

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

The present invention relates to an improvement in a method for producing thallium type superconductor. More particularly, it relates to a method for producing superconducting compound oxides containing thallium (Tl), such as a Tl-Ba-Ca-Cu type oxide, which show the perfect superconducting property (resistance $R = 0$) at a very high temperature.

Description of the related art

Superconductivity is a phenomenon which is described as a kind of phase change of electrons under which an electric resistance become zero and the perfect diamagnetism is observed. When superconductor technology is applied to electric power transmission, power loss of about 7% which is experienced in the electric power transmission systems today can be greatly reduced. Development of superconductor technology is also expected in the field of measurement and in the field of medical treatment such as NMR, π neutron medical treatment or high-energy physical experiments. In the electromagnet devices for generating strong magnetic fields, superconductor technology is expected to accelerate development of the technology of fusion power generation, MHD power generation, magnetic levitation trains and magnetically propelled ships.

The critical temperature "Tc" of superconductors, however, had not exceed 23,2 K exhibited in Nb₃Ge which was the highest Tc reported over the past ten years.

The existence of new types of superconducting materials having much higher Tc was revealed by Bednorz and Müller, who discovered a new oxide type superconductor in 1986 (Z.Phys. B64, 1986 p 189).

The new compound oxide type superconductor discovered by Bednorz and Müller is represented by [La, Sr]₂CuO₄, which is referred to as a K₂NiF₄-type oxide having a crystal structure which is similar to known perovskite type oxides. The K₂NiF₄-type compound oxides, have exhibited a higher Tc on the order of 30 K which are much higher than previously known superconducting materials.

It was also reported in February 1987 that C. W. Chu et al. discovered, in the United States of America, another superconducting material of the so called YBCO type represented by YBa₂Cu₃O_{7-x} having a critical temperature of about 90 K (Physical Review letters, Vol.58, No. 9, p 908).

Other new superconducting materials have been reported recently such as a compound oxide a Bi-Sr-Ca-Cu-O system reported by Maeda et al (Japanese Journal of Applied Physics. Vol. 27, NO. 2, p.L209, (1988) L210) and a Tl-Ba-Ca-Cu-O system, which exhibit a Tc in excess of 100 K (Sheng et al. Appl. Phys. Lett. 52(20) p 1738 (1988) and which are chemically more stable than the above mentioned YBCO type compound oxide or the like. Hence, the possibility of actual utilization of the high Tc superconductors has burst onto the scene.

A variety of compound oxides which show high critical temperatures have subsequently been reported. Among them, thallium (Tl) type compound oxides have the significant advantage that high Tc superconductors having a Tc higher than 100 K can be realized without using rare earth elements as a material, so that the production cost can be reduced.

The above-mentioned oxide type superconducting materials can be prepared in a bulk form as a sintered block obtained by sintering a powder mixture of oxides or carbonates of constituent metal elements, or can be deposited on a substrate in the form of a thin film by a physical vapour deposition (PVD) technique or a chemical vapor deposition (CVD) technique.

In the case of production of thallium type oxide superconductors, however, there is a special problem because thallium (Tl) is a very volatile element and toxic to humans. Therefore, it is necessary to adopt a special sintering technique when the thallium type compound oxides are produced by sintering a material powder mixture.

Heretofore, when the material powder mixture for thallium type compound oxides have been sintered, it has been usual practice to wrap the material powder mixture in a foil made of gold in order to prevent volatile thallium vapour from escaping. However, it has proven to be difficult to completely suppress the escape of thallium vapour out of the gold foil, so that the atomic ratios of the component elements in the resulting sintered mass will deviate from desired values. In fact, it is difficult to produce a sintered mass having consistent quality and a stable high-Tc value by this process.

It has been also proposed to carry out the sintering of material powder mixture for the thallium type compound oxides in a pipe made of gold ("Science" vol. 240, page 631 to 634, April 29, 1988). As a variation, it is proposed to sinter the material powder mixture wrapped in a gold foil in a sealed pipe made of quartz [Report

submitted to "Phys. Review Letter" by S. S. P. Parkin et al. RJ 6147 (60857) 3/18/88].

These methods, however, have the problem that oxygen supply to the material powder mixture during the sintering operation is impossible or difficult, so that the oxygen content in the resulting sintered mass will be insufficient. In fact, the products obtained by these methods show rather poor superconducting property. Further, there is a danger of breakage of the pipe if the pipe is sealed in an air tight manner.

An object of the present invention is to overcome the problem exhibited in prior arts processes and to provide an improved method for producing thallium (Tl) type compound oxide superconductors.

Summary of the Invention

The present invention provides an improved method for producing superconductors of thallium (Tl) type compound oxide by sintering a material powder including at least one thallium-containing powder, the improvement comprising wrapping said material powder mixture in a metallic foil made of precious metals or their alloys, placing the material powder mixture wrapped in the metallic foil in a metallic pipe made of precious metals or their alloys and having a closed end and an opening at the opposite end and then firing said metallic pipe at a sintering temperature between 880 and 920°C while oxygen gas is supplied into the metallic pipe through the opening for a time duration between 1 minute and 40 hours so that the material powder mixture wrapped in the metallic foil is sintered.

The process of the present invention is applicable to any superconductor composed of compound oxide containing thallium (Tl). One of the typical thallium type compound oxides is represented by the general formula:



In which m, n, x and y are numbers each satisfying the ranges of

$$6 \leq m \leq 16, 4 \leq n \leq 12, 0.2 < x < 0.8 \text{ and } -2 \leq y \leq +2,$$

respectively and $p = (6+m+n)$ such as $\text{Tl}_4\text{Ca}_4\text{Ba}_4\text{Cu}_6\text{O}_{20+y}$ or $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10+y}$.

Examples of other thallium-containing compound oxide systems (critical temperatures noted in parentheses) to which the present invention is applicable, are:

Tl-Sr-Ca-Cu-O system	(75 to 100 K),
Tl-Pb-Sr-Ca-Cu-O system	(80 to 122 K),
Tl-Ba-(Y,Ca)-Cu-O system	(92 K),
(Tl, Ln)-Sr-Ca-Cu-O system	(80 to 90 K),
(Tl, La, Pb)-Sr-Ca-O system	(100 K),
(Bi, Tl)-Sr-Cu-O system	(90 K),
Pb-Tl-Sr-Cu-O system	(42 K),
La-Tl-Sr-Cu-O system	(37 K) and
Nd-Tl-Sr-Cu-O system	(44 K).

(note) Ln:lanthanoid

The metallic foil is preferably made of gold (Au), platinum (Pt) or their alloys. The metallic pipe is preferably made of silver (Ag), gold (Au), platinum (Pt) or their alloys.

The sintering operation can be effected in an ordinary furnace. The interior of the furnace is preferably in the condition of an oxygen-rich atmosphere, but, according to the present invention, the sintering can be carried out in the atmosphere of air.

According to the present invention, oxygen gas is fed continuously into the metallic pipe during the sintering operation. The oxygen gas is supplied preferably at a rate of more than 0.1 liter per minute at 1 atm. Usually, the oxygen gas pressure can be about at ambient pressure (1 atm). The sintering can be effected also at a higher oxygen pressure than 1 atm.

The sintering is effected at a temperature between 880 and 920°C. When the sintering temperature is not higher than 880°C, the resulting sintered mass becomes a mixture of different phases each having a different critical temperature, so that the overall T_c of the sintered mass becomes lower. To the contrary, if the sintering temperature is not lower than 920°C, the evaporation of thallium (Tl) increases excessively making it difficult to adjust the composition of the sintered mass to the desired atomic ratios, and increasing precipitates which

do not to contribute the superconductivity of the material.

The sintering can be effected for a time duration between 1 minute and 40 hours, preferably between 1 and 40 hours. When the sintering time is not longer than 1 minute, the material powder mixture is not sintered satisfactorily and a desired superconductive material will not be obtained. A sintering time longer than 40 hours may not generally be effective in improving the superconducting property.

The material powder mixture can be a mixture of powders selected from a group comprising elemental powders of constituent elements (Ti, Ba, Ca, Cu etc), oxide powders (Ti_2O_3 , CaO, BaO, CuO etc) containing at least one constituent element of the compound oxide or carbonate powders ($Ti_2(CO_3)_3$, $Ca(CO_3)_3$, $Ba(CO_3)_3$, etc). The material powder mixture is preferably pressed into a compact before the material powder mixture is wrapped in the metallic foil.

The method according to the present invention has the following merits:

(1) It is possible to adjust the atomic ratio of thallium in the compound oxide to a desired value, because the evaporation of volatile thallium is suppressed by the metallic foil and by the surrounding oxygen gas.

(2) It is also possible to adjust the oxygen content in the compound oxide to a desired value because the sintering operation is carried out in oxygen-rich condition.

(3) The sintered mass is not contaminated by the wrapping foil because the foil is made of precious metal which is not reactive with the material powder.

In a conclusion, according to the method of the present invention, it becomes possible to produce high-quality superconductors of thallium-containing compound oxides such the Ti-Ba-Ca-Cu type oxide superconductors which have improved superconducting properties, particularly stable condition of the critical temperature T_c .

The method according to the present invention is described with reference to Fig. 1 which illustrates one embodiment of how to carry out the present method.

Brief Description of the Drawings

Fig. 1 is a drawing illustrating a substantially schematic cross section of an apparatus for carrying out the present method.

Fig. 2A is a graph showing a temperature dependency of the AC susceptibility of a superconductor produced according to the present invention.

Fig. 2B is a graph showing a temperature dependency of the AC susceptibility of a superconductor produced according to one of prior arts.

Fig. 3 is a graph showing critical temperatures (T_c) (resistance $R=0$) measured on four different compositions when the sintering temperature (T : °C) is varied.

Fig. 4 is a graph showing critical temperatures (T_c) (resistance $R=0$) measured on the four different compositions when the sintering time (t : hr) is varied.

Detailed description of the preferred embodiments

The material powder mixture 1 is wrapped in a metallic foil 2 made of precious metal to prepare a package. This package is placed in a metallic pipe 3 made of precious metal and having a closed end and an opening at an opposite end. Then, the metallic pipe 3 is placed in a furnace (not shown). While oxygen gas is fed by a nozzle (not shown) through the opening of the pipe 3, the temperature of the furnace is elevated gradually to a predetermined sintering temperature which is maintained for a predetermined time duration which is necessary to sinter the material powder mixture.

The method according to the present invention will be described by the following examples. However, the scope of the present invention is not to be limited to the following specific examples.

Example 1

Powders of $BaCO_3$ and CuO are kneaded in a mortar and the resulting powder mixture is sintered preliminarily at 900°C for 8 hours. The resulting sintered mass is pulverized into a powder to which powders of Ti_2O_3 and CaO are admixed uniformly to prepare a material powder mixture. The atomic ratios of Ti:Ca:Ba:Cu in the material powder mixture are adjusted to 2.4 : 2.3 : 2.0 : 3.0.

The material powder mixture is pressed to a compact which is then wrapped in a foil made of gold (Au). The compact wrapped by the gold foil is then placed in a pipe made of silver (Ag) having a closed end and an opening at an opposite end.

After the silver pipe containing the wrapped compact is set in a sintering furnace, oxygen gas is supplied

into the silver pipe through the opening and the temperature of the sintering furnace is elevated to 905°C. Sintering is effected for 3 hours.

Fig. 2A shows a temperature dependency of the AC susceptibility of a superconductor of Example 1 according to the present invention. From Fig. 2A, it is apparent that the superconductor produced according to the present invention exhibits a very sharp curve which means that the superconductor consists of only a high T_c phase.

The critical temperature (T_c at resistance $R = 0$) of Example 1 determined by conventional four probe method is 120 K.

10 Comparative Example 1

As a comparative example 1, a compact which is prepared by the same method as Example 1 is wrapped in a good foil and is sintered in the same sintering furnace at 905°C for 3 hours.

In this case, however, the wrapped compact is sintered directly in the oxygen gas stream without using the silver pipe.

Fig. 2B shows a temperature dependency of the AC susceptibility of a superconductor of the Comparative Example produced by the conventional method. The curve of Fig. 2B is not smooth and has a stepped portion which is caused by the presence of a lower T_c phase in the sintered mass.

20 Comparative Example 2

As a comparative example 2, a compact which is prepared by the same method as Example 1 is wrapped in a gold foil and the resulting wrapped compact is placed in a silver pipe.

In this case, however, opposite ends of the silver pipe are closed in an air-tight manner. Sintering is effected in the same sintering furnace as Example 1 at 905°C for 3 hours in oxygen gas stream.

The critical temperature (T_c at resistance $R = 0$) of this Comparative Example 2 determined by conventional four probe method is 109 K.

30 Example 2 to 5

Example 1 is repeated to prepare the material powder mixture except the atomic ratios of Ti : Ca : Ba : Cu in the material powder mixture are modified as follows:

Example 2: Ti:Ca:Ba:Cu = 2.4:2.3:2.0:3.0

Example 3: Ti:Ca:Ba:Cu = 3.6:2.3:2.0:3.0

Example 4: Ti:Ca:Ba:Cu = 4.9:2.3:2.0:3.0

Example 5: Ti:Ca:Ba:Cu = 1.2:3.5:1.0:3.0

Each compact is wrapped in gold (Au) foil. The compact wrapped by the gold foil is then placed in a pipe made of silver (Ag) having a closed end and an opening an opposite end.

After the silver pipe containing the wrapped compact is set in a sintering furnace, oxygen gas is supplied into the silver pipe through the opening and the temperature of the sintering furnace is elevated. Sintering is effected under different conditions.

Fig. 3 shows the relationships between T_c (resistance $R = 0$) of the superconductors of Example 2 to 5 and the sintering temperature when the sintering time is fixed at 3 hours.

Fig. 4 shows the relationships between T_c (resistance $R = 0$) of the superconductors of Example 2 to 5 and the sintering time when the sintering temperature is fixed at 910°C.

A superconductor obtained from the compact of Example 5 (Ti:Ca:Ba:Cu = 1.2:3.5:1.0:3.0) which is sintered at 910°C for 5 hours shows the highest T_c of 125 K.

Another superconductor obtained from the compact of Example 2 (Ti:Ca:Ba:Cu = 2.4:2.3:2.0:3.0) which is sintered at 910°C for 6 hours also shows a very high T_c of 124 K.

Claims

1. In a method for producing superconductors of thallium (Tl) type compound oxide by sintering a material powder including at least one thallium-containing powder, the improvement comprising wrapping said material powder mixture in a metallic foil made of precious metals or their alloys, placing the material powder mixture wrapped in the metallic foil in a metallic pipe made of precious metals or their alloys and having a closed end and an opening at the opposite end and then firing said metallic pipe at a sintering temper-



into the silver pipe through the opening and the temperature of the sintering furnace is elevated to 905°C. Sintering is effected for 3 hours.

Fig. 2A shows a temperature dependency of the AC susceptibility of a superconductor of Example 1 according to the present invention. From Fig. 2A, it is apparent that the superconductor produced according to the present invention exhibits a very sharp curve which means that the superconductor consists of only a high T_c phase.

The critical temperature (T_c at resistance R = 0) of Example 1 determined by conventional four probe method is 120 K.

Comparative Example 1

As a comparative example 1, a compact which is prepared by the same method as Example 1 is wrapped in a gold foil and is sintered in the same sintering furnace at 905°C for 3 hours.

In this case, however, the wrapped compact is sintered directly in the oxygen gas stream without using the silver pipe.

Fig. 2B shows a temperature dependency of the AC susceptibility of a superconductor of the Comparative Example produced by the conventional method. The curve of Fig. 2B is not smooth and has a stepped portion which is caused by the presence of a lower T_c phase in the sintered mass.

Comparative Example 2

As a comparative example 2, a compact which is prepared by the same method as Example 1 is wrapped in a gold foil and the resulting wrapped compact is placed in a silver pipe.

In this case, however, opposite ends of the silver pipe are closed in an air-tight manner. Sintering is effected in the same sintering furnace as Example 1 at 905°C for 3 hours in oxygen gas stream.

The critical temperature (T_c at resistance R = 0) of this Comparative Example 2 determined by conventional four probe method is 109 K.

Example 2 to 5

Example 1 is repeated to prepare the material powder mixture except the atomic ratios of Ti : Ca : Ba : Cu in the material powder mixture are modified as follows:

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Example 5: Ti:Ca:Ba:Cu = 1.2:3.5:1.0:3.0

Each compact is wrapped in gold (Au) foil. The compact wrapped by the gold foil is then placed in a pipe made of silver (Ag) having a closed end and an opening on opposite end.

After the silver pipe containing the wrapped compact is set in a sintering furnace, oxygen gas is supplied into the silver pipe through the opening and the temperature of the sintering furnace is elevated. Sintering is effected under different conditions.

Fig. 3 shows the relationships between T_c (resistance R = 0) of the superconductors of Example 2 to 5 and the sintering temperature when the sintering time is fixed at 3 hours.

Fig. 4 shows the relationships between T_c (resistance R = 0) of the superconductors of Example 2 to 5 and the sintering time when the sintering temperature is fixed at 910°C.

A superconductor obtained from the compact of Example 5 (Ti:Ca:Ba:Cu = 1.2:3.5:1.0:3.0) which is sintered at 910°C for 5 hours shows the highest T_c of 125 K.

Another superconductor obtained from the compact of Example 2 (Ti:Ca:Ba:Cu = 2.4:2.3:2.0:3.0) which is sintered at 910°C for 6 hours also shows a very high T_c of 124 K.

Claims

1. In a method for producing superconductors of thallium (Tl) type compound oxide by sintering a material powder including at least one thallium-containing powder, the improvement comprising wrapping said material powder mixture in a metallic foil made of precious metals or their alloys, placing the material powder mixture wrapped in the metallic foil in a metallic pipe made of precious metals or their alloys and having a closed end and an opening at the opposite end and then firing said metallic pipe at a sintering temper-



ature between 880 and 920°C while oxygen gas is supplied into the metallic pipe through the opening for a time duration between 1 minute and 40 hours so that the material powder mixture wrapped in the metallic foil is sintered.

- 5 2. The method according to Claim 1 wherein said superconductors of thallium (Tl) type compound oxide are represented by the general formula:

$$\text{Tl}_4(\text{Ca}_{1-x}\text{Ba}_x)_m\text{Cu}_n\text{O}_{p+y}$$
 In which m, n, x and y are numbers each satisfying ranges of
 $6 \leq m \leq 16$, $4 \leq n \leq 12$, $0.2 < x < 0.8$ and $-2 \leq y \leq +2$,
 10 respectively and $p = (6+m+n)$.
3. The method according to Claim 1 or 2 wherein said metallic foil is made of gold (Au), platinum (Pt) or their alloys.
- 15 4. The method according to any one of Claim 1 to 3 wherein said metallic pipe is made of silver (Ag), gold (Au), platinum (Pt) or their alloys.
5. The method according to any one of Claim 1 to 4 wherein the oxygen is supplied at a rate of more than 0.1 liter per minute during the sintering operation.
- 20 6. The method according to any one of Claim 1 to 5 wherein the material powder mixture is a mixture of powders each composed of an elemental powder, an oxide powder or a carbonate powder containing at least one of constituent elements of the compound oxide.
- 25 7. The method according to any one of Claim 1 to 6 wherein the material powder mixture is compacted by a press before the material powder mixture is wrapped by the metallic foil.

Patentansprüche

- 30 1. Verfahren zur Herstellung eines Supraleiters aus einer Verbindung vom Typ des Thallium(Tl)-Oxids durch Sintern eines Materialpulvers, das wenigstens ein Thallium enthaltendes Pulver umfaßt, wobei die Verbesserung beinhaltet, das Materialpulvergemisch in eine Metallfolie aus Edelmetallen oder ihren Legierungen einzuwickeln, das in die Metallfolie eingewickelte Materialpulvergemisch in ein Metallrohr aus Edelmetallen oder ihren Legierungen zu setzen, das ein geschlossenes Ende und eine Öffnung am gegenüberliegenden Ende aufweist, und dann das Metallrohr bei einer Sintertemperatur zwischen 880 und 35 920 °C zu heizen, während Sauerstoffgas über eine Zeitdauer zwischen 1 Minute und 40 Stunden durch die Öffnung in das Metallrohr zugeführt wird, so daß das in die Metallfolie eingewickelte Materialpulvergemisch gesintert ist.
- 40 2. Verfahren nach Anspruch 1, bei welchem die Supraleiter aus der Verbindung vom Typ des Thallium(Tl)-Oxids durch die allgemeine Formel

$$\text{Tl}_4(\text{Ca}_{1-x}\text{Ba}_x)_m\text{Cu}_n\text{O}_{p+y}$$
 dargestellt sind, in der m, n, x und y Zahlen sind, die jeweils den folgenden Bereichen genügen:
 $6 \leq m \leq 16$, $4 \leq n \leq 12$, $0.2 < x < 0.8$ und $-2 \leq y \leq +2$
 45 und $p = (6+m+n)$.
3. Verfahren nach Anspruch 1 oder 2, bei welchem die Metallfolie aus Gold (Au), Platin (Pt) oder ihren Legierungen besteht.
- 50 4. Verfahren nach einem der Ansprüche 1 bis 3, bei welchem das Metallrohr aus Silber (Ag), Gold (Au), Platin (Pt) oder ihren Legierungen besteht.
5. Verfahren nach einem der Ansprüche 1 bis 4, bei welchem der Sauerstoff während der Sinteroperation mit einer Rate von mehr als 0,1 Liter pro Minute zugeführt wird.
- 55 6. Verfahren nach einem der Ansprüche 1 bis 5, bei welchem das Materialpulvergemisch ein Gemisch aus Pulvern ist, die jeweils aus einem reinem Pulver, einem Oxidpulver oder einem Carbonatpulver bestehen, das wenigstens eines der Bestandteile des Verbindungsoxids enthält.



7. Verfahren nach einem der Ansprüche 1 bis 6, bei welchem das Materialpulvergemisch durch eine Presse verdichtet wird, bevor das Materialpulvergemisch durch die Metallfolie eingewickelt wird.

5 Revendications

1. Dans un procédé de fabrication de supraconducteurs d'oxyde composé du type thallium (TI) par frittage de matériaux en poudre comprenant au moins une poudre contenant du thallium, le perfectionnement comprend le fait d'enrober ledit mélange de matériaux en poudre d'une feuille métallique faite de métaux précieux ou de leurs alliages, de placer le mélange de matériaux en poudre enrobés de la feuille métallique dans un tube métallique fait de métaux précieux ou de leurs alliages et ayant une extrémité fermée et une ouverture à l'extrémité opposée, et ensuite de chauffer ledit tube métallique à une température de frittage située entre 880 et 920°C tout en amenant de l'oxygène dans le tube métallique par l'ouverture pendant une durée située entre 1 minute et 40 heures de telle manière que le mélange de matériaux en poudre enrobé de la feuille métallique est fritté.
2. Procédé selon la revendication 1, dans lequel lesdits supraconducteurs d'oxyde composé du type thallium (TI) sont représentés par la formule générale :

$$\text{Ti}_4 (\text{Ca}_{1-x} \text{Ba}_x)_m \text{Cu}_n \text{O}_{p+y}$$
 où m, n, x et y sont des valeurs qui remplissent chacune respectivement les conditions
 $6 \leq m \leq 16$, $4 \leq n \leq 12$, $0,2 < x < 0,8$ et $-2 \leq y \leq +2$,
 et $p = (6+m+n)$.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel ladite feuille métallique est faite d'or (Au), de platine (Pt) ou de leurs alliages.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ledit tube métallique est fait d'argent (Ag), d'or (Au), de platine (Pt) ou de leurs alliages.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'oxygène est amené avec un débit supérieur à 0,1 litre par minute pendant l'opération de frittage.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le mélange de matériaux en poudre est un mélange de poudres dont chacune est composée d'une poudre élémentaire, d'une poudre d'oxyde ou d'une poudre de carbonate contenant au moins l'un des éléments constitutants de l'oxyde composé.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le mélange de matériaux en poudre est compacté par une presse avant que le mélange de matériaux en poudre ne soit enrobé de la feuille métallique.