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Electrically superconducting compositions and processes for their preparation

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ELECTRICALLY SUPERCONDUCTING COMPOSITIONS AND PROCESSES FOR THEIR PREPARATION

The present invention is concerned with electrically superconducting compositions which are useful at a temperature above 77K and with methods for the preparation of such compositions.

The technical breakthrough of Bednorz and Muller, Z. Phys. B, 64, 189 (1986), was the first major improvement in the superconducting transition temperature in the last decade. The material was of nominal composition $La_{2-x}M_xCuO_y$ where M=Ca, Ba or Sr, x was typically >0 and <0.3 and y was variable depending on preparation conditions. Superconductivity was found only over this narrow range of doping of M. The highest superconducting transition (Tc) was obtained for Sr doping and x equal to approximately 0.15-0.20 with Tc in the mid forty degree Kelvin range, Cava et al, Phys. Rev. Letters, 58, 408 (1987). Subsequently, it was reported in March 1987, Chu et al, Phys. Rev. Letters, 58, 405 (1987) that $Y_{1.2}Ba_{0.8}CuO_y$ displayed the onset of superconductivity in the mid ninety degree Kelvin range. In contrast to the earlier work on $La_{2-x}M_xCuO_y$, this higher temperature superconductor has been only prepared as a mixture of several unknown phases and only a minor fraction of the material actually goes superconducting. Experimentation has revealed that superconductivity is not a general phenomenon in this class of materials. Even minor composition variations or isoelectronic atom substitutions will not show superconductivity. For example, Sr or Ca substitution for Ba in $Y_{1.2}Ba_{0.8}CuO_y$ did not produce superconductors.

It has now been discovered that compositions having the formula $A_{1\pm x}M_{2\pm x}Cu_3O_y$, wherein A is Y, or a combination of Y, La, Lu, Sc or Yb, M is Ba, or a combination of Ba, Sr or Ca, x is typically a value in the range from 0 to 0.5 and y is sufficient to satisfy the valence demands, are single phase bulk electrical superconductors at a temperature above that of liquid nitrogen, namely 77K. The compositions have a perovskite-like crystalline structure.

European patent application EP 0,274,407, prior art by virtue of Section 2(3) of the Patents Act 1977, discloses:

$Ba_2\ Y\ Cu_3\ O_{9-\delta}$
$Ba_{1.5}\ Sr_{0.5}\ Y\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y_{0.75}\ Sc_{0.25}\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y_{0.75}\ La_{0.25}\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y\ Cu_3\ O_{6.9}$
$Ba\ Ca\ Y\ Cu_3\ O_{9-\delta}$

where δ is numerically at least 1.

The compositions of the present invention are made by intimately mixing in the form of powders the metal oxides or precursors of metal oxides such as carbonates or hydroxides. The heating of the mixture is conducted at a temperature between about 800°C and about 1100°C in the presence of oxygen. The preferred temperature is about 900° to 1000°C, suitably 950°C. The heating is preferably carried out for a period of time from about 10 to about 40 hours. In general, the lower the temperature, the longer the time required for heating. It is also a critical feature of the present invention that following the heating, the composition is slowly cooled to room temperature in the presence of oxygen over a period of at least four hours, suitably over a period of 5 to 10 hours. Preferred compositions have formulas very close to $A_1M_2Cu_3O_y$ wherein A is Y, or a combination of Y, La, Lu, Sc or Yb and M is Ba, or a combination of Ba, Sr or Ca and y is sufficient to satisfy the valence demands. The most preferred compositions are those in which A is Y and M is Ba. This most preferred composition exhibits single phase bulk electrical superconductivity at a temperature well above 77K. It has a perovskite-like crystalline structure and consists essentially of a metal compound having one atom of yttrium, two atoms of barium and three atoms of copper and a non-metal component of oxygen.

Example

Oxides or carbonates of Y, Ba and Cu are thoroughly mixed, preferably in the mole ratio of 0.5:2:3, or alternately their soluble nitrate or chloride compounds are coprecipitated as their hydroxide or carbonate salts. The mixed powders are heated in an oven at 800-1100 degrees C in either oxygen or air for periods ranging from 10-40 hours. (Oxygen gives better results.) Longer heating times ensure more homogeneous reaction of the starting compounds. Longer reaction times are required at the lower temperatures. To prepare rigid samples, the powders from the initial heating procedure are compressed into pellets or combined in polymeric binders and heated again under similar conditions. The use of an oxygen atmosphere when heating, and slow cooling of the oven to room temperature are important for realizing the sharpest and highest superconducting transitions, and more bulk superconductivity. Typically, the oven is cooled from 900-1000 degrees C over about 5 hours to room temperature.

The compositions obtained by the above process have a perovskite-like structure which can have variable oxygen content depending upon the final annealing and cooling steps. Removal of oxygen, for example, by heating in an inert or reducing atmosphere suppresses superconductivity. Higher oxygen content leads to improved and higher superconducting properties. As mentioned above, it is essential that following the heating step, the compositions be cooled slowly. It is believed that this slow cooling is required because when the material is cooled slowly, it retains slightly more oxygen than when it is cooled rapidly.

The following materials have all demonstrated bulk superconductivity at a temperature above 77°K. They are all single phase perovskite-like crystalline structures within the general formula $A_{1\pm x}M_{2\pm x}Cu_3O_y$.

The materials are:

$(Y_{0.8}Lu_{0.2})_{1.0}Ba_{2.0}Cu_3O_y$
$(Y_{0.5}Lu_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$
$(Y_{0.5}La_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$
$(Y_{0.5}Sc_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$
$(La_{0.5}Sc_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$
$Y_{1.0}(Ba_{0.5}Ca_{0.5})_{2.0}Cu_3O_y$
~~$Y_{1.0}Sr_{0.5}Ca_{0.5})_{2.0}Cu_3O_y$~~
$Y_{0.8}Ba_{2.0}Cu_3O_y$
$Y_{1.2}Ba_{2.0}Cu_3O_y$
$Y_{1.0}Ba_{1.8}Cu_3O_y$
$Y_{1.0}Ba_{1.5}Cu_3O_y$
$Y_{1.2}Ba_{1.8}Cu_3O_y$

All the above samples were confirmed to be superconductive by the AC magnetic susceptibility test method and by electrical resistivity measurements also.

To date, the following materials have not been found to be bulk single phase superconductors above 77°K when formulated and tested by the procedures described above:

$Lu_{1.0}Ba_{2.0}Cu_{3}O_{y}$
$Lu_{1.0}Ca_{2.0}Cu_{3}O_{y}$
$La_{1.0}Ba_{2.0}Cu_{3}O_{y}$
$La_{1.0}Ca_{2.0}Cu_{3}O_{y}$
$Sc_{1.0}Ba_{2.0}Cu_{3}O_{y}$
$Y_{1.0}Ca_{2.0}Cu_{3}O_{y}$
$Y_{1.0}Ba_{1.0}Cu_{2.0}O_{y}$
$Y_{2.0}Ba_{1.0}Cu_{1.0}O_{y}$

Perhaps it is necessary that either yttrium be most of the A component, or that the combination of two or more related A components have an average atomic size approximately that of yttrium.

The range of compositions are not exactly defined as whole number atomic ratios of A and M because it seems that the crystalline structure can accommodate vacancies of these metals and still retain the necessary structure for the high temperature superconductivity. In these cases, as in all others, the oxygen is present in an amount to satisfy the valence demands.

There are a wide variety of current uses of superconductivity at liquid helium temperatures which will be cheaper and more convenient to use at liquid nitrogen temperatures. The use of thin film and ceramic processing technologies will enable these materials to find applications in microelectronics, high field magnetics, energy transmission, and electromechanical devices. In particular, these materials are useful in logic devices in computers (for example Josephson logic devices) and for interconnect metallurgy on and between chips as a means of improving speed and packaging density.

CLAIMS

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1. A composition which is a single phase bulk electrical superconductor at a temperature above 77K, said composition having a perovskite-like crystalline structure and having the formula $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein A is Y, or a combination of Y, La, Lu, Sc or Yb; M is Ba, or a combination of Ba, Sr or Ca; x is a value in the range from 0 to 0.5 and y is sufficient to satisfy the valence demands, with the proviso that said composition is not one of the following compositions:

$Ba_2\ Y\ Cu_3\ O_{9-\delta}$
$Ba_{1.5}\ Sr_{0.5}\ Y\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y_{0.75}\ Sc_{0.25}\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y_{0.75}\ La_{0.25}\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y\ Cu_3\ O_{6.9}$
$Ba\ Ca\ Y\ Cu_3\ O_{9-\delta}$

where δ is numerically at least 1.

2. A composition which is a single phase bulk electrical superconductor at a temperature above 77K, said composition having a perovskite-like crystalline structure and having the formula $A_1M_2Cu_3O_y$, wherein A is Y, or a combination of Y, La, Lu, Sc or Yb; M is Ba, or a combination of Ba, Sr or Ca and y is sufficient to satisfy the valence demands, with the proviso that said composition is not one of the following compositions:

$Ba_2\ Y\ Cu_3\ O_{9-\delta}$
$Ba_{1.5}\ Sr_{0.5}\ Y\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y_{0.75}\ Sc_{0.25}\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y_{0.75}\ La_{0.25}\ Cu_3\ O_{9-\delta}$
$Ba_2\ Y\ Cu_3\ O_{6.9}$
$Ba\ Ca\ Y\ Cu_3\ O_{9-\delta}$

where δ is numerically at least 1.

3. A composition which is a single phase bulk electrical superconductor at a temperature above 77K, said composition having a perovskite-like crystalline structure and having the formula $Y_{0.8}\ Ba_{2.0}\ Cu_3\ O_y$.

4. A composition which is a single phase bulk electrical superconductor at a temperature above 77K, said composition having a perovskite-like crystalline structure and having the formula $Y_{1.2}\ Ba_{2.0}\ Cu_3\ O_y$.

5. A composition which is a single phase bulk electrical superconductor at a temperature above 77K, said composition having a perovskite-like crystalline structure and having the formula $Y_{1.0}\ Ba_{1.5}\ Cu_3\ O_y$.

6. A process for making a single phase bulk electrical superconductor at a temperature above 77K comprising the steps of:

1) intimately mixing in the form of powders metal oxides or their precursors having a composition $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein A is Y, or a combination of Y, La, Lu, Sc or Yb; M is Ba, or a combination of Ba, Sr or Ca; x is a value in the range from 0 to 0.5 and y is sufficient to satisfy the valence demands,

2) heating the mixture to a temperature in the range from 800°C to 1100°C in the presence of oxygen,

3) slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

7. A process for making a single phase bulk electrical superconductor at a temperature above 77K comprising the steps of:

1) intimately mixing in the form of powders metal oxides or their precursors having a composition $A_1M_2Cu_3O_y$, wherein A is Y, or a combination of Y, La, Lu, Sc or Yb; M is Ba, or a combination of Ba, Sr or Ca and y is sufficient to satisfy the valence demands,

2) heating the mixture to a temperature in the range from 800°C to 1100°C in the presence of oxygen,

3) slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

8. A process for making a single phase bulk electrical superconductor at a temperature above 77K comprising the steps of:

1) intimately mixing in the form of powders yttrium oxide (Y_2O_3) or a precursor thereof, barium oxide (BaO) or a precursor thereof and cupric oxide (CuO) or a precursor thereof, in the mole ratio of 0.5:2:3

2) heating the mixture to a temperature in the range from 800°C to 1100°C in the presence of oxygen,

3) slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

9. A process as claimed in any of Claims 6, 7 or 8 wherein the temperature of the heating is between 900°C and 950°C.

10. A process as claimed in any of Claims 6, 7 or 8 wherein the time of the heating is between 10 hours and 40 hours.

11. A process as claimed in any of Claims 6, 7 or 8 wherein the cooling takes place over a period of from 5 to 10 hours.