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(Hg or Pb)-Pr-Tl-Sr-Cu-O based superconductors

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[54] **(HG OR PB)-PR-TL-SR-CU-O BASED SUPERCONDUCTORS**

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[21] Appl. No.: **198,214**

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Related U.S. Application Data

[63] Continuation of Ser. No. 865,669, Apr. 8, 1992, abandoned, which is a continuation of Ser. No. 581,324, Sep. 12, 1990, abandoned.

[51] **Int. Cl.**^{6} **H01L 39/12**; C04B 35/45; C04B 35/50

[52] **U.S. Cl.** **505/120**; 505/779; 505/783; 505/126; 423/263; 423/593; 252/521; 501/126; 501/127

[58] **Field of Search** 505/779, 783, 505/120, 126; 423/263, 600, 604, 593; 252/521; 501/126, 127

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[57] **ABSTRACT**

A high temperature superconducting system comprising M—R—Tl—Sr—Cu—O wherein: M is at least one compound selected from the group consisting of Hg, Pb, K, and Al; and R represents rare earth metals. In one embodiment, a composition forms a 93K superconducting phase having the composition: M—R—Tl—Sr—Cu—O wherein: M is selected from the group consisting of Hg and Al; and R is a rare earth metal. In another embodiment, the composition comprises M—R—Tl—Sr—Cu—O wherein: M is selected from the group of Pb and/or K; and R is a rare earth metal.

2 Claims, 2 Drawing Sheets

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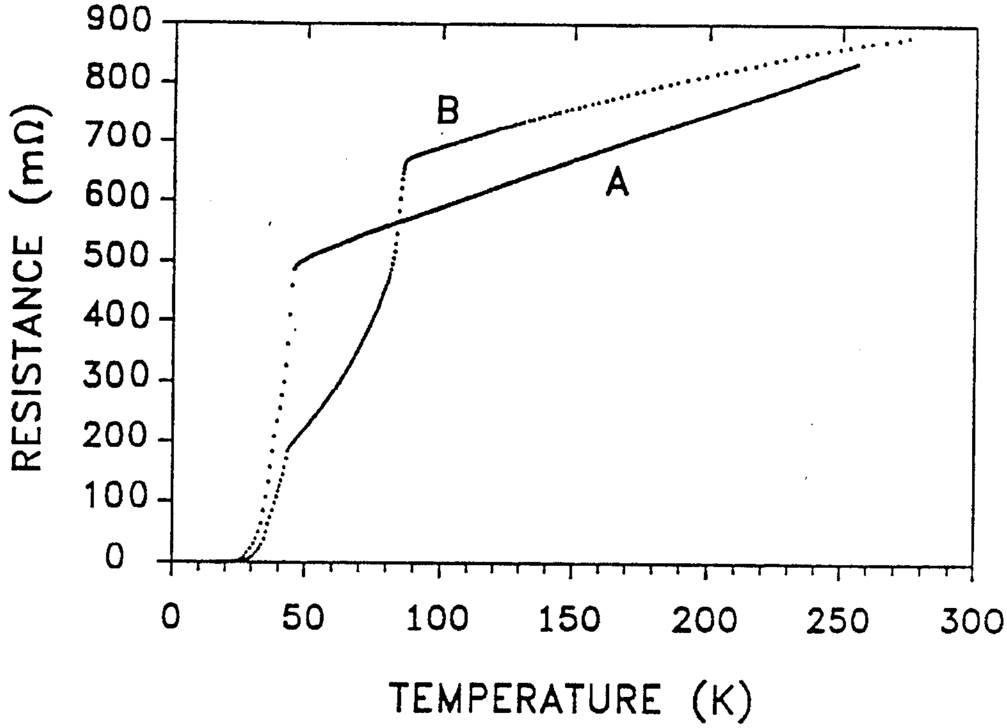
FIG. 1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800
700
600
500
400
300
200
100
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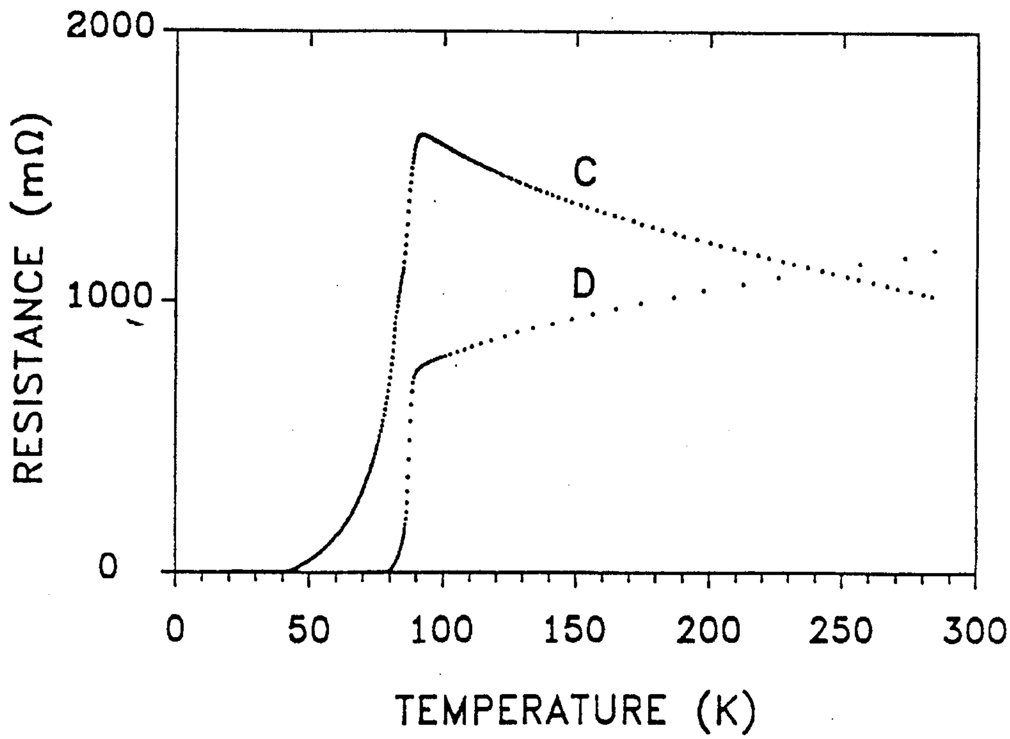
A
0
50
100
150
200
250
300
TEMPERATURE (K)

FIG. 2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100
150
200
250
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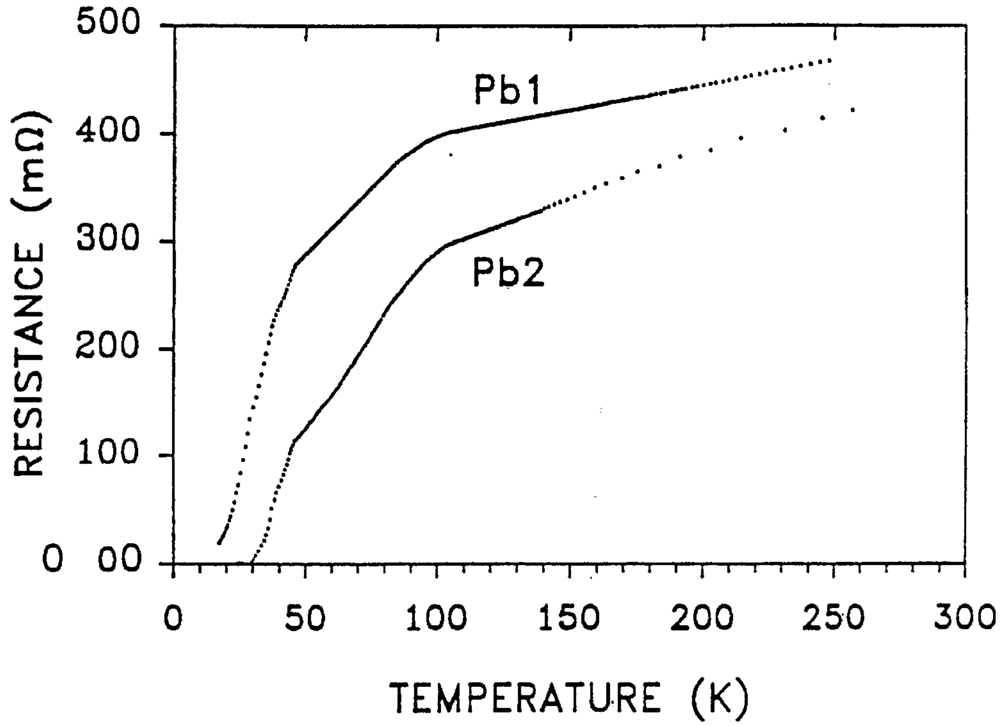
TEMPERATURE (K)

FIG. 3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400
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Pb2
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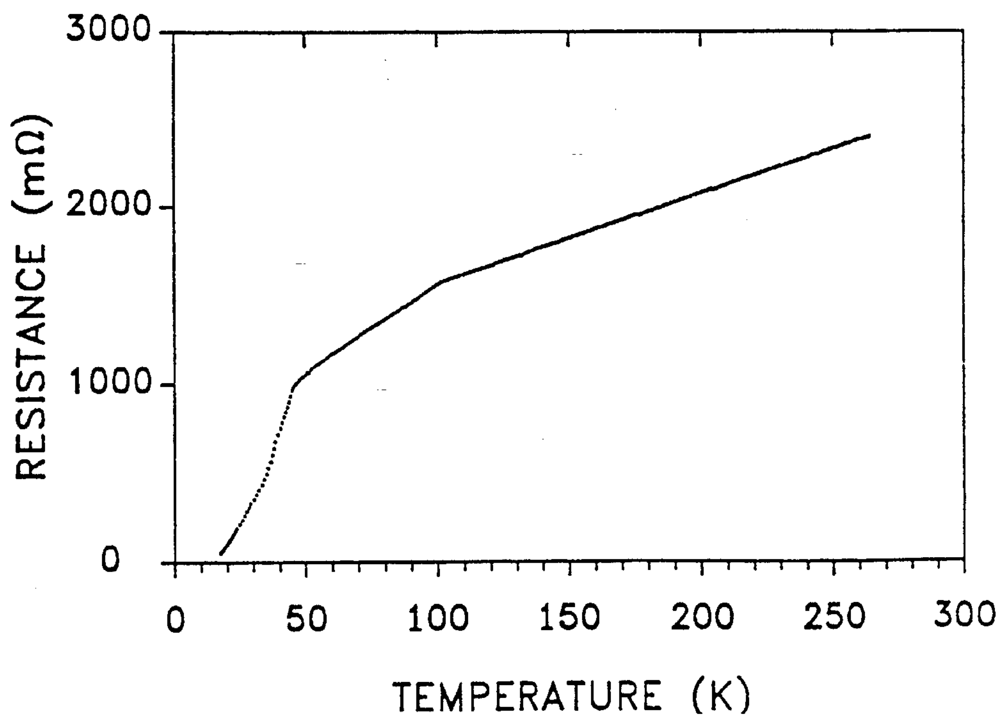
50
100
150
200
250
300
TEMPERATURE (K)

FIG. 4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RESISTANCE (mΩ)
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50
100
150
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TEMPERATURE (K)

(HG OR PB)-PR-TL-SR-CU-O BASED SUPERCONDUCTORS

This is a continuation of application Ser. No. 07/865,669, filed Apr. 8, 1992, now abandoned, which is a continuation of application Ser. No. 07/581,324, filed Sep. 12, 1990 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to high temperature superconducting systems and the processes for making same.

A variety of high temperature superconducting systems have been developed. Such superconducting systems include: Y—Ba—Cu—O; Bi—Sr—Ca—Cu—O; Tl—Ba—Cu—O; and Tl—Ba—Ca—Cu—O. A number of such systems are set forth in pending patent applications of which one of the inventors of the present invention is a coinventor.

For example, U.S. Pat. No. 4,962,083 discloses Tl—Ba—Ca—Cu—O superconductors and processes for making same. Additionally, that application discloses TlSrBaCuO superconductors and processes for making same. U.S. Pat. No. 4,994,432 discloses TlBaCuO superconductors and processes for making same. U.S. Pat. No. 5,036,044 discloses RTlSrCaCuO superconductors and process for making same, wherein R is a rare earth metal. U.S. Pat. No. 5,164,362 discloses TlSrCaCuO superconductors and processes for making same.

Despite the existence of known superconducting systems, and the fact that the above-identified patent applications provide superconductors and methods for making same, new superconducting systems are desirable for several reasons. A new system could provide a basis for the discovery of higher-temperature superconductors. In turn, higher-temperature superconductors could provide low cost processing and manufacturing.

SUMMARY OF THE INVENTION

The present invention provides a composition having superconductive properties comprising M—R—Tl—Sr—Cu—O, wherein R represents rare earth metals and M is at least one compound selected from the group consisting of Hg, Pb, K, and Al.

In an embodiment, the present invention provides a composition having superconductive properties at a temperature of approximately 93K comprising M—R—Tl—Sr—Cu—O wherein:

R is selected from the rare earth metals; and

M is selected from the group consisting of Hg and Al.

In another embodiment, the present invention provides a composition having a Tc of at least approximately 93K to approximately 100K. The composition comprising M—R—Tl—Sr—Cu—O wherein:

R is Pr; and

M is at least one element selected from the group consisting of Pb and K.

In an embodiment, the invention provides a material having superconductive properties having the nominal composition $HgPr_2Tl_2Sr_2Cu_3O_{12}$.

In an embodiment, the invention provides a material having superconductive properties having the nominal composition $HgPr_2Tl_2Sr_2Cu_3O_{13}$.

In an embodiment, the invention provides a material having superconductive properties having the nominal composition $Pb_{0.5}Pr_2Tl_2Sr_3Cu_3O_{13}$.

In an embodiment, the invention provides a material having superconductive properties having the nominal composition $KPb_{0.5}Pr_2Tl_2Sr_3Cu_3O_{13}$.

In a further embodiment, the present invention provides a method of preparing the high-temperature superconductors. The method includes the steps of: mixing together the components of the composition; and heating the mixture.

In an embodiment, the mixture is heated at a temperature of approximately 1000° C. for about 5 minutes in flowing oxygen.

In an embodiment, the mixture is pressed into a pellet prior to being heated.

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

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates resistance versus temperature for a nominal $Pr_2Tl_2Sr_2Cu_3O_{11}$ sample (designated "A") and for a nominal $HgPr_2Tl_2Sr_2Cu_3O_{12}$ sample (designated "B"). Both samples were prepared at 925° C.

FIG. **2** illustrates resistance versus temperature for two nominal $HgPr_2Tl_2Sr_3Cu_3O_{13}$ samples (designated "C" and "D"). Both samples were prepared at 1000° C.

FIG. **3** illustrates resistance versus temperature for two Pb-doping samples with a nominal composition of $Pb_{0.5}Pr_2Tl_2Sr_3Cu_3O_{13}$.

FIG. **4** illustrates resistance versus temperature for a nominal $KPb_{0.5}Pr_2Tl_2Sr_3Cu_3O_{13}$ sample.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

The present invention provides new high-temperature superconductors and the processes for making them. To this end, the present invention provides a composition having super-conductive properties comprising the elements:

M—R—Tl—Sr—Cu—O

wherein:

M is at least one compound selected from the group consisting of Hg, Pb, K, and Al; and

R is selected from the group consisting of rare earth metals.

In an embodiment, R is Pr. In a further embodiment, R is Pr and M is Pb and/or K.

The inventors of the present invention have found that particular elemental dopings with Hg, Al, Pb, and/or K into a Pr— Tl—Sr—Cu—O system results in a compound having a higher Tc. Specifically, Hg- or Al-doping produced a 93K superconducting phase, while Pb- or K-doping increased the temperature from 93K to 100K.

The present invention also provides methods for preparing high-temperature superconductors. Pursuant to the present invention, samples are prepared by mixing the components and heating the mixture in flowing oxygen. For example, compounds selected from the group consisting of HgO, Al_2O_3, PbO_2, KO_2, RE_2O_3 (RE=rare earths), Tl_2O_3, SrO or $Sr(NO_3)_2$, and CuO can be mixed to achieve the desired composition.

In an embodiment of the procedure, the components are completely mixed, ground, and pressed into a pellet having a diameter of 7 mm and a thickness of 1–2 mm. The pellet is then heated in a tube furnace at a temperature of approximately 1000° C. for about 5 minutes in flowing oxygen. The pellet can then be subjected to furnace-cooling or quenching.

By way of example, and not limitation, examples of the superconducting composition and processes for making them are set forth below. For analyzing the resultant compositions created in the examples, resistance (ac, 27 Hz) was measured by a standard four-probe technique with silver paste contacts. All measurements were performed in a commercial APD refrigerator with computer control and processing.

EXAMPLE 1

A nominal $Pr_2Tl_2Sr_2Cu_3O_{11}$ Sample (A) and a nominal $HgPr_2Tl_2Sr_2Cu_3O_{12}$ Sample (B) were prepared according to the above method. The pellet was heated in a tube furnace at approximately 925° C.

FIG. **1** illustrates the resistance-temperature dependence for Sample A and Sample B. While Sample A had an onset temperature of 45K, Sample B exhibited a two-step transition at 88K and 43K, respectively. These results indicate that the addition of HgO facilitated the formation of a new superconducting phase with higher temperatures (approximately 90K). As set forth in Example 2, the superconducting behavior of the Hg—Pr—Tl—Sr—Cu— O samples was further enhanced by increasing the preparation temperature.

EXAMPLE 2

Two nominal $HgPr_2Tl_2Sr_3Cu_3O_{13}$ Samples (C and D) were prepared at a higher temperature, by the method previously described, except that the temperature of the furnace was heated to approximately 1000° C. Sample C was then furnace-cooled to 700° C. and remained at this temperature for 6 minutes. Sample D, on the other hand, was then furnace-cooled to room temperature.

As illustrated in FIG. **2**, Sample C exhibited a semimetallic resistance-temperature behavior at the normal state. It had an onset temperature of 93K, and a zero-resistance temperature of 40K. Sample D had a similar onset temperature to Sample C, but reached zero-resistance at a much higher temperature (78K). Although not illustrated, Al-doping samples also exhibited a superconducting behavior similar to the Hg-doping samples.

The results suggest to the inventors that: 1) either Hg or Al does not form a lattice in the superconducting phase, but only promotes the formation of the 93K superconducting phase; or 2) Hg or Al enters into the lattice but does not influence the conductivity temperature.

EXAMPLE 3

Pb-doping Pr—Tl—Sr—Cu—O samples exhibited different superconducting behavior as compared to the other doping elements.

FIG. **3** illustrates resistance-temperature dependence for two Pb-doping samples (Pb1 and Pb2), consisting of a nominal composition of $Pb_{0.5}Pr_2Tl_2Sr_3Cu_3O_{13}$. The samples were prepared using the method previously described.

As depicted in FIG. **3**, both samples demonstrated a two-step superconducting transition at approximately 100K and 45K. The superconductivity at about 100K in these Ca-free samples was reproducible. Further, this onset temperature of around 100K was higher than other doping elements. This 100K superconducting transition was also observed in K-added Pb samples (K—Pb—R—Tl—Sr—Cu—O) as illustrated in FIG. **4**.

Compared with the Pr—Tl—Sr—Cu—O sample system, Pb (or Pb, K)-doping Pr—Tl—Sr—Cu—O samples do exhibit a higher superconducting temperature (about 100K). The inventors believe that these results indicate that Pb has entered the lattice structure of the superconducting phase, and has changed the superconducting behavior of the samples. Further, the Pb-doped Pr—Tl—Sr—Cu—O samples did not contain calcium as do other superconductors with conductivity temperatures at about 100K. Accordingly, the Pb—Pr—Tl—Sr—Cu—O system may be the first Ca-free superconducting system with reproducible temperatures of about 100K.

The results also indicate that higher temperature superconductivity for Pb- and/or K-doping systems may be achieved by optimizing initial compositions and preparation conditions. Moreover, further elemental substitutions in these systems may lead to higher superconducting temperatures.

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 superconducting composition comprising a composition having the nominal composition $Pb_{0.5}Pr_2Tl_2Sr_3Cu_3O_{13}$, said composition having a superconducting phase having an onset temperature of at least about 90° K.

2. A superconducting composition comprising: a composition having the nominal formula:

$$HgPr_2Tl_2Sr_2Cu_3O_{12},$$

said composition having an onset temperature of at least about 90° K. and exhibiting a two-step superconducting transition at about 88° K. and about 43° K., respectively.

* * * * *