

TITLE

PROCESS FOR PRODUCING THIN FILMS OF INORGANIC
OXIDES OF CONTROLLED STOICHIOMETRY

FIELD OF THE INVENTION

5 This invention relates to methods for producing thin
films of high temperature superconducting oxides and
other materials.

GOVERNMENT FUNDING

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10 Wright-Patterson Air Force Base. The United States
Federal Government may have license rights to the
invention claimed herein.

BACKGROUND OF THE INVENTION

Thin-films have been prepared by a number of
15 deposition methods including evaporation, sputtering,
laser ablation, and metallo-organic chemical vapor
deposition (MOCVD), see, for example, "Thin Film
Processes II", (J. L. Vossen and W. Kern, eds.), Academic
Press, New York, 1991; Handbook of Thin Film Technology",
20 (L. I. Maissel and R. Glang, eds.) McGraw Hill, New York,
1970, and R. W. Simon, Solid State Technology, p. 141,
September, 1989.

The thin film deposition processes of the prior art
typically depend on the substrate temperature. When the
25 temperature of the substrate onto which the thin film of
YBa₂Cu₃O_{7-x} is being deposited is low, the resulting film
is amorphous and insulating. A high-temperature post-
deposition anneal at 800-900°C in oxygen is required to
convert the amorphous precursor film into a
30 superconducting film with the correct crystal structure.
This two-step process is referred to as a "post-anneal"
process. However, when a thin-film such as YBa₂Cu₃O_{7-x} is
deposited onto a substrate heated to about 550-750°C, the
resulting thin-film is crystalline and superconducting as

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deposited. This process is referred to as an "in-situ" process.

Films produced by an in-situ process have less surface roughness and generally superior properties when
5 compared to films from a post anneal process. In-situ deposition has the added advantage of lower processing temperature requirements which makes in-situ deposition compatible with a wider variety of substrate materials.

In-situ processes require heating the substrate
10 uniformly and reproducibly to the required deposition temperature. These methods involve direct thermal and mechanical anchoring of the substrates to a heated block as discussed in R. W. Simon, SPIE Proceedings Vol. 1187, p. 2, edited by T. Venkatesan, published by SPIE
15 Bellingham, WA (1989). The heated block is made of a material that is compatible with an oxygen atmosphere and has good thermal conductivity such as nickel. Good thermal contact between the substrate and the block is usually provided by a compound with high thermal
20 conductivity such as silver paste.

The methods of the prior art have been useful to provide thin films of oxides of relatively involatile oxides (as defined below). The prior art methods of forming in-situ films by vapor deposition onto substrates
25 heated to elevated temperatures, however, tend to cause loss of volatile oxides from the film during the deposition. The resulting film tends to lack sufficient volatile oxide to produce the desired stoichiometry and crystal structure. Although substrates heated to lower
30 temperatures may be employed during deposition, the films deposited on those substrates are amorphous and therefore must be subjected to an additional annealing step subsequent to deposition.

A need therefore exists for a method of producing
35 in-situ thin films of materials that comprise volatile



oxides but which avoids the disadvantages of the prior art methods.

SUMMARY OF THE INVENTION

This invention comprises an in-situ process for
5 preparing thin films of material containing volatile and relatively involatile oxides which employs separate sources of the volatile and relatively involatile oxides during depositon of the thin film. In particular, the process may be employed to prepare in-situ, crystalline
10 thin films of oxide superconductors. In-situ crystalline thin films of oxides that include both relatively involatile oxides as well volatile oxides that tend to be lost from the thin film during its formation by vapor deposition are produced. The process also enables
15 deposition on substrates heated to relatively low temperatures to provide a crystalline thin film.

Thus, the present invention comprises a method of forming in-situ crystalline thin films from materials that include both relatively involatile oxides and
20 volatile oxides that are susceptible to evaporative loss from said thin film during vapor deposition comprising,
providing a first source of said volatile oxides,

providing a second source of said relatively
25 involatile oxides,

depositing said involatile oxides from said second source onto a substrate while concurrently depositing a sufficient amount of volatile oxides from said first source onto said substrate to provide a
30 crystalline thin film of the specified stoichiometry.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an x-ray diffraction pattern on a linear (Fig. 1a) and a log (Fig. 1b) scale of a "phase pure" $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ film made by the present invention.



FIG. 2 shows a plot of the resistivity versus temperature for a $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ film made by the present invention.

FIG. 3 shows an x-ray diffraction pattern of a superconducting thin film made by the invention.

FIG. 4 shows a plot of the inductive frequency response vs. temperature indicating the onset of superconductivity in a film made by the present invention.

FIG. 5 shows an x-ray diffraction pattern on a log scale of a $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7$ film made by the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the following detailed description, unless otherwise specified, all percentages are by weight and all temperatures are in degrees Celsius.

Relatively volatile and involatile oxides are defined as follows. A thin film in accordance with this invention can generally be characterized by the general formula



where "y" is the relative number of moles of oxide A and "z" is the relative number of moles of oxide B, wherein oxide B can be a single or multicomponent oxide, required to form the desired stoichiometric compound relative to A and B per se. In some cases, additional oxygen may be required to satisfy the stoichiometry. When "A" and "B" are involatile oxides, stoichiometric thin film growth requires that

$$[d(A)/dt] = [d(B)/dt] \times (y/z)$$

where $[d(A)/dt]$ and $[d(B)/dt]$ are the relative deposition rates of A and B in units of moles/second.



When oxide A is relatively volatile compared to oxide B, it evaporates from the surface of the growing film and causes the actual stoichiometry of the film (A_yB_z) to deviate significantly from the ideal A_yB_z stoichiometry. For example, in the case of a $TlBa_2CaCu_2O_7$ film, A is $[Tl_2O]$, B is $[Ba_2CaCu_2O_5]$, $y = 1/2$ and $z = 1$. To compensate for this evaporation effect, the deposition rate of the relatively volatile oxide A must be increased to a rate greater than $[d(B)/dt] \times (y/z)$.

10 In accordance with this invention, for oxide A to be a relatively volatile oxide compared to oxide B, the deposition rate of oxide A must be at least twice as great, and preferably more than a factor of two greater than $[d(B)/dt] \times (y/z)$, i.e., the deposition rate of
15 oxide B times the stoichiometric ratio of oxide A to oxide B to obtain the desired stoichiometric film of composition A_yB_z under the desired deposition conditions (i.e., for a given substrate temperature, background gas pressure, and total deposition rate).

20 In accordance with the present invention, separate sources of the volatile oxides and the relatively involatile oxides of the film material are employed during vapor deposition of the material onto a substrate. The sources of volatile and/or involative oxides need not
25 contain oxygen per se, so long as the species produced therefrom can be converted to an oxide, such as by reacting with oxygen in the deposition atmosphere, or can be converted to an oxide at the surface of the growing film, such as by reacting with oxygen at the surface of
30 the film. Control of the amount of volatile oxide in the film is achieved by varying the substrate temperature, the composition of the atmosphere employed during vapor deposition, and rate of deposition of the volatile oxides onto the substrate.



Control of substrate temperature, choice of atmosphere, as well as the rate of deposition of the volatile oxides depends on the composition desired in the film. Generally, the volatile and involatile oxide components of the film are placed into an atmosphere of a mixture of an inert gas and an additional gaseous component for deposition onto the substrate. The atmosphere selected depends on the composition sought in the resultant film. Typically, where the film to be formed is an oxide, the additional gaseous component is an oxygen containing gas such as oxygen. Although the percentages of inert gas and the additional gaseous component may vary, a sufficient amount of inert gas should be present to enable deposition of the oxides on the substrate. The partial pressure of the additional gaseous component is sufficient to reduce evaporation of the volatile oxide from the film. Accordingly, where oxide films of Tl-B-Ca-Cu are to be formed, such as oxide films of $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, and $\text{TlBa}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ wherein x is 0 to 0.6, the additional gaseous component in the atmosphere is oxygen. The partial pressure of oxygen in that atmosphere may vary from about 3 to about 133 Pa (0.5 mtorr to 1 torr), preferably about 13 Pa (100 mtorr) in order to reduce evaporation of Tl_2O from the film being deposited.

The substrate temperature employed during deposition of the film also depends on the composition of the film to be deposited. Generally, the temperature is sufficient to cause growth of the desired composition but less than that which might cause the film to be deficient in the volatile oxide species. Accordingly, where the film to be deposited is a Tl-Ba-Ca-Cu oxide such as $\text{TlBa}_2\text{Ca}_2\text{Cu}_2\text{O}_7$, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, and $\text{TlBa}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ where x is 0 to



0.6, substrate temperatures of from about 400°C to about 700°C, preferably about 550°C may be employed.

Similarly, the rate of deposition of the volatile oxide species depends on the material to be deposited.

5 Generally, the rate of deposition of the volatile oxide species is at least twice as great as the rate of deposition of the relatively involatile oxide or oxides times the stoichiometric ratio of volatile to relatively involatile oxide or oxides during deposition. Where the
10 film material to be deposited is a Tl-Ba-Ca-Cu oxide such as $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, and $\text{TlBa}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ where $x = 0$ to 0.6, a minimum deposition rate of the volatile Tl oxide is about 10 nm/hour, preferably about 360 nm/hour.

15 The involatile oxides to be deposited can be provided in several well known ways. For example, when the sources of involatile oxides are inorganic oxides, radio frequency sputtering or laser ablation of the inorganic oxide can be used to provide the involatile
20 oxide. Preferably, radio frequency sputtering is employed. If the sources of nonvolatile oxides are organometallic compounds, the compounds are volatilized and the organic component thereof is burned off as the compound is deposited onto the substrate.

25 A variety of materials that comprise both volatile and involatile oxides may be deposited in accordance with the invention. Accordingly, oxides of Tl-Ba-Ca-Cu, preferably $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$, where $n = 1, 2, 3$ or 4; $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, where $n = 1, 2, 3$ or 4; and
30 $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$, where $n = 1, 2$ or 3; and $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7$; most preferably $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, $\text{TlBa}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, and $\text{TlBa}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ wherein $x = 0$ to 0.6 are employed.

35 Deposition of oxides of TlBaCaCu to provide thin films of, for example, $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$,



TlBa₂CaCu₂O₈, Tl₂Ba₂Ca₂Cu₃O₁₀, and TlBa₂(Ca_{1-x}Y_x)Cu₂O₇ wherein x = 0 to 0.6 is accomplished by sputter deposition of Ba, Ca and Cu from oxide targets in the presence of Tl₂O vapor. The amounts of Ba, Ca and Cu in the target depends on the composition sought in the Tl-Ba-Ca-Cu thin films. Accordingly, targets of Ba₂CaCu₂O_x are used in forming TlBa₂CaCu₂O₇ and TlBa₂CaCu₂O₈ films. Targets of Ba₂Ca₂Cu₃O_x are used in forming TlBa₂Ca₂Cu₃O₉ and Tl₂Ba₂Ca₂Cu₃O₁₀, and targets of Ba₂(Ca_{1-x}Y_x)Cu₂O₇ are used to produce TlBa₂(Ca_{1-x}Y_x)Cu₂O₇, wherein x = 0 to 0.6 films.

Generally, and in accordance with the invention, a substrate to be coated with the film is mounted onto a substrate block heater. The substrate-heater assembly is placed into a sputtering chamber that contains the desired atmosphere for deposition. The choice of substrate may vary depending on the film that is to be deposited, provided that the substrate and film have a close lattice match. Where oxide materials such as Tl-Ba-Ca-Cu are deposited, suitable substrates include LaAlO₃, NdGaO₃, SrTiO₃, preferably LaAlO₃ and NdGaO₃.

Together with the substrate heater assembly, separate sources of the involatile and the volatile oxides that provide the film are placed into a sputtering deposition chamber. Typically, the sources of involatile oxides are targets that contain those oxides. The targets are vaporized by conventional methods such as radio frequency sputtering or laser ablation to provide the relatively involatile oxides to the substrate. Such relatively involatile oxides comprise oxides of Ba, Ca and Cu, for example, BaO, CaO and CuO.

The separate source of the volatile oxides, for example, PbO and Tl₂O, to be deposited onto the substrate can be heated, for example, in the deposition chamber to volatilize those oxides for deposition onto the film.



EXAMPLE 1

A thin film of $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ on a LaAlO_3 substrate was prepared. A 12 mm square [100] oriented single crystal LaAlO_3 substrate 0.5 mm thick was ultrasonically cleaned
5 in VLSI (very large scale integration) grade 1,1,1-tri-chloroethane for 5 minutes. Without drying, the substrate was immersed in VLSI grade acetone with ultrasonic agitation for 5 minutes. Without drying, the substrate then was immersed in VLSI grade isopropanol
10 with ultrasonic agitation. Finally, the substrate was spray rinsed with VLSI grade isopropanol and blown dry with clean filtered nitrogen.

After cleaning, the substrate was mounted onto the solid nickel (resistively heated) substrate heater block
15 with silver paint. The substrate heater/holder assembly was placed into the vacuum sputter deposition chamber and electrical connections to the resistive heating element were made. A thermocouple temperature probe (standard type K inconel sheathed thermocouple) was inserted into
20 the heater block to provide a temperature signal for a standard feedback type programmable temperature controller (model 818P4 from Eurotherm Corp., 11485 Sunset Hills Rd., Reston, VA 22090-5286). The sputtering chamber was equipped with two standard rf magnetron
25 sputter guns (model TRS-5M from Kurt J. Lesker Co., 1515 Worthington Ave., Clairton, PA 15025) with a 3" (7.6 cm) diameter $\text{Ba}_2\text{CaCu}_2\text{O}_x$ target in each gun. The targets were made by standard hot pressing of a stoichiometric powder mixture of the individual oxides (BaO , CaO , and CuO).
30 The guns were oriented in an "off-axis" configuration to reduce negative ion bombardment effects on the substrates.

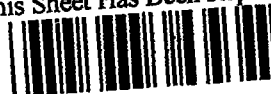
A separate vapor source of Tl_2O from either Tl_2O_3 or Tl_2O powder was included in the sputtering chamber. The
35 vapor source was a hollow crucible of nickel that was



filled with either Tl_2O_3 or Tl_2O powder. The nickel was heated by standard resistive heating elements. The vapor source was placed into the sputtering chamber directly below the substrate heater. A thermocouple temperature probe (standard type K inconel sheathed thermocouple) was inserted into the nickel crucible to provide a temperature signal for a standard feedback type programmable temperature controller.

The sputtering chamber was evacuated to less than 10^{-5} torr (1.33×10^{-3} Pa) by a standard turbo pump (model TPU 330 with a TCP 305 electronic drive from Balzers, 8 Sagamore Park Rd., Hudson, NH 03051) backed by a standard chemical series mechanical pump (model 2020CP from Alcatel vacuum Products, 40 Pond Rd., South Shore Park, Hingham, MA 02043). An Ar gas flow of 25 sccm (standard cubic centimeters per minute) and an O_2 gas flow of 25 sccm into the sputtering chamber were established by standard mass flow controllers. The electronic drive unit for the turbo pump was placed in the pressure feedback mode to control the sputtering pressure at 200 mtorr (26.7 Pa).

The substrate heater temperature and the vapor source temperature were raised to $550^\circ C$ at a rate of $15^\circ C/min$. After reaching $550^\circ C$, the temperature of the vapor source was adjusted to give a deposition rate of $0.6 \text{ \AA/sec}$ (0.06 nm/sec.) on a quartz crystal rate monitor (model IC6000 from Leybold Inficon, 6500 Fly Rd., East Syracuse, NY 13057) located near the substrate heater. The rf magnetron sputter guns then were activated with 100 watts of rf power to each gun to generate a deposition rate of about $450 \text{ \AA/hr}$ (45 nm/hr) at the substrate. After one hour, the rf power was turned off, the gas flows turned off, and the system was backfilled with O_2 to a pressure of 500 torr ($6.65 \times 10^4 \text{ Pa}$). At



the same time, the substrate heater and the vapor source began cooling back to room temperature at about 15°C/min.

The x-ray diffraction pattern of the film produced by the in-situ method of this example is shown in Fig. 1. The black triangles A represent LaAlO_3 (h00) and the white triangles B represent the 1212 (001) phase of $\text{TlBa}_2\text{CaCu}_2\text{O}_7$. The diffraction pattern showed well defined peaks of the $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ phase with no other phases detected. These peaks also showed that the film is highly oriented with the c-axis perpendicular to the substrate surface. The resistivity versus temperature for a similar film which was grown at 565°C instead of 550°C is shown in Fig. 2. The film showed an onset of superconductivity at about 80°K, but did not reach zero resistance until about 8°K.

EXAMPLE 2

The procedure of example 1 was followed except that $\text{Ba}_2(\text{Ca}_{0.6}\text{Y}_{0.4})\text{Cu}_2\text{O}_x$ sputtering targets were used (in place of $\text{Ba}_2\text{CaCu}_2\text{O}_x$), Ar/ N_2O was used in place of Ar/ O_2 as the sputtering gas mixture, the thallium oxide evaporation rate was increased to 1.0 Å/sec (0.1 nm/sec), and deposition was followed by raising the substrate heater temperature to 725°C in 500 torr (6.65×10^4 Pa) of O_2 and holding at that temperature for 240 minutes before cooling to room temperature.

The x-ray diffraction pattern of the $\text{TlBa}_2(\text{Ca}_{0.6}\text{Y}_{0.4})\text{Cu}_2\text{O}_7$ film produced by this example is shown in Fig. 3. The diffraction pattern showed well defined peaks of the $\text{TlBa}_2(\text{Ca}_{0.6}\text{Y}_{0.4})\text{Cu}_2\text{O}_7$ phase with no other phases detected. These peaks also showed that the film is highly oriented with the c-axis perpendicular to the substrate surface. This x-ray diffraction pattern was nearly identical to that shown for the Example 1 except that the crystalline lattice constant was reduced due to the partial substitution of Y for Ca in the



lattice and the increased oxygen content due to the 240 minute soak in O₂ after deposition. An inductive eddy current measurement (taken using the model 7500 from Lake Shore Cryotronics, 64 East Walnut St, Westerville, OH 43081-2399) of the film produced by Example 2 is shown in Fig. 4. Fig. 4 showed the onset of super-conductivity in this sample at about 55°K.

EXAMPLE 3

The procedure of Example 1 was followed except that Pb_{0.5}Sr₂Ca₂Cu₃O_x sputtering targets were used (in place of Ba₂CaCu₂O_x), Ar/N₂O was used in place of Ar/O₂ as the sputtering gas mixture, and the thallium oxide evaporation rate was increased to 1.0 Å/sec (0.1 nm/sec).

The x-ray diffraction pattern of the Tl_{0.5}Pb_{0.5}Sr₂CaCu₂O₇ film produced by this example is shown in Fig. 5. The diffraction pattern showed well defined peaks of the Tl_{0.5}Pb_{0.5}Sr₂CaCu₂O₇ phase. The excess Ca and Cu from the targets relative to the desired Tl_{0.5}Pb_{0.5}Sr₂CaCu₂O₇ phase likely formed a CaCuO_x phase intermixed with the desired Tl_{0.5}Pb_{0.5}Sr₂CaCu₂O₇ phase. The x-ray diffraction peaks also showed that the film is highly oriented with the c-axis perpendicular to the substrate surface.

Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification, or from practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the scope and spirit of the invention being indicated by the following claims.





WHAT IS CLAIMED IS:

1. A method of forming in-situ crystalline thin films from materials that include both relatively involatile oxides and volatile oxides that are
5 susceptible to evaporative loss from said thin film during vapor deposition comprising,
providing a first source of said volatile oxides,
providing a second source of said relatively
10 involatile oxides,
depositing said involatile oxides from said second source onto a substrate while concurrently depositing a sufficient amount of volatile oxides from said first source onto said substrate to provide a
15 crystalline thin film of the specified stoichiometry.
2. The method of Claim 1 wherein said volatile oxides are deposited at a rate at least twice as great as the rate of deposition of the relatively involatile oxides times the stoichiometric ratio of volatile to
20 relatively involatile oxides in the crystalline thin films.
3. The method of Claim 2 wherein said materials are selected from the group consisting of $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, and
25 $\text{TlBa}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ wherein x is 0 to 0.6, said source of volatile oxide is Tl_2O , and said source of relatively involatile oxides comprising an oxide of Ba, Ca and Cu.
4. The method of Claim 3 wherein said substrate is heated to 400-700°C.
- 30 5. The method of Claim 4 wherein said vapor deposition occurs in an atmosphere of a mixture of inert gas together with either oxygen or N_2O .
6. The method of Claim 5 wherein the partial pressure of said oxygen or N_2O in said atmosphere is





sufficient to reduce evaporative loss of Tl oxide from said film during deposition.

7. The method of Claim 3 wherein said Tl_2O is deposited at the rate of 10 to 360 nm per hour.

5 8. The method of Claim 6 wherein said partial pressure is 3 to 133 Pa.

9. The method of Claim 2 wherein said materials are selected from the group consisting of $Tl_{0.5}Pb_{0.5}Sr_2Ca_{n-1}Cu_nO_{2n+3}$ wherein n is 1, 2 or 3, said
10 source of volatile oxides is Tl_2O and PbO and said source of relatively involatile oxides comprises an oxide of Sr, Ca and Cu.

10. The method of Claim 2 wherein said materials are selected from the group consisting of
15 $TlBa_2(Ca_{1-x}Y_x)Cu_2O_7$ wherein x is 0 to 0.6, said source of volatile oxides is Tl_2O and said source of relatively involatile oxides comprises an oxide of Ba, Ca, Y and Cu.

