Assistant Examiner—A. Pal
Attorney, Agent, or Firm—Janet E. Hasak; Henry E. Naylor

[57] ABSTRACT

A class of cation-reordered, bismuth-containing compounds having a perovskite-type structure of the formula

$$Ba_2La_yBi_{2-y}O_6$$

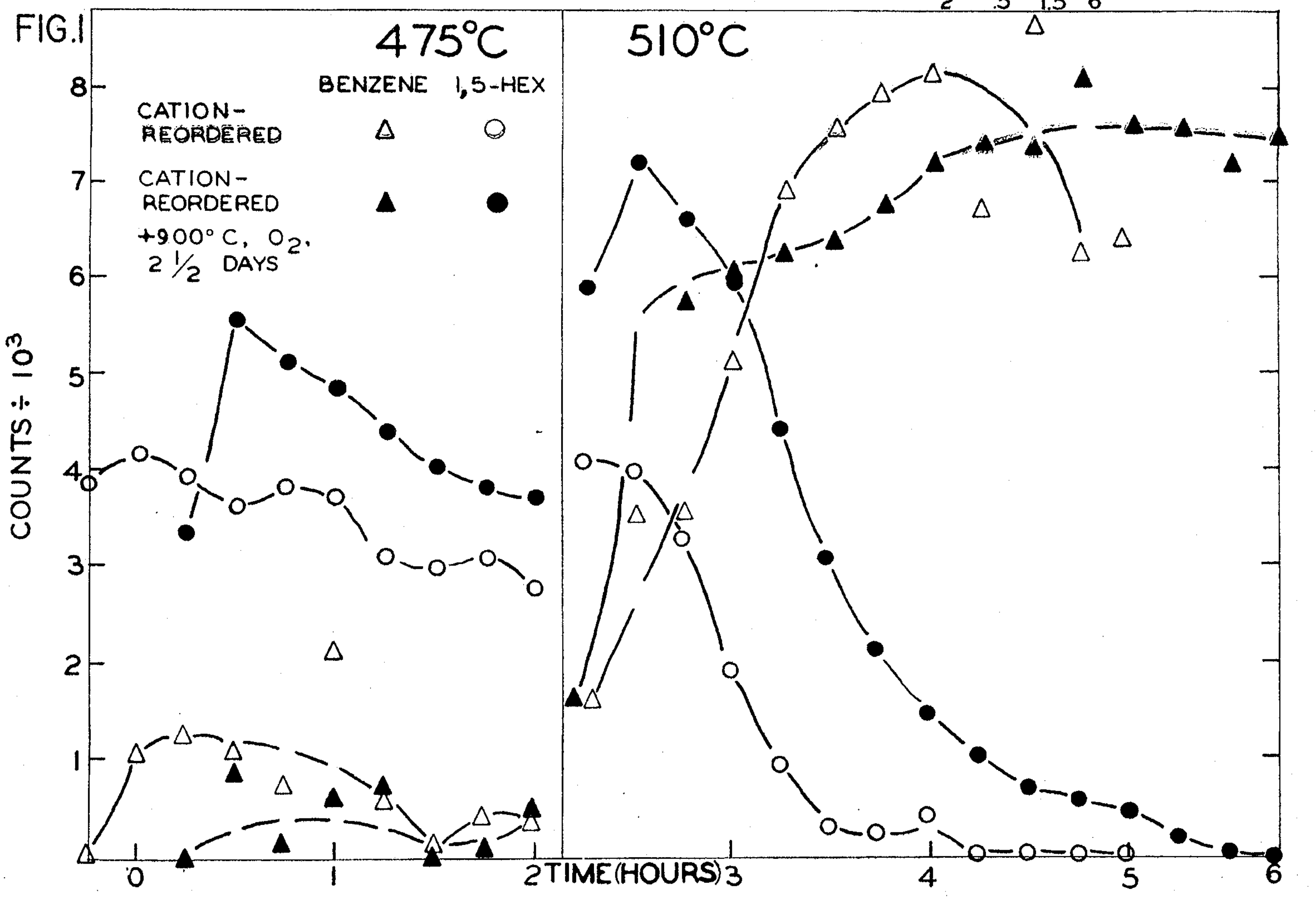
wherein y is greater than 0 but less than 1, is provided. Preferably, y is from 0.25 to 0.75, and most preferably y is 0.5.

The compositions herein are found to be particularly advantageous in the selective production of aromatic compounds from acyclic olefins, particularly in the production of benzene from propylene.

16 Claims, 4 Drawing Figures

FIG.1

PROPYLENE CONVERSION OVER $Ba_2La_{.5}Bi_{1.5}O_6$



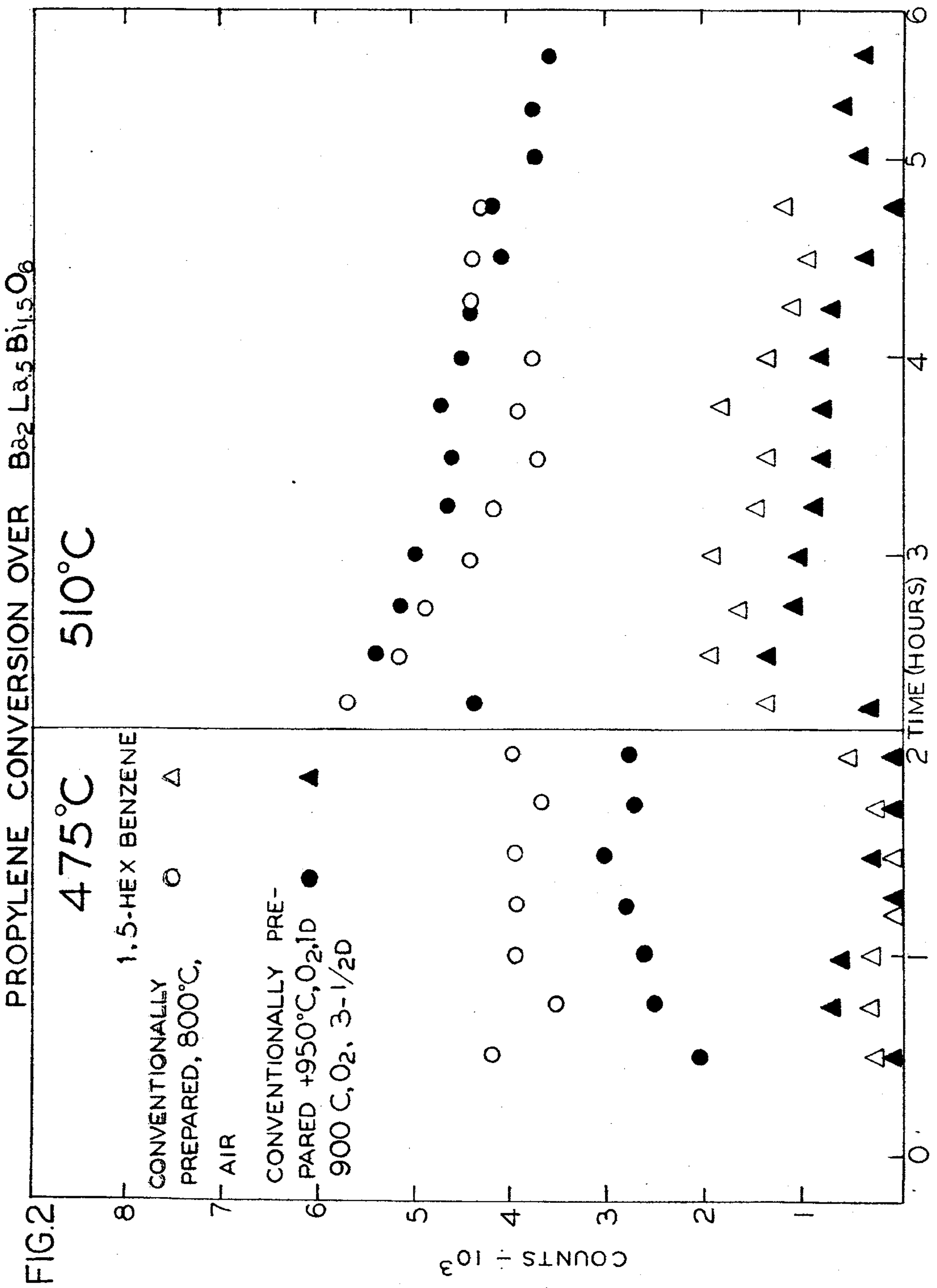

PROPYLENE CONVERSION OVER $Ba_2La_{.5}Bi_{1.5}O_6$
475°C
510°C
1,5-HEX BENZENE
CONVENTIONALLY PREPARED, 800°C, AIR
CONVENTIONALLY PREPARED +950°C, O_2, 1D 900 C, O_2, 3-1/2D
COUNTS ÷ 10^3
TIME (HOURS)
0
1
2
3
4
5
6
7
8

FIG.2

FIG.3

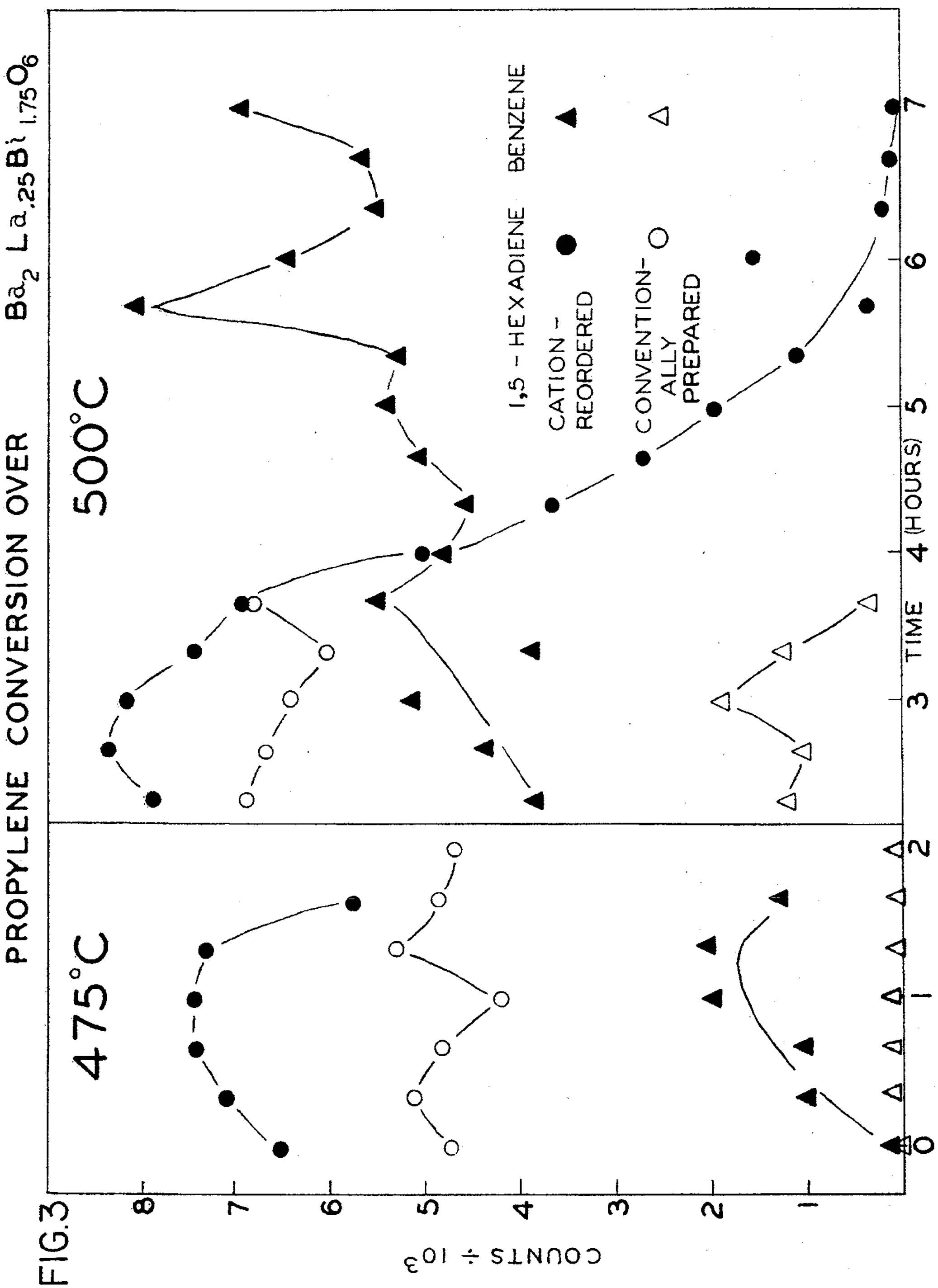
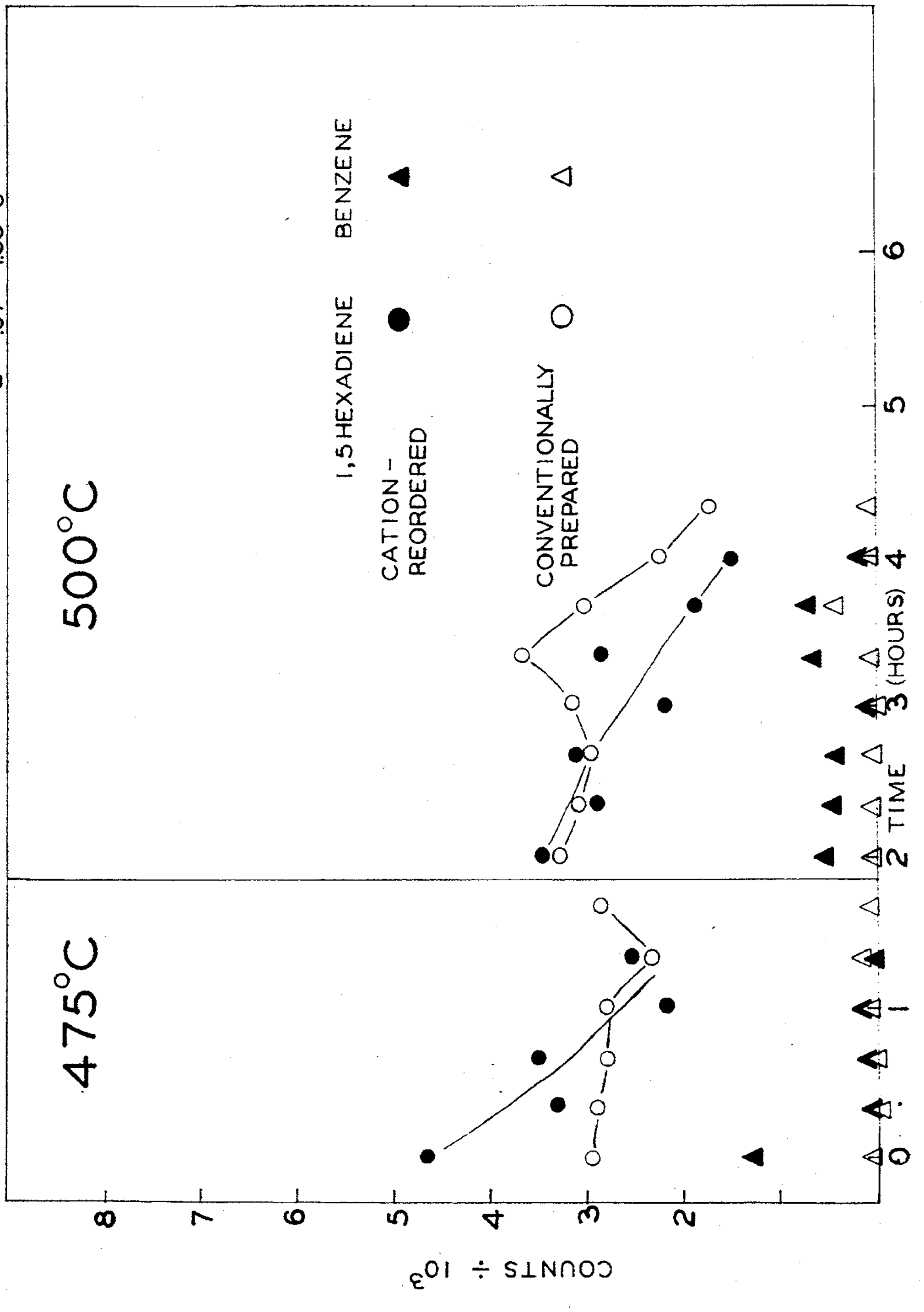

PROPYLENE CONVERSION OVER $Ba_2La_{.25}Bi_{1.75}O_6$
475°C
500°C
1,5 - HEXADIENE
BENZENE
CATION - REORDERED
CONVENTION-ALLY PREPARED
● ▲
○ △
TIME (HOURS)
0
1
2
3
4
5
6
7
COUNTS ÷ 10^3
1
2
3
4
5
6
7
8

FIG. 4


PROPYLENE CONVERSION OVER $Ba_2La_{.67}Bi_{1.33}O_6$
475°C
500°C
1,5 HEXADIENE
BENZENE
CATION - REORDERED
CONVENTIONALLY PREPARED
COUNTS ÷ 10^3
8
7
6
5
4
3
2
0
1
2
3
4
5
6
TIME (HOURS)

CATION-REORDERED, BISMUTH-CONTAINING PEROVSKITES

BACKGROUND OF THE INVENTION

This invention relates to a class of cation-reordered, bismuth-containing compounds having a perovskite-type structure useful in oxidative dehydrogenation reactions and a process for their preparation. In addition, the invention relates to a process for selectively producing aromatic compounds from acyclic olefins, preferably propylene and isobutylene.

During a typical petroleum refining operation large quantities of low molecular weight paraffins and olefins are produced. Unlike paraffins which may be sold for fuels, olefins have undesirable combustion properties which hamper their potential use as fuels. Thus, much research effort has been directed to upgrading the olefins, either for use as fuel or as chemical intermediates in the chemical industry. For those olefins containing three and four carbon atoms much research has been directed toward obtaining reaction products such as dimer and aromatic products having greater potential commercial value, with bismuth oxide representing a conventional oxidation catalyst, particularly for producing dimers.

Oxidative conversions of unsaturated hydrocarbons have recently been conducted using various catalyst combinations. A recently published comprehensive review article on oxidative dehydrogenation of olefins is E. A. Mamedov, *Russ. Chem. Reviews,* 50, 291 (1981), which lists numerous references disclosing use of catalysts containing bismuth oxide in combination with other elements to convert olefins to dienes and aromatic products in the presence or absence of molecular oxygen.

SUMMARY OF THE INVENTION

In accordance with this invention a novel class of cation-reordered, bismuth-containing compounds having a perovskite-type structure of the formula:

$$Ba_2La_yBi_{2-y}O_6$$

wherein y is greater than 0 but less than 1 is provided. These compounds are further characterized by having the x-ray powder diffraction pattern as set forth in Table II hereof. Preferably, y is from 0.2 to 0.75, most preferably 0.5.

The above class of compounds may be prepared by heating a first precursor compound represented by the formula:

$$Ba_2La_yBi_{2-y}O_6$$

where y is defined above and which is characterized by having the x-ray diffraction pattern as set forth in Table I hereof, in the presence of an effective amount of oxygen at a temperature from about 600° C. to its melting temperature, for a sufficient period of time to produce a second precursor compound which is oxygen deficient and which has a perovskite-type structure and which is represented by the formula:

$$Ba_2La_yBi_{2-y}O_{6-x}$$

where y is as defined above and x is from about 0 to 1; and heating the second precursor compound to a temperature from about 400° C. to about 650° C. in an oxidizing environment.

The class of compounds herein, which are stable in air to at least 600° C., may be used in oxidative dehydrogenation reactions or in similar processes requiring solid oxidizing agents. In particular, the compounds herein are especially effective as catalysts in selectively producing aromatic products from C_3 and C_4 acyclic olefins, preferably benzene and xylene from propylene and isobutylene, respectively.

Specifically, most of the cation-reordered materials of this invention show nearly 100% selectivity for converting propylene to benzene at 510° C., as compared to a much lower selectivity observed when the first precursor compound described above, or the first precursor compound treated at high temperatures in flowing oxygen, is employed under identical conditions. Furthermore, the oxygen-deficient catalyst obtained after the propylene has been converted in accordance with the present invention can be regenerated by oxidation to yield a catalyst showing further improved performance in the conversion reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation showing the relative amounts of 1,5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at two different temperatures, 475° C. and 510° C., by use of two materials, (A and B) both of which are represented by the formula $Ba_2La_{0.5}Bi_{1.5}O_6$. Both are re-ordered but one (B) was obtained by treating (A) in flowing oxygen at 900° C. for 2.5 days prior to use.

FIG. 2 is a graphical representation showing the relative amounts of 1,5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at two different temperatures, 475° C. and 510° C., by use of two conventional cation ordered materials (C and D) both of which are represented by the formula $Ba_2La_{0.5}Bi_{1.5}O_6$ wherein material C is a first precursor compound as herein described and material D is the product of heating a sample of material C in flowing oxygen at 950° C. for one day followed by heating at 900° C. for 3.5 days.

FIG. 3 is a graphical representation showing the relative amounts of 1,5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at temperatures of 475° C. and 500° C. by use of two materials (E and F), both of which are represented by the formula $Ba_2La_{0.25}Bi_{1.75}O_6$ wherein material E is cation re-ordered and F is conventionally cation ordered.

FIG. 4 is a graphical representation showing the relative amounts of 1,5 hexadiene and benzene produced from propylene (5% in helium) as a function of time at temperatures of 475° C. and 500° C. by use of two materials (G and H), both of which are represented by the formula $Ba_2La_{0.67}Bi_{1.33}O_6$ wherein material G is cation-reordered and H is conventionally cation ordered.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The class of cation-reordered bismuth-containing compounds of the present invention are found by x-ray diffraction analysis to have the perovskite-type structure as described in A. F. Wells, Structural Inorganic

Chemistry, Fourth Edition, Chapter 4, Clarendon Press (1975), and incorporated herein by reference.

The first precursor compounds, $Ba_2La_yBi_{2-y}O_6$, where y is greater than 0 but less than 1, used as starting materials to prepare the novel compounds herein, may be prepared by any convenient means known to those skilled in the art. For the investigations and experiments herein disclosed, they were obtained from a mixture containing barium nitrate, bismuth nitrate pentahydrate and lanthanum oxide. In this technique the nitrates and oxide in the appropriate amounts are oxidatively decomposed in air at 400° C. for 2 to 3 hours followed by successive regrinding and refining in air at temperatures of 800° to 900° C. for about 10 to 70 hours until no unreacted nitrate or lanthanum oxide can be detected in either the x-ray powder diffraction patterns or the infrared spectra of the oxygenated precursor compound product.

The x-ray pattern obtained for the conventional class of compounds $Ba_2La_yBi_{2-y}O_6$ thus obtained are shown in Table I for materials where $y=0.25$, 0.50, and 0.67. These patterns are typical of conventionally ordered $A_2BB'O_6$ pseudo-cubic perovskites. Here B is La^{+3} and Bi^{+3} and B' is Bi^{+5}. The appearance of certain ordering lines (hhh, $h=2n+1$) such as (111) and (333) is representative of such compounds. These same ordering lines are absent in the x-ray pattern of the novel compositions of the present invention as shown in Table II, indicating that cation reordering has occurred such that all B layers have the same stoichiometry. Thus, the compounds of the present invention have a different structure from the conventionally ordered $A_2BB'O_6$ structure.

The cation-reordered compounds of the present invention are prepared by heating the first (fully oxidized) precursor compound which is conventionally ordered and which can be prepared by any of the convenient methods previously described in the presence of an amount of oxygen effective for a particular temperature to obtain a second precursor compound which is an oxygen-deficient perovskite type structure of the formula $Ba_2La_yBi_{2-y}O_{6-x}$ where y is defined above and x is greater than 0 but no greater than 1. The amount of oxygen which is effective to produce the second precursor compound will depend primarily on the type of first precursor compound employed, the temperature at which the first precursor compound is heated, and the length of time for which the first precursor compound is heated. Typically, the heating will take place under a flow of a mixture of oxygen and an inert gas such as helium, or argon, at a flow rate of about 200 to 400 cm^3/minute. Higher or lower flow rates may be employed depending primarily on sample and reactor size.

The temperature at which the first precursor compound is heated is likewise dependent on many factors such as the type of first precursor compound and the amount of oxygen present. At minimum, the temperature should be about 600° C., but the temperature is preferably higher, for example about 600° C. to 1000° C. The time of heating will similarly depend on several factors such as the type of first precursor, temperature, and oxygen partial pressure. The interrelationships among the amount of oxygen employed, the temperature, and the type of first precursor compound can be expressed as follows: When the temperature is decreased, a lower oxygen pressure is required to obtain the product. As the content of lanthanum in the first precursor compound is increased, either the temperature must be increased or the oxygen partial pressure decreased and the time for heating must be increased to obtain the reduced product. Even when these parameters are adjusted, however, if y in the formula is increased beyond about 0.7 the second precursor obtained on cooling will generally not be a single-phase material but rather will comprise two phases which may be a mixture of the fully oxidized material ($x=0$) and the fully reduced material ($x=1$). If the first precursor compound is such that y is 0.5, when the compound is heated at between about 600° C. and 1000° C. the oxygen partial pressure will be between about 0.001 and 0.00001 atm, depending on the temperature. The preferred temperature range for heating is about 800° C. to 1000° C. and most preferred is about 900° C. to 1000° C. When a temperature of about 1000° C. is employed when y is 0.5, the oxygen partial pressure must be about 0.001 atm to obtain the second precursor compound, whereas if the temperature is about 950° C., the oxygen partial pressure is generally about 0.0001 atm and the time required is at least 8 hours, preferably 10 to 12 hours. When y is increased to 1, no oxygen-deficient precursor will be obtained unless the oxygen partial pressure is reduced or the temperature is increased.

The second precursor compound thus obtained is then oxidized to form the cation-reordered product by heating the compound at a temperature no greater than about 650° C. in an oxidizing environment, preferably at about 400° C. to 600° C., and more preferably 600° C. The time required for this oxidation will depend on the type of precursor employed, the temperature, the oxygen partial pressure, and the rate of gas flow, but is generally from about 1 to 4 hours, more preferably from about 2 to 3 hours.

The cation-reordered compound of this invention can be converted to an ordering similar to that of the conventionally ordered fully oxidized compound by heating in flowing oxygen at a temperature of at least about 800° C., preferably about 900° C. to 1000° C. for at least one day, depending on the temperature. The x-ray powder diffraction pattern of the compound which resulted when the cation-reordered material with $y=0.5$ was heated at 900° C. in flowing oxygen for 2.5 days, shown in Table III hereof, displays a clear (111) and a weak (333) reflection as does the diffraction pattern for the first precursor compound for $y=0.5$ shown in Table I hereof.

The novel compounds of the present invention are particularly useful for the selective production of aromatic products from C_3 and C_4 acyclic olefins. The process comprises contacting the acyclic olefin in the essential absence of oxygen and at a temperature of about 425° C. to 600° C. with the cation-reordered compound herein, preferably with y from 0.25 to 0.5, and recovering the aromatic product. The use of the compounds herein as catalysts has the advantage that substantial quantities of aromatic compounds are selectively produced relative to dimerized products. Moreover, when propylene is employed as olefin, the catalyst herein selectively produces benzene as substantially the only aromatic product, whereas bismuth oxide as catalyst produces substantial quantities of aromatic side products, which are difficult to separate from one another.

The acyclic olefins capable of being converted to higher molecular weight aromatic compounds are C_3-C_4 terminally or internally unsaturated linear or branched olefins such as, for example, propylene, 1-

butene, 2-butene, isobutylene or mixtures of the same. The preferred olefins herein are propylene, which is selectively converted to benzene, and isobutylene, which is selectively converted to para-xylene.

Although the catalysis reaction hereof can be conducted in the presence of oxygen, it is desirable to keep the amount of oxygen at a minimum. It is preferred that less than about 5 volume %, more preferably less than about 1 volume % of oxygen be present. It is most preferred to carry out the catalysis reaction under substantially anaerobic conditions. The volume percents are based on the total volume of gases. In the typical process herein a feedstock containing the olefin substrate is passed through a bed containing the catalyst (the cation-reordered compound of this invention), which is preferaably unsupported. An inert diluent gas such as nitrogen, methane, helium, argon, or the like is preferably added to the feedstock containing the olefinic hydrocarbon to minimize risk of explosion and complete oxidation of the olefin. Typically, the feedstock contains at most 5% olefin with the remainder being helium gas.

A temperature of about 425° C. to 600° C. is generally required to achieve significant conversion of the olefins to aromatic products. If the temperature is increased much above 600° C., decomposition may occur so as to form by-products or degradation products and problems may arise with respect to any regeneration of catalyst. The preferred temperature range for the process herein is about 450° C. to 520° C.

The duration of the reaction is governed by such factors as, for example, the temperature, the amount and type of catalyst, and the rate at which the feedstock passes through the catalyst bed, which is preferably about 10 cc/min. to 50 cc/min. for a bed diameter of about 2 cm, but may be varied in accordance with the specific conditions employed. If the rate is too fast, of course, there will be a significant decrease in conversion of the feed, whereas if the rate is too slow, undesirable by-reactions may begin to occur.

After the reaction has proceeded for such a period of time that the catalyst has lost a significant amount of its lattice oxygen but prior to any destruction of the complex (for example, at about 450° C.-520° C. at 30 cc/min. for about 4 to 6 hours), the catalyst is preferably regenerated by reoxidation thereof with an oxidizing gas such as oxygen or air. The regeneration may take place at the reaction temperature or higher, preferably at 550° C.-600° C. The reaction can thus be conducted in a cyclic operation so that reaction occurs in one cycle and regeneration in a second cycle, or in a continuous operation wherein preferably two reactors are employed and a continuous stream of olefin flows through one reactor while the catalyst is regenerated in the second reactor. These cycles may be periodically reversed.

The aromatic product may be recovered by any suitable manner known in the art.

The invention is further described in the examples which follow. In the examples, all parts and percentages are by weight, and all temperatures are in °C., unless otherwise noted.

EXAMPLE 2

Preparation of $Ba_2La_{0.5}Bi_{1.5}O_6$

A mixture of 12.000 g $Ba(NO_3)_2$, 16.701 g $Bi(NO_3.5$-H_2O and 1.870 g La_2O_3 was heated in air to 400° C. for two hours. The sample was reground and fired at 800° C. in air for one hour followed by regrinding and refiring at 800° C. for 60 hours. The resulting first precursor product was determined by x-ray diffraction to be a pseudo cubic perovskite material which could be indexed using a lattice parameter $a_o=8.74(1)$ Å, (also written as $a_o=8.74\pm0.01$ Å). Comparison with the lattice parameters for $Ba_2Bi_2O_6$ and Ba_2LaBiO_6 shows that the oxygen composition for this material is specified by $Ba_2La_{0.5}Bi_{1.5}O_6$. This material was placed in an alumina boat in a Lindberg tube furnace and heated in flowing oxygen to 950° C. for 18 hours to ensure a fully oxidized starting material, which was then cooled without removal from the furnace. The gas stream was changed to a stream consisting of oxygen and air containing 100 ppm oxygen (0.0001 atm partial pressure of oxygen) flowing at 300 cm³/min. The temperature was then raised to 950° C. and maintained for 16 hours before cooling in the same atmosphere to produce a light-brown oxygen-deficient material representing the second precursor. Without removal of the material from the furnace, the atmosphere was changed to pure oxygen flowing at 300 cm³/min. and the temperature was raised to 600° C. and maintained there for 2.5 hours before cooling in flowing oxygen to room temperature. Ancillary TGA experiments showed that these conditions were sufficient to re-oxidize fully the oxygen-deficient material formed during the treatment with 100 ppm oxygen to yield the compound of this invention.

The x-ray diffraction data for the first precursor and for the cation-reordered material obtained by re-oxidation at 600° C. of the second precursor are shown in Tables I and II respectively. The data were recorded with a Philips diffractometer using CuK radiation. The x-ray diffraction data of the material obtained by heating the cation-reordered material at 900° C. in flowing oxygen for two days is shown in Table III. It can be seen from this data that the compounds represented in Tables I and III are conventionally cation-ordered materials having a (111) and (333) reflection whereas the compounds represented in Table II are cation-reordered, and do not exhibit reflections of the type (111) and (333).

TABLE I

X-Ray Powder Diffraction Data for $Ba_2La_yBi_{2-y}O_6$, Conventional Preparation

	y = 0.25 a_o = 8.722(5) Å		y = 0.50 a_o 8.737(5) Å		y = 0.67 a_o 8.747(5) Å	
hkl	Intensity	d-spacing (Å)	Intensity	d-spacing (Å)	Intensity	d-spacing (Å)
111	w	5.036	w	5.044	w	5.050
200	m	4.361	m	4.369	m^-	4.374
220	s^{++}	3.084	s^{++}	3.089	s^{++}	3.093
311	w	2.630	w	2.634	w	2.637
400	s	2.181	s	2.184	s	2.187
331	N.O.		w^-	2.004	N.O.	
420	w^+	1.950	w^+	1.954	w^+	1.956
422	s^+	1.780	s^+	1.783	s^+	1.785
333	N.O.		w^-	1.681	w	1.683
440	m^+	1.542	m	1.544	m	1.546
531	N.O.		w^-	1.477	N.O.	
442,600	w	1.454	w	1.456	w^-	1.458
620	m^+	1.379	m	1.381	m	1.383
622	w^-	1.315	N.O		N.O.	
444	w^+	1.259	w^+	1.261	w^+	1.263
640	w^-	1.210	w^-	1.212	N.O.	
642	m	1.166	m^+	1.168	m	1.169

NOTE:
w = weak; m = medium, s = strong, N.O. = not observed.

TABLE II

X-Ray Powder Diffraction Data for $Ba_2La_yBi_{2-y}O_6$, Cation Reordered

	y = 0.25 a_o 8.722(5) Å		y = 0.50 a_o 8.755(5) Å		y = 0.67 a_o 8.77(5) Å	
hkl	Intensity	d-spacing (Å)	Intensity	d-spacing (Å)	Intensity	d-spacing (Å)
111	N.O.		N.O.		N.O.	
200	m	4.361	m^{+}	4.378	m	4.387
220	s^{++}	3.084	s^{++}	3.095	s^{++}	3.102
311	w^{-}	2.360	w	2.640	w^{-}	2.646
			w^{-}	2.350		
400	s	2.181	s	2.189	s	2.194
			w	2.032		
331	N.O.		N.O.		N.O.	
420	w^{+}	1.950	w^{+}	1.958	w^{+}	1.962
422	s^{+}	1.780	s^{+}	1.787	s^{+}	1.791
333	N.O.		N.O.		N.O.	
440	m^{+}	1.542	m^{+}	1.548	m	1.551
531	N.O.		N.O.		N.O.	
442,600	w	1.454	w	1.459	w	1.463
620	m^{+}	1.379	m^{+}	1.384	m	1.387
622	w^{-}	1.315	w^{-}	1.320	N.O.	
444	w^{+}	1.259	w^{+}	1.264	w^{+}	1.267
640	w^{-}	1.210	w^{-}	1.214	N.O.	
642	m	1.166	m^{+}	1.170	m	1.173

NOTE:
w = weak; m = medium, s = strong, N.O. = not observed.

TABLE III

X-ray Powder Diffraction Data for $Ba_2La_{.5}Bi_{1.5}O_6$ After Cation-Reordering Followed by 900° C., O_2, 2½ days

hkl	Intensity	d*-spacing (Å)
111	w	5.044
200	m	4.369
220	s^{++}	3.089
311	w	2.634
400	s	2.184
331	w^{-}	2.004
420	w^{+}	1.954
422	s^{+}	1.783
333	w^{-}	1.681
440	m^{+}	1.544
531	N.O.	
442,600	w	1.456
620	m^{+}	1.381
444	w^{+}	1.261
640	w^{-}	1.212
642	m^{+}	1.168

NOTE:
w = weak, m = medium, s = strong, N.O. = not observed.
*The pseudo-cubic lattice constant for this material, a_o = 8,737(5) Å, is equivalent to that for the conventional preparation of the same composition (See Table I).

EXAMPLE 2

Preparation of $Ba_2La_{0.25}Bi_{1.75}O_6$

A mixture of 10.454 g of $Ba(NO_3)_2$, 16.974 g of $Bi(NO_3)_3.5H_2O$ and 0.815 g of La_2O_3 was heated as described in Example 1 except that the final firing in air was done at 900° C. instead of 800° C. The resulting first precursor product was determined by x-ray diffraction to be a pseudo-cubic perovskite material which could be indexed with a lattice parameter a_o=8.72(1) Å. Comparison with the lattice parameters for $Ba_2Bi_2O_6$ (a_o=8.71(1) Å) and for Ba_2LaBiO_6 (a_o=8.77(1) Å) shows that the oxygen composition of this material is given by $Ba_2La_{0.25}Bi_{1.75}O_6$. This material was placed in an alumina boat in a Lindberg tube furnace and heated at 920° C. for 14 hours in a gas stream consisting of oxygen and argon containing 1000 ppm oxygen (0.001 atm partial pressure of oxygen) flowing at 300 cm³/min. before cooling in the same atmosphere to produce an oxygen-deficient material, light brown in color, representing the second precursor. Ancillary TGA experiments showed that these conditions were sufficient to form $Ba_2La_{0.25}Bi_{1.75}O_5$. Without removal of the material from the furnace, the atmosphere was changed to pure oxygen flowing at 300 cm³/min. and the temperature was raised to 600° C. and maintained there for 2 hours before cooling in flowing oxygen to room temperature. Ancillary TGA experiments showed that these conditions were sufficient to fully reoxidize the oxygen-deficient material formed during the treatment with 1000 ppm oxygen to yield the compound of the invention.

The x-ray diffraction data for the first precursor and for the cation-reordered material obtained by re-oxidation at 600° C. of the second precursor are shown in Tables I and II, respectively. It can be seen that the (111) and (333) reflections are absent for the compound of composition $Ba_2La_{0.25}Bi_{1.75}O_6$ in Table II, indicating that this compound has been cation-reordered.

EXAMPLE 3

Preparation of $Ba_2La_{0.67}Bi_{1.33}O_6$

A mixture of 10.454 g of $Ba(NO_3)_2$, 2.183 g of La_2O_3 and 12.9 g of $Bi(NO_3)_3.5H_2O$ was heated as described in Example 1 except that the final heating was done at 900° C. instead of 800° C. The resulting first precursor product was determined by x-ray diffraction to be a pseudo-cubic perovskite with lattice parameter a_o=8.75(1) Å. Comparison with the lattice parameters for $Ba_2Bi_2O_6$ (a_o=8.71 Å) and Ba_2BiLaO_6 (a_o=8.77 Å) shows that the oxygen composition for this material is given by $Ba_2La_{0.67}Bi_{1.33}O_6$. A 6 g sample of this material was placed in an alumina boat in a Lindberg tube furnace and heated in flowing oxygen to 900° C. for 2 hours to ensure a fully oxidized starting material which was cooled without removal from the furnace. The gas stream was charged to a stream of purified argon (0.000002 atm partial pressure of oxygen) flowing at 300 cm³/min. The temperature was raised to 950° C. and maintained there for 16 hours and then increased to 1000° C. for an additional 24 hours before cooling in the same atmosphere to obtain a bright yellow oxygen-deficient material representing the second precursor. Ancillary TGA experiments showed that these conditions were sufficient to form $Ba_2La_{0.67}Bi_{1.33}O_5$. Without removal of the sample from the furnace the atmosphere was changed to pure oxygen flowing at 300 cm³/min. and the temperature was raised to 600° C. and maintained for 2 hours before cooling in the same atmosphere to room temperature. Ancillary TGA experiments showed that these conditions were sufficient to fully reoxidize the oxygen deficient material formed in the previous step to yield the compound of the invention.

The x-ray diffraction pattern for the first precursor and for the cation-reordered material obtained by reoxidation at 600° C. of the second precursor are shown in Tables I and II. It can be seen that the (111) and (333) reflections are absent for the compound of composition $Ba_2La_{0.67}Bi_{1.33}O_6$ in Table II indicating that this compound has been cation-reordered.

EXAMPLE 4

Selective Production of Benzene

In four separate experiments, each of the four materials A–D, having the composition $Ba_2La_{0.5}Bi_{1.5}O_6$, was singly deposited in an amount of 3 grams in a quartz upflow reactor with a 0.75 inch (1.9 cm) diameter. Material A was the final product of Example 1. Material B was the material resulting when Material A was heated in flowing oxygen at 900° C. for 2.5 days. Material C was the first product of Example 1, i.e., the material obtained on successive regrindings and refirings to 800° C. of a mixture of $Ba(NO_3)_2$, $Bi(NO_3)_3.5H_2O$ and La_2O_3 heated in air. Material D was obtained by heating Material C in flowing oxygen at 950° C. for one day followed by 3.5 days at 900° C. Thus, Material A is a cation-reordered material of this invention and Material B is obtained by high temperature treatment of Material A. Materials C and D represent conventionally ordered materials as a comparison.

A feedstream consisting of about 5% propylene and 95% helium flowing at a rate of 30 cc min^{-1} was passed through the reactor which was heated to a temperature of 475° C. After about 2¼ hours of reaction at 475° C. the temperature was increased to 510° C. and the reactions proceeded at the higher temperature to yield a total reaction time of six hours. Each reaction was monitored by injecting, at regular intervals, a sample of each product reaction mixture into a gas chromatograph. The identity and relative amounts of each product were thereby determined.

The results obtained for Materials A and B, on the one hand, and Materials C and D, on the other hand, are shown in FIGS. 1 and 2, respectively, which represents plots of the relative amounts of 1,5-hexadiene and benzene formed as a function of time. All four materials showed low production of carbon oxides, low benzene make, and comparable production of the 1,5-hexadiene dimer which was the dominant product during the initial reaction at 475° C. Materials A and B did, however, show a small early build-up of benzene which was much less pronounced with Materials C and D at 475° C. The most dramatic differences among the four materials occurred upon increasing the reaction temperature from 475° to 510° C. Both Materials A and B, representing the cation-reordered material and its high temperature oxygen treated counterpart, respectively, showed a substantial build-up of benzene production with an accompanying rapid decrease in the production of the dimer. Thus, the selectivity for conversion of propylene to benzene at 510° C. was nearly 100% after an initial induction period of about 1.5 hours and 3 hours for Materials A and B, respectively. On comparing the results in FIG. 1 with those in FIG. 2, it can be seen that the steady-state production of benzene by the materials which have undergone cation reordering (of FIG. 1) is greater by a factor of six to eight than the production of benzene by the conventionally ordered materials (of FIG. 2), which were tested under identical conditions. Moreover, when a perovskite of the composition Ba_2LaBiO_6, prepared by mixing appropriate molar amounts of barium nitrate, bismuth nitrate pentahydrate, and lanthanum oxide, heating the mixture to 400° C. for 2 to 3 hours then cooling and grinding in air and reheating to 800° C. in air for 60 hours in a furnace with an intermediate regrind, was tested under identical conditions for conversion of propylene to benzene, it was found to have a lower conversion rate than Materials A and B by about a factor of one-half, even though the latter materials have a lower La to Bi ratio.

X-ray diffraction analysis of the solid reaction products obtained after the catalytic reactions were completed showed that for Materials A and B significant quantities of the oxygen-deficient material $Ba_2La_{0.5}Bi_{1.5}O_5$ were present, while for comparative Materials C and D, which exhibited much lower conversion rates, the dominant phase was the fully oxidized material $Ba_2La_{0.5}Bi_{1.5}O_6$ and little if any $Ba_2La_{0.5}Bi_{1.5}O_5$ was present.

In an additional experiment, the solid product material produced by reacting Material A with propylene was removed from the reactor and was regenerated by reoxidation at 600° C. in flowing oxygen. Using a mixture of 5% propylene in helium and conditions identical to those described above, the results showed that the regenerated material produced approximately equal amounts of the 1,5-hexadiene and benzene at 475° C. at a level very comparable to that obtained using Material A. When the temperature was increased to 500° C., the benzene production rapidly increased to about 150% of the maximum level shown in FIG. 1. As observed with Material A the production of 1,5-hexadiene rapidly decreased, so that after two hours at 510° C. the regenerated material effected essentially 100% conversion of propylene to benzene with a slow decrease in benzene production as time progressed. The results thus show that the loss in activity due to depletion of lattice oxygen may be avoided by treatment of the oxygen-deficient cation-reordered material with oxygen.

EXAMPLE 5

Selective Production of Benzene from $Ba_2La_{0.25}Bi_{1.75}O_6$

In two separate experiments, each of two materials E and F, having the composition $Ba_2La_{0.25}Bi_{1.75}O_6$, was separately deposited in the amount of 3 grams in a quartz upflow reactor with a 0.75 inch (1.9 cm) diameter. Material E was cation reordered while Material F was conventionally ordered, each having each prepared as described in Example 2 where Material E is the final product and Material F is the first precursor product of Example 2.

A feedstream consisting of about 5% propylene and 95% helium flowing at a rate of 30 cc min^{-1} was passed through the reactor which was heated to a temperature of 475° C. After about 2¼ hours of reaction at 475° C., the temperature was increased to 500° C., and the reactions proceeded at the higher temperature to yield a total reaction time of seven hours. Each reaction was monitored by injecting, at regular intervals, a sample of each product reaction mixture into a gas chromatograph. The identity and relative amounts of each product were thereby determined.

The results obtained for Materials E and F are shown in FIG. 3 which represents plots of the relative amounts of 1,5-hexadiene and benzene formed as a function of time. Both materials showed low production of carbon oxides, low benzene make, and comparable production of the 1,5-hexadiene dimer which was the dominant product during the initial reaction at 475° C. At 475° C., material E did show a small early build-up of benzene which was absent for Material F. A dramatic difference between these two materials occurred upon increasing the reaction temperature from 475° to 500° C. Material E, representing the cation-reordered material, showed a substantial build-up of benzene production with an accompanying rapid decrease in the production of the dimer, while Material F, representing the conventionally ordered material, continued to produce the dimer as the dominant product. For the cation-reordered Material E, the selectivity for conversion of propylene to benzene at 500° C. was nearly 100% after an initial induction period of about four hours. Comparing the results for Materials E and F given in FIG. 3, it is clear that the cation reordered process increases the overall propylene conversion rate and dramatically improves selectivity toward the aromatic product as the reaction temperature is increased from 475° C. to 500° C.

EXAMPLE 6

Selective Production of Benzene from $Ba_2La_{0.67}Bi_{1.33}O_6$

In two separate experiments, each of two Materials G and H, having the composition $Ba_2La_{0.67}Bi1.33O_6$, was separately deposited in the amount of 3 grams in a quartz upflow reactor with a 0.75 inch (1.9 cm) diameter. Material G was cation reordered, while Material H was conventionally ordered each having been prepared as described in Example 3 where Material G is the final product and Material H is the first precursor product of Example 3.

A feedstream consisting of about 5% propylene and 95% helium flowing at a rate of 30 cm min^{-1} was passed through the reactor which was heated to a temperature of 475° C. After about 1¾ hours of reaction at 475° C., the temperature was increased to 500° C. and the reactions proceeded at the higher temperature to yield a total reaction time of 4¼ hours. Each reaction was monitored by injecting, at regular intervals, a sample of each product reaction mixture into a gas chromatograph. The identity and relative amounts of each product were thereby determined.

The results obtained for Materials G and H are shown in FIG. 4 which represents plots of the relative amounts of 1,5-hexadiene and benzene formed as a function of time. Both materials showed low production of carbon oxides, low benzene make, and comparable production of the 1,5-hexadiene dimer which was essentially the only product during the initial reaction at 475° C. Material G showed a slight build-up of benzene as the temperature was increased to 500° C., while Material H showed essentially no benzene yield even at 500° C. Both materials showed a gradual decline over several hours in production of the dimer as the reactor temperature was held at 500° C.

In summary, the present invention is seen to provide a class of fully oxidized, cation-reordered, bismuth- and lanthanum-containing compounds having a perovskite-type structure and a process for the preparation thereof. Also provided is a process for selectively producing aromatic products from C_3–C_4 acyclic olefins using the class of compounds herein.

What is claimed is:

1. A cation-reordered, bismuth-containing compound having a perovskite-type structure of the formula:

$$Ba_2La_yBi_{2-y}O_6$$

wherein y is greater than 0 but less than 1, the compound being further characterized by having the x-ray powder diffraction pattern indicated in Table II.

2. A compound according to claim **1** which is prepared by heating a compound having a perovskite-type structure of the formula:

$$Ba_2La_yBi_{2-y}O_{6-x}$$

wherein y and x are greater than 0 but less than 1, at a temperature no greater than about 600° C. in flowing oxygen.

3. A compound according to claim **1** wherein y is from 0.25 to 0.75.

4. A compound according to claim **1** wherein y is 0.5.

5. A process for preparing a cation-reordered, bismuth-containing compound having a perovskite-type structure of the formula:

$$Ba_2La_yBi_{2-y}O_6$$

wherein y is greater than 0 but less than 1, the compound having the x-ray powder diffraction pattern indicated in Table II, which process comprises:

(a) heating a first precursor compound of the formula:

$$Ba_2La_yBi_{2-y}O_6$$

wherein y is defined above and having the x-ray diffraction pattern given in Table I, in the presence of an effective amount of oxygen at a temperature of at least about 600° C., depending on the particular precursor compound and the amount of oxygen present, for a sufficient period of time to produce a second precursor compound which is oxygen deficient and has a perovskite-type structure of the formula:

$$Ba_2La_yBi_{2-y}O_{6-x}$$

where y is defined above and x is greater than 0 but no greater than 1; and

(b) heating the second precursor compound at a temperature no greater than about 650° C. in flowing oxygen for a sufficient period of time to reoxidize the second precursor compound.

6. A process according to claim **5** wherein y is 0.25 to 0.75.

7. A process according to claim **5** wherein y is 0.5.

8. A process according to claim **5** wherein the first precursor compound is prepared from a mixture of $Ba(NO_3)_2$, $Bi(NO_3)_3.5H_2O$ and La_2O_3.

9. A process according to claim **8** wherein the mixture is heated in air to about 800° C.

10. A process according to claim **5** wherein the first precursor compound is heated at from about 600° C. to 1000° C., depending on the particular precursor compound and the amount of oxygen present.

11. A process according to claim **5** wherein the first precursor compound is heated at from about 800° C. to 1000° C., depending on the particular precursor compound and the amount of oxygen present.

12. A process according to claim **5** wherein the amount of oxygen present is sufficient to yield an oxygen partial pressure of between about 0.001 and 0.000001 atm.

13. A process according to claim **5** wherein the first precursor compound is heated at an oxygen partial pressure of between about 0.001 and 0.00001 atm and at a temperature of 900° C. to 1000° C., depending on the oxygen partial pressure.

14. A process according to claim **5** wherein the first precursor compound is heated at 950° C. at an oxygen partial pressure of 0.0001 atm for at least 8 hours and y is 0.5.

15. A process according to claim **5** wherein the second precursor compound is heated at a temperature of about 250° to 650° C.

16. A process according to claim **14** wherein the second precursor compound is heated at a temperature of about 600° C. for at least 2.5 hours.

* * * * *

DECEMBER 1986

SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	SATURDAY
30	1 NEW MOON	2	3 note to [illegible] Bednorz Müller.	4 Boston MRS Pre-view LaBCO w/ Kitazawa Ask Wu to join the project. Lunch together	5 THO gave Kitazawa [illegible] presented his paper 1201 [illegible] who mentioning UH. >7:PM Back to Hou.	6 Called CY MK Wu for Michael + Raveau paper
7 Told GTH result Not encouraging [illegible] [illegible]	8 Talked to David Voss very encouraging. GTH - not encouraging. Immaculate Conception FIRST QUARTER	9 Decided to go to PRL Called Strongin (positive but [illegible]) Called Ashcroft Maple! APS Meeting	10 Müller called + thanked	11	12 PRL paper sent. [illegible]	13
14 Post card to [illegible] 40.2K 50K next wk >70 - possible. To DC.	15 Ashcroft - Yes panel disc.	16 Piscataway Army Integrated Optical Conf - Banquet Speaker - announced >50K. Agreed to Send [illegible] a sample FULL MOON	17 (?) UH Press release on Jan. 5/87. (Müller rejected 12/24) ~~to Boston~~	18 ~~[illegible]~~ complete replacement of La by smaller Y, Yb, Lu ...	19 [illegible]	20
21 Winter Begins	22 Our PRL accepted	23 In two days Bell will submit ~~[illegible]~~ paper ~~[illegible]~~ re. Lee's Nos. - NSF release Decided - ~~UH~~ release on 1/30/86 [illegible]	24 Facs Sci. News to UH go to Boston LAST QUARTER	25 Christmas Sicked (3 [illegible])	26 Rec. UH release Call. Müller - will be out 1/[illegible] Worked on UH release Y. [illegible] Yes!	27 Send Release to RW. F. Exp. New Hampshire! O.K. ~~[illegible] disc [illegible]~~ Hanukkah ~~[illegible]~~ O.K.
28 Magic Show	29 6:30 a.m. to DC - MK Wu + Jim Ashburn - + 1:11 [illegible]) 7:40 to Houston	30 Took [illegible] [illegible] Müller [illegible] [illegible] RW coordinated w/ NSF Press Conf. 2pm Hou. Post, Chronicle NY Times, [illegible]	31 Ch. 13, Ch. 11. Business wk. Radio sts + more [illegible] - [illegible] results? call [illegible] NEW MOON	1	2	3 Called to contact Zhao - [illegible] (Beijing)

1986

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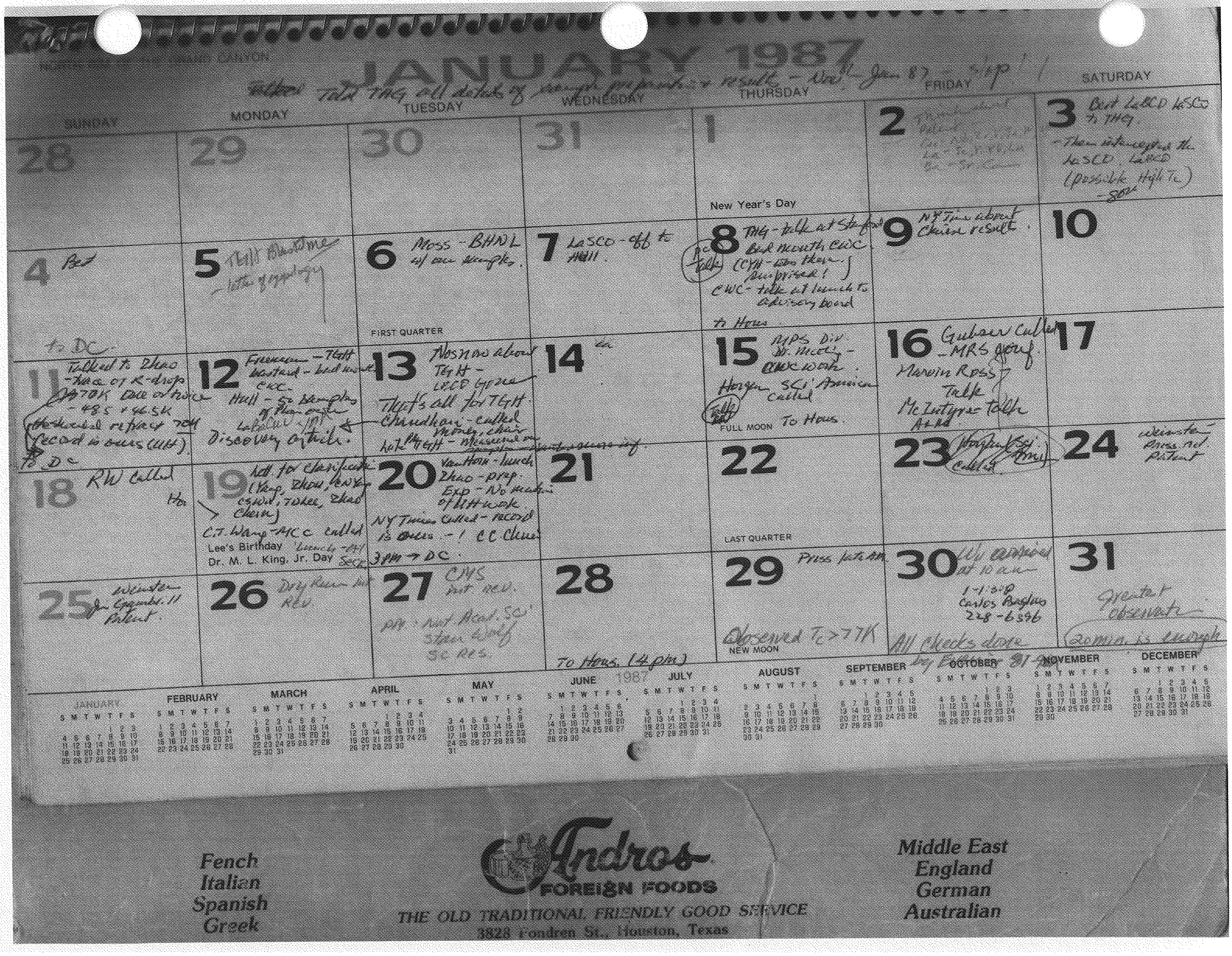

JANUARY 1987

~~[illegible]~~ Told THG all details of sample preparation + results – Wed. Jan 87 – slip!!

SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	SATURDAY
28	29	30	31	1 New Year's Day	2 [illegible]	3 Brt LaBCD LaSCO to THG. – Then [illegible] the LaSCO, LaBCD (possible High Tc) – 80K
4 Bed	5 THG [illegible] – letter of apology	6 Moss – BHNL w/ our samples. FIRST QUARTER	7 LaSCO – off to Hull.	8 THG – talk at Stanford. Bad mouth CWC (CYH – was there – surprised!) PC talk CWC – talk at lunch to advisory board to Hous.	9 NY Times about Chinese result.	10
to DC. 11 Talked to Zhao – trace of R-drop 70K once or twice – 48.5 + 46.5K [illegible] reflect TGH record is ours (UH). to DC	12 Freeman – TGH [illegible] – bad mouth CWC. Hull – 50 samples of [illegible] [illegible] Discovery article.	13 Nosanow about TGH – LBCO [illegible] That's all for TGH. Chaudhari – called Money, chair [illegible] TGH – [illegible]	14 [illegible]	15 MPS Div. Dr. McCoy – CWC work. Horgan SCI' American called Talk FULL MOON To Hous.	16 Gubser called – MRS conf. Marvin Ross Talk McIntyre Talk Add.	17
18 RW called Hou	19 Call for clarification (Yang, Zhou, [illegible], CSWU, [illegible], Zhao Chem) C.T. Wang – ACC called Lee's Birthday Lunch – AH Dr. M. L. King, Jr. Day Secy	20 VanHorn – lunch Zhao – prep. Exp – No mention of UH work NY Times called – record is ours. – 1 CC Chu 3PM → DC.	21	22 LAST QUARTER	23 Horgan Sci. Amer. called	24 Weinstein – Press rel. Patent
25 Weinstein – [illegible] 11 Patent.	26 Dry Run [illegible] Rel.	27 CMS Pat. rel. PR: Nat. Acad. Sci' Stan Wolf SC Res.	28 To Hous. (4 pm)	29 Press [illegible] Observed Tc > 77K NEW MOON	30 [illegible] at 10 a.m. 1-1:30 Carlos [illegible] 228-6596 All checks done by [illegible] 31 [illegible]	31 Greatest observation 20 min. is enough

FEBRUARY 1987

SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	SATURDAY
1	2 Even'g 180K cont. to [illegible] Ground Hog Day	3	4	5 FIRST QUARTER	6 Weinstock ~~[illegible]~~ 1 p.m. lunch [illegible] 717 [illegible] [illegible]!	7
8	9 3pm	10 2 PM 21 [illegible] Joseph Henry Bldg Rm 406 –	11 Hous	12 UH Talk Lincoln's Birthday	13 8pm – [illegible] FULL MOON	14 Lv to Houston Valentine's Day
15	16 Board of Regents Meeting 8:30am H Washington's Birthday Observed	17 [illegible] 8:30am ABC CBS Conf. Call from Natalie [illegible]	18 4pm Van Horn Cocanougher Ammann 3:30pm 4 [illegible]	19 News Release [illegible] (614) 821-4882 [illegible] 9 am – [illegible]	20 Van Horn 12 noon [illegible] 10 am – daily Cougar 11 am – [illegible]	21 Albert's B'day LAST QUARTER
22 Traditional Washington's Birthday	23 rt.	24 [illegible] EPB. Bill Graham 3:30 pm Japan & Taiwan [illegible] (6 pm)	25 [illegible]	26 [illegible] UCSB	27 Gordon Cook (Cal.) SC. above 50K Call [illegible] [illegible] [illegible] aircraft	28 NEW MOON
1	2 MCB aircraft.	3 Stanford.	4	5	6	7

1987

JANUARY

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MOBILE, ALABAMA

MARCH 1987

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1	2 ~~Hughes~~ Berkeley	3 Stanford.	4 Weinstock AIR FORCES [illegible] Ash Wednesday	5	6 [illegible] (Chem Sci [illegible]) McDonald, [illegible] (Chem. Higher Ed.) 9 am	7 H FIRST QUARTER
8	9 7:00 pm Gambrell	10	11 TI (214)	12 TI (214) 995-2784 Dallas News Morning Gayle Golden (214) 571-8768	13	14
15 FULL MOON	16 Harvard Roy Glauber — Seminar	17 Evening – [illegible] (LCI) St. Patrick's Day	18 7:30 pm HPS Panel disc.	19 du Pont : Sleight 1 pm	20 Mary + kids here du Pont Sleight	21 W Spring Begins
22 LAST QUARTER	23 [illegible] 12:30 [illegible] pictures	24 8 pm [illegible] (WSF) 2 pm [illegible]	25 Stony Brook	26 Litton, Ray Bell (Litton) Arthur Fisher AM Popular Sci 1 pm	27 VCU Illinois UI	28 H
29 NEW MOON	30 [illegible] UCB.	31	1	2 TI (214) 995-2784 [illegible]	3	4

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JANUARY
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FEBRUARY
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