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R-Tl-Sr-Ca-Cu-O superconductors and processes for making same

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United States Patent [19][11] **Patent Number:** **5,597,781****Sheng et al.**[45] **Date of Patent:** ***Jan. 28, 1997**[54] **R-TL-SR-CA-CU-O SUPERCONDUCTORS AND PROCESSES FOR MAKING SAME**[75] Inventors: **Zhengzhi Sheng; Allen M. Hermann,**
both of Fayetteville, Ark.[73] Assignee: **University of Arkansas,** Little Rock,
Ark.[*] Notice: The portion of the term of this patent
subsequent to Jul. 30, 2008, has been
disclaimed.[21] Appl. No.: **480,258**[22] Filed: **Feb. 15, 1990****Related U.S. Application Data**[63] Continuation of Ser. No. 251,348, Sep. 29, 1988, Pat. No.
5,036,044.[51] Int. Cl.⁶ **H01B 12/00; H01L 39/12**[52] U.S. Cl. **505/120; 505/783; 252/518;**
252/521[58] Field of Search **505/783, 1; 252/518,**
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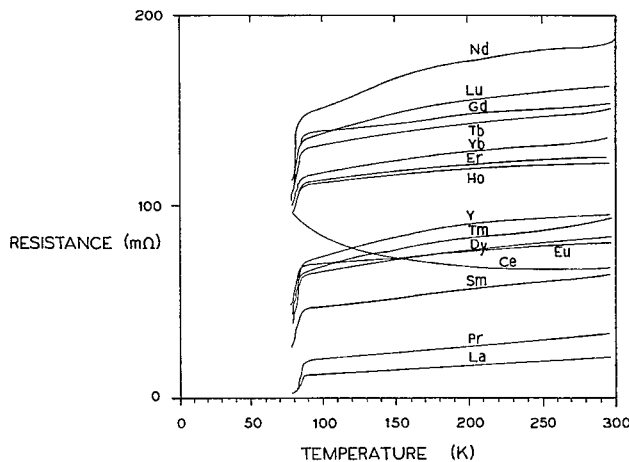
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Primary Examiner—Paul Lieberman*Assistant Examiner*—M. Kopec*Attorney, Agent, or Firm*—Hill, Steadman & Simpson[57] **ABSTRACT**

A high temperature superconductor system is provided having the following formula: M-A-B-C-D-E, wherein, M is a metallic element. A is an element in Group 3A, B is an element in Group 2A, C is another element in Group 2A, D is an element in Group 1B, and E is an element in Group 6A. In an embodiment, the high temperature superconductor has the following formula: R-Tl-Sr-Ca-Cu-O (wherein R is chosen from the group consisting of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y). Processes for making these high temperature superconductors are also disclosed.

4 Claims, 3 Drawing Sheets

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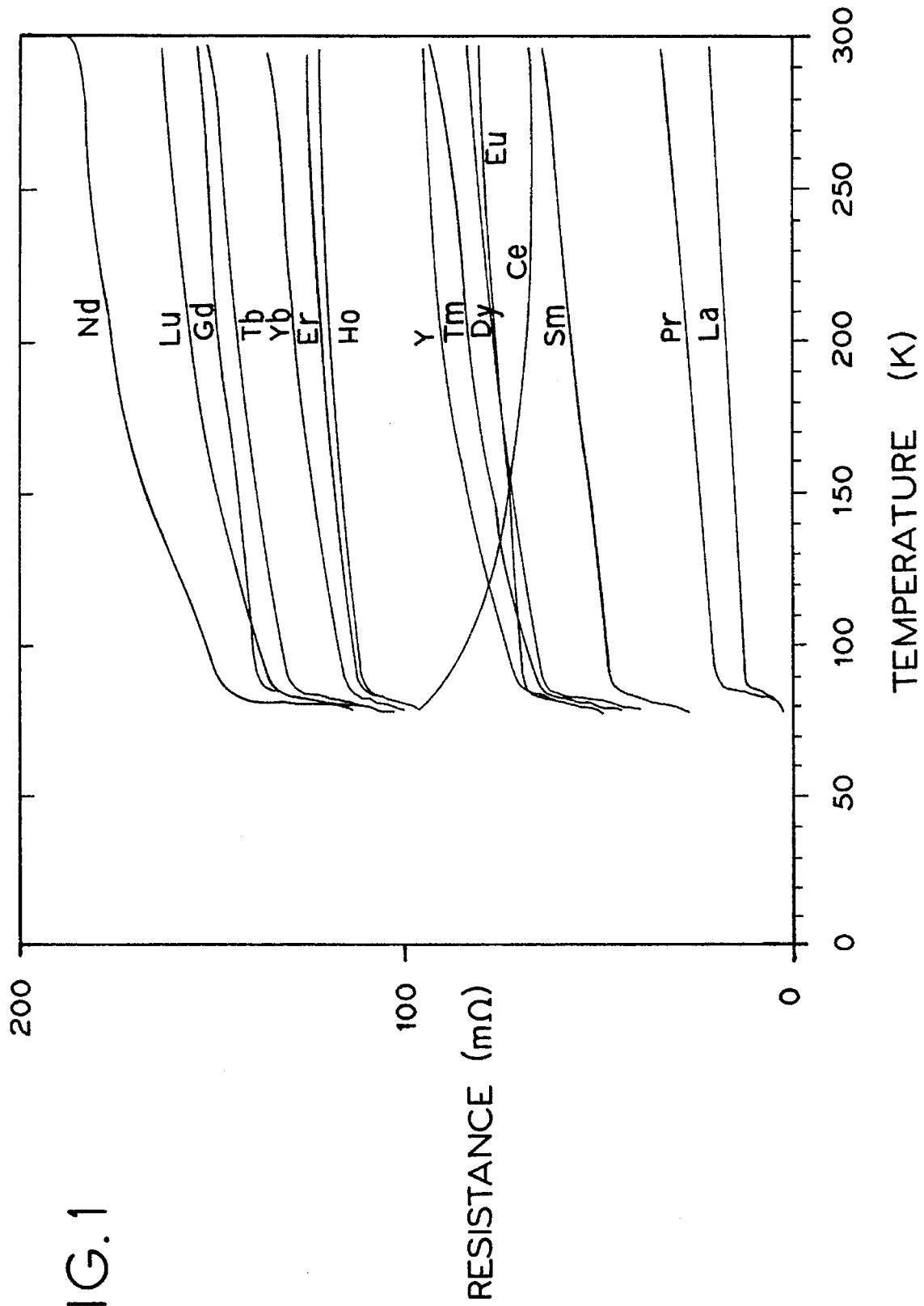


FIG.1

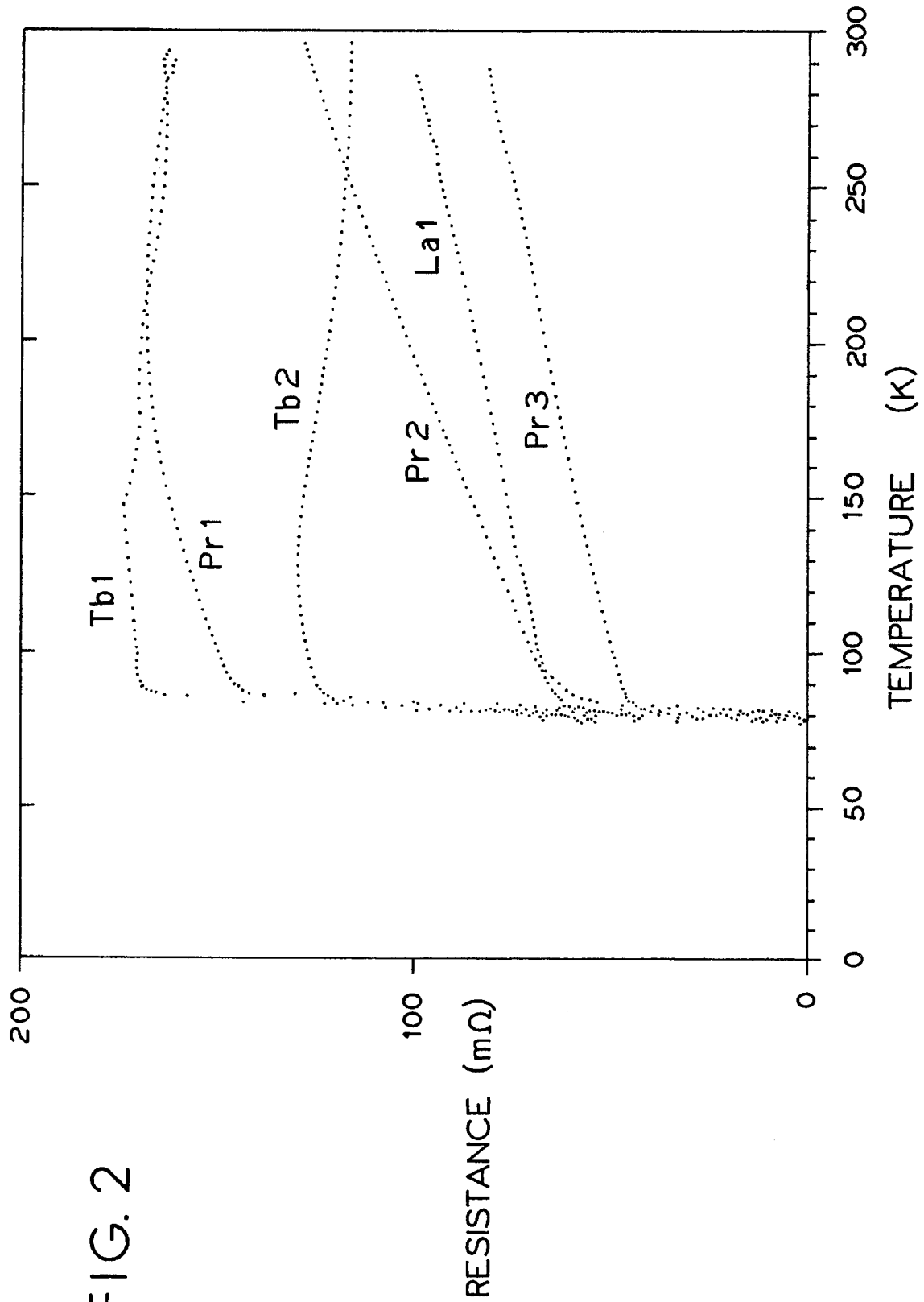


FIG. 2

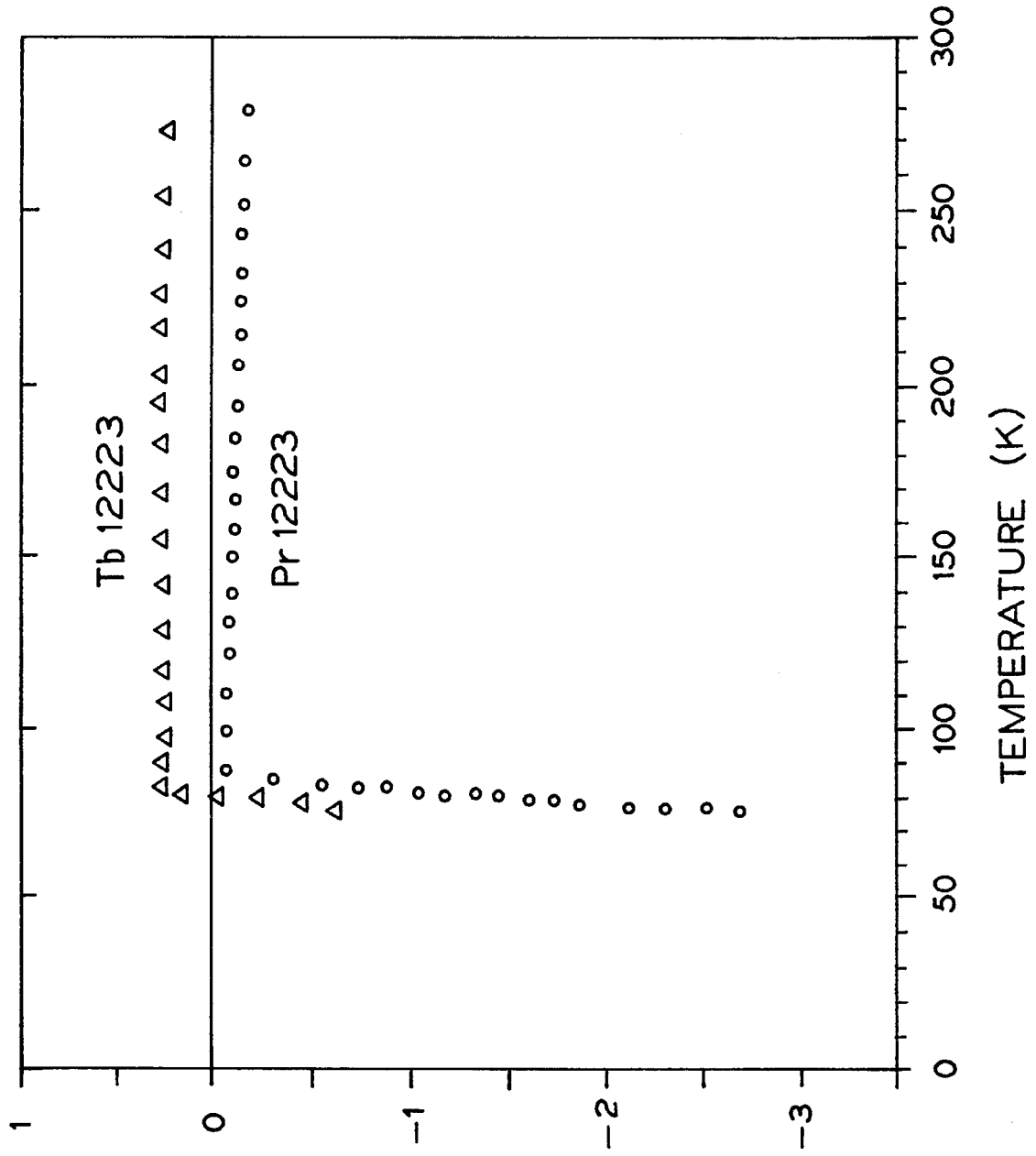


FIG. 3

AC Susceptibility
(arb. unit)

R-Tl-Sr-Ca-Cu-O SUPERCONDUCTORS AND PROCESSES FOR MAKING SAME

This is a continuation of application Ser. No. 251,348, filed Sep. 29, 1988, now U.S. Pat. No. 5,036,044.

The present invention relates generally to high temperature superconductors. More specifically, the present invention relates to a new high temperature superconductor system and processes for making same.

A variety of superconducting systems are known. The inventors of the present patent application have filed the following patent applications that disclose superconductors and/or methods of making same.

U.S. patent application Ser. No. 144,144 discloses a high temperature superconductor having the composition Tl-R-X-Y wherein: R is an element chosen from Group 2A; X is an element chosen from Group 1B; and Y is an element chosen from Group 6A.

U.S. patent application Ser. No. 155,247 discloses a high temperature superconductor having the composition: Tl-R-Ba-Cu-O wherein R is a Group 2A element excluding barium; or Tl-Sr-Cu-O. In an embodiment, R is either strontium or calcium.

U.S. patent application Ser. No. 082,222 discloses a high temperature superconductor having the composition: Tb-R-Ba-Cu-O wherein R is chosen from the group of rare earth metals excluding: praseodymium; cerium; and terbium.

U.S. patent application Ser. No. 089,067 discloses a high temperature superconductor having the composition: R-Ba-Cu-O wherein R is chosen from the group of rare earth metals excluding: praseodymium; terbium; and cerium.

U.S. patent application Ser. No. 236,502 discloses a process for making Tl-Ba-Ca-Cu-O superconductors.

Applicants have also filed, on the same day as the instant patent application, a patent application entitled: "Tl-Sr-Ca-Cu-O SUPERCONDUCTORS AND PROCESSES FOR MAKING SAME". The patent application discloses a high temperature superconductor having the formula Tl-Sr-Ca-Cu-O and processes for making same.

A new superconductor would be desirable for many reasons. Such a superconductor would: (1) facilitate the discovery of the correct theory on oxide superconductivity; (2) provide a framework for the search for higher temperature, even room temperature superconductors; (3) allow superconducting components to operate with lower cost; and (4) provide low cost processing and manufacturability. Furthermore, in superconducting systems including Tl, there is a drawback in that Tl is toxic. Therefore, a superconducting system with a reduced amount of Tl would be desirable.

Accordingly, there is a need for new high temperature superconductors.

SUMMARY OF THE INVENTION

the present invention provides a new superconductor system that yields a number of new high temperature superconductors with transition temperatures above liquid nitrogen temperature that are unique to date among all high temperature superconductors.

The present invention comprise a system containing six elements:

M-A-B-C-D-E

wherein:

M, A, B, C, and D are metallic elements; and
E is a non-metallic element.

Preferably, M is a metallic element, A is an element in Group 3A, B, and C are elements in Group 2A, D is an element in Group 1B, and E is an element in Group 6A.

In a preferred embodiment, M is a rare earth, including La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y; A is thallium (Tl); B is strontium (Sr); C is calcium (Ca); D is copper (Cu); and E is oxygen (O).

In an embodiment, the superconductor of the present invention has the following formula:

Pr-Tl-Sr-Ca-Cu-O.

In an embodiment, the superconductor of the present invention has the following formula:

Tb-Tl-Sr-Ca-Cu-O.

In an embodiment, the superconductor of the present invention has the following approximate stoichiometry:

$RTl_xSr_yCa_zCu_uO_v$,

wherein:

- x is greater than 0.1 and less than 10;
- y is greater than or equal to 0 and less than or equal to 10;
- z is greater than or equal to 0 and less than or equal to 10;
- y+z is greater than 0.1 and less than 20;
- u is greater than 0.1 and less than 20;
- v is greater than x+y+z+u and less than 5+x+y+z+u; and
- R is a rare earth metal.

Methods for producing the high temperature superconductors of the present invention are also provided. The methods allow the superconductors to be prepared at temperatures of approximately 850° to about 1000° C. in flowing oxygen.

Accordingly, an advantage of the present invention is to provide a number of new superconducting systems having high transition temperatures.

A further advantage of the present invention is to provide a number of material systems that may produce higher temperature, even room temperature superconductors.

A still further advantage of the present invention is that it provides a number of new high temperature superconductors that can be rapidly fabricated.

Furthermore, an advantage of the present invention is that it provides processes for making new high temperature superconductors.

Still another advantage of the present invention is that it provides processes for rapidly making high temperature superconductors.

Additional features and advantages of the present invention will be apparent from the detailed description of the presently preferred embodiments and from the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates graphically ac (5 KHz) resistance versus temperature for nominal $RTl_2Sr_2Ca_2Cu_3O_{12}$ samples with R=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y.

FIG. 2 illustrates graphically dc resistance versus temperature for La-Tl-Sr-Ca-Cu-O, Pr-Tl-Sr-Ca-Cu-O, and Tb-Tl-Sr-Ca-Cu-O samples.

FIG. 3 illustrates graphically ac (5 KHz) susceptibility versus temperature dependences for a Pr-Tl-Sr-Ca-Cu-O sample and a Tb-Tl-Sr-Ca-Cu-O sample.

DETAILED DESCRIPTION OF THE
PRESENTLY PREFERRED EMBODIMENTS

The present invention provides a new superconductor system that provides a number of new superconductors with phases whose transition temperatures are above liquid nitrogen temperature. The present invention also provides a number of new material systems that may produce higher temperature, even room temperature superconductors by further elemental substitution and variation of preparation procedures. In addition, the present invention provides processes for making these new high temperature superconductors.

The present invention comprises a superconducting system containing six elements:

M-A-B-C-D-E

wherein:

M, A, B, C, and D are metallic elements; and
E is a non-metallic element.

Preferably, M is a metallic element, A is an element in Group 3A, B and C are elements in Group 2A, D is an element in Group 1B, and E is an element in Group 6A.

In a preferred embodiment, M is a rare earth (including La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y), A is thallium, B is strontium (Sr), C is calcium (Ca), D is copper (Cu), and E is oxygen (O).

In a preferred embodiment, the superconductor of the present invention has the following formula:

R-Tl-Sr-Ca-Cu-O

wherein: R=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y.

The inventors of the present invention have found that superconductors having this formula are superconducting above liquid nitrogen temperature. To date, the following above-liquid-nitrogen-temperature superconducting systems are known: rare earth-Ba-Cu-O (90K); Tl-Ba-Cu-O (90K); Bi-Sr-Ca-Cu-O (110K); and Tl-Ba-Ca-Cu-O (120K). The R-Tl-Sr-Ca-Cu-O systems of the present invention are the fifth above-liquid-nitrogen-temperature superconducting systems.

The present invention provides a number of new superconductors that can be operated at higher temperature with lower cost. Furthermore, the new high temperature superconductors of the present invention can be rapidly produced.

In a preferred embodiment, the superconductors in the new superconductive systems having the following approximate stoichiometry:

$RTl_xSr_yCa_zCu_uO_v$

wherein:

x is greater than 0 and less than 10;

y is greater than or equal to 0 and less than or equal to 10;

z is greater than or equal to 0 and less than or equal to 10;

y+z is greater than 0.1 and less than 20;

u is greater than 0.1 and less than 20;

v is greater than x+y+z+u and less than 5+x+y+z+u; and
R is a rare earth metal.

By way of example and not limitation, examples of methods for making the new high temperature R-Tl-Sr-Ca-Cu-O superconductors will now be given.

EXAMPLE 1

A. The following reagents were utilized:

1. La_2O_3

2. Tl_2O_3

3. $SrCO_3$

4. $CaCO_3$

5. CuO

B. The following procedure was followed:

1. A mixture of $SrCO_3$, $CaCO_3$, and CuO with a molar ratio of 2:2:3 was completely ground.

2. The mixture was heated at 950° C. in air for at least 24 hours with several intermediate grindings.

3. The heated mixture was cooled and ground, so that a powder with a nominal composition of $Sr_2Ca_2Cu_3O_7$ was obtained.

4. A mixture of La_2O_3 , Tl_2O_3 , and $Sr_2Ca_2Cu_3O_7$ with a molar ratio of 1:2:2:23 (La:Tl:Sr:Ca:Cu) was ground and pressed into a pellet.

5. A tube furnace was heated to 900° C. in flowing oxygen.

6. The pellet was put in a platinum boat, and the boat was placed in the tube furnace, maintaining the temperature and oxygen flow for 3 minutes.

7. The pellet was then furnace-cooled to room temperature.

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is shown in FIG. 1 (curve La) and FIG. 2 (curve La1). This sample reached zero resistance at liquid nitrogen temperature.

EXAMPLE 2

The procedure was the same as that set forth Example 1 except that La_2O_3 was replaced by Pr_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example illustrated in FIG. 1 (curve Pr) and FIG. 2 (curve Pr3). This sample reached zero resistance at liquid nitrogen temperature. FIG. 3 illustrates ac susceptibility-temperature dependence for this sample (curve Pr12223 in FIG. 3).

EXAMPLE 3

The same procedure as that used in Example 1 was followed except that La_2O_3 was replaced by Nd_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Nd).

EXAMPLE 4

The same procedure as that set forth in Example 1 was used except that La_2O_3 was replaced by Sm_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The ac resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Sm).

EXAMPLE 5

The same procedure as that set forth in Example 1 was used except that La_2O_3 was replaced by Eu_2O_3 .

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The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Eu).

EXAMPLE 6

The same procedure as that set forth in Example 1 was used except that La_2O_3 was replaced Gd_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Gd).

EXAMPLE 7

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by Tb_4O_7 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Tb). The ac susceptibility-temperature dependence for the sample is illustrated in FIG. 3 (curve Tb12223).

EXAMPLE 8

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by DY_2O_3 .

The sample prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Dy).

EXAMPLE 9

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by HO_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Ho).

EXAMPLE 10

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by Er_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Er).

EXAMPLE 11

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by Tm_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Tm).

EXAMPLE 12

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by Yb_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Yb).

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EXAMPLE 13

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by Lu_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Lu).

EXAMPLE 14

The same procedure as that set forth in Example 1 was followed except that La_2O_3 was replaced by Y_2O_3 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 1 (curve Y).

EXAMPLE 15

A. The following reagents were utilized:

1. La_2O_3
2. Tl_2O_3
3. SrCO_3
4. CaCO_3
5. CuO

B. The following procedure was followed:

1. A mixture of SrCO_3 , CaCO_3 , and CuO with a molar ratio of 2:2:3 was completely ground.
2. The mixture was heated at 950°C . in air for at least 24 hours with several intermediate grindings.
3. The heated mixture was cooled and ground, so that a powder with a nominal composition of $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ was obtained.
4. A mixture of La_2O_3 and $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ with an atomic molar ratio of 1:2:2:3 (La:Sr:Ca:Cu) was ground and pressed into a pellet.
5. The pellet was heated at 950°C . in air or flowing oxygen for 3-10 minutes.
6. A tube furnace was heated to 900°C . in flowing oxygen.
7. 0.1 to about 0.2 gram of Tl_2O_3 was put in a platinum boat which was put in a quartz boat, and the heated pellet was put over the platinum boat.
8. The quartz boat and its contents was placed in the tube furnace, maintaining the temperature and oxygen flow for 2 to about 5 minutes.
9. the quartz boat with its contents was then furnace-cooled to room temperature.

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature.

EXAMPLE 16

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Pr_2O_3 .

EXAMPLE 17

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Nd_2O_3 .

EXAMPLE 18

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Sm_2O_3 .

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EXAMPLE 19

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Eu_2O_3 .

EXAMPLE 20

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Gd_2O_3 .

EXAMPLE 21

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Tb_4O_7 .

EXAMPLE 22

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Dy_2O_3 .

EXAMPLE 23

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by HO_2O_3 .

EXAMPLE 24

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Er_2O_3 .

EXAMPLE 25

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Tm_2O_3 .

EXAMPLE 26

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Yb_2O_3 .

EXAMPLE 27

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Lu_2O_3 .

EXAMPLE 28

The same procedure as that set forth in Example 15 was followed except La_2O_3 was replaced by Y_2O_3 .

EXAMPLE 29

A. The following reagents were utilized:

1. Pr_2O_3

2. Tl_2O_3

3. SrCO_3

4. CaCO_3

5. CuO

B. The following procedure was followed:

1. A mixture of SrCO_3 , CaCO_3 , and CuO with a molar ratio of 2:2:3 was completely ground.

2. The mixture was heated at 950°C . in air for at least 24 hours with several intermediate grindings.

3. The heated mixture was cooled and ground, so that a powder with a nominal composition of $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ was obtained.

4. A mixture of Pr_2O_3 , Tl_2O_3 , and $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ with an atomic molar ratio of 1:2:2:2:3 (Pr:Tl:Sr:Ca:Cu) was ground and pressed into a pellet.

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5. A tube furnace was heated to 950°C . in flowing oxygen.

6. The pellet was put in a platinum boat, and the boat was placed in the tube furnace, maintaining the temperature and oxygen flow for 2 minutes.

7. The platinum boat with the pellet was then furnace-cooled to room temperature.

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The dc resistance-temperature dependence for a sample prepared pursuant to this example is illustrated in FIG. 2 (curve Pr2). This sample reached zero resistance at liquid nitrogen temperature.

EXAMPLE 30

A. The following reagents were utilized:

1. Pr_2O_3

2. Tl_2O_3

3. SrCO_3

4. CaCO_3

5. CuO

B. The following procedure was followed:

1. A mixture of SrCO_3 , CaCO_3 , and CuO with a molar ratio of 2:4:5 was completely ground.

2. The mixture was heated at 950°C . in air for at least 24 hours with several intermediate grindings.

3. The heated mixture was cooled and ground, so that a powder with a nominal composition of $\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_{11}$ was obtained.

4. A mixture of Pr_2O_3 , Tl_2O_3 , and $\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_{11}$ with an atomic molar ratio of 1:1:2:4:5 (Pr:Tl:Sr:Ca:Cu) was ground and pressed into a pellet.

5. A tube furnace was heated to 900°C . in flowing oxygen.

6. The pellet was put in a platinum boat, and the boat was placed in the tube furnace, maintaining the temperature and oxygen flow for 3 minutes.

7. The pellet was annealed at 710°C . in flowing oxygen for 10 hours, followed by furnace-cooling to room temperature.

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The dc resistance-temperature dependence for a sample prepared pursuant to the method of this example is illustrated in FIG. 2 (curve Pr1).

EXAMPLE 31

The same procedure as that set forth in Example 30 was followed except that Pr_2O_3 was replaced by Tb_4O_7 .

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The dc resistance-temperature dependence for a sample prepared pursuant to the method of this example is illustrated in FIG. 2 (curve Tb2).

EXAMPLE 32

A. The following reagents were utilized:

1. Tb_4O_7

2. Tl_2O_3

3. SrCO_3

4. CaCO_3

5. CuO

B. The following procedure was followed:

1. A mixture of SrCO₃, CaCO₃, and CuO with a molar ratio of 2:4:5 was completely ground.
2. The mixture was heated at 950° C. in air for at least 24 hours with several intermediate grindings.
3. The heated mixture was cooled and ground, so that a powder with a nominal composition of Sr₂Ca₄Cu₅O₁₁ was obtained.
4. A mixture of Tb₄O₇, Tl₂O₃, and Sr₂Ca₄Cu₅O₁₁ with an atomic molar ratio of 1:1:2:4:5 (Tb:Tl:Sr:Ca:Cu) was ground and pressed into a pellet.
5. A tube furnace was heated to 950° C. in flowing oxygen.
6. The pellet was put in a platinum boat, and the boat was placed in the tube furnace, maintaining the temperature and oxygen flow for 3 minutes.
7. The pellet was then quenched in air to room temperature.

The samples prepared by this procedure were found to be superconducting above liquid nitrogen temperature. The dc resistance-temperature dependence for a sample prepared pursuant to this method is illustrated in FIG. 2 (curve Tb1).

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the present invention and without diminishing its attendant advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

We claim:

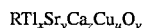
1. A composition having superconductive properties the composition comprising a melt produced complex having the nominal formula:



wherein R is chosen from the group consisting of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y; and

wherein the atomic molar ratio of R:Tl:Sr:Ca:Cu is 1:2:2:2:3.

2. A composition having superconductive properties having the following approximate stoichiometry:



wherein:

R is a single rare earth metal is chosen from the group consisting of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y;

x is greater than 0.1 and less than 10;

y is greater than or equal to 0 and less than or equal to 10;

z is greater than or equal to 0 and less than or equal to 10;

y+z is greater than 0.1 and less than 20;

u is greater than 0.5 and less than 20; and

v is greater than x+y+z+u and less than 5+x+y+z+u.

3. The composition of claim 2 wherein R is Pr.

4. The composition of claim 2 wherein R is Tb.

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