Center: Consortium for Materials Development in Space
The University of Alabama in Hunstville (UAH)

Project Name: **"High Temperature Superconductors"**

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Introduction

Our laboratory was the first in the world to develop a material with a transition temperature to superconductivity (Tc) above the temperature of liquid nitrogen. Despite efforts by other well-known laboratories around the world there still have been no other major breakthroughs eclipsing our work. This puts us in a good position to continue our leading role in this area.

The two principal objectives of our present work are to develop materials that superconduct at higher temperatures and to better understand the mechanisms behind high temperature superconductivity. To achieve these goals we are carrying out detailed experiments on the thermal reaction, structure, and physical properties of materials that exhibit superconductivity at high temperatures.

If the results of our studies lend credence to some theories now under consideration, we may wish to combine immiscible alloys with proper normal state properties, such as resistivity, crystal structure, and presence of appropriate excitation. If this is the case we will develop a plan to produce superconducting materials in the freefall environment of space.

Areas of Study

1. Development of high-Tc superconductors.

Our breakthrough work evolved from the knowledge that pressure has an effect on the transition temperature of the La-Ba-Cu-O compound. We decided to simulate a high pressure environment by replacing the Ba and La with other differently-sized atoms, thereby changing the interatomic distances. After several configurations we estimated an optimal chemical composition of Y(1.2)Ba(0.8)CuO(4). On January 29, 1987, using this formula, we created the first superconductor in a liquid nitrogen environment, approximately 95 K. Subsequent work has raised the Tc to 98 K.

Recent work has demonstrated that Yttrium can be replaced with a wide variety of rare earth elements and the Tc will still remain around 90 K. Others the field claim to have achieved a Tc as high as 240 K, although these results are unstable, inconsistent, and not reproducible.

2. Understanding the mechanisms behind superconductivity.

The complexity of the compounds involved makes understanding the mechanism of superconductivity difficult, but it is this understanding that will be required to make stable superconductors at high Tc ranges. It has been determined that the traditional theories of superconductivity, primarily the theory of electron-phonon interaction, are insufficient to explain the processes we are observing, but we are finding some tendencies that appear to be related to the superconductivity effect.

Our research indicates that the appearance of superconductivity depends on the heat treatment process, the size of the divalent (Ba) and trivalent (Y) atoms, and the crystal structure, which may be related to the size of the ions.

The following research is being initiated to study these and other aspects of the superconductivity mechanism:

a) Investigation of the thermal processes by simultaneously monitoring the weight loss, the thermal reaction, and the chemical species involved in sample preparation.

b) Investigation of the Ionic Size Effects through further substitutions and partial substitutions of the divalent and trivalent constituents of the compounds.

c) Study of possible infrared electronic excitation at room temperature and at low temperatures.

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STUDY OF HIGH TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

High temperature superconductors with Tc above liquid nitrogen temperature was first discovered in our laboratory. The impact of this discovery to both the science and technology is tremendous. An extensive follow up study of this discovery is in urgent need to better understand the science and to improve the material characteristic for practical application. We propose in this study to carry out detailed experiments on the thermal reaction, structure and physical propertis of the high Tc superconductors. The success of this study is expected to provide important insight into the mechanism responsible for the occurrence of high Tc.

INTRODUCTION

For the last three quarters of a century, since the discovery of superconductivity in 1911, great efforts have been made in an attempt to raise the superconducting transition temperature Tc. In spiter of the efforts, not until recently has Tc exceeded 23.2 K first observed in 1973.[1] In the spring of 1986, Bednorz and Muller reported [2] the observation of superconductivity in the La-Ba-Cu-O compound system. Subsequent magnetic measurements [3-5], indeed, confirmed the report and suggested the role [6] of the K_2NiF_4 phase in the superconductivity observed. Pressure was found [5,7] to enhance the superconducting transition temperature of La-Ba-Cu-O compound in an unusually high rateof > 10^{-3} $Kbar^{-1}$ and to raise the onset temperature Tco to about 57 K. To simulate the pressure effects, we have replaced the Ba atoms in the K2NiF4 structure La-Ba-Cu-O compound by smaller Sr and even smaller Ca-atoms. We found [8] that the Tc of La-Sr-Cu-O is enhanced while the Tc of La-Ca-Cu-O is suppressed as compared with La-Ba-Cu-O, suggesting the existence of an optimal interatomic distance for high Tc in this oxide compound system. Further studies by substituting the alkaline earth ion by other divalent ions suggest that the size of the trivalent ion (La) is also important for the occurrence of superconductivity. Based on this observation, we decided to substitute the La atom by smaller size Y atom but with different composition which match the optimum size condition. The composition we estimated is $Y_{1.2}Ba_{0.8}CuO_4$. In January 29, 1987, we demonstrated the first time in history the appearance of superconductivity in a liquid nitrogen environment.[9] The Tc of

Keynote Address

Study of high temperature oxide superconductors

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ABSTRACT

Superconducting 123 films can be fabricated using the green 211 phase as a substrate. The superconducting characteristics of these films are better than the characteristics found when other oxide compounds are used as substrates. Using high temperature processing, 211 phase oxide can be partially converted to 123 phase. Using the same process, a new high T_c copper oxide compound with non-rare earth elements was prepared. High temperature processing presents an alternative synthetic route in the search for new high T_c superconductors.

1. INTRODUCTION

The discovery of superconductivity in the La-Ba-Cu-O system (referred to as the "214" phase) in the 30K range by Bednorz and Muller in 1986[1] has stimulated much interest among scientists of many disciplines. Perturbations to the crystal lattice by applying high pressure[2] or by replacing Ba^{2+} with other ions[3] have raised the superconducting transition temperature T_c to above 50K. These results suggested that higher T_c compounds might be made by substituting the appropriate ion into this cuprate oxide system. This supposition led us to the discovery of superconductivity at 90K in multiphase $Y_{1.2}Ba_{0.8}CuO_{4-y}$.[4] Within weeks of our discovery the superconducting phase was identified to be the black $Y_1Ba_2Cu_3O_7$ phase (referred to as the "123" phase).[5] Subsequently, many research groups have directed their research efforts toward this class of materials and have generated voluminous data on their normal and superconducting properties. Improved processing techniques have led to the preparation of single-phase bulk polycrystalline materials, single crystals, and oriented films. The extent of the research being done on 90K superconductors is amply demonstrated by the number of conferences held and journal articles published last year.[6]

About a year ago we began an extensive search for new superconductors by chemical substitution on the 40K superconducting cuprate oxides. While most of our experiments ended in failure, some important observations[7] pertaining to improvements in T_c gradually emerged: (1) the proper combination of a stable trivalent ion and a divalent alkaline-earth ion is essential, (2) the size of the ions is an important factor, and (3) proper heat treatment is required. Based on these observations and the assumption that an optimal interatomic distance might exist in the K_2NiF_4 structure for a high T_c compound,[7] we successfully produced the first Y-Ba-Cu-O compound with a superconducting transition at 90K. Immediately after this discovery we found that Bi-Sr-Cu-O,[8] when prepared under certain conditions, exhibited an anomaly indicative of superconductivity with an onset temperature at about 60K. However, an equilibrium phase of this system was found to have a T_c of only 20K.

During the process of making the first 90K multiphase Y-Ba-Cu-O material, which was soon shown to be composed of the green Y_2BaCuO_7 phase (referred to as the "211" phase) and the superconducting 123 phase, we observed samples which were reacted at a temperature higher than 950°C but for a comparatively short time exhibited sharper T_c transitions.[7] We also observed that an extremely careful heat treatment procedure is required to obtain single phase 123 compound. These results suggested that: (1) the presence of the 211 phase may be thermodynamically favorable to the formation of the superconducting 123 phase, and (2) processing at higher temperatures may stabilize some phases unstable at lower processing temperatures. These results led us to attempt fabrication of superconducting films at higher temperatures using the 211 phase as a substrate material. In this paper we report on recent advances made in our laboratories.

2. EXPERIMENTAL

The compounds used as film substrates and for high temperature processing were prepared in the following manner. Appropriate amounts of metal oxides were mixed, pressed into pellets, heated at 950°C for 12 hours, and then quenched to room temperature. Annealing procedures depended on the particular study being conducted and are described in detail in appropriate sections. Electrical resistivity measurements were made with the conventional