(54) Title: METHOD AND COMPOSITION FOR IMPROVING FLUX PINNING AND CRITICAL CURRENT IN SUPERCONDUCTORS

Superconducting materials and methods of forming superconducting materials are disclosed. Highly oxidized superconductors are heated at a relatively high temperature so as to release oxygen, which migrates out of the material, and form a non-superconducting phase which does not diffuse out of grains of the material. The material is then reoxidized at a lower temperature, leaving the non-superconducting inclusions inside a superconducting phase. The non-superconducting inclusions act as pinning centers in the superconductor, increasing the critical current thereof.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>ES</td>
<td>Spain</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>FI</td>
<td>Finland</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GA</td>
<td>Gabon</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GB</td>
<td>United Kingdom</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BI</td>
<td>Benin</td>
<td>IT</td>
<td>Italy</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>JP</td>
<td>Japan</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SU</td>
<td>Soviet Union</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LU</td>
<td>Luxembourg</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>DE</td>
<td>Germany, Federal Republic of</td>
<td>MC</td>
<td>Monaco</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
METHOD AND COMPOSITION FOR IMPROVING FLUX PINNING AND CRITICAL CURRENT IN SUPERCONDUCTORS

GOVERNMENT RIGHTS NOTICE
The inventions herein arose in the course of, under, or in connection with Contract No. DE-AC03-76-SF-00098 between the Department of Energy and the University of California at Berkeley.

CROSS-REFERENCE TO RELATED APPLICATION
This application is a continuation-in-part of co-pending application Serial No. 263,750, filed October 28, 1988 and incorporated herein by reference for all purposes.

BACKGROUND OF THE INVENTION
This invention relates to superconductor systems, and in particular to crystalline structures having superconducting properties.

Theoretical and experimental research in the field of superconducting materials by thousands of researchers has led to the discovery of a variety of oxide compounds which become superconducting at relatively high temperatures ($T_c$), i.e., above about 20°K. The widely known high temperature superconductors are oxides, and presently contain (1) copper and/or bismuth, (2) barium or other alkaline earths such as strontium or calcium, and (3) trivalent elements such as yttrium. Rare earth elements having atomic numbers ranging from 57 to 71 (lanthanum to lutecium), are substituted for yttrium in some materials, as are thallium or bismuth. Representative of superconductors are the following:

(1) oxide materials containing lanthanum, strontium and copper, bearing the formula $La_{2-x}Sr_xCuO_4$, commonly referred to as L-S-C-O, and recently discovered variants thereof such as materials in which La substituted with, for
example, praseodymium, neodymium, uranium, thorium, cerium and others containing a tetravalent ion in place of Sr;

(2) oxide materials containing yttrium, barium and copper, bearing the formula $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, commonly referred to as 1-2-3 (rare earth elements can be substituted for yttrium, and the resulting compounds are also superconducting). Other $\text{Y-Ba-Cu}$ materials include 1-2-4 and 2-4-7;

(3) oxide materials containing bismuth, strontium, calcium and copper, bearing such formulas as $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8-x}$ and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10-x}$, commonly referred to as B-C-S-C-O, and related materials including those in which Pb and copper replace Bi;

(4) oxide materials containing thallium, barium, calcium and copper, bearing such formulas as $\text{Tl}_2\text{Ba}_2\text{Cu}_2\text{O}_x$, $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_x$, $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$, $\text{Tl}_2\text{Ca}_3\text{Ba}_2\text{Cu}_4\text{O}_x$, $\text{TlCaBa}_2\text{Cu}_2\text{O}_x$, and $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_x$, commonly referred to as T-C-B-C-O, and related materials including those in which Pb and/or Cu replace Tl; and

(5) oxide materials containing bismuth, barium, potassium and copper, bearing the formula $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, identified as B-K-B-O.

Copending application Serial No. 263,750 discloses certain improved superconductor materials and methods of manufacture thereof, and is incorporated herein by reference for all purposes. See also Morris et al., "Eight New High Temperature Superconductors With the 1:2:4 Structure", Phys. Rev., 39, 7347 (April, 1989), which is also incorporated herein by reference for all purposes.
Introduction of defects in intermetallic type II superconductors was proposed to increase their critical current density. See, for example, Campbell et al., "Pinning of Flux Vortices in Type II Superconductors," Phil. Mag., 18, 313 (1968). Thermally activated flux creep has also been recognized as a problem with high-temperature superconductors.

However, in the case of high-temperature superconductors, the introduction of defects to increase critical current density to a useful level has met with only limited success. For example, in Gammel et al., Phys. Rev. Lett., 59, 2592 (1987), an increased density of twin boundaries provides only moderate improvement in flux pinning. Some increase in low temperature $J_c$ in YBa$_2$Cu$_3$O$_y$ in strong magnetic fields was achieved by the introduction of point defects by neutron irradiation in, for example, Willis et al., "Radiation Damage in YBa$_2$Cu$_3$O$_{y-x}$ By Fast Neutrons", High Temperature Superconductors, MRS Symposium Proceedings Vol. 99, 391-94 (1988). However, even in Willis et al., the increase in $J_c$ was limited and at 7°K and B = 4T increased to only about $10^4$ A/cm$^2$ after about $10^{18}$ n cm$^{-2}$ above which value superconductivity was adversely effected by the neutron dose. This may limit the wide application of neutron irradiation to provide improvement in flux pinning.

Critical currents in polycrystalline high-temperature superconductors are still further reduced by weak links at the grain boundaries, which are made worse by high porosity, misalignment of the crystalline axis of adjacent grains, and by formation and accumulation of non-superconductor phases (compounds) at boundaries between superconducting grains.

The need for additional high temperature superconductors and methods of manufacturing superconductors is great, not only to achieve superconductors with higher $T_c$'s, but also to achieve superconductors with improved
J_c's in magnetic fields, improved mechanical properties, stability, and ease of processing.

SUMMARY OF THE INVENTION

Improved superconductors and methods of manufacturing superconductors are disclosed. In one embodiment the invention provides a method of producing pinning centers in the grains of superconductor material and in some embodiments controlling and optimizing the size, shape, and distribution of pinning centers within grains of superconductors which have multiple phases whose stability depends on oxygen content, especially including high temperature superconductors. The invention, further, provides for suppression of the formation of non-superconducting phases at grain boundaries and preparation of dense superconductors with low porosity.

Accordingly, in one embodiment the invention provides a method of forming a superconductor comprising the steps of heating a starting material to form a first, non-superconducting immobile phase, and an intermediate phase; and oxidizing or reducing the intermediate phase to form a superconductor phase which is interspersed by the non-superconducting phase.

A high-temperature superconductor is also disclosed. The superconductor comprises a first, superconducting phase and a second phase dispersed within crystals of said first, superconducting phase. The second phase may be a superconducting or non-superconducting phase and, in some embodiments, a third phase is provided which may also be either superconducting or non-superconducting.

In an alternative embodiment the superconductor material is formed by the steps of heating a starting material, the step of heating forming a second phase, and an intermediate phase; and oxidizing or reducing the
intermediate phase to form a superconductor phase interspersed by the second phase.

A method of using a superconductor is also disclosed. In one embodiment the superconductor has a first, superconducting phase and a second phase. The superconductor is placed in a magnetic field and oriented such that magnetic flux lines are substantially parallel to planes of the second phase.

In alternative embodiments, the method of forming a superconductor comprises the step of mixing a superconducting material or its formation materials in the presence of a nucleation center under conditions that form a superconducting phase and a non-superconducting phase by removal of oxygen.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a Pseudo-ternary phase diagram of the Y₂O₃-BaO-CuO system at P(O₂) = 100 bar and T = 930°C. The positions of dots and crosses indicate the starting stoichiometries - the corresponding cation ratios are indicated. The dots indicate compositions which resulted in formation of the 124 phase;

Fig. 2 shows x-ray powder diffraction patterns for the 124 and 247 phases in the Dy-Ba-Cu-O system. Each pattern shows a single phase, except for additional peaks identified as CuO and Y₂Ba₁Cu₁O₅;

Fig. 3 shows low angle x-ray powder diffraction curves taken with Cu kα radiation: (a) Dy-Ba-Cu-O synthesized at 930°C in 35 bar O₂; the peak at d spacing = 13.6 Å indicates the 124 phase. (b) Dy-Ba-Cu-O synthesized in 17 bar O₂; the peak at 12.55 Å indicates the 247 phase. (c) Dy-Ba-Cu-O synthesized in 6 bar O₂; the peak at 11.7 Å indicates the 123 phase. (d) Eu-Ba-Cu-O processed in 100 bar O₂. The two peaks at 13.6 Å and 12.55 Å indicated that the sample contains both 124 and 247 phases;
Fig. 4 is a phase diagram of the 1-2-4, 1-2-3, 2-4-7 system for Dy-Ba-Cu-O;

Fig. 5 is a set of susceptibility curves for 1-2-4 and material formed according to one embodiment of the invention;

Fig. 6 is a Transmission Electron Micrograph (TEM) of material formed according to one embodiment of the invention;

Fig. 7 is a TEM of another portion of the material shown in Fig. 6;

Fig. 8 is a weight loss curve for material formed according to one embodiment of the invention;

Fig. 9 is a set of susceptibility curves for additional materials formed according to one embodiment of the invention;

Fig. 10 is a set of susceptibility curves for additional materials formed according to one embodiment of the invention;

Fig. 11 is a weight loss curve for a sample "J";

Fig. 12 is a weight loss curve for a sample "H";

Fig. 13 is a TEM of a mixed phase Eu-Ba-Cu-O superconductor; and

Fig. 14 illustrates the stability regions of 1-2-3.
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Contents

I. General

II. Overall Description of Synthesis
   A. 1-2-4 Starting Material
   B. 1-2-3 Starting Material
   C. Other Starting Materials

III. Detailed Description of the Synthesis
   A. Synthesis of Starting Materials
   B. Formation of Non-Superconducting Phase
   C. Formation of Nucleation Regions
   D. Re-Diffusion of Oxygen

IV. Example 1 - Conversion of 1-2-4 into 1-2-3 with Flux Pinning Centers
   A. Synthesis of 1-2-4
   B. Formation of Flux Pinning Centers in 1-2-3 from 1-2-4
   C. Formation of Flux Pinning Centers in 1-2-3

V. Example 2 - Synthesis of Y-Ba-Cu and Dy-Ba-Cu Interspersed by Non-Superconductor

VI. Example 3 - Partial Conversion of 1-2-4 to 1-2-3 Plus a Non-Superconducting Phase

VII. Use of Materials Disclosed Herein

I. General

In general, the invention herein is applied to materials in which two phases can be found by means of the addition or removal of an easily diffused material such as oxygen and concurrent production of a second
phase which is non-superconducting or has different superconducting characteristics than a first, superconducting phase. The invention in some aspects provides for the partial reaction of a first superconducting material to a second superconducting material within crystals of the first superconducting material. Lattice boundaries of the first and the second superconducting materials will act as effective pinning centers. In another aspect of the invention, a material including the first and second superconducting materials is formed, along with a third, non-superconducting phase within crystals of the superconducting materials. In still another aspect of the invention, a starting material is used to form a superconducting material and a non-superconducting material, crystals of the superconducting material interspersed within the crystals of the non-superconducting material.

By way of example, the invention is illustrated herein with regard to the formation of superconducting or non-superconducting phases within the grains of yttrium-barium-copper oxide superconductors, but the invention is not so limited. Examples of other materials suitable to such a process are materials which have multiple phases whose stability depends upon oxygen content. Such materials include but are by no means limited to the Y-Ba-Cu-O materials, the Tl-Ca-Ba-Cu-O materials, the Bi-Ca-Sr-Cu-O materials, the La-Sr-Cu-O materials, the Ba-K-Bi-O materials, and other high $T_c$ oxide superconductors.

One important aspect of the invention is that a composition which forms two stable phases which vary in their oxygen content is used to form a superconducting phase interspersed by second regions which act as flux pinning centers and which do not migrate significantly to grain boundaries. Therefore, the invention will find use not only in the above-mentioned materials, but also in
many materials of which exemplary materials are discussed in detail herein.

In some embodiments the invention provides magnetic flux pinning centers having controllable or predictable size and shape within the grains of the crystals. By varying the size of the pinning centers, the pinning strength of the material may readily be adjusted. In preferred embodiments the size of the pinning center is adjusted to be about the coherence size, and in some embodiments between 1 and 1000 Å, in preferred embodiments between 10 and 100 Å in the plane of the material, and in 1-2-3, for example, the pinning centers have dimensions of about 20 Å in the plane of the superconducting material and about 2 Å perpendicular to the plane. Even atomic scale defects such as partial dislocations which produce strain fields will be sufficient in some embodiments to substantially increase (i.e., increase by about 5% or more) the critical current of the material.

Flux pinning centers may also have improved orientations according to the invention herein. One embodiment of the invention herein provides pinning centers of a desired orientation such that the fluxoids may be pinned in point or line defects that lie substantially along lines or planes, rather than points. The material may then be optimally used in an orientation wherein such planes or lines of defects lie in the planes of or parallel to direction of the fluxoid. These planes or lines in some embodiments lie along the a·b plane of the superconductor while in other embodiments they lie along the C axis. Current is, similarly, passed along the plane of the defects. In Cu-based superconductors, this plane will generally lie in the plane of CuO₂ sheets. It is preferred that while the current and magnetic flux lines lie in the same or parallel planes, that they be substantially perpendicular to each other since the magnetic field produced by a current is perpendicular to
the current and the objective is to transmit strong or concentrated currents or strong magnetic fields.

II. Overall Description of Synthesis

A. 1-2-4 Starting Material

In one preferred embodiment, the invention utilizes the \( \text{YBa}_2\text{Cu}_4\text{O}_6 \) (1-2-4) phase or one of its rare earth analogues as a starting material. The 1-2-4 phase is heated in low pressure oxygen such that it decomposes at least in part into a 1-2-3 tetragonal (non-superconducting) phase plus one or more non-superconducting copper rich phase(s) such as \( \text{CuO} \) and/or \( \text{BaCuO}_2 \) and/or \( \text{Y}_2\text{BaCuO}_5 \) and/or \( \text{Cu}_2\text{O} \). This treatment of the 1-2-4 phase is carried out at a temperature such that oxygen from the reaction diffuses out of the grains of superconductor but, in this embodiment, the temperature and pressure are adjusted to prevent decomposition of 1-2-3. This will leave a multiphase system with small Cu-rich phase regions within the 1-2-3 crystallites and any remaining 1-2-4 crystallites if present. The temperature and \( P(\text{O}_2) \) is, in preferred embodiments, chosen such that \( x \) is between about 6.1 and 6.6 in \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \) under equilibrium conditions. The step of heating in low pressure oxygen is optionally followed by the step of heating at somewhat higher temperatures such that the Cu diffuses small distances and increases the size scale of the pinning centers for further optimized flux pinning.

The 1-2-3 material is then treated with oxygen at lower temperatures and re-oxidized to the orthorhombic superconducting phase, leaving the Cu-rich non-superconducting inclusions trapped inside the 1-2-3 material, plus any remaining 1-2-4 phase. Superconducting materials prepared according to the invention will be particularly useful in conditions under which thermally activated flux creep is important. For example, the materials will find use in high temperature conditions in strong magnetic fields.
B. 1-2-3 Starting Material

In a second preferred embodiment, the starting material is the 123 material \( \text{YBa}_2\text{Ca}_3\text{O}_{x} \) or its rare earth substituted analogues. The 123 phase is heated in a low partial pressure oxygen \((\text{P(O}_2\text{)})\) or in a partial vacuum. The \( \text{P(O}_2\text{)} \) is chosen low enough, e.g., between about \( 10^{-1} \) bar to \( 10^{-6} \) bar or less (about 1 ppm \( \text{O}_2 \) or less) at temperatures about 500 to 600°C so that \( x \) is less than about 6.2 to 6.0 in \( \text{YBa}_2\text{Cu}_3\text{O}_x \) under equilibrium conditions. The required pressure will depend on temperature. Increasing the distance below the stability line in Fig. 14 at a given temperature will be preferred to increase the driving force of the reaction. Under these conditions the 123 compound is destabilized and begins to separate locally into non-superconductors such as \( \text{Y}_2\text{Ba}_1\text{Cu}_1\text{O}_5 \), \( \text{BaCuO}_2 \), \( \text{CuO}_4 \), \( \text{Cu}_2\text{O} \), etc. In this embodiment the decomposition is preferably halted before the decomposition is complete. The temperatures and pressures selected for decomposition of 1-2-3 will vary over a wide range of values in addition to the above-cited values. Temperatures and pressures for decomposition may be selected for 1-2-3 based upon the stability information presented in Borman et al., Appl. Phys. Lett., 54 (21) (May 22, 1989), which is incorporated herein by reference. The sample is cooled and then re-oxygenated at a higher \( \text{P(O}_2\text{)} \) (e.g., \( \text{P(O}_2\text{)} \) of \( \approx 1 \) bar). The re-oxidation could, alternatively, be done before cooling. The result is non-superconducting inclusions precipitated within the superconducting grains. The result is similar to the first embodiment, except the chemical composition of the inclusions is different and their morphology will also differ.

C. Other Starting Materials

In a third preferred embodiment, the starting material is the bismuth-strontium-calcium-copper-oxide
superconductor. The 2122 phase Bi$_2$Sr$_1$Ca$_2$Cu$_2$O$_{x}$ and the 2223 phase Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{x}$ are each stable at different P(O$_2$) at the same temperature (e.g., see Endo et al., "Preparation of High Tc Phase of Bi-Sr-Ca-Cu-O Superconductor," Jap. Journal of App. Phys., August 1988, pp. 1446, which is incorporated herein by reference). Thus interconversion of 2223 → 2122 + CaCuO$_2$ and/or other non-superconducting phases is possible by heating 2223 in an increased P(O$_2$) of ≈ 10$^{-3}$ atm or above following a procedure similar to that set forth above.

In another preferred embodiment a high P(O$_2$) is applied to a BSCCO 2-1-2-2 superconductor of the general formula Bi$_2$Ca$_{1-2x}$Sr$_x$Cu$_2$O$_{x}$. This composition has been shown to be unstable at high P(O$_2$) at, for example, 600-800°C (see, for example, Morris et al., "Oxygen Concentration Effect on Tc of the Bi-Ca-Sr-CuO Superconductor," Phys. Rev. B., Vol. 39, No. 10, pp. 6612 (1989), which is incorporated herein by reference) as shown by a decreasing low temperature Meissner diamagnetism with increasing treatment time or temperature, but with an unchanging diamagnetism onset temperature. Therefore, heating BSCCO superconductor in high P(O$_2$) will cause precipitation of non-superconducting phases in a manner similar to 1-2-3 heated in low P(O$_2$). A subsequent anneal at a lower temperature will optimize the superconducting properties and T$_c$ while avoiding diffusion of the non-superconducting precipitate which could make pinning centers unduly large.

In an alternative embodiment, a high P(O$_2$) is applied at elevated temperature to the Ba$_{1-x}$K$_x$BiO$_3$ (BKBO) superconductor. This causes oxidation of Bi to Bi$^{+5}$ and thereby de-stabilizes the superconductor. The rest of the procedure follows the above embodiment. In the case of BKBO an added advantage is that evaporation of K is suppressed by the high P(O$_2$).
In another alternative embodiment, the above process is applied to BSCCO 2223 (Bi₂Sr₂Ca₂Cu₃Oₓ). Instability of the superconducting compound will result from the reaction Bi⁻³ to Bi⁺⁵.

In yet another embodiment, applicable to thallium-containing superconductors such as Tl₂Ba₂CaCu₃Oₓ, reduced P(O₂) reduces Tl⁺³ to Tl⁺¹ and de-stabilizes the superconductor. Superconductivity may then be restored by re-oxidation, leaving non-superconducting inclusions for pinning. Application of high P(O₂) prevents the reaction:

\[ \text{Tl}_2(\text{III})\text{O}_3 \rightarrow \text{Tl}_2(\text{I})\text{O} + \text{O}_2 \]

so as to prevent evaporation and consequent loss of Tl and permits controlling the synthesis of Tl superconductor with more uniform structure since the Tl concentration does not vary. Also, the resulting fully oxidized Tl will give an optimal T_c.

Other materials to which the invention herein may be applied will be readily apparent to those skilled in the art.

III. Detailed Description of the 1-2-4/1-2-3 Synthesis

A. Synthesis of Starting Materials

The present invention is, by way of example, applicable to superconductor materials which contain or are fabricated from metals or metal oxides. Preferred metals have several valence states. Among these, copper and bismuth are particularly preferred.

These metals or metal oxides may be combined with other metals or metal oxides. Included among the latter are divalent metals such as, for example, barium, strontium, calcium and cadmium; trivalent metals such as, for example, yttrium, scandium, bismuth, thallium; transition metals; the rare earth elements (lanthanum through lutecium); and metals in general which are
highly electro-positive, or have large electric polarizabilities. Preferred among the rare earth elements are neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium and thulium.

In addition to the elemental metals and the metal oxides, the metals used in the preparation of the superconductors of the present invention may be in the form of nitrates, carbonates, oxalates, tartrates, and any other form which yields the oxide upon heating in oxygen. The metals used in the process may also be in the form of mixed oxides or compounds, that is to say, compounds each of which incorporate more than one of the metals.

In preferred embodiments, metal oxides are used in a chemical and physical form which will render them highly reactive at elevated temperatures. Examples include the use of finely divided particles to provide large surface energies, and chemical forms such as per-oxides or mixed oxides which have lower chemical binding energy than either the desired product or other compounds which can be formed from the metals or metal oxides. In the case of barium, the preferred form is BaO. In the case of copper, the preferred form is CuO. In the case of yttrium, the preferred form is Y₂O₃.

The metals or metal compounds may be combined in relative amounts such that the atomic ratio of the metals is approximately the same as that of the superconductor to be formed. For example, when the desired compound is YBa₂Cu₄O₈, the yttrium, barium and copper metals are combined in the atomic ratios of about 1:2:4.

As an alternative, the metals or metal compounds can be combined by applying them as an intimate mixture to a suitable substrate in the form of a film on the substrate. Such application may be done by high vacuum evaporation, plasma coating, decomposition of
organometallics, laser ablation coating or other known coating methods.

As another alternative specifically involving formation of the 1-2-4 compound which is used as an example herein, a substrate including the 1-2-3 compound or another compound containing one or more of the constituent metals of the 1-2-4 compound may be heated in concentrated or high pressure oxygen and thereby converted to the 1-2-4 compound or may be treated at pressures and temperatures such that 1-2-3 is not the stable phase as shown in Fig. 4. If all of the constituents of the 1-2-4 compound are incorporated in the substrate, a superconducting film may be formed without film deposition.

The supply of oxygen at a high oxidizing potential in the practice of the present invention may be achieved in a variety of ways. Molecular oxygen at hyperbaric pressure, or preferably appropriate combinations of temperature and pressure as indicated in Fig. 4 may be used. Ozone and atomic oxygen may be used in the alternative.

Further means of supplying oxygen at high oxidizing potential are the use of oxygen incorporated in a highly oxidized chemical compound which under appropriate conditions will release the oxygen, thus making it available for the formation of a second highly oxidized compound which is a superconductor. Such oxygen-supplying compounds include, but are not limited to, peroxides or nitrates of the constituent metals, as well as other highly oxidized compounds which may themselves be superconductors. To form the desired product, these oxygen-supplying compounds are placed in contact, and preferably mixed intimately, with the other constituent materials.

Still further means of supplying oxygen at high oxidizing potential are those involving the use of electrical current. Such means may for example involve
placing the constituent starting materials in an electrochemical cell containing an electrolyte which releases oxygen when exposed to an electric current. One example of such an electrolyte is ZrO₂. This method and that of the preceding paragraph may reduce or eliminate the need for elevated temperature during synthesis of the superconductor.

In preferred embodiments of the invention, the high oxidizing potential oxygen supply is molecular oxygen, ozone, or atomic oxygen, either alone or combined with each other or with inert gases. Molecular oxygen is preferred. When molecular oxygen is used, the gas mixture is preferably at least about 50% molecular oxygen, more preferably at least about 90% oxygen, and most preferably substantially 100% molecular oxygen. With molecular oxygen, the pressure is higher than the boundary region of 1-2-4 at a given temperature. Pressures less than 200 bar may readily be used through the use of temperatures below about 1050°C.

The temperature and heating time may vary, depending on the materials used. Higher temperatures will generally require less heating time. In preferred embodiments, the heating is done at a temperature of at least about 700°C for at least 10 hours, or at least about 800 to 850°C for about 1 hour. If the material is finely divided, lower temperatures (e.g., 600 to 700°C) may be used.

Since superconducting phases of a highly oxidized state are formed herein, many new materials having superconducting capabilities, particularly with high superconducting transition temperatures, may be formed. It is thus expected that many new superconductors will be discovered by virtue of and through the practice of the methods disclosed herein.

Also by virtue of the methods disclosed herein, 1-2-4 materials can be reacted and/or sintered at significantly higher temperatures than 1-2-3 materials,
without loss of phase identity. This is useful in the
densification of the materials for enhancement of the
superconducting current density $J_c$. Similar procedures
may be applied to 1-2-3 by appropriate selection of
temperature and pressure to suppress decomposition of
1-2-3. A preferred method of densification is hot
isostatic pressing (HIP), a procedure known in the art.
Upon applying the HIP technique to single-phase 1-2-4
materials, any initial conversion of the 1-2-4 to the
1-2-3 phase will terminate at an early stage once the
internal oxygen pressure reaches about 5 to 30 bar at
temperatures of 950 to 850°C.

B. Formation of Non-Superconducting Phase

According to one embodiment of the invention,
oxidized superconductor or non-superconductor materials,
of which the above-described materials are used herein as
examples, are further treated to provide improved flux
pinning characteristics. In one embodiment, an oxidized
material is heated at a temperature and a pressure which
permits diffusion and removal of oxygen in the material,
but which does not permit rapid diffusion of an excess
second superconducting or non-superconducting phase to
grain boundaries. In one embodiment, 1-2-4 is heated at
a temperature of between about 400 and 1000°C and in an
oxygen-containing atmosphere at a $P(O_2)$ of between about
.0001 atm and 100 atm to destabilize the 1-2-4 to form
1-2-3. In preferred embodiments, referring to Fig. 4,
the 1-2-4 is heated to a temperature and at a pressure in
which 1-2-3 becomes the equilibrium phase. Pressure and
temperature conditions which provide 1-2-3 with an oxygen
content of below about 6.5 and preferably above about 6.1
in the formula YBa$_2$Cu$_3$O$_x$ are most preferred. The pressure
and temperature conditions that produce a given oxygen
content in 1-2-3/1-2-4 have been estimated by Lindemer et
al., "Review of Non-Stoichiometry in YBa$_2$Cu$_3$O$_{6.7}$x," Chemical
Tech. Div., Oak Ridge Laboratory, TM-10827, November
1988, which is incorporated herein by reference. For example, the following equation may be used to estimate \( x \) (oxygen stoichiometry) for a given \( P(O_2) \) and temperature:

\[
\ln(P(O_2)) = \frac{\Delta H^\circ_{\text{rxn}}}{RT} - \frac{\Delta S^\circ_{(O_2)}}{R}
\]

where:
\[
\Delta H^\circ_{\text{rxn}} = -160,700 \text{ (orthorhombic)}
\]
\[
-146,300 \text{ (tetragonal)}
\]

\( \Delta S^\circ_{(O_2)} \) is selected from the following values:

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \Delta S^\circ_{(O_2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>-159.6</td>
</tr>
<tr>
<td>6.6</td>
<td>-146.6</td>
</tr>
<tr>
<td>6.5</td>
<td>-135.9</td>
</tr>
<tr>
<td>6.4</td>
<td>-126.3</td>
</tr>
<tr>
<td>6.3</td>
<td>-116.7</td>
</tr>
<tr>
<td>6.2</td>
<td>-105.9</td>
</tr>
<tr>
<td>6.1</td>
<td>-91.0</td>
</tr>
</tbody>
</table>

\( R \) is the gas constant
\( T \) is temperature (K).

When 1-2-3 is used as a starting material, the \( P(O_2) \) and temperature can be selected to provide decomposition of 1-2-3 according to, for example, the data shown in Bormann et al., Appl. Phys. Lett., Vol. 54 (21), May 22, 1989, which has previously been incorporated herein by reference. The equation of the line for 1-2-3 stability is about:

\[
\log_{10}(P(O_2)) = 10.18 - 1.41 \times 10^4 / T(\degree\text{K})
\]

For a given \( T \), the pressure should be maintained below the \( P(O_2) \) given by the above equation.

Fig. 14 illustrates the decomposition line of 1-2-3 described by the above equation. The step of heating the superconductor results in an intermediate
material with a first superconducting or non-superconducting phase plus a relatively immobile second phase. Heating of the superconductor is optionally followed by a step of heating the intermediate material at a temperature and pressure which permits slight diffusion of the excess second and/or third phase, so as to allow for control of the size and distribution of the resulting pinning centers.

The optional heating step is preferably limited such that significant amounts of non-superconducting material (e.g., copper oxide) do not diffuse to grain boundaries of the superconductor, which would be detrimental to performance of the material. The optional step of heating is preferably performed until just before a significant decrease in critical current is caused due to the existence of the non-superconducting phase at the grain boundaries of the superconductor. Alternatively, the optional heating step is performed until the pinning energy of the material is on the order of a few electron volts such that thermally activated flux creep becomes negligibly small. The optional heating step may be carried out at, for example, a temperature of between about 0 and 500°C higher than the initial conversion within a preferred range of about 50 to 150°C higher for a few minutes up to several hours. The pressure may be preferably below the pressure at which the starting material is stable at the temperature chosen (e.g., atmospheric may be convenient).

C. Formation of Nucleation Regions

In the preparation of 1-2-3, 1-2-4, or other superconducting materials, non-superconducting materials are formed. The method may also be supplemented by the step of forming nucleation centers in the superconductor so as to better form non-superconducting regions. The nucleation centers may be formed by one of a variety of methods and serve to improve formation of regions of non-
superconducting phases of a very small size. Such methods may include, for example, electron irradiation, ion irradiation, neutron irradiation, gamma irradiation, x-ray irradiation, or the like, so as to provide point defects in the crystal which significantly reduce nucleation energy for the formation of a non-superconducting phase. The pinning centers are optimally arranged along more or less straight lines. This can be accomplished for example by the use of charged particle irradiation such as electrons, H', He'', H-, He', or other negative ions, etc., which would deposit energy and displace atoms of the superconductor each of which can act as a nucleation center along the track of the charged particle through the superconductor.

The irradiation step is preferably carried out with electron or proton (hydrogen ion) irradiation at an energy of between 25 keV and 100 MeV, depending upon the thickness of the material. The step is preferably carried out before heating the material for removal of oxygen and formation of the non-superconducting phase.

In alternative embodiments, the nucleation centers are formed by the addition of metals or metal oxides or compounds that produce metal oxides which are of limited solubility and whose solubility depends on temperature, pressure, or oxygen concentration in the formation of the starting materials.

D. Re-Diffusion of Oxygen

The intermediate product is, thereafter, treated under temperature and pressure conditions which re-diffuse or implant or otherwise re-introduce oxygen into the intermediate product to produce a material which is more fully oxidized with good superconducting properties. The step of re-introducing oxygen is conducted in some embodiments by diffusion at a temperature of between about 200 and 750°C and in an oxygen-containing atmosphere at a P(O₂) of between about
0.0001 atm and 200 atm. In preferred embodiments the step of re-diffusing oxygen is carried out at a temperature of between about 350 and 450°C and at a pressure of between about 0.1 and 10 atm. In most preferred embodiments the step of re-diffusing oxygen is carried out at a temperature of about 400°C and at a pressure of about 1 atm. In some embodiments, the step of re-diffusing oxygen is carried out for between about 0.1 and 1000 hours. In preferred embodiments, the step of re-diffusing oxygen is carried out for between about 1 and 100 hours with a most preferred embodiment of about 10 hours.

The following examples are offered primarily for purposes of illustration, and are intended neither to limit nor define the invention in any manner.

IV. Example 1 - Conversion of 1-2-4 into 1-2-3 with Flux Pinning Centers
A. Synthesis of 1-2-4

Polycrystalline materials bearing the empirical formula $R_1Ba_2Cu_4O_x$ where $R$ is $Y$, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm may be prepared as follows. Stoichiometric quantities of R oxide, BaO, and CuO powders (all 99% or better) may be mixed thoroughly and pressed at 25 kg/mm$^2$ into 6 mm diameter pellets, which may be calcined in oxygen held at 120 atmospheres pressure for 7 hours at 930°C. The reacted mixtures may then be cooled at 5°C per minute to 700°C, 2°C/min to 600°C, 1°C/min to 500°C, 0.5°C/min to 450°C, 1°C/min to 390°C, and furnace cooled at about 4°C/min. The mixtures may then be finely ground with an agate mortar and pestle, pressed into 6-mm-diameter tablets at 25 kg/mm$^2$, and sintered in oxygen at the same temperature, pressure and time schedule as used for the calcining. In the case of the Ho, Er and Tm compounds, the calcining and sintering may both be carried out at 60 atmospheres pressure at a maximum temperature of 980°C. Cooling rates may be the same as
described above. The pellets may be wrapped in gold foil before the calcining and sintering operations are carried out; no reaction with the gold should be observed. If the constituent oxides are mixed in the 1-2-3 stoichiometry instead of the 1-2-4 stoichiometry and then the process given in the first example herein is carried out, the result should be the formation of the desired 1-2-4 compound along with residual phases which incorporate the excess Y and Ba oxides which are left over.

Table 1 illustrates the properties of various superconductors which have been synthesized according to the above method and which are exemplary of the materials which may be used according to further aspects of the invention. In the table, the superconducting temperature $T_c$ was determined by observation of bulk diamagnetism. Note that the $T_c$'s of the different compounds are significantly different, and are correlated with lattice parameters $a$ and $b$, and with orthorhombic distortion which is larger for the heavier (smaller) rare earth ions. The symbol $\chi_{20K}$ represents the flux expulsion on cooling to 20 K in a constant Oe field, and is expressed in units of $10^{-4}$ emu/g. The symbol $4\pi\rho\chi_{20K}$ represents the diamagnetic volume fraction. The density $\rho$ is calculated from the measured unit cell volume. The superconducting fraction may be larger, because some expelled flux will be trapped in the pores of these ceramic samples. The relative amounts of the phases were estimated from x-ray powder diffraction patterns and Reitveld refinements. To determine the lattice parameters, the Reitveld procedure was used and a sample displacement correction was refined along with the unit-cell parameters. The refinement included 1-2-3 or 2-4-7 phases when present. The unit-cell parameters found for the Dy compound did not differ significantly from those determined using a Cr$_2$O$_3$ internal standard.
### Table 1

**SUPERCONDUCTING AND STRUCTURAL PARAMETERS OF RBA$_2$Cu$_4$O$_8$ COMPOUNDS**

<table>
<thead>
<tr>
<th>R</th>
<th>$T_c$(K)</th>
<th>$\chi_{20K}$</th>
<th>$\frac{\mu}{\mu_{20K}}$</th>
<th>Phases Present</th>
<th>Lattice Parameters of 1-2-4 [2-4-7] Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1-2-4</td>
<td>2-4-7</td>
</tr>
<tr>
<td>Y</td>
<td>80.5</td>
<td>-25</td>
<td>20%</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Nd</td>
<td>57</td>
<td>-3.5</td>
<td>3%</td>
<td>trace</td>
<td>no</td>
</tr>
<tr>
<td>Sm</td>
<td>70</td>
<td>-11</td>
<td>10%</td>
<td>70%</td>
<td>no</td>
</tr>
<tr>
<td>Eu</td>
<td>68.5</td>
<td>-24</td>
<td>21%</td>
<td>no</td>
<td>40%</td>
</tr>
<tr>
<td>Gd</td>
<td>73</td>
<td>-18</td>
<td>16%</td>
<td>no</td>
<td>60%</td>
</tr>
<tr>
<td>Dy</td>
<td>77</td>
<td>-19</td>
<td>17%</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Ho</td>
<td>77</td>
<td>-20</td>
<td>18%</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Er</td>
<td>78</td>
<td>-22</td>
<td>20%</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Tm</td>
<td>77</td>
<td>-11</td>
<td>10%</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
B. Formation of Flux Pinning Centers in 1-2-3 from 1-2-4

According to one embodiment of the invention, an oxidized superconducting material selected from the above materials or other highly oxidized materials may be heated to a temperature which facilitates removal and diffusion of oxygen, but which does not permit significant diffusion of an associated second phase to grain boundaries.

When using the 1-2-4 material as a starting compound, a wide variety of pressure and temperature conditions may be selected for use. Fig. 4 illustrates the stability of the Dy-Ba-Cu-O system as an example. To form materials according to one aspect of the invention, one would begin with 1-2-4 and subject it to temperature and partial pressures of oxygen which cause the 1-2-4 phase to at least partially convert to form the 1-2-3 phase. As shown in Fig. 4, pressure and temperature conditions which provide materials having an oxygen content of about 6.6 or less will be desirable. Pressure and temperature conditions which form materials having an oxygen content of below about 6.5 would be desirable with oxygen contents below 6.3 preferred, so long as 1-2-3 is not decomposed. As a general rule, pressures between about 0.1 and 300 bar will be used. Increasing temperature will have the effect of driving the material to the 1-2-3 phase, but increasing temperature will only be desirable within limits. At any given temperature lower pressure will be desirable. At elevated temperatures (e.g., above about 800°C), diffusion of the non-superconducting phase becomes excessive. Lower pressures will tend to be desirable because the driving force of the reaction will be higher. Again, however, this will not be without limit because the 1-2-3 phase will become unstable at lower pressures (e.g., less than about 0.1 bar at 970°C to 0.001 bar at 800°C). Synthesis in a range of the diagram where the equilibrium oxygen
content of the 1-2-3 is about 6.1 to 6.2 is most desirable. For example, $10^{-3}$ to $10^{-2}$ bar at 700°C and $10^{-4}$ bar at 600°C may be used.

The optional heating step may, thereafter, be followed by treatment at a higher temperature of about 800°C in an oxygen environment having a $P(O_2)$ of about 0.1 atm. The intermediate 1-2-3 phase is then re-oxidized for a period of about 10 hours at 400°C to again form a superconducting phase. Copper-rich non-superconducting inclusions will be trapped inside the grain boundaries of 1-2-3. It is believed that the presence of such inclusions will increase the critical current of the superconductor by 50 to 200% or more over that of the 1-2-4 material alone. It is further believed that the inclusions will provide critical currents of between about 50 to 200% or greater than 1-2-3 material alone.

C. Formation of Flux Pinning Centers in 1-2-3

When 1-2-3 is the starting material and it is desirable to precipitate other phases, it will be desirable to treat the 1-2-3 under temperature and oxygen partial pressure conditions which render the 1-2-3 unstable. Synthesis of 1-2-3 itself is well known. When the equilibrium oxygen content of the 1-2-3 is lowered to below about 6.1, it will tend to become unstable. Lower pressure (e.g., below about $10^{-3}$ bar at 800°C or $10^{-5}$ bar at 700°C or $10^{-7}$ bar at 600°C) will be desirable within limits such as those imposed by mechanical constraints of vacuum pumps, diffusion rates of $O_2$, and the like. High temperatures will also tend to be desirable to increase the driving force of the reaction, but again, excess diffusion of the non-superconducting phase should be avoided.

While the invention is illustrated above with regard to the reaction control by way of reduced oxygen partial pressure, it should be recognized that reducing
agents could be effectively utilized to produce the same effect. Such reducing materials would include, for example, hydrogen, carbon monoxide, ammonia, methane, hydrogen sulfide, borane, phosphine, arsine, or the like as well as elemental reducing agents that may be incorporated into the final composition, e.g. La, Y, K, Rb, Ba, etc.

V. Example 2 - Synthesis of Y-Ba-Cu-O and Dy-Ba-Cu-O Interspersed by Non-Superconductor

A series of two experiments were carried out. In the first series, the starting stoichiometry was varied over a wide range while $P(O_2)$, temperature and time were held constant. In the second series, the oxygen pressure in which the solid state reaction took place was varied in small steps. Temperature and time were held constant and starting stoichiometries were 1:2:3, 1:2:4 and 1:2:3.5. The superconducting phases present in the products of all three series of experiments were identified by XRD, and bulk superconductivity was confirmed and $T_c$ determined by measurement of Meissner diamagnetism in a SQUID magnetometer.

Samples were prepared by solid state reaction of $Y_2O_3$ or a rare earth oxide $R_2O_3$ ($R = \text{Nd, Sm, Eu, Gd, Er, Dy, Ho, Er, or Tm}$) (all 99.9%), with BaO (99.99%) and CuO (99.99%). All ingredients were fine powders (~325 mesh), which were ground together in a mortar and pestle and pressed into 6 mm tablets at 3500 kg/cm$^2$. The samples were wrapped individually in Au foil and calcined for 8 hours in high pressure $O_2$ in a commercially available externally heated high pressure oxygen furnace. Calcining was followed by slow cooling to room temperature. To maximize homogeneity, each sample was then re-ground, pressed, fired and cooled a second time under the same conditions.

In the first series of experiments, conducted at $P(O_2) = 100$ bar and synthesis temperature of 930°C, the
starting cation ratio was varied over a wide range, but only the 124 phase formed (see Figure 1). With Y:Ba:Cu ratios of 1:2:3, 1:2:3.5, 1:2:4, and 1:2:5, the 124 phase alone, without 123 or 247, was detected by low-angle XRD (described below). At still greater CuO content (1:2:6), and in samples richer in Ba (Y:Ba:Cu ratios 1:3:4, 1:3:5, 1:3:6), or rich in yttrium (1:1:2), no low angle peaks appeared. These experiments indicate that 124 is the stable phase in high P(O₂) over a considerable range of starting compositions.

In the second series of experiments, starting stoichiometries (cation ratios) of 1:2:3, 1:2:3.5 and 1:2:4 were used. Experiments were conducted on the Dy-Ba-Cu-O system as well as on Y-Ba-Cu-O. Samples were processed at a series of closely spaced pressures between 9 and 47 bar (1 bar = 0.1 Mpa = 0.987 atm). The temperature was 930°C.

The reacted samples were examined by x-ray powder diffraction (XRD). The count rate patterns in Figure 2 indicated that in addition to one or more of the superconducting phases, most samples contained some CuO and BaO, as indicated by the peaks at 29.8 and 45.5 degrees, as well as small quantities of the 211 "green phase" R₂BaCuO₅. The three superconducting phases were distinguished by their characteristic low-angle powder diffraction peaks as shown in the upper portion of Figure 3. The [0 0 2] peak of the 124 phase is found at d spacing ≈ 13.6 Å, clearly distinct from the position of the [0 0 1] peak of 123 at 11.7 Å and the [0 0 4] peak of 247 at 12.55 Å. The 2-4-7 peak is significantly broadened. This method is quite sensitive when applied to the Dy-Ba-Cu-O system, because the low-angle reflections from the rare earth compounds are quite strong, as shown in Fig. 2.

Fig. 13 is a TEM of Eu-Ba-Cu-O illustrated in Table 1 and with the low angle diffraction pattern shown in the lower portion of Fig. 3. Note that the 2-4-7 peak
in Fig. 3 is substantially broadened, indicating 2-4-7. This is shown directly in the TEM. The TEM shows many interspersed regions of the 2-4-7 and 1-2-4 materials. Above the $T_c$ of 2-4-7, the 2-4-7 will act as flux pinning centers. In any event, the boundaries will also act as pinning centers.

VI. Example 3 - Partial Conversion of 1-2-4 to 1-2-3 Plus A Non-Superconducting Phase

In order to further test the invention, a variety of samples were prepared using $\text{YBa}_2\text{Cu}_4\text{O}_8$ as a starting material.

The first series of experiments utilized three samples, which are elsewhere referred to herein as A, B, and C. Sample A was 1-2-4 material which has been discussed at length above. Sample B was 1-2-4 treated at 775°C for 160 hours in 1 atm of $\text{O}_2$. Sample C was treated at 930°C for 5 hours in 1 atm $\text{O}_2$. All samples were cooled to room temperature during which time, reoxidation of 1-2-3 occurred.

Susceptibility curves for samples A, B, and C are provided in Fig. 5. As would be expected, the 1-2-4 sample begins to show negative susceptibility at about 80K, indicating superconductivity, and shows a rapid drop in susceptibility, indicating a relatively pure sample. Sample B shows a stepped falloff starting 92K indicating the presence of finely divided superconducting 1-2-3 phase within the crystals and a large falloff at 80K indicating a large fraction of 1-2-4. Sample C shows a negative susceptibility starting at about 95K, which is more closely correlated with the $T_c$ of 1-2-3 and a gradual falloff in susceptibility, indicating finely divided regions with differing $T_c$'s, i.e. 1-2-4 and 1-2-3. At a temperature of about 70K, the susceptibility is smaller than its maximum value, indicating non-superconducting regions are present at that temperature. These regions should act as pinning centers. It should be noted that
the $T_c$ of sample C is, however, significantly higher than the value normally reported for 1-2-3 or 1-2-4. For reasons which are not entirely understood to the inventor herein, the presence of finely divided multiple phases or intergrowths in the superconductor will, in addition to increasing critical current, provide a $T_c$ above that of either phase alone.

Fig. 6 provides an atomic resolution TEM of sample B. The distance indicated by "1" is 11.6 Å. The distance indicated by "2" is 13.6 Å. The distance indicated by "3" is 25.7 Å. 13.6 Å is the C axis unit cell spacing of the 1-2-4 phase while 11.6 Å is the C axis unit cell spacing of the 1-2-3 phase. This TEM illustrates the presence of 1-2-4 in contact with 1-2-3 within a crystal.

Fig. 7 shows another region in sample B. In the upper right-hand portion of the figure, a partial dislocation is shown, i.e., a region where 1-2-3 and 1-2-4 meet. The extra copper layer which distinguishes 1-2-4 from 1-2-3 ends at the interface. Therefore, copper oxide has likely been removed in this region, and gone upward extending along a line perpendicular to the plane of the figure, leaving the boundary between the 1-2-4 and 1-2-3. This dislocation should act as an effective pinning center extending along the line. Note that the strain field extends about 10 to 15 Å around the defect in the plane of the figure.

Similar meeting points of layers of differing thickness are observed throughout Fig. 7. Note that strain fields around the dislocations are produced throughout the area due to the dislocations. The dislocations and regions within these strain fields should also act as effective pinning centers.

On the left-hand portion of Fig. 7, a "checkerboard" meeting point is found, i.e., a region in which, in an imaginary square, 1-2-3 is found in the upper right- and lower left-hand portion of the "square"
while 1-2-4 is found in the lower right- and upper left-hand portions of the square. The strain field produced in this region should also act as an effective pinning center.

Fig. 8 shows the weight-versus-temperature curve during preparation of sample C. The sample shows a weight loss as it is heated, particularly after it reaches about 900°C where it was held for 5 hours. The sample eventually had about a 1.6% weight loss, corresponding to the loss of about 2/3 of an oxygen per formula unit. When the sample was cooled, the weight gain was slower because the temperature was lowered at a slow rate. This curve is typical of 1-2-3 which gains oxygen as it is cooled. The oxygen content of 1-2-3 is reversibly variable as a function of temperature. This confirms the formation of 1-2-3 from 1-2-4.

Fig. 9 shows the susceptibility curve for additional samples. Again, the curve for sample A (1-2-4) is shown for comparison. Sample D was 1-2-4 heated at 950°C in 1 atm of O₂ for 5 hours, and cooled over 1.5 hours to ambient. Sample E was heated at 890°C for 6 hours in 1 atm of O₂ and cooled to ambient over 6 hours. Sample F was heated at 775°C for 140 hours in 1 atm O₂ and cooled to ambient over 1 hour. Sample G was heated at 775°C for 100 hours in 0.0001 atm O₂ and cooled to ambient over 6 hours.

Based upon the susceptibility curves, sample D has clearly been converted to 1-2-3. The T_c is, however, somewhat lower than observed with sample C. It is believed this occurs because only a single phase is present. The drop-off in susceptibility is also much sharper, indicating a nearly complete conversion to 1-2-3, as opposed to the somewhat less complete conversion obtained in samples B and C and, therefore, the gradual transition in susceptibility, indicating multiple superconducting phase and fine division of the two phases. Curve E shows a similar result. While it is
believed that sample D would have improved flux pinning ability due to the formation of CuO within the crystal. The CuO may have reached the grain boundaries since the temperature was high, or at least may have agglomerated into larger regions than desired for efficient flux pinning. The retention of at least some 1-2-4, as shown in samples B may produce better results due to the presence of multiple superconducting phases within the crystal. By contrast, sample E shows only a minimum amount of conversion to 1-2-3 and sample F nearly no conversion. By reducing O₂ pressure, in this case, to 0.0001 atm at 77°C, it is seen that conversion to 1-2-3 takes place and a more gradual transition in susceptibility beginning at 92K is obtained, indicating the presence of finely divided 1-2-3.

Fig. 10 shows magnetic susceptibility curves for additional samples H, I, and J. Sample J (treated at 700°C for 60 min in 1% O₂, cooled over 85 min to 100°C) shows little conversion to 1-2-3, while samples H (1-2-4 treated at 800°C for 100 min in 1% O₂, and cooled to 200°C in 160 min) and I (1-2-4 treated at 850°C for 60 min in 1% O₂, and cooled to 200°C in 85 min) show the more gradual drop-off in susceptibility characteristic of substantially mixed 1-2-4, 1-2-3 phases. In general, it would be desirable to treat the materials under conditions such that the transition in susceptibility from one susceptibility level to the next as a function of temperature is broadened at least to about 5°C and preferably at least 10°C.

Figs. 11 and 12 provide weight loss curves for samples J and H, respectively. The susceptibility curve of Fig. 10 shows sample J to be largely 1-2-4, the weight loss curve of Fig. 11 shows that, in fact, a measurable conversion to 1-2-3 has occurred since some weight gain takes place on cooling.

VII. Use of Materials Disclosed Herein
Without in any way limiting the scope of the invention it is believed that the invention may frequently provide defects in the form of flakes, or generally planar structures, which extend along lines or planes rather than simply points. Hence, magnetic flux lines or planes are pinned along a more reasonable distance. Accordingly, improved results in use of a superconductor synthesized according to the invention may be obtained by using the material in an orientation in which magnetic fields are substantially parallel or, at a maximum within ±30 degrees or less of the planes of the defects. This will substantially increase pinning energy without substantially increasing resistance in the superconductor. The material is also preferably oriented such that the flow of current is along planes of the defects or, at a maximum within about ±30 degrees or less of the plane of the defects and substantially perpendicular to the lines of magnetic flux or, at a maximum, within about ±30 degrees or less of the perpendicular to the flux lines.

The foregoing is offered primarily for illustrative purposes. It will be readily apparent to those skilled in the art that substitutions, modifications and variations in the procedures and materials disclosed above may be made without departing from the spirit and scope of the invention.
WHAT IS CLAIMED IS:

1. A method of forming a superconductor comprising the steps of:
   a) heating a starting material to form a first, stationary phase, and an intermediate phase; and
   b) oxidizing or reducing said intermediate phase to form a superconductor phase, crystals of the superconductor phase interspersed by said stationary phase.

2. A method of forming a superconductor comprising oxidizing or reducing a first phase to produce a superconducting phase, crystals of which are interspersed by a non-superconducting phase.

3. The method as recited in claim 1 wherein the step of heating a starting material is a step of heating at a temperature and pressure under which said intermediate phase is an equilibrium phase.

4. The method as recited in claim 3 wherein said starting material comprises $R_1Ba_2Cu_4O_{x}$ and said intermediate phase comprises $R_1Ba_2Cu_3O_y$ where $R$ is selected from the group yttrium and rare earth metals.

5. The method as recited in claim 4 wherein $y$ is below about 6.6.

6. The method as recited in claim 4 wherein $y$ is below about 6.4.

7. The method as recited in claim 4 wherein $y$ is between about 6.1 and 6.2.
8. The method as recited in claim 1 wherein said starting material comprises $R_1^{3-x}$Ba$_2$Cu$_3$O$_x$ where R is selected from the group yttrium or rare earth metals.

9. The method as recited in claim 4 wherein said stationary phase comprises a material selected from the group CuO, BaCu$_2$O$_2$, $Y_2$BaCuO$_5$, and Cu$_2$O.

10. The method as recited in claim 8 wherein said stationary phase comprises a material selected from the group $Y_2$Ba$_1$Cu$_1$O$_5$, BaCu$_2$O$_2$, CuO, and Cu$_2$O.

11. The method as recited in claim 1 wherein said starting material comprises Bi$_2$Sr$_1$Ca$_2$Cu$_2$O$_x$ or materials which react to form it upon heating.

12. The method as recited in claim 1 wherein said starting material comprises Bi$_2$CaSr$_2$Cu$_2$O$_{6-x}$ or materials which react to form it upon heating.

13. The method as recited in claim 1 wherein said starting material comprises Ba$_{1-x}$KBiO$_3$ or materials which react to form it upon heating.

14. The method as recited in claim 1 wherein said starting material comprises TlBa$_2$CaCu$_3$O$_x$ or materials which react to form it upon heating.

15. The method as recited in claim 1 wherein the step of oxidizing is preceded by the step of heating at a temperature and a pressure so as to increase the scale of said non-superconducting phase.

16. The method as recited in claim 1 wherein said starting material comprises a metal selected from the group where R is selected from the group yttrium and rare earth metals.
17. The method as recited in claim 1 wherein said starting material comprises a metal or metal oxide selected from the group barium, copper, silver, and gold.

18. The method as recited in claim 1 wherein said starting material comprises yttrium, barium, and copper.

19. The method as recited in claim 1 wherein said starting material is a substantially single-phase lattice structure of the empirical formula R\(\text{Ba}_2\text{Cu}_4\text{O}_8\) where R is selected from the group yttrium and rare earth metals.

20. The method as recited in claim 1 wherein the starting material is formed by the process of:
   a) forming a composition by combining (i) a compound of a metal selected from the group consisting of yttrium and rare earth metals with (ii) a compound of barium and (iii) a compound of copper, said compounds selected from the group consisting of oxides, nitrates and carbonates thereof, in relative amounts such that the atomic ratio of said metal-to-barium-to-copper in said composition is approximately 1:2:4; and
   b) heating said composition in an oxidizing environment having an oxidizing potential to a temperature and for a length of time sufficient to effect interdiffusion of said compounds and the formation of a substantially single-phase lattice structure having approximately the empirical formula R\(\text{Ba}_2\text{Cu}_4\text{O}_8\) where R is said metal of compound (i).

21. The method as recited in claim 1 wherein said stationary phase comprises regions of a non-superconducting phase.
22. The method as recited in claim 21 wherein said regions of non-superconducting phase have dimensions of the order of a coherence length of the superconductor.

23. The method as recited in claim 1 wherein said stationary phase comprises said starting material.

24. The method as recited in claim 21 wherein regions of said non-superconducting phase regions are about 20 Å in the plane of the material and about 2 Å perpendicular to said plane.

25. The method as recited in claim 21 wherein said regions of non-superconducting material lie substantially along planes parallel to a·b planes of said superconductor.

26. The method as recited in claim 25 further comprising the step of flowing current through said superconductor, said current flowing along a·b planes of said superconductor and substantially perpendicular to flux lines of a magnetic field in said superconductor.

27. The method as recited in claim 21 wherein said non-superconducting phase comprises sheets of CuO.

28. The method as recited in claim 1 further comprising the step of irradiating said starting material.

29. The method as recited in claim 28 wherein said step of irradiating produces defects aligned along lines, said lines being paths of irradiating particles.

30. The method as recited in claim 28 wherein said step of irradiating uses a beam energy of between about 25 KeV and 100 MeV.
31. A high-temperature superconductor comprising a first, superconducting phase, and a second phase, said second phase dispersed within crystals of said first, superconducting phase.

32. The superconductor as recited in claim 31 wherein said superconducting phase comprises a metal oxide.

33. The superconductor as recited in claim 31 wherein said superconducting phase comprises metal oxides selected from the group barium, strontium, calcium, cadmium, yttrium, scandium, bismuth, thallium, transition metals, and rare earth metals.

34. The superconductor as recited in claim 31 wherein said second phase comprises copper oxide.

35. The superconductor as recited in claim 31 wherein said second phase comprises a second superconducting phase.

36. The superconductor as recited in claim 35 wherein said first superconductor comprises a material having the form \( R_2 \text{Ba}_2 \text{Cu}_4 \text{O}_x \) and said second superconductor comprises a material having the form \( R_2 \text{Ba}_2 \text{Cu}_3 \text{O}_x \), where \( R \) is selected from the group yttrium and rare earth metals.

37. The superconductor as recited in claim 31 wherein said superconducting phase comprises a material of the formula \( R\text{Ba}_x \text{Cu}_y \text{O}_z \), where \( R \) is a member of the group yttrium and rare earth metals.

38. The superconductor as recited in claim 31 wherein said superconducting phase comprises \( R\text{Ba}_x \text{Cu}_y \text{O}_{z-\delta} \) and said non-superconducting phase comprises a material
selected from the group copper oxide, $R_2B_1Cu_1O_5$, and barium cuprate where $R$ is selected from the group yttrium and rare earth metals.

39. The superconductor as recited in claim 31 wherein said superconducting phase comprises a material of the formula $Bi_{1}Sr_{m}C_{n}O_{x}$ and wherein Pb or Sb is partially substituted for Bi.

40. The superconductor as recited in claim 31 wherein said superconducting phase comprises a material of the formula $Tl_{1}Ba_{m}C_{n}O_{x}$.

41. The superconductor as recited in claim 40 wherein Tl is partially substituted by Bi, Sb, In and/or Pb.

42. The superconductor as recited in claim 31 wherein said second phase comprises substantially sheets of material in planes substantially parallel to a $a$ $b$ planes of said superconducting phase.

43. The superconductor as recited in claim 31 wherein said second phase comprises a non-superconductor material and further comprising a third material, said third material comprising a second superconductor.

44. The superconductor as recited in claim 31 and further comprising a means for flowing a current through said superconductor in a direction substantially parallel to a $a$ $b$ planes of said superconducting phase and substantially perpendicular to magnetic flux lines in said superconductor.

45. The superconductor as recited in claim 31 wherein said second phase comprises regions having at least one dimension between about 1 and 1000 Å.
46. The superconductor as recited in claim 31 wherein said non-superconducting phase comprises regions having at least one dimension of about 10 Å.

47. The superconductor as recited in claim 31 wherein said non-superconducting phase comprises regions of about 20 Å in size in the a•b plane of the superconducting phase and about 2 Å perpendicular to the a•b plane of the superconducting phase.

48. A bulk superconducting material comprising a crystalline lattice structure interspersed by non-superconducting regions, said crystalline lattice structure comprising a material of the empirical formula RBa$_2$Cu$_3$O$_{7-x}$ where R is a member selected from the group yttrium and rare earth metals.

49. A method of using a superconductor having a first, superconducting phase and a second, non-superconducting phase in a magnetic field comprising the step of orienting said superconductor such that magnetic flux is substantially parallel to planes of the non-superconducting phase.

50. A method of forming a superconductor comprising metals and metal oxides in the presence of a nucleation center under conditions that form a superconducting phase and a non-superconducting phase by removal or addition of oxygen, formation of said non-superconducting phase enhanced by said nucleation center.

51. The method as recited in claim 50 wherein said nucleation center is formed by a material having at least two metals therein, said metals only partially soluble during cooling said second metal forming nucleation
centers when said first material is oxidized or reduced into a superconductor.

52. The method as recited in claim 51 wherein said second metal is yttrium or rare earth.

53. A method of forming a two-phase metal oxide comprising removal or addition of oxygen from a first oxidized material to form a first crystalline phase interspersed by a substantially immobile second phase.

54. The method as recited in claim 53 further comprising the step of oxidizing or reducing said first crystalline phase to form a third crystalline phase interspersed by said second phase.

55. The method as recited in claim 54 wherein said third crystalline phase is a superconductor at temperatures above about 30*K and said second phase is a non-superconductor at temperatures above about 30*K.

56. A bulk superconducting material comprising a first, superconducting phase and a second superconducting phase within grains of said bulk superconducting material, said bulk superconducting material having a higher critical current density than said first or said second superconducting phases.

57. The superconducting material as recited in claim 56 wherein said first, superconducting phase is 1-2-4 and said second phase is 1-2-3.

58. A superconductor comprising at least one highly oxidized metal, defects selected from the group tilt boundaries, partial dislocations, intercalations, crystals of said highly oxidized metal containing
dislocations, said dislocations substantially increasing the critical current of said superconductor.

59. The superconductor as recited in claim 58 formed by the process of reducing a first material.

60. The superconductor as recited in claim 58 formed by the process of oxidizing a first material.

61. A superconducting material comprising a first superconducting phase and a finely divided second superconducting phase, said superconducting material having a critical temperature above a critical temperature of said first superconducting phase and said second superconducting phase.

62. The material as recited in claim 61 wherein said first phase is $R_1Ba_2Cu_4O_8$ and said second phase is $R_1Ba_2Cu_3O_x$ where $R$ is selected from the group yttrium and rare earth metals.
FIG. 2.

Dy$_2$B$_4$Cu$_7$O$_{15-x}$

DyBa$_2$Cu$_4$O$_8$
FIG. 3.
FIG. 4.
SAMPLE J, Y124 TREATED IN 1% O2 AT 700 C
HEATED TO 200 C IN 200 DEG/MIN SOAKED FOR 5MM, HEATED TO 700 IN 200 DEG/MIN SOAKED FOR 100
MIN. COOLED AT 5 DEG/MM BASELINE SUBTRACTED

FIG._II.
SAMPLE H. Y124 TREATED 1% O2 AT 800 C
HEATED TO 200 C IN 200 DEG/MM SOAKED FOR 5MIN HEATED TO 800 IN 200 DEG/MM SOAKED FOR 100 MIN. COOLED AT 5 DEG/MIN
BASELINE SUBTRACTED

FIG. 12.

SUBSTITUTE SHEET
INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classifications:

IPC(5): CO1F 11/02; CO1G 3/02; CO1G 5/7007; CH01L 39/12

U.S. Cl. 252/509; 423/583, 604, 617, 618, 624, 635; 505/725, 727, 775, 781

II. FIELDS SEARCHED

Minimum Documentation Searched:

Classification System Classification Symbols

U.S. 252/509; 423/583, 604, 617, 618, 624, 635;
505/725, 727, 775, 781

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched:

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category Citation of Document, with indication, where appropriate, of the relevant passages Relevant to Claim No.

Y US, A, 4,826,808 (YUREK ET AL) 02 May 1989, See entire document 1-10.15-38 and 42-62


Y Communication of the American Ceramic Society, November 1988, Peterson et al., "Magnetic Inducement of Texture in 49

IV. CERTIFICATION

Date of the Actual Completion of the International Search: 26 January 1990

Date of Mailing of this International Search Report: 15 FEB 1990

International Searching Authority: ISA/US

Signature of Authorized Officer:

Form PCT/ISA/210 (second sheet) (Rev.11-87)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>in Ba$_2$YCu$<em>3$O$</em>{6.9}$ Particle Assemblies under Cryogenic conditions&quot;, pages 458-459</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Physical Review B, volume 37, Number 1 01 January 1988, Tranquada et al., Observation of alignment of Superconducting YBa$_2$Cu$_3$O$_7$ particles in a magnetic field using neutron diffraction&quot;, page 519-521</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Applied Physics A, volume 47, September 1988, Ferreira et al., &quot;Magnetic Field Alignment of High-Tc Superconductors RBa$_2$Cu$_3$O$_7$-x -R= Rare Earth&quot;, pages 105-110</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Applied Physics Letters, volume 52(25), 20 June 1888, Tamura et al., Ozone UV irradiation effects on Ba$_2$YCu$_3$O$_7$-x thin films&quot;, pages 2183-2185</td>
<td>28-30 and 58-60</td>
</tr>
<tr>
<td>Y</td>
<td>Nature, volume 334, 14 July 1988, Marsh et al., &quot;Crystal Sturture of the 80K Superconductor YBa$_2$Cu$_4$O$_8&quot;&quot;, pages 141-143</td>
<td>1-10,12-38 and 42-62</td>
</tr>
<tr>
<td>Y</td>
<td>Physical Review B, volume 38, Number 1, 01 July 1988, Char et al., &quot;Properties of Y-Ba$_2$-Cu-O thin films with ordered defect structure: Y$_2$Ba$_4$Cu$<em>8$O$</em>{20}$-x&quot;, pages 834-837</td>
<td>1-10,15-38 and 42-62</td>
</tr>
<tr>
<td>Category</td>
<td>Citation of Document, with indication, where appropriate, of the relevant passages</td>
<td>Relevant to Claim No</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Y</td>
<td>Nature, volume 331, 21 January 1988, Karpinski et al., &quot;Equilibrium pressures of oxygen above YBa₂Cu₃O₇₋ₓ up to 2,000 bar&quot;, pages 242-245</td>
<td>9-10,38</td>
</tr>
<tr>
<td>Y</td>
<td>Solid State Communications, volume 65, number 7, February 1988, Wisniewski et al., &quot;Magnetization studies of YBa₂Cu₃O₇₋ₓ irradiated by fast neutrons&quot;, pages 577-580</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Chemical and Engineering, 13 November 1989, Dayani, &quot;New Milestonse Set with bulk, thin-film Superconductors&quot;, pages 22-23</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Physics Review B, volume 36, number 13, 01 November 1987, Umezawa et al., &quot;Enhanced critical magnetization currents due to fast neutron irradiation in single-crystal YBa₂Cu₃O₇₋ₓ&quot;, pages 7151-7154</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Physical Review B, volume 37, number 4, 01 February 1988, Cost et al., &quot;Fast-neutron irradiation of YBa₂Cu₃Oₓ&quot; pages 1563-1568</td>
<td>49</td>
</tr>
<tr>
<td>Category</td>
<td>Citation of Document, with indication, where appropriate, of the relevant passages</td>
<td>Relevant to Claim No.</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------------------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Y</td>
<td>Physical Review B, volume 39, Number 10, 01 April 1989, Bourgault et al., &quot;Modifications of the physical properties of the high-Tc superconductors YBa$_2$Cu$<em>3$O$</em>{7-x}$ (0.1 &lt; X &lt; 0.7) by 3.5 GeV xenon ion bombardment&quot;, pages 6549-6554</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Physical Review B, volume 27, number 9, 01 May 1983, Kerchner et al., &quot;Low-temperature irradiation study of flux-line pinning in type II superconductors&quot;, pages 5467-5478</td>
<td>49</td>
</tr>
<tr>
<td>Y</td>
<td>Zeitschrift Physik B: Condensed Matter, volume 69, Number 1, Kupfer et al., &quot;Fast neutron irradiation of YBa$_2$Cu$_3$O$_7$&quot;, pages 167-171</td>
<td>49</td>
</tr>
</tbody>
</table>
V. **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE**

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. **Claim numbers**, because they relate to subject matter not required to be searched by this Authority, namely:

2. **Claim numbers**, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. **Claim numbers**, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING**

This International Searching Authority found multiple inventions in this international application as follows:

1. **As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.**

2. **As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:**

   1-10, 15-38 and 42-62

3. **No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:**

4. **As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.**

**Remark on Protest:**

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.