

Description**Background of the Invention**5 **Field of the invention**

The present invention relates to a method for preparing a superconducting material. More particularly, it relates to a process for preparing a novel superconducting material composed of compound oxide having a higher critical temperature.

10

Description of the related art

Under the phenomenon of superconductivity, the perfect diamagnetism is observed and no difference in potential is observed for all that an electric current of a constant finite value is observed internally.

15

The superconductivity can be utilized in the field of power electric applications such as MHD power generation, fusion power generation, power transmission, electric power reservation or the like; in the field of transportation for example magnetic levitation trains, magnetically propelling ships or the like; in the medical field such as high-energy beam radiation unit; in the field of science such as NMR or high-energy physics; a high sensitive sensors or detectors for sensing very weak magnetic field, microwave, radiant ray or the like, or in the field of fusion power generation. In addition to the abovementioned power electric applications, the superconducting materials can be used in the field of electronics, for example, as a device using the Josephson device which is expected to be a high-speed and low-power consuming switching device.

20

The phenomenon of superconductivity, however, is observed only at very low cryogenic temperatures. In fact, a relatively lower temperature of 23.2 K which was the critical temperature (T_c) of a superconductor composed of Nb_3Ge have been the top record of the critical temperature among known superconducting materials.

25

This means that liquidized helium (boiling point of 4.2 K) is only one cryogen which can realize such very low temperature of T_c . However, helium is not only a limited costly resource but also require a large-scaled system for liquefaction. Therefore, there had been strong demand for another superconducting materials having higher T_c . But no material which exceeded the abovementioned T_c had been found for all studies for the past ten years.

30

Possibility of existence of a new type of superconducting materials having much higher T_c was revealed by Bednorz and Müller who discovered a new oxide type superconductor in 1986 [Z. Phys. B64 (1986) 189]. It was also reported in the news paper that C. W. Chu et al. discovered in the United States of America another superconducting material so called YBCO type represented by $YBa_2Cu_3O_{7-x}$ having the critical temperature of about 90 K in February 1987. It was also disclosed in J. Am. Chem. Soc, vol 109, N°9, 29th April 1987, pages 2848-2849 a family of perovskite-based superconductors consisting of $Y_1Ba_2Cu_3O_y$ derivatives wherein Y is totally or partially replaced by rare earths, and/or Ba is totally or partially replaced by Sr and/or Ca. And hence, possibility of existence of high-temperature superconductors have burst on the scene.

35

It had been known that certain ceramics material of compound oxides exhibit the property of superconductivity. For example U.S. patent No. 3,932,315 discloses Ba-Pb-Bi type compound oxide which shows superconductivity and Japanese patent laid-open No. 60-173,885 discloses that Ba-Bi type compound oxides also show superconductivity. These superconductors, however, possess rather low transition temperatures of about 10 K and hence usage of liquidized helium (boiling point of 4.2 K) as cryogen had been indispensable to realize superconductivity. Therefore, the abovementioned new type compound oxides in which superconductivity is realized in liquid nitrogen which is a relatively cheap cryogen will accelerate actual usage of superconductors.

40

An object of the present invention is to provide a process for preparing a new system of compound oxides which possess a higher critical temperature.

50 **Summary of the Invention**

A process for producing a superconducting material according to the present invention comprise preparing a material powder, compacting the material powder and then subjecting the resulting compact to a final sintering operation, the process is characterized in that said material powder is one of following (A), (B), (C) and (D):

55

(A) a powder mixture consisting of powders of elemental Sr, La, Cu, Ca, δ and Bi, in which, " δ " is Sm or Yb,

(B) a powder mixture consisting of powders of compounds each containing at least one of said elements

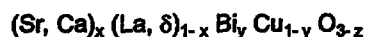
Sr, La, Cu, Ca, δ and Bi,

(C) a sintered powder obtained by sintering preliminarily said powder mixture (A) or (B) and then pulverizing the resulting preliminarily sintered mass, and

(D) a powder mixture of said powder mixture (A) and (B) and said sintered powder (C),

5 wherein, an atomic ratio of (Sr, Ca):(La, δ):Bi:Cu in said material powder satisfies a ratio of $x:(1-x):y:(1-y)$, in which an atomic ratio of Ca to Sr is selected in a range between 1 % and 90 %, an atomic ratio of δ to La is selected in a range between 1 % and 90 %, "x" is a number of about 0.66 and "y" is a number of about 0.11 respectively, and

10 said superconducting material is a compound oxide having a crystal structure of perovskite represented by the general formula:



in which δ , x and y have the same meaning as above and z is a number in a range of $0 \leq z < 1$.

The expression of (Sr, Ca) and (La, δ) mean that the respective elements position predetermined sites in a crystal in a predetermined proportion.

15 The atomic ratio of Ca with respect to Sr can be selected in a range between 1 % and 90 % but a preferred result is obtained in a range between 1 % and 50%.

The essence of the present invention resides in that the compound oxide is composed of specified elements and oxygen. This is a unique point of the present invention, comparing to the abovementioned known new type superconductors composed of four elements. Namely, the compound oxide according to the present invention, two pairs of elements each pair of which belongs to the same group of the periodic table. It is thought that an advantageous result of the present invention is obtained when each of these elements occupies a predetermined site in the crystal in a predetermined proportion.

We found that precise control of the following factors is indispensable in order to obtain a sintered compound oxide possessing superior superconducting properties:

- 25 (i) particle size of the material powder,
- (ii) temperature during the preliminary sintering operation,
- (iii) particle size of the preliminarily sintered and pulverized powder, and
- (iv) temperature during the final sintering operation.

30 In fact, if an average particle size of the material powder exceed $10 \mu\text{m}$, a fine particle which is satisfactory in uniformity can not be obtained easily even after such material powder is subjected to the preliminary sintering operation. Therefore, the average particle size of the material powder is preferably less than $10 \mu\text{m}$.

In case that a sintered powder (B) which is prepared by preliminary sintering of the powder mixture (A) is used as the material powder, the preliminary sintering is preferably carried out at a temperature which is higher than 700°C but is not higher than the lowest melting point of any compound which is contained in the powder mixture (A) for a duration of from 1 to 50 hours and preferably in an atmosphere containing oxygen gas of 0.135 to 1.35 Pa (10^{-3} to 10^2 Torr). It is also preferable that, after the preliminary sintering complete, the resulting sintered mass is cooled at a cooling rate which is not slower than $1^\circ\text{C}/\text{min}$ but not higher than $1,000^\circ\text{C}/\text{min}$. A particle size of the pulverized powder obtained from the preliminarily sintered mass influence directly upon a particle size of a crystal which is obtained after the final sintering operation, so that the preliminarily sintered mass is preferably pulverized to powder having an average particle size of less than $5 \mu\text{m}$. Such fine particles increase the area of grain boundaries which is one of critical factors for realizing the superior superconductor which is particularly improved in the critical temperature of superconductivity. Pulverization or reduction of the preliminarily sintered mass to less than $1 \mu\text{m}$ is not only economical or practicable but also increase possibility of contamination of the material powder. Therefore, the average particle size of the preliminarily sintered powder is preferably adjusted to a range between $1 \mu\text{m}$ and $5 \mu\text{m}$.

45 A series of operations of preliminary sintering, pulverization and compacting is preferably repeated for several times to homogenize the material powder.

The sintering temperature is one of the critical factors in the process for producing the superconducting compound oxide, so that the sintering temperature is controlled and adjusted to a temperature at which the sintering proceed in a solid reaction without substantial fusing of the material powder and excessive crystal growth is not occur in the resulting sintered compound oxide. In fact, the sintering temperature should not exceed the lowest melting point of any component in the material powder such as the powder mixture, the compound powder or the preliminarily sintered powder. To the contrary, satisfactory sintering can not be effected if the sintering temperature is too low. Therefore the sintering must be carried out a temperature which is higher than 700°C . Duration of sintering operation is generally for 1 hour to 50 hours in actual practice, although longer sintering time is preferable.

The abovementioned preliminary sintering operation should be also controlled precisely in the same manner as above because of the same reason.

According to a preferred embodiment, the sintered compound oxide is further heat-treated in order to homogenize the crystal structure. This heat-treatment improves the critical temperature and reduces remarkably the discrepancy between the terminal temperature of phase change where perfect zero resistance is observed and the critical temperature.

This heat-treatment is preferably carried out in an oxygen containing atmosphere at a temperature of 500 to 900 °C. Under this condition of heat-treatment, the crystal structure of sintered compound oxide is stabilized and the oxygen deficient perovskite structure which is desired for realizing the superconductivity is obtained, resulting in that the lower critical temperature where perfect zero resistance is observed becomes much higher and a lasting and stable superconductor is assured. If the temperature of heat-treatment is not higher than 500 °C the abovementioned effect is not obtained or it takes longer time before realization of the objective crystal structure. To the contrary, if the temperature of heat-treatment exceeds 900 °C, the abovementioned perovskite type crystal structure is lost.

The superconducting material according to the present invention can be used in a form of a sintered mass or article as it is and is also used in a form of a powder which is prepared by pulverizing the sintered mass. This powder-formed superconducting compound oxide can be used for producing a superconducting wire or the like. For example, the superconducting compound oxide powder according to the present invention is compacted in a metallic pipe which is then drawn into a fine wire or is mixed with suitable binder such as polybutylbutylal (PVB) to prepare a paste which can be molded into a desired configuration or which is coated or applied in a desired pattern. The resulting wire and the paste molded or coated are then sintered finally.

When the superconducting compound oxide according to the present invention is used in the form of a paste, it is preferable to heat the coated or molded paste at 400 to 700 °C in air before the final sintering operation in order to remove the binder previously.

When a self-supporting article is molded with the paste, it is preferable to select a thickness of the paste to be molded to less than 1.2 mm and when a thick film is coated on a support, the thickness of a layer of paste to be coated on a support is adjusted to less than 0.6 mm. In practice, since a pre-form of paste molded or coated by a doctor blade coating technique or extrusion technique shrinks during the final sintering stage, the dimension of the final product becomes smaller. Therefore, when the paste is shaped into a form of a tape or wire or is coated into a thick film, their thickness or diameter of paste molded or coated is preferably controlled to less than 1.2 mm or 0.6 mm respectively.

The superconducting material according to the present invention can be formed into a thin film by the conventional physical vapor deposition (PVD) technique such as vacuum deposition, sputtering, ion-plating or molecular beam epitaxial growth technique in the presence of oxygen gas. In this case, the abovementioned sintered mass or block is used as a vapor source or target which is evaporated in a vacuum chamber to produce a thin film deposited on a substrate. Namely, the vapor source may be a block prepared by sintering the material powder such as (i) powders of metal elements of Sr, La, Cu, γ , δ and ϵ (elements γ , δ and ϵ have the same definition as above) as they are, (ii) a powder mixture of compounds of these elements or (iii) their combination. The vapor source may be a powder which is obtained by pulverizing the sintered block. The proportion or atomic ratio of the elements in the vapor source is selected in such manner that the desired atomic ratio of the elements are realized in the deposited thin film in consideration of vaporization rate or sputtering rate or the like. The oxygen pressure in the vacuum chamber should be controlled so that the partial pressure of oxygen gas is adjusted to a range between $0.135 \cdot 10^{-3}$ to 1.35 Pa (10^{-6} and 10^{-2} Torr). The substrates on which the thin film are deposited are preferably those that have similar crystal structure or lattice constant and may be a single crystal of MgO, sapphire or SrTiO_3 . Desirably, the superconducting thin film is deposited on a {001} plane or {110} plane of a single crystal of MgO or SrTiO_3 to improve the critical current density (J_c) owing to ordering of crystal to c-axis.

In this case of thin film also, the abovementioned heat-treatment of the deposited thin film is very effective. The heat-treatment is carried out at a temperature of 500 to 900 °C for more than 1 hour in oxygen containing atmosphere in which the partial pressure of oxygen is adjusted to 0.135 to $135 \times 10^2 \text{ Pa}$ (10^{-3} to 10^2 Torr). After the heat-treatment, the resulting thin film is cooled slowly at a cooling rate of less than 10 °C/min .

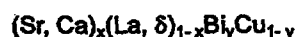
The superconducting material according to the present invention shows a very high critical temperature comparing to the conventional materials. This might come from their characteristic feature of the composition and their uniform and fine crystal structure which is assured by the present process.

The novel superconducting materials according to the present invention have improved stability and a high critical temperature, so that they can realize superconductivity by means of relatively cheaper cryogen in a small liquefaction system and hence they can be utilized advantageously in applications of superconducting wire, rod, parts such as magnets, thick film or thin film devices, such as Matisoo switching elements or Josephson device, Anacker memory device, a variety of sensors or Superconducting Quantum Interference Device (SQUID).

Now, embodiments of the process according to the present invention will be described by Examples, but the scope of the present invention should not be limited thereto.

Examples

Powders of commercially available CuO and carbonate powders of Sr, Ca, La, Sm, Yb and Bi, namely SrCO_3 , CaCO_3 , $\text{La}_2(\text{CO}_3)_3$, $\text{Sm}_2(\text{CO}_3)_3$, $\text{Yb}_2(\text{CO}_3)_3$, $(\text{BiO})_2\text{CO}_3$ are mixed in such an atomic ratio that satisfies the following general formula:



in which,

δ represents Sm or Yb, the value of x and y are shown in Table 1, and the proportion (%) of Ca with respect to Sr and the proportion (%) of δ with respect to La are also shown in Table 1.

The respective powder mixtures are pulverized in a ball mill to be reduced to an average particle size of 4 μm and then sintered at 750 °C for 15 hours. The resulting sintered mass or cake is pulverized again. The steps of sintering and pulverization are repeated two times under the same condition as above. The finally obtained powder of less than 4 μm is charged in a rubber mold and compressed hydrostatically under a pressure of 1.5 ton/cm² to obtain tablets of 4 x 10 x 30 mm. The tablets are sintered at 950 °C for 8 hours in air.

Resistance is measured on the tablets on which electrodes are secured with silver electroconductive paste to determine the critical temperature.

Measurement of an upper critical temperature T_c and a lower critical temperature T_{cf} is effected by a conventional four probe method. Temperature is measured by a calibrated Au(Fe)-Ag thermocouple.

The result are shown in Table 1.

Table 1

Sample No	(Sr,Ca)x (x)	Bi (y)	Ca (%)	δ	δ (%)	T_c	T_{cf}
1	0.66	0.11	10	Sm	30	148	129
2	0.66	0.11	10	Yb	30	130	116

Claims

1. A process for preparing a superconducting material including the steps of preparing a material powder, compacting said material powder and then subjecting the resulting compact to a final sintering operation, characterized in that

said material powder is one of following (A), (B), (C) and (D):

(A) a powder mixture consisting of powders of elemental Sr, La, Cu, Ca, δ and Bi, in which, " δ " is Sm or Yb,

(B) a powder mixture consisting of powders of compounds each containing at least one of said elements Sr, La, Cu, Ca, δ and Bi,

(C) a sintered powder obtained by sintering preliminarily said powder mixture (A) or (B) and then pulverizing the resulting preliminarily sintered mass, and

(D) a powder mixture of said powder mixture (A) and (B) and said sintered powder (C),

wherein, an atomic ratio of (Sr, Ca):(La, δ):Bi:Cu in said material powder satisfies a ratio of x:(1-x):y:(1-y), in which an atomic ratio of Ca to Sr is selected in a range between 1 % and 90 %, an atomic ratio of δ to La is selected in a range between 1 % and 90 %, "x" is a number of about 0.66 and "y" is a

Now, embodiments of the process according to the present invention will be described by Examples, but the scope of the present invention should not be limited thereto.

Examples

Powders of commercially available CuO and carbonate powders of Sr, Ca, La, Sm, Yb and Bi, namely SrCO_3 , CaCO_3 , $\text{La}_2(\text{CO}_3)_3$, $\text{Sm}_2(\text{CO}_3)_3$, $\text{Yb}_2(\text{CO}_3)_3$, $(\text{BiO})_2\text{CO}_3$ are mixed in such an atomic ratio that satisfies the following general formula:



in which,

δ represents Sm or Yb, the value of x and y are shown in Table 1, and the proportion (%) of Ca with respect to Sr and the proportion (%) of δ with respect to La are also shown in Table 1.

The respective powder mixtures are pulverized in a ball mill to be reduced to an average particle size of 4 μm and then sintered at 750 °C for 15 hours. The resulting sintered mass or cake is pulverized again. The steps of sintering and pulverization are repeated two times under the same condition as above. The finally obtained powder of less than 4 μm is charged in a rubber mold and compressed hydrostatically under a pressure of 1.5 ton/cm² to obtain tablets of 4 x 10 x 30 mm. The tablets are sintered at 950 °C for 8 hours in air.

Resistance is measured on the tablets on which electrodes are secured with silver electroconductive paste to determine the critical temperature.

Measurement of an upper critical temperature T_c and a lower critical temperature T_{cf} is effected by a conventional four probe method. Temperature is measured by a calibrated Au(Fe)-Ag thermocouple.

The result are shown in Table 1.

Table 1

Sample No	(Sr,Ca) (x)	Bi (y)	Ca (%)	δ	δ (%)	T_c	T_{cf}
1	0.66	0.11	10	Sm	30	148	129
2	0.66	0.11	10	Yb	30	130	116

Claims

1. A process for preparing a superconducting material including the steps of preparing a material powder, compacting said material powder and then subjecting the resulting compact to a final sintering operation, characterized in that

said material powder is one of following (A), (B), (C) and (D):

(A) a powder mixture consisting of powders of elemental Sr, La, Cu, Ca, δ and Bi, in which, " δ " is Sm or Yb,

(B) a powder mixture consisting of powders of compounds each containing at least one of said elements Sr, La, Cu, Ca, δ and Bi,

(C) a sintered powder obtained by sintering preliminarily said powder mixture (A) or (B) and then pulverizing the resulting preliminarily sintered mass, and

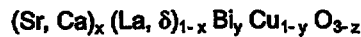
(D) a powder mixture of said powder mixture (A) and (B) and said sintered powder (C),

wherein, an atomic ratio of (Sr, Ca):(La, δ):Bi:Cu in said material powder satisfies a ratio of $x:(1-x):y:(1-y)$, in which an atomic ratio of Ca to Sr is selected in a range between 1 % and 90 %, an atomic ratio of δ to La is selected in a range between 1 % and 90 %, " x " is a number of about 0.66 and " y " is a



number of about 0.11 respectively, and

said superconducting material is a compound oxide having a crystal structure of perovskite represented by the general formula:



in which δ , x and y have the same meaning as above and z is a number in a range of $0 \leq z < 1$.

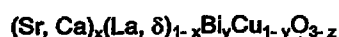
2. The process set forth in claim 1 wherein the atomic ratio of Ca to Sr is selected in a range between 1 % and 50 %.
3. The process set forth in claim 1 or 2 wherein said sintered powder is obtained by repeating a series of operations of sintering of the powder mixture (A) or (B) and pulverization of the resulting sintered mass for at least two times.
4. The process set forth in any one of claim 1 to 3 wherein said compound in (B) is oxide, carbonate, sulfate, nitrate or oxalate each containing at least one of said elements of Ba, Cu, δ , Ca and Bi.
5. The process set forth in any one of claim 1 to 4 wherein said compound in (B) is powder having an average particle size of less than 10 μm .
6. The process set forth in any one of claim 1 to 5 wherein the final sintering operation is effected at a temperature which is higher than 700 °C but is not higher than the lowest melting point of said compounds for a duration of from 1 to 50 hours.
7. The process set forth in any one of claim 1 to 6 wherein the final sintering is carried out in an atmosphere containing oxygen gas of 0.135 Pa to 13.5 kPa (10^{-3} to 10^2 Torr).
8. The process set forth in any one of claim 1 to 7 wherein, after the final sintering complete, the resulting sintered mass is cooled at a cooling rate which is not slower than 1 °C/min but not higher than 1,000 °C/min.
9. The process set forth in any one of claim 1 to 8 wherein, after the final sintering complete, the resulting sintered mass is heat-treated at a temperature between 500 and 800 °C.
10. The process set forth in any one of claim 1 to 9 wherein said heat-treatment is carried out in an atmosphere containing oxygen gas whose partial pressure is from 0.135 Pa to 13.5 kPa (10^{-3} to 10^2 Torr).
11. The process set forth in any one of claim 1 to 10 wherein said superconducting material is used as a vapor source to prepare a thin film thereof on a substrate by physical vapor deposition technique.
12. The process set forth in claim 11 wherein the resulting thin film is heat-treated at a temperature between 500 and 900 °C.
13. The process set forth in claim 11 or 12 wherein the heat-treatment is carried out in oxygen containing atmosphere.

Patentansprüche

1. Verfahren zur Herstellung eines supraleitenden Materials, bei dem man stufenweise ein Materialpulver herstellt, das Materialpulver verdichtet und danach die anfallende verdichtete Masse einem End-Sintervorgang unterwirft, dadurch gekennzeichnet, daß es sich bei dem Materialpulver um eines der Pulver (A), (B), (C) und (D) handelt:
 - (A) Pulvergemisch aus Pulvern der Elemente Sr, La, Cu, Ca, δ und Bi, wobei δ Sm or Yb bedeutet,
 - (B) Pulvergemisch aus Pulvern von Verbindungen, die jeweils mindestens eins der Elemente Sr, La, Cu, Ca, δ und Bi enthalten,
 - (C) Sinterpulver, erhalten durch Vorsintern des Pulvergemischs (A) oder (B) und danach Pulverisieren der vorgesinterten Masse, und
 - (D) Pulvergemisch der Pulvergemische (A) und (B) und des gesinterten Pulvers (C),
 wobei das Atomverhältnis von (Sr, Ca):(La, δ):Bi:Cu im Materialpulver das Verhältnis $x:(1-x):y:(1-y)$ befriedigt, wobei das Atomverhältnis von Ca:Sr im Bereich von 1 bis 90 % gewählt ist, das Atomverhältnis von δ :La im Bereich von 1 bis 90 % gewählt ist, x eine Zahl von etwa 0,66 bedeutet



und y eine Zahl von etwa 0,11 bedeutet, und wobei
das supraleitende Material ein Mischoxid mit einer Perovskit-Kristallstruktur der folgenden allgemeinen Formel ist:



5 worin δ , x und y die vorstehend angegebenen Bedeutungen be sitzen und z eine Zahl im Bereich von $0 \leq z < 1$ ist.

2. Verfahren nach Anspruch 1, wobei das Atomverhältnis von Ca:Sr im Bereich von 1 bis 50 % gewählt ist.
- 10 3. Verfahren nach Anspruch 1 oder 2, wobei das Sinterpulver dadurch erhalten ist, daß man eine Reihe von Sintervorgängen der Pulvergemische (A) oder (B) wiederholt und die resultierende gesinterte Masse mindestens zweimal pulverisiert.
- 15 4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die Verbindung im Pulvergemisch (B) ein Oxid, Carbonat, Sulfat, Nitrat oder Oxalat ist und jeweils mindestens eins der Elemente Ba, Cu, δ , Ca und Bi enthält.
5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Verbindung im Pulvergemisch (B) ein Pulver mit einer mittleren Teilchengröße von weniger als 10 μm ist.
- 20 6. Verfahren nach einem der Ansprüche 1 bis 5, wobei der End-Sintervorgang bei einer Temperatur, die höher als 700 °C ist, jedoch nicht höher als der niedrigste Schmelzpunkt der Verbindungen, für 1 bis 50 h durchgeführt wird.
7. Verfahren nach einem der Ansprüche 1 bis 6, wobei der End-Sintervorgang in einer Atmosphäre mit einem Gehalt an gasförmigem Sauerstoff von 0,135 Pa bis 13,5 kPa (10^{-3} bis 10^2 Torr) durchgeführt wird.
- 25 8. Verfahren nach einem der Ansprüche 1 bis 7, wobei nach abgeschlossenem End-Sintervorgang die anfallende gesinterte Masse mit einer Kühlrate abgekühlt wird, die nicht langsamer als 1 °C/min., jedoch nicht größer als 1000 °C/min. ist.
- 30 9. Verfahren nach einem der Ansprüche 1 bis 8, wobei nach abgeschlossenem End-Sintervorgang die resultierende gesinterte Masse bei einer Temperatur von 500 bis 800 °C wärmebehandelt wird.
- 35 10. Verfahren nach einem der Ansprüche 1 bis 9, wobei die Wärmebehandlung in einer Atmosphäre mit einem Gehalt an gasförmigem Sauerstoff durchgeführt wird, dessen Partialdruck, 0,135 Pa bis 13,5 kPa (10^{-3} bis 10^2 Torr) beträgt.
- 40 11. Verfahren nach einem der Ansprüche 1 bis 10, wobei das supraleitende Material als Dampfquelle zur Herstellung eines daraus bestehenden Dünnschichtfilms auf einem Substrat mit Hilfe einer physikalischen Dampfabscheidungstechnik verwendet wird.
12. Verfahren nach Anspruch 11, wobei der resultierende Dünnschichtfilm bei einer Temperatur von 500 bis 900 °C wärmebehandelt wird.
- 45 13. Verfahren nach Anspruch 11 oder 12, wobei die Wärmebehandlung in einer sauerstoffhaltigen Atmosphäre durchgeführt wird.

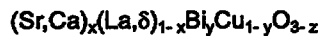
Revendications

- 50 1. Procédé pour préparer un matériau supraconducteur, incluant les étapes de préparation d'une poudre de matériaux, de compactage de la poudre de matériaux puis de soumission du produit compact obtenu à un frittage final, caractérisé en ce que
ladite poudre de matériaux est l'une des (A), (B), (C) et (D) suivantes :
(A) un mélange de poudres constitué de poudres de Sr, La, Cu, Ca, δ et Bi élémentaires, où " δ " est Sm ou Yb,
55 (B) un mélange de poudres constitué de poudres de composés contenant chacun au moins l'un desdits éléments Sr, La, Cu, Ca, δ et Bi,
(C) une poudre frittée obtenue en frittant préliminairement ledit mélange de poudres (A) ou (B) puis en pulvérisant la masse préliminairement frittée obtenue, et



(D) un mélange de poudres desdits mélanges de poudres (A) et (B) et de ladite poudre frittée (C),
 où le rapport atomique de (Sr,Ca) : (La, δ) : Bi : Cu dans ladite poudre de matériaux satisfait au rapport $x:(1-x):y:(1-y)$, dans lequel le rapport atomique de Ca à Sr est choisi dans la gamme entre 1 % et 90 %, le rapport atomique de δ à La est choisi dans la gamme entre 1 % et 90 %, "x" est un nombre d'environ 0,66 et "y" est un nombre d'environ 0,11, respectivement, et

ledit matériau supraconducteur est un oxyde composé ayant une structure cristalline de perovskite, représenté par la formule générale :



dans laquelle δ , x et y ont la même définition que ci-dessus et z est un nombre dans la gamme de $0 \leq z < 1$.

2. Procédé selon la revendication 1, dans lequel le rapport atomique de Ca à Sr est choisi dans la gamme entre 1 % et 50 %.
3. Procédé selon la revendication 1 ou 2, dans lequel ladite poudre frittée est obtenue en répétant une série d'opérations de frittage du mélange de poudres (A) ou (B) et en pulvérisant la masse frittée obtenue au moins deux fois.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ledit composé (B) est un oxyde, un carbonate, un sulfate, un nitrate ou un oxalate, chacun contenant au moins l'un desdits éléments Ba, Cu, δ , Ca et Bi.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit composé dans (B) est une poudre ayant une taille moyenne des particules inférieure à 10 μm .
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'opération de frittage final est effectuée à une température qui est supérieure à 700 °C mais non supérieure au point de fusion le plus bas desdits composés pendant une durée de 1 à 50 heures.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le frittage final est effectué dans une atmosphère contenant du gaz oxygène à 0,135 Pa à 13,5 kPa (10^{-3} à 10^2 torrs).
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel, au terme du frittage final, la masse frittée obtenue est refroidie à une vitesse de refroidissement qui n'est pas plus lente que 1 °C/min mais pas plus élevée que 1 000 °C/min.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel, au terme du frittage final, la masse frittée obtenue est traitée thermiquement à une température entre 500 et 800 °C.
10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel ledit traitement thermique est effectué dans une atmosphère contenant du gaz oxygène dont la pression partielle va de 0,135 Pa à 13,5 kPa (10^{-3} à 10^2 torrs).
11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel ledit matériau supraconducteur est utilisé en tant que source de vapeur pour préparer une pellicule mince de celui-ci sur un substrat par une technique de dépôt physique en phase vapeur.
12. Procédé selon la revendication 11, dans lequel la pellicule mince obtenue est traitée thermiquement à une température entre 500 et 900 °C.
13. Procédé selon la revendication 11 ou 12, dans lequel le traitement thermique est effectué dans une atmosphère contenant de l'oxygène.

