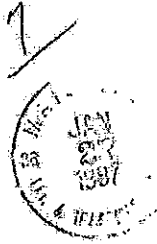


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APPLICATION FOR PATENT

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Title: SUPERCONDUCTING COMPOSITIONS AND METHOD
FOR ENHANCING THEIR TRANSITION TEMPERATURES
BY PRESSURE

Cross-Reference to Related Application

This is a continuation-in-part of Serial No. 4002,089, filed January 12, 1987, entitled "Superconducting Composition and Method."

5 Background of the Invention

This invention relates to superconducting compositions, i.e., compositions offering no electrical resistance at a temperature below a critical temperature; to processes for their production and to methods for their use; and to methods for increasing the superconducting transition temperature of superconducting compositions.

Superconductivity was discovered in 1911. Historically, the first observed and most distinctive property of a superconductive material is the near total loss of electrical resistance by the material when at or below a critical temperature that is a characteristic of the material. This critical temperature is referred to as the superconducting transition temperature of the material, T_c . The criteria by which a selection of the critical temperature value is determined from a transition in the change in resistance observed is often not obvious from the literature. Many past authors have chosen the

mid-point of such curve as the probable critical temperature of their idealized material, while many others have chosen to report as the critical temperature the highest temperature at which a deviation from the normal state resistivity property is observed. Hence, the literature may report differing temperatures within a narrow range as the critical or superconducting transition temperature for the same material, depending on the particular author's method for selecting T_c from the observed data.

The history of research into the superconductivity of specific materials began with the discovery in 1911 that mercury superconducts at a transition temperature of about 4° K. In the late 1920's, NbC was found to superconduct at a higher temperature, namely up to about 10.5° K. Thereafter other compounds and alloys of Nb were examined and various Nb compositions were discovered with progressively, but only slightly higher, superconducting transition temperatures. In the early 1940's NbN was observed with a transition temperature of about 14° K; Nb₃Sn was reported in the early 1950's; Nb₃(Al-Ge) was reported in the late 1960's; and Nb₃Ge was reported in the early 1970's to have a transition temperature of about 17° K. Careful optimization of Nb₃Ge thin films led to an increase of the critical temperature for such material up to 23.3° K. While this work led to progress the maximum temperature at which superconductivity could occur was raised to only 23.3° K since research started three-quarters of a century ago. The existing theories explained the superconductivity of these materials, but did not predict superconductivity of higher than 40° K. Significant progress in finding materials which superconduct at higher transition temperatures than that of Nb₃Ge thin films was not made until 1986.

In 1986, specially prepared coprecipitated and heat treated mixtures of lanthanum, barium, copper and oxygen, that have an abrupt decrease in resistivity at an onset

temperature as high as 30° K exhibited a phenomena
"reminiscent of the onset of percolative
superconductivity" were reported by J.G. Bednorz and R.A.
Muller, "Possible High T_c Superconductivity In The
5 Ba-La-Cu-O System," Z.Phys.B.-Condensed Matter, 64, pp.
189-193 (1986). Under atmospheric pressure conditions,
the abrupt change in resistivity for these compositions --
i.e., that temperature at which a portion of the material
begins to show properties reminiscent of percolative
10 superconductivity -- were reported to approach the 30° K
range. The authors refer to this phenomenon as a
"possible" case of superconductivity. The compositions
reported by Bednorz et al to have such properties at a
temperature as high as 30° K comprise $La_{5-x}Ba_xCu_5O_{(3-y)}$
15 where $X = 0.75$ to 1 and $Y > 0$. The Bednorz et al
compositions are prepared by coprecipitation of Ba-, La-
and Cu- nitrate solutions by addition to an oxalic acid
solution followed by decomposition and solid-state
reaction of the coprecipitate at 900°C for 5 hours.
20 Thereafter, the composition is pressed to pellets at 4
kilobars and the pellets are sintered at a temperature
below 950°C in a reduced oxygen atmosphere of 0.2×10^{-4}
bar. Bednorz et al reported that this method of sample
preparation is of crucial importance to obtaining the
25 observed phenomena.

Superconductivity is a potentially very useful
phenomenon. It reduces heat losses to zero in electrical
power transmission, magnets, levitated monorail trains and
many other modern devices. However, superconductivity of
30 a material occurs only at very low temperatures.
Originally, and until the inventions outlined herein,
liquid helium was the required coolant to provide the
conditions necessary for superconductivity to occur.

It would be desirable to produce a superconducting
35 composition that has a transition temperature which
exceeds those of 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° K or higher. Such a composition would enable the use of liquid nitrogen instead of liquid helium to cool the superconducting equipment and would
5 dramatically decrease the cost of operating and insulating superconducting equipment and material.

Summary of the Invention

Described is a superconducting composition comprising an oxide complex of the formula $[L_{1-x}M_x]_aA_bO_y$ wherein L is
10 lanthanum, lutetium or yttrium; A is copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, or vanadium; M is barium, strontium, calcium or magnesium; and "a" is 1 to 2; b is 1; x is about 0.01 to about 0.5 and preferably 0.075 to 0.5; and y is about 2 to about 4.
15 The oxide complexes of the invention are prepared by a solid-state reaction procedure which produce oxide complexes having enhanced superconducting transition temperatures compared to an oxide complex of like empirical composition prepared by a coprecipitation -- high
20 temperature decomposition procedure.

When M is barium, the transition temperatures of onset and complete superconductivity, T_{c0} and T_{c1} (as seen in Fig. 5), respectively, may be increased by subjecting the barium species of the oxide complex to pressure up to
25 18 kilobars. Likewise the non-barium species of the oxide complexes of the invention exhibit an enhancement to higher limits of their superconducting transition temperatures when subjected to high pressures.

The application and maintenance of high pressure on
30 such oxide complexes is believed to enhance the transition temperature to higher limits by reducing the interatomic spacings between elements L, A, M and O compared to their respective spacings when the oxide complex is under atmospheric pressure only.

35 Alternatively, an alkaline earth metal having atomic radius smaller than barium may be used in whole or in part

to fulfill the alkaline earth metal constituent requirement to provide an oxide complex having reduced interatomic spacings between elements, L, A, M and O even when the oxide complex is under only atmospheric pressure, compared to a pure barium species, thus increasing T_{co} and T_{cl} . Application of pressure up to 18 kilobars will even further enhance the T_{co} and T_{cl} of such substituted or non-barium oxide complex species.

With a solid-state reaction prepared oxide complex of the invention a transition temperature as high as 100° K has been observed even under atmospheric pressure.

Brief Description of the Drawings

Fig. 1 illustrates the reduction in electrical resistance as temperature is decreased of a La-Ba-Cu-O composition as prepared according to Example V.

Fig. 2 illustrates the enhancement towards higher temperatures of the onset transition temperature (T_{co}) as applied pressure is increased upon a La-Ba-Cu-O composition as prepared according to Example V.

Fig. 3 illustrates the magnetic field effect on resistivity of a La-Ba-Cu-O composition as prepared according to Example V.

Fig. 4 illustrates the magnetic susceptibility as a function of temperature of a La-Ba-Cu-O composition as prepared according to Example V.

Fig. 5 illustrates the resistivity and diamagnetic shift as a function of temperature of a La-Ba-Cu-O composition prepared according to Example III.

Fig. 6 illustrates the resistivity as a function of temperature under different applied pressures of 5.7 kilobars, 10.5 kilobars and 16.8 kilobars of a La-Ba-Cu-O composition as prepared according to Example III.

Fig. 7 illustrates the effect of applied pressure on onset temperatures (T_{co}), midpoint temperature (T_{cm}) and temperature for complete superconductivity (T_{cl}) of a La-Ba-Cu-O composition prepared according to Example III.

Detailed Description of the Preferred Embodiments

Superconducting compositions of this invention comprise an oxide complex defined by the following formula:



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 from about 0.01 to about 0.5, and preferably 0.075 to 0.5; "a" is 1 to 2, "b" is 1, and "y" is about 2 to about 4. 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 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 preceding equation. Lanthanum is the preferred "L" component, barium and strontium are the preferred "M" components, and copper is the preferred "A" component.

It has been observed that the transition temperature of such an oxide complex is increased by the application of pressure to the composition. It is believed that subjecting the oxide complex to high pressures decreases the interatomic distances or lattice spacing in such complexes and that this may, at least in part, account for the enhancement of transition temperatures that has been observed. Another way to obtain a decrease of the interatomic distances or lattice spacings is during the preparation of the oxide complex. Thus, for example, an

alkaline earth metal having an atomic radius smaller than barium may be used in whole or in part to fulfill the alkaline earth metal requirement to produce an oxide complex having reduced interatomic distances or lattice spacing compared to an oxide complex with barium alone, with a consequent increase in the transition temperature of the non-barium oxide complex resulting compared to one produced with barium alone. The transition temperature is increased in such an oxide complex even as measured under atmospheric pressure.

The present invention also provides a solid-state reaction method for making such superconducting oxide complexes which comprises: thoroughly mixing selected amounts of solid powdered compounds containing L, M, A, and O, preferably by selecting appropriate amounts of L_2O_3 , $L(OH)_3$, MCO_3 , and AO ; heating the powdered mixture in an oxygen containing atmosphere, at an appropriate pressure, and at a temperature of between about $640^\circ C$ and $800^\circ C$ for a time sufficient to react the mixture in the solid state; heating the resulting mixture at a temperature between about $900^\circ C$ and $1100^\circ C$, preferably for at least twelve hours; homogenizing said reaction mixture; heating the homogenized reaction mixture at a temperature between about $900^\circ C$ and about $1100^\circ C$, preferably for at least six hours; compressing said composition with a pressure of at least one kilobar to produce pellets; sintering said pellets; and quenching said sintered pellets rapidly from the sintering temperature to room temperature in air or in an inert gas atmosphere such as Ar. Preferably mixing of the solid powder compounds is performed by an intensive mixer such as a ball mill.

An alternative method for making such oxide complex superconductive compositions includes the following steps: thoroughly mixing selected amounts of solid powdered compounds containing L, M, A, and O, preferably by selecting appropriate amounts of L_2O_3 or $L(OH)_3$, MCO_3 and AO ; compressing said mixture into pellets; reacting said

mixture at a temperature between about 900°C and about 1100°C for a time sufficient to complete the solid state reaction; and rapidly quenching said pellets to room temperature. Again, mixing is preferably accomplished by an intensive mixer such as a ball mill.

Still another alternative method includes the immediately foregoing steps and the step of reducing interatomic distances, either by the application of pressure to the oxide complex or by the use of atomic elements which provides smaller lattice spacings.

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 procedure 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. 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.

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. 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_c of the composition.

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

1. Appropriate amounts of L_2O_3 or $L(OH)_3$, MCO_3 and AO are thoroughly mixed. This mixing is preferably done mechanically, as in a jar mill or more preferably in an intensive mixer such as a ball 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 solid-state mixture to react. Preferably, the mixture is allowed to react for about an hour. After this reaction step, the temperature is raised to about 900 to about 1100°C, conveniently at a rate of about 30°C per minute. The samples are kept at the 900 to 1100°C temperature for 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 and more preferably in a ball mill for at least 1 hour. The pulverized mixture is then heated

rapidly to between 900 - 1100°C. The mixture is maintained at this temperature preferably 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 or some other coherent compacted form as desired. 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 air, or an 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 range is the range of temperatures between the point when a portion of the material shows superconductive properties (onset transition temperature) and the temperature at which the composition shows complete superconductive properties.

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

2. A second process for producing superconducting compositions of the present invention comprises: thoroughly mixing, preferably for at least about 12 hours, appropriate amounts of L_2O_3 or $L(OH)_3$, MCO_3 , and AO, by mechanical means, such as in a jar mill or more preferably in a ball mill, compressing the mixture into pellets; reacting the pellets at about 900 - 1100°C preferably for at least 12 hours, and more preferably at least twenty-four hours. This reaction preferably takes place in an

air atmosphere; after which the reacted pellets are rapidly quenched to room temperature.

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

5 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, 10 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 15 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 20 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.

25 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 30 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 35 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 $\text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_1\text{O}_y$. This corresponds to an oxide complex of the general formula $[\text{La}_{1-x}\text{Sr}_x]_a\text{Cu}_b\text{O}_y$ wherein "x" is 0.1, "a" is 2, "b" is 1 and "y" is 2 to 4. The oxide complex composition had an onset 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 $\text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_1\text{O}_y$. This corresponds to an oxide complex of the general formula $[\text{La}_{1-x}\text{Sr}_x]_a\text{Cu}_b\text{O}_y$ 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
5 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
10 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
15 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
20 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
25 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 $\text{La}_{1.8}\text{Ba}_{0.2}\text{Cu}_1\text{O}_y$. The oxide
30 complex so formed was of the formula $[\text{La}_{1-x}\text{Ba}_x]_a\text{Cu}_b\text{O}_y$
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
35 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.

5 A sample prepared as described above exhibits only X-ray powder diffraction patterns characteristic of the single K_2NiF_4 phase with a resolution ~5%. The resistivity of this sample at ambient pressure decreases monotonically with decreasing temperature but at a reduced
10 rate below 60° K. A large drop in resistivity sets in at ~39° K, indicative of the onset of a superconducting transition, and resistivity becomes zero at T_{c1} ~20° K as shown in Fig. 5. Preliminary ac χ -measurement showed diamagnetic shift starting at ~32° K and reaching a
15 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}
20 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.

25 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
30 is also detected upon removal of pressure, as evidenced by the dramatic increase 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
35 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 $\text{La}(\text{OH})_3$, 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 $[\text{La}_{1-x}\text{Ba}_x]_a\text{Cu}_b\text{O}_y$ 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
5 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
10 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
15 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 and "y" is 2 to 4.

The resulting lanthanum-barium-copper-oxide
20 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 medium. Pressure was measured using a superconducting Pb-manometer situated next to the sample at room temperature. As this
25 compressed composition was cooled, it began showing superconductivity properties at a temperature of 40.2° K.

Powder X-ray diffraction patterns at room temperature showed that the sample was multiphased, consisting
predominantly of K_2NiF_4 (~90%) and unidentified phases
30 (<10%). Under applied pressures, resistivity at 300° K is suppressed and the drop in resistivity is broadened slightly, but with an overall shift toward higher temperature as shown in Fig. 1. T_{co} increases rapidly
with pressures as shown in Fig. 2. At 13 kilobars, T_{co} is
35 ~40.2° K. Under pressure, T_{co} increases from 32° to 40.2° K at 13 kilobars at a rate $\sim 0.9 \times 10^{-3}$ ° K bar⁻¹. Above 13 kilobars, the sample was damaged due to a shear strain

introduced accidentally by applying pressure below -20°C , as evidenced by the appearance of a rapid resistivity increase following the resistivity drop at T_{co} on cooling and the irreversibility of resistivity after the pressure was reduced.

Fig. 3 displays the magnetic field effect on 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 $[\text{La}_{1-x}\text{Sr}_x]_a\text{Cu}_b\text{O}_y$ 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 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^{-4} microns Hg at a temperature of about 1000°C for about twenty-four hours. The resulting product formed a magnetic compound with a 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^{-4} 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 $(\text{La}_{1-x}\text{Ba}_x)_a\text{Cu}_b\text{O}_y$ 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 so 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
5 appropriate to provide an oxide complex of the formula $[\text{La}_{1-x}\text{Ba}_x]\text{Cu}_b\text{O}_y$ 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
10 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
15 and CuO were used in the amounts appropriate to provide an oxide complex of the formula $[\text{La}_{1-x}\text{Ba}_x]\text{Cu}_b\text{O}_y$ 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
20 complex so produced showed superconductive properties at an onset temperature of 100°K .

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
25 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.

1 7. The method of claim 1, wherein said sintering is
2 at a temperature of 900-1100°C.

1 8. The method of claim 1, further comprising
2 quenching the sintered pellets.

1 9. The method of claim 1, wherein said mixture is
2 pelletized before said heating.

1 10. The method of claim 1, wherein L is lanthanum
2 and A is copper.

1 11. The method of claim 10, wherein M is barium.

1 12. The method of claim 10, wherein M is strontium.

1 13. A superconducting metal oxide complex having the
2 formula $(L_{1-x}M_x)_aA_bO_y$, wherein L is lanthanum, lutetium,
3 yttrium or a combination thereof; M is barium, strontium,
4 calcium, magnesium or a combination thereof; A is copper
5 bismuth, titanium, tungsten, zirconium, tantalum, niobium,
6 vanadium or a combination thereof; "a" is 1 to 2; "b" is
7 1; "x" is about 0.01 to about 0.5; and "y" is about 2 to
8 about 4; said complex made by a process comprising the
steps of:

10 heating a mixture of solid compounds containing
11 L, M, A and O in proportions appropriate to yield
12 said formula to a temperature and for a time
13 sufficient to react the mixture in the solid state;
14 pelletizing the mixture; and
15 sintering the pellets.

1 14. The complex of claim 13, wherein said reaction
2 is at a temperature of 640-800°C in an oxygen atmosphere.

1 15. The complex of claim 13, wherein said process
2 further comprises heating the mixture at 900-1100°C for a
3 period of at least about 12 hours subsequent to said
4 reaction.

1 16. The complex of claim 15, wherein said process
2 further comprises homogenizing the mixture subsequent to
3 said reaction and heating.

1 17. The complex of claim 16, wherein said process
2 further comprises heating said homogenized mixture at
3 900-1100°C for at least about 6 hours.

1 18. The complex of claim 13, wherein the mixture is
2 pelletized by compressing the mixture with a pressure of
3 at least 1 kilobar.

1 19. The complex of claim 13, wherein said sintering
2 is at a temperature of 900-1100°C.

1 20. The complex of claim 13, wherein said process
2 further comprises quenching the sintered pellets.

1 21. The complex of claim 13, wherein said mixture is
2 pelletized before said heating.

1 22. The complex of claim 13, wherein L is lanthanum
2 and A is copper.

1 23. The complex of claim 22, wherein M is barium.

1 24. The complex of claim 22, wherein M is strontium.

1 25. The complex of claim 13, wherein M is strontium,
2 calcium, or magnesium and essentially free of barium.

1 26. The complex of claim 13, wherein "x" is about
2 0.01 to about 0.03.

1 27. The complex of claim 13, wherein "x" is about
2 0.075 to about 0.5.

1 (A) 28. A superconducting metal oxide complex, having
2 the formula $(L_{1-x}M_x)_aA_bO_y$, wherein L is lanthanum,
3 lutetium, yttrium or a combination thereof; M is barium,
4 strontium, calcium, magnesium, or a combination thereof;
5 A is bismuth, titanium, tungsten, zirconium, tantalum,
6 niobium, vanadium or a combination thereof;
7 "x" is about 0.01 to about 0.03;
8 "a" is 1 to 2;
9 "b" is 1; and
10 "y" is about 2 to about 4.

1 29. The complex of claim 28, wherein M is
2 substantially free of barium.

1 30. The complex of claim 28, wherein M includes a
2 combination of two or more of elements selected from the
3 group consisting of: barium, strontium, calcium and
4 magnesium.

1 31. The complex of claim 28, wherein L is lanthanum
2 and A is copper.

1 32. The complex of claim 31, wherein M is barium.

1 33. The complex of claim 31, wherein M is strontium.

1 (B) 34. A method of increasing superconducting
2 temperature of a metal oxide, comprising the steps of:
3 subjecting to superatmospheric pressure a metal
4 oxide complex of the formula $(L_{1-x}M_x)_aA_bO_y$, wherein L is
5 lanthanum, lutetium, yttrium or a combination thereof; M

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6 is barium, strontium, calcium, magnesium or a combination
7 thereof; A is copper, bismuth, titanium, tungsten,
8 zirconium, tantalum, niobium, vanadium or a combination
9 thereof; "a" is 1 to 2; "b" is 1; "x" is about 0.01 to
10 about 0.5; and "y" is about 2 to about 4; and
11 cooling said complex to a temperature at or
12 below its superconducting onset temperature.

1 35. The method of claim 34, wherein said pressure is
2 up to about 18 kilobars.

1 36. The method of claim 34, wherein said pressure is
2 from 1 to 18 kilobars.

1 37. The method of claim 34, further comprising
2 reducing the pressure to which said complex is subjected
3 before said cooling thereof.

1 38. The method of claim 34, wherein said pressure is
2 maintained during said cooling.

1 39. The method of claim 34, wherein said oxide is
2 simultaneously subjected to said pressure and said onset
3 temperature.

1 40. The method of claim 34, wherein L is lanthanum
2 and A is copper.

1 41. The method of claim 40, wherein M is barium.

1 42. The method of claim 40, wherein M is strontium.

ABSTRACT

Described is a superconducting composition comprising an oxide complex of the formula $[L_{1-x}M_x]_aA_bO_y$, wherein L is lanthanum, lutetium or yttrium; A is copper, bismuth, titanium, tungsten, zirconium, tantalum, niobium, or vanadium; M is barium, strontium, calcium or magnesium; and "a" is 1 to 2; b is 1; x is a number in the range of 0.01 to 0.5 and preferably 0.075 to 0.5; and y is about 2 to about 4. The oxide complexes of the invention are prepared by a solid-state reaction procedure which produces oxide complexes having enhanced superconducting transition temperatures compared to an oxide complex of like empirical composition prepared by a coprecipitation - high temperature decomposition procedure.

When M is barium, the transition temperatures of onset and complete superconductivity, T_{CO} and T_{CI} , respectively, may be increased by subjecting the barium species of the oxide complex to pressure up to 18 kilobars. Likewise the non-barium species of the oxide complexes of the invention exhibit an enhancement to higher limits of their superconducting transition temperatures when subjected to high pressures.

The application and maintenance of high pressure on such oxide complexes is believed to enhance the transition temperature to higher limits by reducing the interatomic spacings between elements L, A, M and O compared to their respective spacings when the oxide complex is under atmospheric pressure only.

Alternatively, an alkaline earth metals having atomic radius smaller than barium may be used in whole or in part to fulfill the alkaline earth metal constituent requirement to provide an oxide complex having reduced interatomic spacings between elements, L, A, M and O even when the oxide complex is under only atmospheric pressure, compared to a pure barium species, thus increasing T_{CO} and T_{CI} . Application of pressure up to 18 kilobars will even

further enhance the T_{CO} and T_{Cl} of such substituted or non-barium oxide complex species.

With a solid-state reaction prepared oxide complex of the invention a transition temperature as high as 100° K
5 has been observed even under atmospheric pressure.