

Description

This invention pertains to methods of producing mixed metal oxide material, and of making a body that comprises the material. In a particular embodiment the body is a superconductive body.

Background of the Invention

The recent discovery of superconductivity in a (La, Ba) cuprate led to worldwide research activity which quickly resulted in the discovery of other metal oxides having relatively high superconductive transition temperature T_c . In particular, it was discovered that $\text{YBa}_2\text{Cu}_3\text{O}_7$ can have T_c of about 90K. To date, the research efforts have resulted in the identification of several classes of high T_c oxide superconductors.

One class of metal oxide superconductors has nominal composition $\text{Ba}_{2-y}(\text{M}_{1-x}\text{M}'_x)_{1+y}\text{Cu}_3\text{O}_{9-z}$, where M and M' are chosen from Y, Eu, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, Lu, La, Sc, Sr or combinations thereof. Typically, $0 \leq x \leq 1$, $0 \leq y \leq 1$, and $1 < z < 3$. This class will be referred to as the Ba-cuprate system. Many members of the Ba-cuprate system have T_c greater than 77K the boiling point of liquid nitrogen. Exemplary of the Ba-cuprate system are $\text{YBa}_2\text{Cu}_3\text{O}_7$ (frequently referred to as the "1:2:3" compound), $\text{EuBa}_2\text{Cu}_3\text{O}_7$, and $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_7$. (It will be understood that chemical formulae of oxide superconductors and other mixed metal oxides herein are approximate only, and that deviations may occur. For instance, the optimal oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_7$ frequently is not 7 but about 6.9.)

Other classes of oxide superconductors are the Ti-Ba-Ca-Cu oxides (exemplified by $\text{Ti}_2\text{Ba}_2\text{CaCuO}_8$, see, for instance, *Nature* Vol. 332, March 31, 1988, page 420), the Bi-Sr-Ca-Cu oxides (exemplified by $\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8+x}$; *ibid*, page 422), and the copper-free bismates (exemplified by $\text{Ba}_8\text{K}_4\text{BiO}_3$).

A multitude of applications for the novel high T_c oxide superconductors have been proposed, and many of the proposed applications require the formation of bulk bodies comprising superconductive material. For a general overview of some potential applications of superconductors see, for instance, B. B. Schwartz and S. Foner, editors, *Superconductor Applications: SQUIDS and MA-CHINES*, Plenum Press 1977; and S. Foner and B. B. Schwartz, editors, *Superconductor Materials Science, Metallurgy, Fabrications, and Applications*, Plenum Press 1981. Among the applications are power transmission lines, rotating machinery, and superconductive magnets for e.g., fusion generators, MHD generators, particle accelerators, levitated vehicles, magnetic separation, and energy

storage, as well as junction devices, interconnects, and detectors. It is expected that many of the above and other applications of superconductivity would materially benefit if high T_c superconductive material could be used instead of the previously considered relatively low T_c materials.

In general, bulk superconducting bodies (including relatively thick films such as are produced by application of a paste to a substrate) are made from a starting material that comprises a powder of the appropriate metal oxide or oxides. Similarly, bulk bodies of non-superconductive metal oxides (e.g., ferrite bodies) can be produced from a starting material that comprises powder of the appropriate oxide or oxides. In all these cases the overall metal composition of the starting material corresponds directly to the desired metal composition of the body to be produced, but the powder can be a mixture of metal oxides. The oxygen content of the powder typically does not correspond to the desired final oxygen content.

Production of high T_c metal oxide powder is frequently accomplished by reaction of the component oxides and/or carbonates, involving typically repeated calcining and comminution steps, which is not only time consuming but may lead to the introduction of contaminants (it is well known that the presence of many common elements leads to poisoning of the superconducting properties such as high T_c). However, other approaches, (including co-precipitation) have also been used to produce the metal oxide powder for bulk superconductors. For instance, J. G. Bednort and K. A. Muller, *Zeitschrift für Physik B-Condensed Matter*, Vol. 64, pp. 189-193 (1986) report on page 190 the preparation of multiphase (Ba, La) cuprate by means of co-precipitation from an aqueous solution of the nitrates, using oxalic acid as the precipitant, and heating of the oxalate precipitate. See also A. Manthiram et al, *Nature*, Vol. 329, October 22, 1987, page 701.

Chung-Tse Chu et al, *Journal of the American Ceramic Society*, Vol. 70(12), 1987, C-375, report the preparation of high T_c superconducting oxide powder by a citrate process which involves dissolving in water the nitrate salts of the metal constituents of the oxide, adding citric acid to the solution, optionally adding NH_4OH to bring the pH of the solution to about 6, heating the solution to evaporate the water, and firing the resulting residue to form the desired oxide.

X. Z. Wang et al, *Solid State Communication*, Vol. 64(6), 1987, page 881 report on the formation of high T_c oxide powder ($\text{YBa}_2\text{Cu}_3\text{O}_x$) by a process that comprises dissolving copper acetate and yttrium nitrate in water, dissolving barium hydroxide in acetic acid, and pouring the resulting solution into an aqueous solution of oxalic acid. The result-

ing precipitate is then fired to produce the oxide.

Oxalic acid co-precipitation of aqueous metal nitrate solutions is also reported by A. Koyanagi et al, *Seissan Kenkyu* (Japan), Vol. 39(11), 1987, page 8, M. Hirabayashi et al, *Japanese Journal of Applied Physics*, vol. 26(4), 1987, page L454, K. Kaneko et al, *ibid*, Vol. 26(5), 1987, page L734, D.W. Capone et al, *Applied Physics Letters*, Vol. 50(9), 1987, page 543, and by T. Kawai et al, *Japanese Journal of Applied Physics*, vol. 26(5), 1987, page 736.

R.J. Clark et al, *High-Temperature Superconducting Materials*, edited by W.E. Hatfield et al, University of North Carolina, pp. 153-158 report, inter alia, treating "1:2:3" solutions of the nitrates with about 75% excess of oxalic acid to precipitate the bulk of the metals, evaporating the suspension to dryness, and heat treating the resulting solid. The procedure is reported to result in an exothermic reaction between nitrate and oxalate. The authors caution that this heat treatment should be done with care using limited quantities of material. European patent application EP-A-0 309 322 teaches forming sinterable superconductor powders by a process that comprises preparing an aqueous solution with a base of nitrates and/or acetates of at least one rare earth, at least one alkaline earth metal, and at least one transition metal, spray-drying the solution, and calcining the dried product. The application discloses that it is preferred to use nitrates. PCT patent application WO 88/10009 teaches making a superconducting composition $M_wA_zCu_xO_x$ by a process that comprising mixing $A(OH)_2$, OA or AO_2 and M_2O with an aqueous solution of cupric carboxylate or cupric nitrate, or mixing $A(OH)_2$ with an aqueous solution of Cu carboxylate and/or Cu nitrate and M carboxylate and/or M nitrate.

The prior art methods of forming mixed metal oxide powder material typically are time consuming and generally not easily adapted to continuous processing and/or scaling up to industrial scale. Furthermore, prior art coprecipitation methods typically depend on control of a variety of parameters such as pH and solubility product.

In view of the potential importance of bulk high T_c metal oxide superconductors and other articles that comprise mixed metal oxide powder, it would be highly desirable to have available a simple, fast, inexpensive, easily controllable, and efficient method for producing mixed metal oxide powder that is suitable for scale-up to industrial quantities. Desirably such a method also would be able to produce essentially single phase material that is essentially free of contaminants and has relatively uniform and relatively small particle size. Furthermore, such a method desirably would have broad applicability and permit the production of a wide range of com-

positions, including for high T_c superconductive oxides. This application discloses such a method.

DEFINITIONS

A "metal" herein is an element that forms positive ions when its compounds are in solution, and whose oxides form hydroxides rather than acids with water.

By "salt" we mean herein a compound which dissolves in water and is composed of one or more anions and one or more cations.

A "mixed metal oxide" herein is a compound of oxygen and two or more metals, an intimate mixture of the oxides of two or more metals, or a combination of the above.

All terms not explicitly defined herein have their customary meaning as defined in "The Condensed Chemical Dictionary", 10th edition, revised by G.G. Hawley.

According to the present invention there is provided a method as defined in claim 1.

Disclosed is a novel method for producing an article, (e.g., a superconductive magnet or a microwave component) that comprises a body that comprises a mixed metal oxide. Exemplarily the body is a superconductive wire or tape, or is a ferrite bead.

The mixed oxide has nominal composition $M_xM'_yO_z$, where M , M' ... are metal elements (exemplarily chosen from the alkalis, alkaline earths, the transition metals of atomic number 21-30, 39-48, 57-80, the column III elements Al, Ga, In, and Tl, and the column IV elements Sn and Pb), and $x, y, \dots$ and z can have any appropriate (not necessarily integer) non-negative value, with at least x, y , and z being non-zero.

The method comprises forming a mixture of salts that comprises at least one salt of each of $M, M' \dots$. At least one of the salts is an oxidizing agent with respect to at least one of the other salts, such that an oxidation-reduction reaction (in which the reactive anion species are essentially completely consumed to give gaseous decomposition products, leaving essentially no residue as an impurity) can occur in the mixture at an appropriate reaction temperature. This oxidation-reduction (redox) reaction will also be referred to as a "self-propagating chemical decomposition" (SCD). It will be appreciated that the metal ions are present in the mixture in proportions such that the final oxide has the desired composition. Typically, this means that the metals $M, M' \dots$ are present in atomic ratio $x:y: \dots$

In exemplary embodiments, one or more metal nitrates serve as the oxidizing agent, and one or more metal formates, acetates, propionates, and/or other appropriate metal-organic salts serve as the

reducing agent. The ratio of oxidizing agent (or agents) to reducing agent (or agents) is chosen such that the oxidation-reduction reaction proceeds at a desired rate at a desired reaction temperature. It is to be noted that the results generally do not depend on which metal is associated with the oxidizing agent or with the reducing agent. Instead, the results generally depend, for a given oxidizing agent and reducing agent, only on the ratio of oxidizing agent to reducing agent.

The method typically comprises forming a (non-explosive) aqueous solution of the salts, drying the solution (resulting in formation of a residue that comprises a mixture of the salts), and heating the residue to the reaction temperature such that the SCD occurs, with the metal oxide or, more typically, a precursor material of the mixed metal oxide being formed. If precursor material was formed then the method further comprises heating the precursor material in an oxygen-containing atmosphere such that the desired mixed metal oxide powder is formed from the precursor material.

The typical product of the SCD, the precursor material of the desired mixed metal oxide, typically is a mixture of oxides of M, M' that can be essentially free of contaminants. Significantly, the reaction can be carried out at a relatively low temperature, due to its exothermic character. For instance, we have formed the precursor material for $\text{YBa}_2\text{Cu}_3\text{O}_{x(z \sim 7)}$ from a mixture of nitrates and acetates at 270°C , which is significantly lower than the decomposition temperature of the acetate or nitrate salts alone.

The precursor material typically is heated in an oxygen-containing atmosphere such that the desired mixed metal oxide results. For instance, maintaining the above referred to precursor material at 910°C for 5-10 minutes in air resulted in essentially single phase ($> 90\%$, frequently $> 95\%$) $\text{YBa}_2\text{Cu}_3\text{O}_x$. Bodies made from this material by a conventional technique were superconductive, with $T_c(R=0)$ of about 91K.

The mixed oxide powder produced according to the invention can be used in the same way as such powders produced by prior art methods are used. For instance, they can in a conventional manner be formed into a desired body, and the body can be incorporated into an appropriate article, also in conventional manner. Exemplarily, if the mixed oxide is an appropriate ferrite then the body can be a ferrite bead or other ferrite body, and the article can be a microwave device or apparatus; if the oxide powder is high T_c superconductive powder then the body can be magnetic tape or wire and the article can be a superconductive magnet.

Brief Description of the Drawings

FIG. 1 shows, in form of a flow chart, major steps in a preferred embodiment of the invention;

FIG. 2 illustrates the dependence of the heat of reaction on the acetate:nitrate ratio of exemplary salt mixtures that are useful in the practice of the invention; and

FIGS. 3 and 4 give differential scanning calorimetry results for a salt mixture according to the invention, and for a mixture of metal acetates; respectively.

Detailed Description of Some Exemplary Embodiments

In many currently preferred exemplary embodiments the oxidizing agent is a nitrate or nitrates and the reducing agent is one or more acetates, formates, and/or propionates. Although the invention is not so limited, the discussion below will be primarily in terms of these particular salts. Some major steps in an exemplary preferred embodiment of the inventive process are indicated in FIG. 1.

A significant aspect of the invention is the ability to, at least to some extent, control the heat of reaction and the reaction temperature of the SCD by simple means, namely, appropriate choice of oxidizing and reducing agents, and of the molar ratio of oxidizing to reducing agents. This is illustrated by FIG. 2, which shows the heat of reaction $-\Delta H$ as a function of the nitrate/acetate ratio in the mixture of salts. As can be seen, the reaction is exothermic for a significant range of the ratio, with the heat of reaction strongly dependent on the ratio of oxidizing agent to reducing agent.

As those skilled in the art will recognize, choice of ΔH through, inter alia, the oxidizing agent/reducing agent ratio offers the possibility of control of the rate of reaction, such that the SCD can be chosen to proceed substantially at any desired rate. Although typically this rate will be non-explosive, under appropriate conditions (e.g., small quantities, confined space) even an explosive reaction may be useful, since it can be expected to result in especially well mixed small grained powder.

Other organic salts (e.g., formates or propionates) yield ΔH -curves that are of similar shape to that obtained for acetate but differ in some details therefrom. In particular, we have found that the maximum value of ΔH for a given cation is greater if propionates are used instead of acetates, and is smaller if formates are used instead of acetates. This offers further means of controlling the redox reaction, namely, forming a mixture containing more than one type of reducing agent.

Choice of the organic salts also affects the reaction temperature. For instance, for a particular NO_3 /organic salt ratio the reaction temperatures were 240°C , 270°C , and greater than 270°C if the organic salts were formates, acetates, or propionates, respectively (the metal ratios were Y:2Ba:3Cu). Thus, appropriate choice of oxidizing agent/reducing agent ratio, together with appropriate choice of reducing agent (typically an organic salt) makes possible control of the reaction rate and, at least to some extent, of the reaction temperature.

In currently preferred embodiments of the invention the metal salts are dissolved in water and the solution is spray dried by conventional means, resulting in an intimate mixture of metal salts. The quantities to be dissolved are selected such that the solution contains the metal ions in the same ratio as is desired to be present in the mixed metal oxide. For instance, in order to produce "1:2:3" material ($\text{YBa}_2\text{Cu}_3\text{O}_x$), x moles of yttrium nitrate; 2x moles of barium formate, and 3x moles of copper nitrate are dissolved. Although nitrates are the currently preferred oxidizers the invention is not so limited, and other oxidizers (e.g., chlorates) are also contemplated.

After formation of the intimate mixture of metal salts (e.g., by spray drying of the solution) the mixture is heated to the reaction temperature, whereby the reaction is initiated. Heating can be, but need not be, in air. Due to its exothermic nature, the reaction typically readily goes to completion, with the mixture of salts being transformed into a mixed metal oxide which, typically, comprises an intimate mixture of metal oxides. The salts are advantageously chosen such that their anionic portions readily decompose at the reaction temperature, with the products of the decompositions being volatile at that temperature. Such a choice of salts can result in a mixed metal oxide that is substantially free of impurities. This is considered to be a significant advantage of the inventive method.

Subsequent to completion of the SCD the resulting material is typically subjected to a heat treatment in an oxygen-containing atmosphere such that the desired mixed oxide results. For instance, the production of superconductive ($T_c \sim 91\text{K}$) "1:2:3" powder exemplarily comprised heating of oxidic precursor material to 910°C for 5-10 minutes. In a variant of this procedure the salt mixture is heated in O_2 to about 900°C , with the reaction occurring at an intermediate temperature, and formation of the 1:2:3 powder occurring at the final temperature.

Example 1: From commercially obtained quantities of hydrated $\text{Ba}(\text{CH}_3\text{COO})_2$, $\text{Ba}(\text{NO}_3)_2$, Y- $(\text{CH}_3\text{COO})_3$, Y $(\text{NO}_3)_3$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{Cu}(\text{NO}_3)_2$,

191.57 g of barium acetate, 84.09 g of yttrium acetate, 44.64 g of yttrium nitrate, and 269.91 g of copper nitrate, were taken and dissolved in water, resulting in a solution that contained Y, Ba, and Cu in the molar ratio 1:2:3, and that contained acetate and nitrate in the molar ratio 6:7. Enough solution to make 250 g of "1:2:3" powder was spray dried using a commercially available conical type laboratory spray drier, resulting in formation of a light blue powder that was an intimate mixture of acetates and nitrates of Y, Ba, and Cu. A sample of the powder was analyzed by differential scanning calorimetry (DSC) in flowing O_2 , with the result of the analysis shown in FIG. 3. As can be seen from the figure, a strongly exothermic reaction ($-\Delta H > 1162 \text{ kJ/mole}$) occurred at about 270°C . The remainder of the salt mixture was put into ceramic boats and placed under flowing O_2 into a furnace that was kept at about 400°C . The SCD reaction occurred as anticipated and yielded a mixed oxide powder. The powder was then heated to 900°C and maintained at that temperature for 10 minutes under flowing O_2 , followed by a slow cool to room temperature, also under flowing O_2 . The resulting powder was analyzed by powder X-ray diffraction, with the result indicating that the powder was single phase $\text{YBa}_2\text{Cu}_3\text{O}_x$ to within the limits of X-ray detection. Similar X-ray analysis of the DSC sample had shown that the reaction had gone to completion. Specifically, no $\text{Ba}(\text{NO}_3)_2$ was detected. From the thus produced 1:2:3 powder pellets were formed by cold pressing. The pellets were superconducting, with T_c ($R=0$) of about 91K. Sintered disks were also formed by a conventional method. The disks were also superconducting, with T_c ($R=0$) of about 91K.

Example 2: Sintered superconducting disks were prepared substantially as in Example 1, except that the salt mixture was placed, under flowing O_2 , into a furnace at 900°C and maintained at that temperature for 10 minutes. The SCD reaction occurred at an intermediate temperature.

In the examples below the salt solution was prepared to contain the metals in the indicated ratios and the indicated reducing agent/oxidizing agent ratio. The preparation procedures were standard and do not require recitation.

Examples 3-6: 1:2:3 powders were prepared substantially as described in Example 1, except that the aqueous salt solutions had acetate:nitrate ratios of 9:4, 7:6, 5:8, and 4:9, respectively. The exothermic SCD reactions had ΔH of -4016, -2406, -890, and -721 kJ/mole, respectively, with the main exotherms of the former two occurring at 326 and 296°C , and the latter two having a single sharp exotherm at about 270°C . The powder resulting from the 5:8 (acetate:nitrate) mixture comprised, in addition to $\text{YBa}_2\text{Cu}_3\text{O}_x$, about 2% BaCuO_2 , and the

4:9 (acetate:nitrate) powder comprised, in addition to the $\text{YBa}_2\text{Cu}_3\text{O}_x$, about 2% BaCuO_2 and less than 1% of BaCO_3 . Sintered pellets were prepared from these powders by a standard technique. The pellets were essentially single phase (>95%) and superconducting, with $T_c(R=0) \geq 88\text{K}$.

Example 7: An intimate mixture of Y, Ba, and Cu salts was prepared substantially as described in Example 1, except that the mixture did not contain any nitrates. The mixture was analyzed by DSC, with the result shown in FIG. 4. As the figure shows, the decomposition is a multi-step process that is not complete until about 400°C . This is in agreement with previous reports on spray-dried acetate salt.

Examples 8-10: 1:2:3 powders were prepared substantially as described in Example 1, except that formates ($\text{Ba}(\text{HCOO})_2$, $\text{Y}(\text{HCOO})_3$, and $\text{Cu}(\text{COO})_2$) were used instead of the acetates. Solutions having a formate:nitrate ratio of 9:4, 8:5, and 6:7 were prepared. DSC analysis determined that the SCD reaction occurred over the ranges $163\text{--}284$, $167\text{--}272$, and $173\text{--}276^\circ\text{C}$, respectively, with the peaks occurring at 210 , 221 , and 253°C , respectively, with $-\Delta H$ of 804 , 770 , and 473 kJ/mole , respectively. Pellets made from the thus produced 1:2:3 powders were essentially single phase superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$, with $T_c(R=0) \geq 88\text{K}$.

Examples 11-12: 1:2:3 powders were prepared substantially as described in Example 1, except that propionates ($\text{Ba}(\text{H}_3\text{C-CH}_2\text{-COO})_2$, etc.) were used instead of the acetates. Solutions having a propionates:nitrate ratio of 4:9 and 7:6 were prepared. DSC analysis determined the peak of the SCD reaction to occur at 264 and 289°C , respectively, with $-\Delta H$ of 1073 and 2058 kJ/mole , respectively. Pellets made from the thus produced 1:2:3 powders are essentially single phase superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$, with $T_c(R=0) \geq 88\text{K}$.

Examples 13-15: 1:2:3 powders were prepared substantially as described in Example 1, except that respective glycine salts ($\text{Ba}(\text{H}_2\text{N-CH}_2\text{-COO})_2$, etc.), β -alanine salts ($\text{Ba}(\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-COO})_2$, etc.) and α -alanine salts ($\text{Ba}(\text{CH}_3\text{-CH}_2\text{NH}_2\text{-COO})_2$, etc.) were substituted for the acetate salts. In all three cases the solutions had a 4:9 amino acid:nitrate ratio. DSC analysis determined that the SCD reactions occurred over the range $201\text{--}216$, $186\text{--}195$, and $201\text{--}216^\circ\text{C}$ respectively, with peak temperatures of 206 , 191 , and 206°C , respectively. Pellets made from the thus produced 1:2:3 powders are essentially single phase superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$, with $T_c(R=0) \geq 88\text{K}$.

Example 16: A spinel powder (NiMn_2O_4) was produced by a method substantially as described in Example 1, except that $\text{Ni}(\text{NO}_3)_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$ were dissolved in water, with the Ni:Mn ratio being 1:2. The intimate salt mixture was heat-

ed on a hot plate, and an exothermic reaction occurred. The resulting precursor material was ground and fired in a Pt boat at 920°C for 6 hours under O_2 . The resulting mixed oxide powder was essentially single phase NiMn_2O_4 , as determined by X-ray diffraction.

Example 17: A ferrite powder (MnFe_2O_4) is produced substantially as described in Example 1, except that $\text{Mn}(\text{NO}_3)_2$ and $\text{Fe}(\text{CH}_3\text{-COO})_2$ were dissolved in water, with the Mn:Fe ratio being 1:2. The salt mixture is reacted in a furnace under O_2 , and the resulting precursor material is heated to 920°C and fired under O_2 for 6 hours. The resulting powder is essentially single phase. A bead is formed from the powder by a conventional technique.

Example 18: A superconducting oxide powder ($\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$) is produced substantially as described in Example 1, except that two molar units each of $\text{Ti}(\text{NO}_3)_3$, $\text{Ba}(\text{CH}_3\text{-COO})_2$, and $\text{Ca}(\text{CH}_3\text{-COO})_2$, and three molar units of $\text{Cu}(\text{NO}_3)_2$ are dissolved in water.

Example 19: 1:2:3 powder is produced substantially as described in Example 1, except that one half molar unit each of $\text{Ba}(\text{NO}_3)_2$ and $\text{Ba}(\text{ClO}_4)_2$, one molar unit each of $\text{Y}(\text{CH}_3\text{-COO})_3$ and $\text{Ba}(\text{CH}_3\text{-COO})_2$, and 3 molar units of $\text{Cu}(\text{NO}_3)_2$ are dissolved in water. The SCD reaction is relatively vigorous.

Claims

1. A method of producing an article that comprises a body comprising a mixed metal oxide of nominal composition $\text{M}_x\text{M}'_{x'}\text{O}_z$ wherein M, M' ... are metal elements and at least each of x, x' and z is greater than zero, with M, M', ..., x, x' ... z selected such that the mixed metal oxide is a Ba-cuprate superconductor, a Ti-Ba-Ca-cuprate superconductor, a Bi-Sr-Ca-cuprate superconductor, a copper-free Bi-oxide superconductor, a spinel or a ferrite, the method comprising forming precursor material consisting essentially of M, M' ... and, optionally, of oxygen; heating the precursor material in an oxygen-containing atmosphere such that the mixed metal oxide is formed from the precursor material; and

forming the body from the mixed metal oxide, and completing

producing the article;

CHARACTERIZED IN THAT forming the precursor material comprises

- a) forming an intimate mixture comprising at least one salt each of M, M' ... such that the mixture contains M, M' ... in essentially the ratio x:x' ...; with the salts chosen such that at least one of the salts is an oxidizing agent with respect to at least one of the



4:9 (acetate:nitrate) powder comprised, in addition to the $\text{YBa}_2\text{Cu}_3\text{O}_x$, about 2% BaCuO_2 and less than 1% of BaCO_3 . Sintered pellets were prepared from these powders by a standard technique. The pellets were essentially single phase (>95%) and superconducting, with $T_c(R=0) \geq 88\text{K}$.

Example 7: An intimate mixture of Y, Ba, and Cu salts was prepared substantially as described in Example 1, except that the mixture did not contain any nitrates. The mixture was analyzed by DSC, with the result shown in FIG. 4. As the figure shows, the decomposition is a multi-step process that is not complete until about 400°C . This is in agreement with previous reports on spray-dried acetate salt.

Examples 8-10: 1:2:3 powders were prepared substantially as described in Example 1, except that formates ($\text{Ba}(\text{HCOO})_2$, $\text{Y}(\text{HCOO})_3$, and $\text{Cu}(\text{COO})_2$) were used instead of the acetates. Solutions having a formate:nitrate ratio of 9:4, 8:5, and 6:7 were prepared. DSC analysis determined that the SCD reaction occurred over the ranges $163\text{--}284$, $167\text{--}272$, and $173\text{--}276^\circ\text{C}$, respectively, with the peaks occurring at 210 , 221 , and 253°C , respectively, with $-\Delta\text{H}$ of 804 , 770 , and 473 kJ/mole , respectively. Pellets made from the thus produced 1:2:3 powders were essentially single phase superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$, with $T_c(R=0) \geq 88\text{K}$.

Examples 11-12: 1:2:3 powders were prepared substantially as described in Example 1, except that propionates ($\text{Ba}(\text{H}_3\text{C-CH}_2\text{-COO})_2$, etc.) were used instead of the acetates. Solutions having a propionates:nitrate ratio of 4:9 and 7:6 were prepared. DSC analysis determined the peak of the SCD reaction to occur at 264 and 289°C , respectively, with $-\Delta\text{H}$ of 1073 and 2058 kJ/mole , respectively. Pellets made from the thus produced 1:2:3 powders are essentially single phase superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$, with $T_c(R=0) \geq 88\text{K}$.

Examples 13-15: 1:2:3 powders were prepared substantially as described in Example 1, except that respective glycine salts ($\text{Ba}(\text{H}_2\text{N-CH}_2\text{-COO})_2$, etc.), β -alanine salts ($\text{Ba}(\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-COO})_2$, etc.) and α -alanine salts ($\text{Ba}(\text{CH}_3\text{-CH}_2\text{NH}_2\text{-COO})_2$, etc.) were substituted for the acetate salts. In all three cases the solutions had a 4:9 amino acid:nitrate ratio. DSC analysis determined that the SCD reactions occurred over the range $201\text{--}216$, $186\text{--}195$, and $201\text{--}216^\circ\text{C}$ respectively, with peak temperatures of 206 , 191 , and 206°C , respectively. Pellets made from the thus produced 1:2:3 powders are essentially single phase superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$, with $T_c(R=0) \geq 88\text{K}$.

Example 16: A spinel powder (NiMn_2O_4) was produced by a method substantially as described in Example 1, except that $\text{Ni}(\text{NO}_3)_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$ were dissolved in water, with the Ni:Mn ratio being 1:2. The intimate salt mixture was heat-

ed on a hot plate, and an exothermic reaction occurred. The resulting precursor material was ground and fired in a Pt boat at 920°C for 6 hours under O_2 . The resulting mixed oxide powder was essentially single phase NiMn_2O_4 , as determined by X-ray diffraction.

Example 17: A ferrite powder (MnFe_2O_4) is produced substantially as described in Example 1, except that $\text{Mn}(\text{NO}_3)_2$ and $\text{Fe}(\text{CH}_3\text{-COO})_2$ were dissolved in water, with the Mn:Fe ratio being 1:2. The salt mixture is reacted in a furnace under O_2 , and the resulting precursor material is heated to 920°C and fired under O_2 for 6 hours. The resulting powder is essentially single phase. A bead is formed from the powder by a conventional technique.

Example 18: A superconducting oxide powder ($\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$) is produced substantially as described in Example 1, except that two molar units each of $\text{Ti}(\text{NO}_3)_3$, $\text{Ba}(\text{CH}_3\text{-COO})_2$, and $\text{Ca}(\text{CH}_3\text{-COO})_2$, and three molar units of $\text{Cu}(\text{NO}_3)_2$ are dissolved in water.

Example 19: 1:2:3 powder is produced substantially as described in Example 1, except that one half molar unit each of $\text{Ba}(\text{NO}_3)_2$ and $\text{Ba}(\text{ClO}_4)_2$, one molar unit each of $\text{Y}(\text{CH}_3\text{-COO})_3$ and $\text{Ba}(\text{CH}_3\text{-COO})_2$, and 3 molar units of $\text{Cu}(\text{NO}_3)_2$ are dissolved in water. The SCD reaction is relatively vigorous.

Claims

1. A method of producing an article that comprises a body comprising a mixed metal oxide of nominal composition $\text{M}_x\text{M}'_{x'}\text{O}_z$ wherein M, M' ... are metal elements and at least each of x, x' and z is greater than zero, with M, M', ..., x, x' ... z selected such that the mixed metal oxide is a Ba-cuprate superconductor, a Ti-Ba-Ca-cuprate superconductor, a Bi-Sr-Ca-cuprate superconductor, a copper-free Bi-oxide superconductor, a spinel or a ferrite, the method comprising forming precursor material consisting essentially of M, M' ... and, optionally, of oxygen; heating the precursor material in an oxygen-containing atmosphere such that the mixed metal oxide is formed from the precursor material; and

forming the body from the mixed metal oxide, and completing

producing the article;

CHARACTERIZED IN THAT forming the precursor material comprises

- a) forming an intimate mixture comprising at least one salt each of M, M' ... such that the mixture contains M, M' ... in essentially the ratio $x:x'$...; with the salts chosen such that at least one of the salts is an oxidizing agent with respect to at least one of the



- other salts (to be referred to as the reducing agent);
b) heating the mixture at least to a reaction temperature such that an exothermic reaction occurs and the precursor material of the mixed metal oxide is formed from the mixture.
2. Method of claim 1, where the Ba-cuprate superconductor has nominal composition $\text{YBa}_2\text{Cu}_3\text{O}_7$, where the Ti-Ba-Ca-cuprate superconductor has nominal composition $\text{Ti}_2\text{Ba}_2\text{CaCuO}_8$, where the Bi-Sr-Ca-cuprate superconductor has nominal composition $\text{Bi}_{2,2}\text{Sr}_2\text{Ca}_{0,8}\text{Cu}_2\text{O}_{8+\delta}$, where the copper-free Bi-oxide superconductor has nominal composition $\text{Ba}_{0,8}\text{K}_{0,4}\text{BiO}_3$, where the spinel has nominal composition NiMn_2O_4 , and where the ferrite has nominal composition MnFe_2O_4 .
 3. Method of any of claims 1 and 2, where a) comprises dissolving the at least one salt each of M, M' ... in an aqueous medium, and drying the solution, whereby the intimate mixture is formed, and wherein the oxidizing agent or agents and reducing agent or agents, as well as the ratio of the former to the latter, are chosen such that the exothermic reaction occurs at a desired rate and at a desired temperature.
 4. Method of any of claims 1-3, wherein the at least one oxidizing agent is a nitrate.
 5. Method of any of claims 1-4, wherein the at least one reducing agent is selected from the group consisting of the acetates, formates, propionates, glycines, and alanines.
 6. Method of any of claims 1-5, wherein the mixed metal oxide is superconducting at a temperature of 77K.
 7. Method of claim 2, wherein the mixed metal oxide has nominal composition $\text{YBa}_2\text{Cu}_3\text{O}_7$.
 8. Method of claim 7, wherein the reaction temperature is a temperature less than 300°C .
 9. Method of claim 6, wherein forming the body and completing producing the article comprises sintering the body in an oxygen-containing atmosphere.
 10. Method of any of claims 1-9, wherein the body is a superconducting body or a ferrite body.

11. Method of claim 10, wherein the superconducting body is adapted for carrying an electric current.

Patentansprüche

1. Verfahren zur Herstellung eines Gegenstandes mit einem Körper, der ein gemischtes Metalloxyd der nominellen Zusammensetzung $\text{M}_x\text{M}'_{x'}\dots\text{O}_z$ enthält, wobei M, M' ... Metallelemente sind und wenigstens jedes x, x' und z größer als null ist, wobei M, M'..., x, x'... z derart ausgewählt sind, daß das gemischte Metalloxyd ein Ba-Kuprat-Supraleiter, ein Ti-Ba-Ca-Kuprat-Supraleiter, ein Bi-Sr-Ca-Kuprat-Supraleiter, ein kupferfreier Bi-Oxyd-Supraleiter, ein Spinell oder ein Ferrit ist, wobei das Verfahren umfaßt, Bilden eines Vorläufermaterials, das im wesentlichen aus M, M'... und wahlweise aus Sauerstoff besteht, Erhitzen des Vorläufermaterials in einer Sauerstoff enthaltenden Atmosphäre derart, daß das gemischte Metalloxyd aus dem Vorläufermaterial gebildet wird, und Bilden des Körpers aus dem gemischten Metalloxyd und Vervollständigen der Herstellung des Gegenstandes, dadurch gekennzeichnet, daß das Bilden des Vorläufermaterials umfaßt
 - a) Bilden einer innigen Mischung mit wenigstens einem Salz von jedem M, M', ... derart, daß die Mischung M, M' ... im wesentlichen in dem Verhältnis $x:x'$... enthält, wobei die Salze derart ausgewählt werden, daß wenigstens eines der Salze ein oxydierendes Agens in Bezug auf wenigstens eines der anderen Salze ist, (das als das reduzierende Agens bezeichnet wird),
 - b) Erhitzen der Mischung wenigstens auf eine Reaktionstemperatur derart, daß eine exotherme Reaktion auftritt und das Vorläufermaterial des gemischten Metalloxydes aus der Mischung gebildet wird.
2. Verfahren nach Anspruch 1, in welchem der Ba-Kuprat-Supraleiter eine nominelle Zusammensetzung $\text{YBa}_2\text{Cu}_3\text{O}_7$ hat, wobei der Ti-Ba-Ca-Kuprat-Supraleiter eine nominelle Zusammensetzung $\text{Ti}_2\text{Ba}_2\text{CaCuO}_8$ hat, wobei der Bi-Sr-Ca-Kuprat-Supraleiter eine nominelle Zusammensetzung $\text{Bi}_{2,2}\text{Sr}_2\text{Ca}_{0,8}\text{Cu}_2\text{O}_{8+\delta}$ hat, wobei der kupferfreie Bi-Oxyd-Supraleiter eine nominelle Zusammensetzung $\text{Ba}_{0,8}\text{K}_{0,4}\text{BiO}_3$ hat, wobei der Spinell eine nominelle Zusammensetzung NiMn_2O_4 hat und wobei der Ferrit eine nominelle Zusammensetzung von MnFe_2O_4 hat.



3. Verfahren nach einem der Ansprüche 1 und 2, wobei a) das Lösen des wenigstens einen Salzes von jedem M, M' ... in einem wässrigen Medium und Trocknen der Lösung umfaßt, wobei die innige Mischung gebildet wird, und wobei das oxydierende Agens oder die mehreren oxydierenden Agens und das reduzierende Agens oder die mehreren reduzierenden Agens sowie das Verhältnis des ersteren zum letzteren bzw. der ersteren zu den letzteren derart gewählt ist, daß die exotherme Reaktion bei einer erwünschten Rate und bei einer erwünschten Temperatur auftritt.

4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem das wenigstens eine oxydierende Agens ein Nitrat ist.

Verfahren nach einem der Ansprüche 1 bis 4, in welchem das wenigstens eine reduzierende Agens aus der Gruppe ausgewählt ist, die aus den Acetaten, Formiaten, Propionaten, Glycinen und Alaninen besteht.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem das gemischte Metalloxyd bei einer Temperatur von 77K supraleitend ist.

7. Verfahren nach Anspruch 2, in welchem das gemischte Metalloxyd eine nominelle Zusammensetzung $YBa_2Cu_3O_7$ hat.

8. Verfahren nach Anspruch 7, in welchem die Reaktionstemperatur eine Temperatur ist, die niedriger als 300 °C ist

9. Verfahren nach Anspruch 6, bei welchem das Bilden des Körpers und das Vervollständigen der Herstellung des Gegenstandes das Sintern des Körpers in einer Sauerstoff enthaltenden Atmosphäre umfaßt.

10. Verfahren nach einem der Ansprüche 1 bis 9, in welchem der Körper ein supraleitender Körper oder ein Ferritkörper ist.

11. Verfahren nach Anspruch 10, in welchem der supraleitende Körper einen elektrischen Strom tragen kann.

Revendications

1. Procédé de fabrication d'un objet qui comprend un corps comprenant un oxyde métallique mixte de composition nominale $M_xM'_x...O_z$ dans laquelle M, M'... sont des éléments métalliques et au moins chacun de x, x' et z est supérieur à zéro, avec M, M',..., x,

x'...z tels que l'oxyde métallique mixte est un supraconducteur à base de cuprate de Ba, un supraconducteur à base de cuprate de Ti-Ba-Ca, un supraconducteur à base de Bi-Sr-Ca, un supraconducteur à base d'oxyde de Bi exempt de cuivre, un spinel ou un ferrite, le procédé consistant à former un précurseur consistant essentiellement en M, M'... et, le cas échéant, en oxygène ; à chauffer le précurseur dans une atmosphère contenant de l'oxygène, de façon à former l'oxyde métallique mixte à partir du précurseur ; et

à former le corps à partir de l'oxyde métallique mixte et à achever la fabrication de l'objet ;

caractérisé en ce que la formation du précurseur consiste

a) à former un mélange intime comprenant au moins un sel de chacun de M, M'... tel que le mélange contienne M, M'... essentiellement en le rapport x:x'... ; les sels choisis étant tels que l'un au moins des sels soit un agent oxydant par rapport à au moins un autre sel (qui sera désigné comme agent réducteur) ;

b) à porter le mélange à au moins une température de réaction telle qu'il se produise une réaction exothermique et que le précurseur de l'oxyde métallique mixte soit formé à partir du mélange.

2. Procédé suivant la revendication 1, dans lequel le supraconducteur à base de cuprate de Ba a la composition nominale $YBa_2Cu_3O_7$, le supraconducteur à base de cuprate de Ti-Ba-Ca a la composition nominale $Ti_2Ba_2CaCuO_8$, le supraconducteur à base de cuprate de Bi-Sr-Ca a la composition nominale $Bi_{2,2}Sr_2Ca_{0,8}Cu_2O_{8+\delta}$, le supraconducteur à base d'oxyde de Bi et exempt de cuivre a la composition nominale $Ba_{0,8}K_{0,4}BiO_3$, le spinel a la composition nominale $NiMn_2O_4$ et le ferrite a la composition nominale $MnFe_2O_4$.

3. Procédé suivant l'une quelconque des revendications 1 ou 2, dans lequel a) consiste à dissoudre ledit au moins un sel de chacun de M, M'... dans un milieu aqueux et à sécher la solution, de manière à former le mélange intime, et dans lequel l'agent oxydant ou les agents oxydants et l'agent réducteur ou les agents réducteurs ainsi que le rapport de celui-là à celui-ci sont choisis de manière que la réaction isothermique ait lieu à une vitesse souhaitée et à une température souhaitée.

4. Procédé suivant l'une des revendications 1 à 3, dans lequel ledit au moins un agent oxydant



est un nitrate.

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel ledit au moins un agent réducteur est choisi parmi les acétates, formiates, propionates, glycines et alanines. 5
6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel l'oxyde métallique mixte est supraconducteur à une température de 77K. 10
7. Procédé suivant la revendication 2, dans lequel l'oxyde métallique mixte a la composition nominale $\text{YBa}_2\text{Cu}_3\text{O}_7$. 15
8. Procédé suivant la revendication 7, dans lequel la température de réaction est une température inférieure à 300°C . 20
9. Procédé suivant la revendication 6, dans lequel la formation du corps et l'achèvement de la fabrication de l'objet comprennent un frittage du corps dans une atmosphère contenant de l'oxygène. 25
10. Procédé suivant l'une quelconque des revendications 1 à 9, dans lequel le corps est un corps supraconducteur ou un corps en ferrite. 30
11. Procédé suivant la revendication 10, dans lequel le corps supraconducteur est destiné au passage d'un courant électrique. 35

40

45

50

55