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SUPERCONDUCTING COMPOSITION AND METHOD

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BACKGROUND OF THE INVENTION

The present invention relates to superconducting compositions, i.e., compositions offering no electrical resistance, processes for their production, and methods for their use.

Mixtures of barium, lanthanum, copper and oxygen, that have superconductive properties at approximately 30° Kelvin have been described. Under atmospheric pressure conditions, the superconducting transition temperature (T_c) for these compositions, i.e., that temperature at which a portion of the material begins to show superconductive properties, appears to be limited to near the 30° Kelvin limit. It would be desirable to produce a superconducting composition that has a T_c which exceeds the T_c of those superconducting compositions previously described. It would be particularly desirable to develop a superconducting composition that has the potential of having a T_c of 77° Kelvin. Such a composition would enable liquid nitrogen to be used to cool the superconducting equipment, which would dramatically decrease the cost of insulating the superconducting material.

SUMMARY OF THE INVENTION

The present invention provides a superconducting composition having a superconducting transition temperature above about 40° Kelvin. A preferred embodiment of this composition includes an alkaline earth metal that has interatomic distances that are less than those of a comparable composition that includes barium as the alkaline earth metal and that is maintained at atmospheric pressure and at room temperature.

A particularly preferred superconducting composition comprises an oxide complex defined by the following formula:

$$[L_{1-x} M_x]_a A_b O_y$$

wherein L is an element selected from the group consisting of lanthanum, lutetium and yttrium, or a mixture of one or more of these elements;

wherein A is an element selected from the group consisting of copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, and vanadium or a mixture of one or more of these elements;

wherein M is an element selected from the group consisting of barium, strontium, calcium and magnesium or a mixture of one or more of these elements; and

wherein x is a number in the range of about 0.075 to about 0.5,

a is a number in the range of 1 and 2,
b is 1, and
y is about 2 to about 4.

wherein the interatomic distances between the elements is reduced from their respective distances when under atmospheric pressure, when M is barium.

In a preferred embodiment of the present invention, the interatomic distances between the atoms of the elements is reduced from their respective distances, when under atmospheric pressure.

The present invention also provides a method for making such compositions which includes:

thoroughly mixing appropriate amounts of L_2O_3, MCO_3 and AO;

heating said mixture in an oxygen containing atmosphere, at an appropriate pressure, and at a temperature of between about 640° C and 800° C for a time sufficient to let the mixture react;

heating the resulting samples at a temperature between about 900° C and 1100° C for at least twelve hours;

homogenizing said reaction mixture;

heating the homogenized mixture at a temperature between about 900° C and about 1100°C for at least six hours;

compressing said composition with a pressure of at least one kilobar to produce pellets;

sintering said pellets;

quenching said samples rapidly from the sintering temperature to room temperature in an inert gas atmosphere.

An alternative method for making such compositions includes the following steps:

thoroughly missing appropriate amounts of L_2O_3, MCO_3 and AO

compressing said mixture into pellets;

reacting said mixture at temperature between about 900° C and about 1100° C for a time sufficient to complete the solid state reaction;

rapidly quenching said pellets to room temperature, and, when M is barium, reducing the interatomic distances of the elements L, A, M and O from their respective distances when under atmospheric pressure.

The present invention also provides for the use of such compositions as superconducting materials.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Reducing the interatomic distances between the atoms of the elements in a lanthanum, barium, copper oxide composition can increase the superconducting transition temperature T_c of the composition. Consequently, any means for reducing this interatomic distance should enhance the T_c of the composition. One means for reducing this distance is to apply a pressure that exceeds atmospheric pressure. The T_c increases as the applied pressure is increased.

Another method for decreasing the interatomic distance is to completely or partially substitute the barium atoms, atomic radius of 2.22 angstroms, with the 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. Similarly, complete or partial substitution of the lanthanum atoms, atomic radius of 1.87 angstroms, with the smaller lutetium, atomic radius 1.75 angstroms, or yttrium, atomic radius 1.78 angstroms, will provide this same effect.

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 distance of the superconducting composition, and thus will increase the T_c of the composition. Further, cladding of a lanthanum, barium, copper oxide composition with metals having smaller thermal expansion coefficients, such as copper, will restrain the interatomic distances between the elements in the composition and increase the T_c of the composition.

The compositions of the present invention may be made, for example, following either of the following processes.

1. Appropriate amounts of L_2O_3, MCO_3 and AO are thoroughly mixed. This mixing is preferably done mechanically in a jar mill for at least 12 hours. The mixing produces finely ground particles. The mixture is then heated in an oxygen containing atmosphere, at an appropriate pressure, and at a temperature between about 640-800° C. The temperature of the mixture is conveniently increased to the 640-800°C target temperature at a rate of 10° C per minute. The mixture is kept at this target temperature for a time sufficient to allow the mixture to react. Preferably the mixture is allowed to react for about an hour. After this reaction step, the temperature is raised to between 900 and 1100° C, conveniently at a rate of about 30° C per minute. The samples are kept a time sufficient to complete the solid state reaction of the materials, the completed solid state reacted product being that product having the components completely diffused through the composition. The samples are then cooled to room temperature.

The next step is to homogenize the sample, preferably by pulverizing the reacted mixture in a jar mill for at least 1 hour. The pulverized mixture is then heated rapidly to between 900 - 1100° C. The mixture remains at this temperature for at least 6 hours. After this step the mixture is compressed under a pressure of at least one kilobar. This compresses the powdered mixture into pellets. The pellets are then sintered into solid cylinders. This sintering process is preferably performed at a pressure between zero to two kilobars at a temperature of between about 900 - 1100° C and for about four hours. Finally, the samples are quenched rapidly from this temperature of between 900 - 1100° C to room temperature, in an argon, or other inert gas, atmosphere. This final step, along with thorough mixing of this mixture, decreases the range of the superconducting transition of the composition: This superconducting transition is the range of temperatures between the point when a portion of the material shows superconductive properties and the temperature at which the entire composition shows superconductive properties.

Compositions made in this process may be compressed to pressures that exceed atmospheric pressure, preferably in the range of 1 to 20 kilobar. This increase in pressure typically increases the T_c of the composition.

2. A second process for producing this superconducting composition of the present invention includes: thoroughly mixing, for at least about 12 hours, appropriate amounts of L_2O_3, MCO_3, and AO, conveniently by mechanical means, such as in a jar mill, compressing the mixture into pellets; reacting the pellets at about 900 - 1100° C for at least 12 hours; preferably at least twenty-four hours, this

reaction preferably takes place in an air atmosphere; and quenching rapidly the reacted pellets to room temperature.

This second method sometimes results in multiphase samples in a less controllable way.

The following examples are representative of the methods of producing the products of the invention.

EXAMPLE I

6.0 grams of La_2O_3, 0.61 grams of $SrCO_3$ 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, 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. 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 kilobar. 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 zero kilobar. Finally, the sample was rapidly quenched from this temperature to room temperature in an argon atmosphere.

The resulting lanthanum-strontium-copper-oxide composition has a superconductivity transition temperature of 45° Kelvin, with a narrow transition width to uniform superconductivity of about 10° Kelvin 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 kilobar. 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 showed superconductive properties at a temperature of about 42° Kelvin, with a narrow transition width of about 6° Kelvin 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, 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 kilobar. 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 a pressure of zero kilobar. Finally, the sample was rapidly quenched from this temperature to room temperature in air.

The resulting lanthanum-barium-copper-oxide composition, superconducting at 39° Kelvin at ambient pressure, was then placed inside a pressure cell. The composition was then compressed to a pressure of 10 kilobar, at room temperature. After this compression step, the temperature was gradually reduced until the composition showed superconductive properties. This composition shows superconductivity properties at a temperature of 52.5° Kelvin.

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, $BaCo_3$ and CuO have been placed in a copper sleeve. 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 kilobar. 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 showed superconductive properties at a temperature of 36° Kelvin 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, 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 kilobar. 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 a pressure of zero kilobar. Finally, the sample was rapidly quenched from this temperature to room temperature in air.

The resulting lanthanum-barium-copper-oxide composition, superconducting at 32° Kelvin at ambient pressure, was then placed under a pressure of 9 kilobar at room temperature. As this compressed composition was cooled, it began showing superconductivity properties at a temperature of 40.2° Kelvin.

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 kilobar. 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 was then placed under a pressure of 16 kilobar, at room temperature. Upon cooling, this composition, it showed superconductive properties at a temperature of 54° Kelvin.

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 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 magnetic layer in such a superconducting-magnetic-superconducting multi-layer device could consist of a lanthanum-barium-copper-oxide base composition. Such a composition was prepared in the following example.

EXAMPLE VII

3.0 grams La_2O_3, 3.6 grams $BaCO_3$ and 2.9 grams CuO were mixed and heated in a vacuum of 10^{-4} Microns at a temperature of about 1000° C for about twenty-four hours. The resulting product formed a magnetic compound with an ordering temperature below 20° Kelvin.

The superconducting-magnetic-superconducting multilayer structures may be formed by subjecting the overlayer, which is separated from the underlayer by an ultra-thin protective covering of SiO_2, to a vacuum of 10^{-4} Microns 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. Heat treatment of such film samples at 15-2000 Microns pressure in an oxygen atmosphere should make the superconducting properties of the film samples similar to those for the sintered samples.

The amount of oxygen present in the compositions of the present invention depends upon the valence requirements of the other elements and the defects resulting heat from the particular heat treatment used to make the composition. The molar oxygen content "y" is about 2 to 4 times "b", as used in the preceeding equation.

As is readily apparent from the above description, additional advantages and modifications will readily occur to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific examples shown and described. Accordingly, departures may be made from the details shown in the examples without departing from the spirit or scope of the disclosed general inventive concept.

WHAT IS CLAIMED IS:

1. A superconducting composition having a superconducting transition temperature above about 40° Kelvin.

2. The composition of claim 1 wherein said composition includes an alkaline earth metal that has interatomic distances that are less than those of such compositions that include barium and that are maintained at atmospheric pressure under room temperature.

3. The composition of claim 2 wherein said composition comprises an oxide complex defined by the following formula:

$$[L_{1-x} M_x]_a A_b O_y$$

wherein L is an element selected from the group consisting of lanthanum, lutetium and yttrium or a mixture of one or more of these elements;

wherein A is an element selected from the group consisting of copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, and vanadium or a mixture of one or more of these elements;

wherein M is an element selected from the group consisting of barium, strontium, calcium and magnesium or a mixture of one or more of these elements; and wherein x is a number in the range of about 0.075 to about 0.5,

a is a number in the range of 1 and 2,
b is 1, and
y is from about 2 to about 4 and

wherein the interatomic distances between the elements is reduced from their respective distances when under atmospheric pressure, when M is barium.

4. The composition of claim 3 wherein L is lanthanum, M is strontium, A is copper, and x is a number in the range of about 0.075 to about 0.185.

5. The composition of claim 4 wherein a is 2.

6. The composition of claim 1 wherein the interatomic distances of the elements L, A, M and O have been reduced from their respective distances, when under atmospheric pressure.

7. The composition of claim 6 wherein L is lanthanum, M is barium, A is copper, x is a number in the range of about 0.075 to about 0.2, and a is 2.

8. The composition of claim 6 wherein L is lanthanum, M is barium, A is copper, x is a number in the range of about 0.3-0.4, and a is 1.

9. The composition of claim 6 wherein the interatomic distances are reduced by the application of a pressure greater than atmospheric pressure.

10. The composition of claim 9 wherein the pressure applied is at least about 1 kilobar.

11. The composition of claim 6 wherein the interatomic distances are reduced by the deposition of a film of said composition onto a substate having smaller lattice parameters.

12. The composition of claim 6 wherein the interatomic distances are reduced by the cladding of said composition with a metal having a relatively smaller thermal expansion coefficient.

13. The composition of claim 12 wherein said metal is copper.

14. The composition of claim 3 in which said composition has a superconducting transition temperature approximately equal to or greater than 42° Kelvin.

15. The composition of claim 6 in which said composition has a superconducting transition temperature approximately equal to or greater than 54° Kelvin.

16. A method of making a superconducting composition comprising an oxide complex defined by the following formula:

$$[L_{1-x} M_x]_a A_b O_y$$

wherein L is an element selected from the group consisting of lanthanum, lutetium and yttrium;

wherein A is an element selected from the group consisting of copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, and vanadium;

wherein M is an element selected from the group consisting of barium, strontium, calcium and magnesium; and

wherein x is a number in the range of about 0.075 to about 0.5,

a is a number in the range of 1 and 2,
b is 1, and
y is a number determined by the valence requirements of the other elements present, and

wherein the interatomic distances of the elements L, A, M and O have been reduced from their respective distances when under atmospheric pressure, when M is barium.

comprising:

thoroughly mixing appropriate amounts of L_2O_3, MCO_3 and AO

compressing said mixture into pellets;

reacting said mixture at a temperature between about 900° C and about 1100° C for at least 21 hours; and quenching said pellets to room temperature, and, when M is barium, reducing the interatomic distances of the elements L, A, M and O from their respective distances when under atmospheric pressure.

17. A method for making a superconducting composition comprising an oxide complex defined by the following formula:

$$[L_{1-x}M_x]_a A_b O_y$$

wherein L is an element selected from the group consisting of lanthanum, lutetium and yttrium;

wherein A is an element selected from the group consisting of copper, bismuth, titanium, tungsten, zirconium, tantalum, noibium, and vanadium;

wherein M is an element selected from the group consisting of barium, strontium, calcium and magnesium; and

wherein x is a number in the range of about 0.075 to about 0.5,

a is a number in the rang of 1 and 2,
b is 1, and
y is about 2 to about 4 and

wherein the interatomic distances of the elements L, A, M and O have been reduced from their respective distances when under atmospheric pressure, when M is barium.

comprising:

thoroughly mixing appropriate amounts of L_2O_3, MCO_3 and AO;

heating said mixture in an oxygen-contained atmosphere under a pressure of between 15 and 2000 Microns at a temperature of between 6409° C and 800° C for a time sufficient to let the mixture react;

heating the resulting samples at a temperature between about 900° C and 1100° C for at least twelve hours;

homogenizing said reaction mixture;

heating the homogenized mixture at a temperature between about 900° C and about 1100° C for at least six hours;

compressing said composition with a pressure of at least one kilobar to produce pellets;

sintering said pellets;

quenching said samples rapidly from the sintering temperature to room temperature in an inert gas atmosphere.

18. A method of using a superconducting composition comprising an oxide complex defined by the following formula:

$$[L_{1-x}M_x]_a A_b O_y$$

wherein L is an element selected from the group consisting of lanthanum, lutetium and yttrium;

wherein A is an element selected from the group consisting of copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, and vanadium;

wherein M is an element selected from the group consisting of barium, strontium, calcium and magnesium; and

wherein x is a number in the range of about 0.075 to about 0.5,

a is a number in the range of 1 and 2,
b is 1, and
y is about 2 to about 4 and

wherein the interatomic distances of the elements L, A, M and O have been reduced from their respective distances when under atmospheric pressure, when M is barium,.

as a superconducting material.

ABSTRACT

A superconducting composition that is an oxide complex of the formula $[L_{1-x} M_x]_a A_b O_y$. L is lanthanum, lutetium or yttrium. A is copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, or vanadium. M is barium, strongium, calcium or magnesium. When M is barium, the interatomic distances of the elements L, A, M and O have been reduced from their respective distances when under atmospheric pressure. "a" is a number between 1 and 2, b is 1, x is a number in the range of 0.075 and .5 and y is about 2 to about 4.

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