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(11) (C) **1,341,623**

(21) 558,109

(22) 1988/02/04

(45) 2011/10/11

(52) C.L. CR 23-228
31-122
31-106
23-295
337-3.1

(51) Int.Cl. ***H01B 12/00*** (2006.01), ***C01G 03/00***(2006.01), ***C01F 17/00*** (2006.01)

(19) (CA) **CANADIAN PATENT** (12)

(54) Electrically Superconducting Compositions and Processes for Their Preparation

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(30 U.S.A. 024,653 1987/03/11

(57) 9 Claims

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Abstract of the Invention

ELECTRICALLY SUPERCONDUCTING COMPOSITIONS AND PROCESSES FOR THEIR PREPARATION

Compositions having the formula $A_{1\pm x}M_{2\pm x}Cu_3Oy$, 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, have been found to be bulk electrical superconductors at a temperature above 77°K. The compositions are single phase perovskite-like crystalline structures. They are made by a process involving intimately mixing the metal oxides or their precursors in the proper molar ratios, heating the mixture in the presence of oxygen to a temperature between about 800°C and about 1100°C and slowly cooling the mixture to room temperature in the presence of oxygen over a period of at least four hours.

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ELECTRICALLY SUPERCONDUCTING COMPOSITIONS AND PROCESSES FOR THEIR PREPARATION

Description

Technical Field

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

Background Art

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 by ourselves and other research groups have revealed that superconductivity is not a general phenomena 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.

Summary of the Invention

In one aspect of the invention there is provided a composition which is a single phase bulk electrical superconductor at a temperature above 77°K, 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 between 0 and 0.5 and y is sufficient to satisfy the valence demands.

In one aspect of the invention there is provided a composition which is a single phase bulk electrical superconductor at a temperature above 77°K, 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.

In one aspect of the invention there is provided a composition which is a single phase bulk electrical superconductor at a temperature above 77°K, said composition having a perovskite-like crystalline structure and consisting essentially of a metal component of one atom of yttrium, two atoms of barium and three atoms of copper and a non-metal component of oxygen.

In one aspect of the invention there is provided a process for making a single phase bulk electrical superconductor at a temperature above 77°K comprising the steps of:

(i) intimately mixing in the form of powders metal oxides or their precursors having a composition of $A_{1\pm x}M_{2\pm x}Cu_3O_y$ 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 between 0 and 0.5 and y is sufficient to satisfy the valence demands,

(ii) heating the mixture to the temperature between about 800°C and about 1100°C in the presence of oxygen,

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

In one aspect of the invention there is provided a process for making a single phase bulk electrical superconductor at a temperature above 77°K comprising the steps of:

(i) intimately mixing in the form of powders metal oxides or their precursors having a composition of $A_1M_2Cu_3O_y$, 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,

(ii) heating the mixture to the temperature between about 800°C and about 1100°C in the presence of oxygen,

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

In one aspect of the invention there is provided a process for making a single phase bulk electrical superconductor at a temperature above 77°K comprising the steps of:

(i) 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 (Cu)) or a precursor thereof, in the mole ration of 0.5 to 2 to 3,

(ii) heating the mixture to the temperature between about 800°C and about 1100°C in the presence of oxygen,

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

In one aspect of the invention there is provided a process for making a crystalline single phase superconductor exhibiting bulk superconductivity above 77°K, including the steps of combining a rare earth (RE) cation, an alkaline earth (AE) cation and copper (Cu) in a cation ratio of about 1-2-3, respectively, said combining occurring in an oxygen containing atmosphere to form a superconducting composition having the general formula RE AE_2 Cu_30_y where y is sufficient to satisfy the valance demands, and cooling said composition in an oxygen containing atmosphere to produce a crystalline essentially single phase superconductor, said cooling being sufficiently slow that oxygen is retained in said composition at a level to ensure that said composition will exhibit bulk superconductivity at temperatures in excess of 77°K.

In one aspect of the invention there is provided a method for producing a crystalline material exhibiting bulk superconductivity above 77°K, including the steps of providing precursors of a rare-earth element (A), an alkaline earth element (M) and copper, mixing said rare earth element, said alkaline earth element and said copper from said precursors at an elevated temperature and in the presence of oxygen, producing a composition having the general formula A_{1+x} M_{2+x} Cu_3 0_y, where x is typically between 0 and 0.5 and y is sufficient to satisfy valence demands of said composition, and cooling said composition to room temperature at a rate sufficiently slowly that said composition has a perovskite - like crystalline structure and exhibits bulk superconductivity at temperatures in excess of 77°K.

In one aspect of the invention there is provided a method for producing an essentially single phase crystalline superconductor exhibiting bulk superconductivity at a temperature of 77°K, comprising the steps of combining copper with an alkaline earth element and another element in the presence of oxygen to produce a composition with a metal component having three atoms of copper, two atoms of said alkaline earth element and one atom of said another element and a non-metal component of oxygen, and cooling said composition in the presence of oxygen at a sufficiently slow rate to essentially maintain the level of oxygen in said composition prior to said cooling step to produce a single phase crystalline superconductor exhibiting superconductivity at a temperature of 77°K.

In one aspect of the invention there is provided a process for making a single phase superconductor exhibiting bulk superconductivity at a temperature above 77°K, said process comprising the steps of mixing in the form of powders, metal oxides or their precursors having a composition A_{1+x} M_{2+x}

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$Cu_3 0_y$ wherein A is either Y or is two or more of Y, La, Lu, Sc or Yb; M is either Ba or is two or more of Ba, Sr or Ca; X is a value greater than or equal to 0 and less than or equal to 0.5; and y is sufficient to satisfy the valence demands; heating the mixture to a temperature between about 800°C and about 1100°C in the presence of oxygen; cooling the mixture to room temperature in the presence of oxygen over a period that is sufficiently long to produce a single phase composition that exhibits bulk superconductivity at a temperature above 77°K.

In one aspect of the invention there is provided a method for producing a single phase copper oxide superconductor having bulk superconductivity above 77°K, said superconductor having a nominal composition $A B_2 Cu_3 0_y$, where A is a rare earth element, B is an alkaline earth element, y is sufficient to enable said bulk superconductivity, said method including the steps of combining said rare earth element, said alkaline earth element and copper in the presence of oxygen to produce a copper oxide mixture in which the metal cations A: B: Cu have the nominal ratio 1: 2: 3, and cooling said mixture to room temperature in the presence of oxygen to produce said single phase superconductor, said cooling being at a sufficiently slow rate that the amount of oxygen in said superconductor after said cooling step is sufficient to enable said superconductor to exhibit bulk superconductivity above 77°K.

In one aspect of the invention there is provided a method for producing a single phase superconductor having bulk superconductivity at a temperature above 77°K, including the steps of combining a rare earth element (A), an alkaline earth element (M) and copper in the presence of oxygen to produce an essentially single phase copper oxide composition in which the metal cation ratio A: M: Cu is nominally 1: 2: 3, and retaining the amount of oxygen in said composition at a level sufficient to enable said composition to exhibit bulk superconductivity at a temperature of 77°K.

Disclosure of the Invention

It has now been discovered that compositions having the formula $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein x is typically between 0 and 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 77°K. The compositions have a perovskite-like crystalline structure. They 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. The heating is 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. 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. The most preferred composition exhibits single phase bulk electrical superconductivity at a temperature well above 77°K. It has a perovskite-like crystalline structure and consists essentially of a metal component having one atom of yttrium, two atoms of barium and three atoms of copper and a non-metal component of oxygen.

As an example of the most preferred method of preparing the most preferred composition, the following procedure is provided:

Oxides or carbonates of Y, Ba and Cu are thoroughly mixed, 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:

$(Y_{0.8}Lu_{0.2})_{1.0}Ba_{2.0}Cu_3O_y$

$(Y_{0.5}Lu_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$(Y_{0.5}La_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$(Y_{0.5}Sc_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$(La_{0.5}Sc_{0.5})_{1.0}Ba_{2.0}Cu_3O_y$

$Y_{1.0}(Ba_{0.5}Ca_{0.5})_{2.0}Cu_3O_y$

$Y_{0.8}Ba_{2.0}Cu_3O_y$

$Y_{1.2}Ba_{2.0}Cu_3O_y$

$Y_{1.0}Ba_{1.8}Cu_3O_y$

$Y_{1.0}Ba_{1.5}Cu_3O_y$

$Y_{1.2}Ba_{1.8}Cu_3O_y$

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:

$Lu_{1.0}Ba_{2.0}Cu_3O_y$

$Lu_{1.0}Ca_{2.0}Cu_3O_y$

$La_{1.0}Ba_{2.0}Cu_3O_y$

$La_{1.0}Ca_{2.0}Cu_3O_y$

$Sc_{1.0}Ba_{2.0}Cu_3O_y$

$Yb_{1.0}Ba_{2.0}Cu_3O_y$

$Y_{1.0}Ca_{2.0}Cu_3O_y$

$Y_{1.0}Ba_{1.0}Cu_{2.0}O_y$

$Y_{2.0}Ba_{1.0}Cu_{1.0}O_y$

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 magnets, 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

WHAT IS CLAIMED IS:

1. A composition which is a bulk electrical superconductor at a temperature above 77°K, 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 the metal Y, or a combination chosen from one or more of the elements of the group consisting of Y, La, Lu, and Sc; M is the metal Ba, or a combination of Ba and Ca; x is a value in the range from 0 to 0.5 and y is sufficient to satisfy the valence demands, said composition retaining an enhanced oxygen content as a result of employing a slow cooling stage of at least four hours in the presence of oxygen following a heating step to a temperature between 800°C and 1100°C during manufacture, whereby a single phase bulk electrical superconductor is formed.

2. A composition as claimed in claim 1, wherein x is zero.

3. A composition as claimed in claim 2, wherein A is Y, and M is Ba.

4. A process of making a single phase bulk electrical superconductor at a temperature above 77°K the composition $A_{1\pm x}M_{2\pm x}Cu_3O_y$ wherein A is the metal Y, or a combination chosen from one or more of the elements of the group consisting of Y, La, Lu, and Sc; M is the metal Ba, or a combination of Ba and Ca; x is between 0 and 0.5 and y is sufficient to satisfy the valence demands, the process comprising the steps of:

1) intimately mixing in the form of powders oxides of said metals or precursors of said oxides,

2) heating the mixture to a temperature between about 800°C and about 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.

5. A process as claimed in claim 4, wherein x is zero.

6. A process as claimed in claim 5, wherein the powders which are intimately mixed are 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.

7. A process as claimed in any of claims 4, 5 or 6 wherein the temperature of the heating is between 900°C and 950°C.

8. A process as claimed in any of claims 4, 5 or 6 wherein the time of the heating is between 10 hours and 40 hours.

9. A process as claimed in any of claims 4, 5 or 6 wherein the cooling takes place over a period of from 5 to 10 hours.