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## 90 K TI-Ba-Ce-Cu-O superconductor and processes for making same

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# United States Patent [19]

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[54] **90 K TL-BA-CE-CU-O SUPERCONDUCTOR AND PROCESSES FOR MAKING SAME**

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[21] Appl. No.: **782,868**

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### Related U.S. Application Data

[63] Continuation of Ser. No. 484,844, Feb. 26, 1990, abandoned.

[51] Int. Cl.<sup>5</sup> ..... **C04B 41/89; H01L 39/12**

[52] U.S. Cl. .... **505/1; 505/783; 501/123; 501/152; 252/518; 252/521**

[58] Field of Search ..... **505/783, 1; 501/123, 501/152; 252/518, 521**

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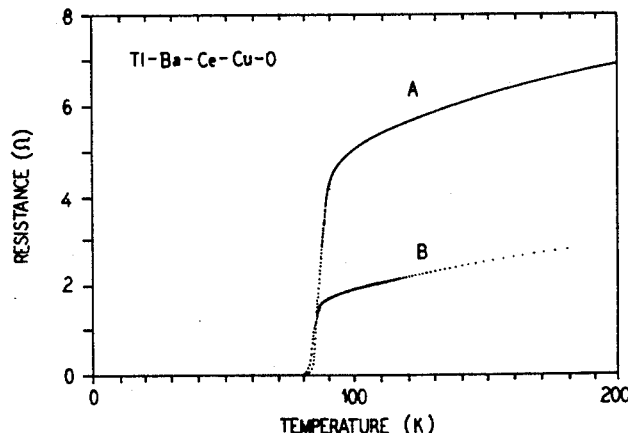
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### [57] ABSTRACT

A high temperature superconductor system having the nominal composition: Tl-Ba-Ce-Cu-O. The high temperature superconductor of the present invention has a transition temperature of about 90 K. Processes for making the high temperature superconductor are also provided.

**19 Claims, 4 Drawing Sheets**



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FIG.1

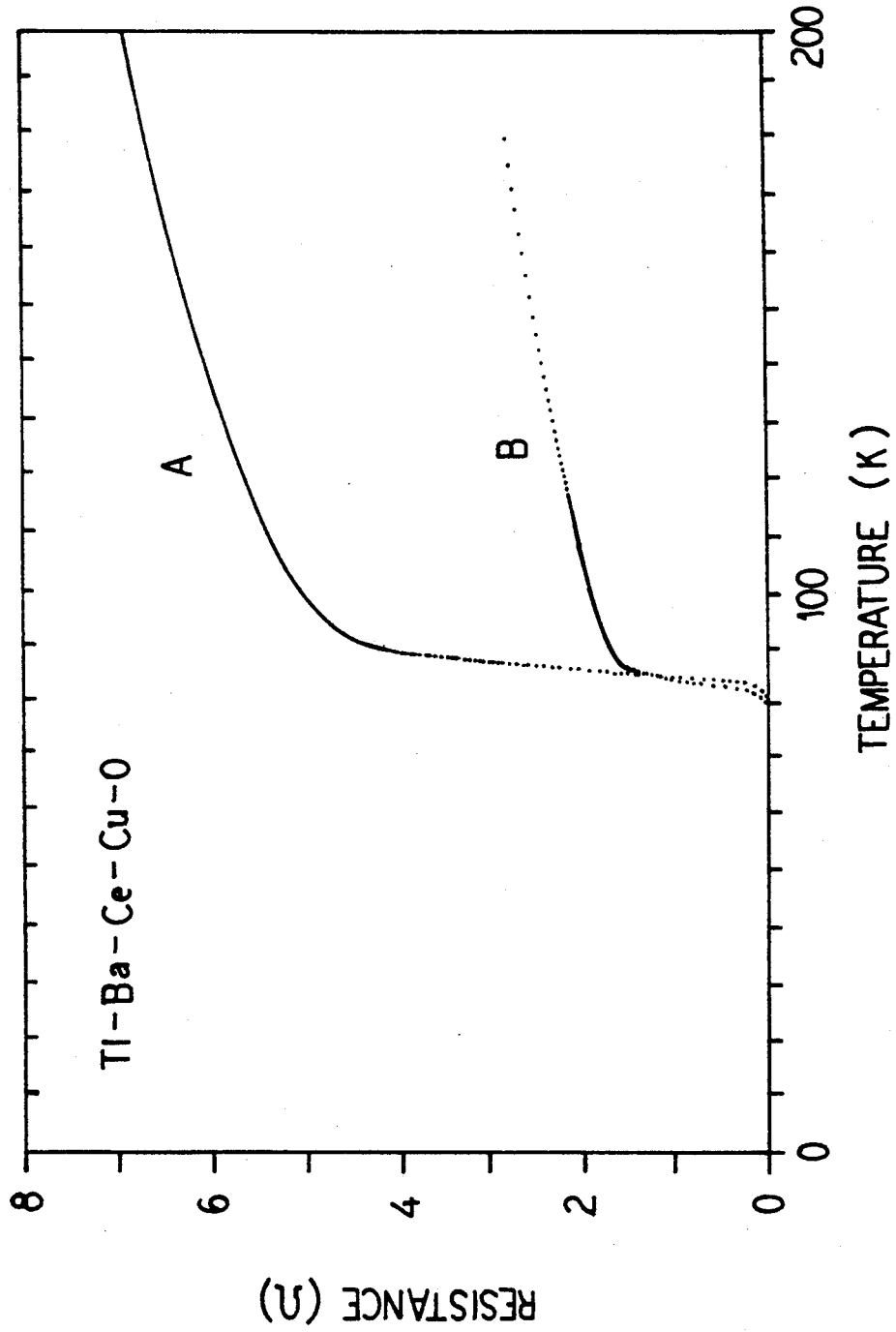


FIG. 2

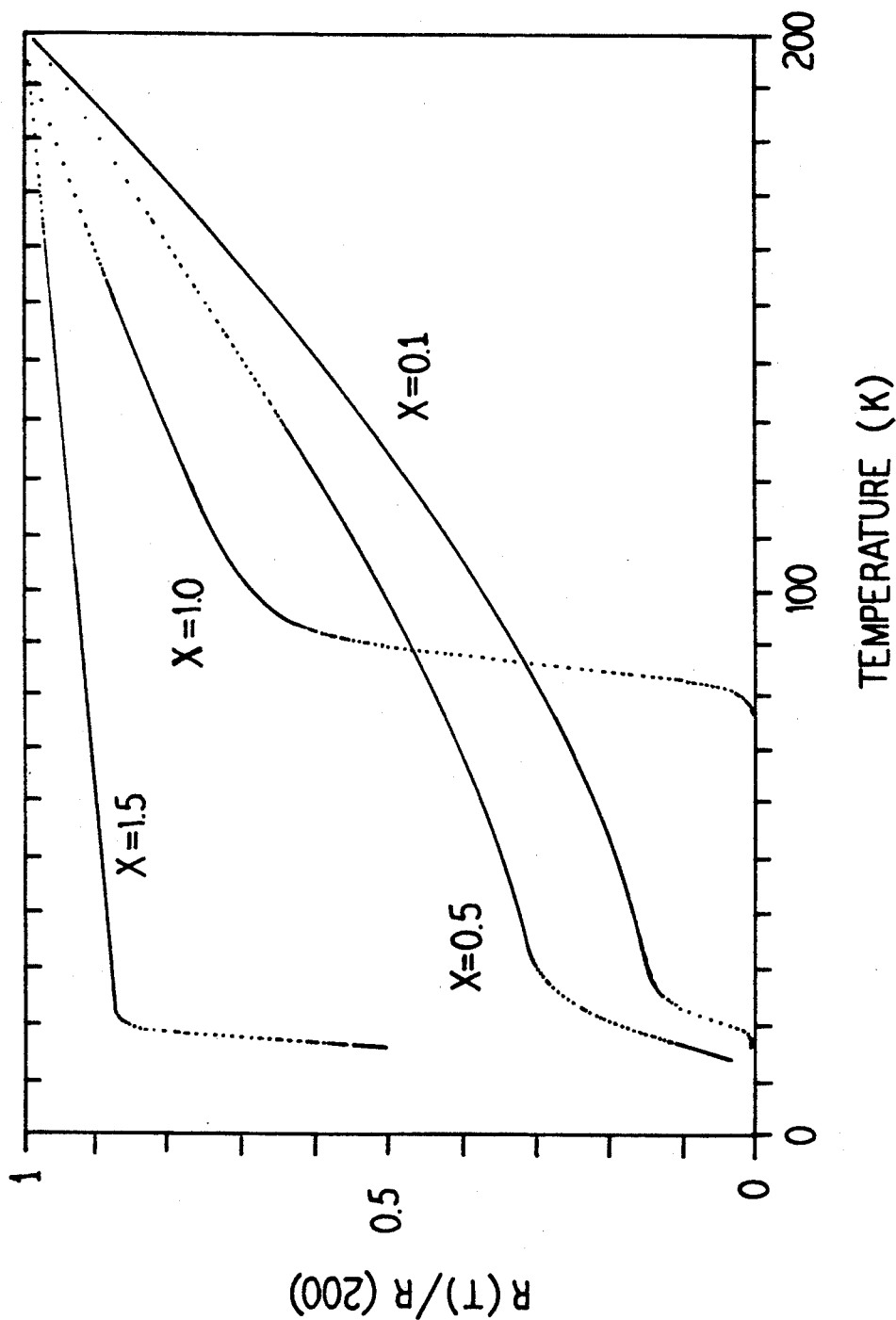


FIG. 3

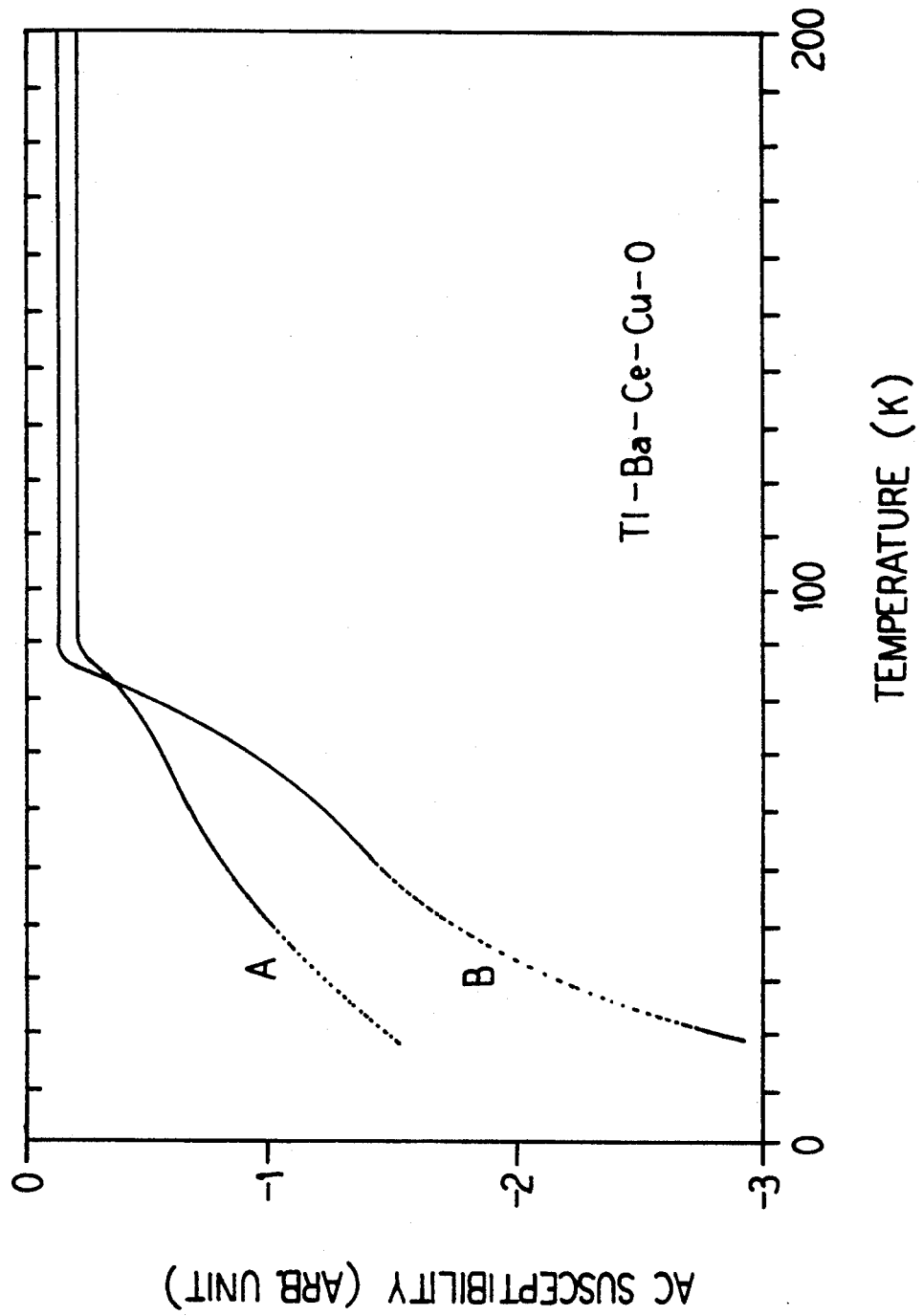
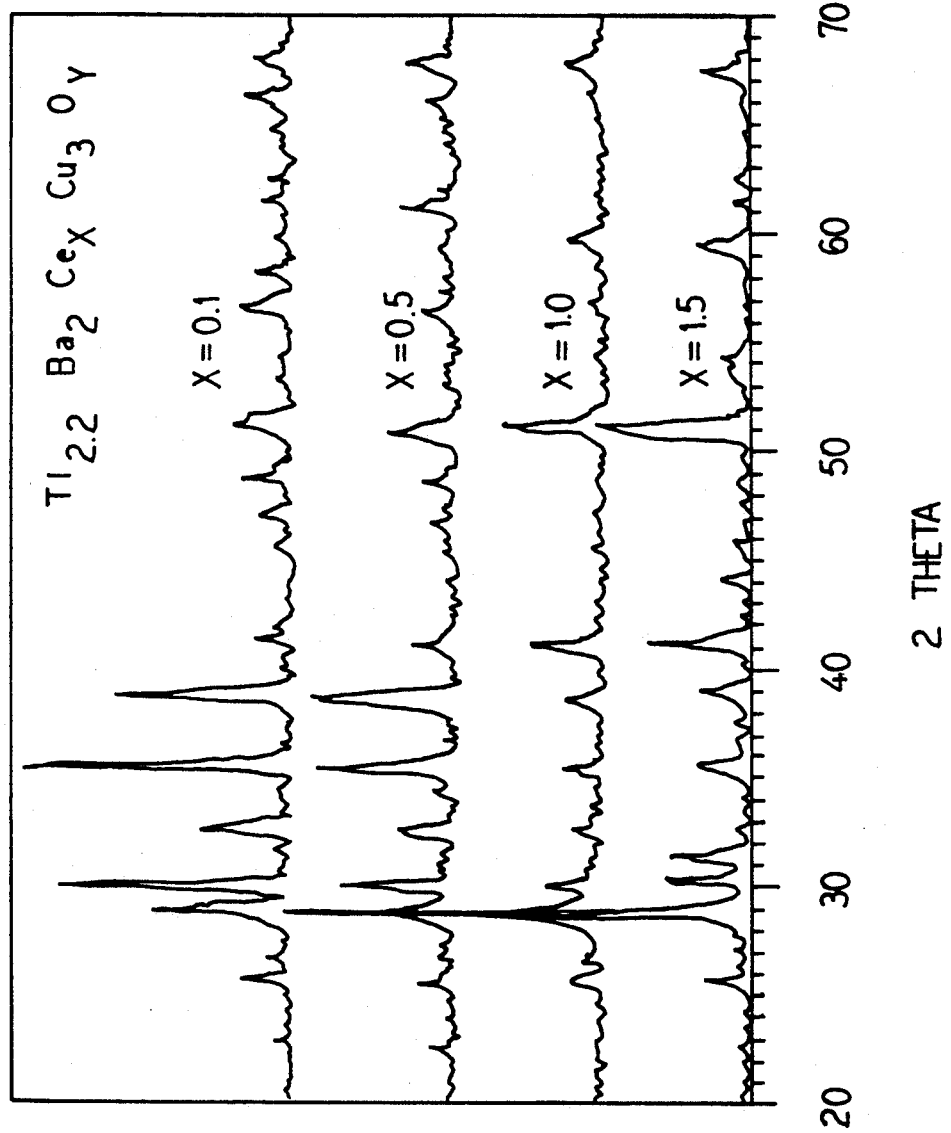


FIG.4





## 90 K Tl-Ba-Ce-Cu-O SUPERCONDUCTOR AND PROCESSES FOR MAKING SAME

This is a continuation of application Ser. No. 484,844, filed Feb. 26, 1990, now abandoned.

### BACKGROUND OF THE INVENTION

The present invention relates generally to high temperature superconductors. More specifically, the present invention relates to Tl-Ba-Ce-Cu-O superconductors and processes for making same.

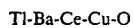
Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O superconducting systems have been identified. U.S. patent application Ser. No. 144,114 and Ser. No. 155,247, now U.S. Pat. No. 4,962,083, issued Oct. 9, 1990 filed in the name of Hermann and Sheng, two of the three inventors of the present invention, disclose, in part, Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O superconductor systems. The discovery of the Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O superconducting systems has led to the identification of a number of Tl-based superconducting compounds, including the series  $Tl_mBa_2Ca_{n-1}Cu_nO_{1.5m+2n+1}$ , wherein  $m=1-2$  and  $n=1-5$ .

One of the phases of the Tl-Ba-Ca-Cu-O system that has been identified is the  $Tl_2Ba_2Ca_2Cu_3O_{10}$  superconductor phase. This phase has a transition temperature of 125 K., which transition temperature, the inventors of the present invention believe, is the highest to date among existing high temperature superconductors.

The presently known phases of such high  $T_c$  superconductors have a tetragonal structure and are p-type. These superconductive phases are also anisotropic. If a new superconductor system was discovered that had a different structure, it could be used for several special applications.

### SUMMARY OF THE INVENTION

The present invention provides a new superconductor system and method for making same. To this end, the present invention provides a high temperature superconductive system containing thallium (Tl), barium (Ba), cerium (Ce), copper (Cu), and oxygen (O):



In a preferred embodiment of the present invention, the superconductive system of the present invention has the following approximate stoichiometry:



wherein:

$$\begin{aligned} 1.1 &\leq a \leq 2.2; \\ 1.8 &\leq b \leq 2.2; \\ 0.5 &< c < 1.5 \\ 1.1 &\leq d \leq 4; \text{ and} \\ 5.55 &< e < 12.5. \end{aligned}$$

In an embodiment of the present invention, the superconductor has a nominal composition of  $Tl_{2.2}Ba_2CeCu_3O_{10.3}$  and is superconducting at 90 K.

A method of producing the high temperature superconductors is also provided. The method of the present invention allows the superconductor to be prepared at temperatures of approximately 900° to about 925° C. in flowing oxygen. Accordingly, the method of the present invention allows the superconductor to be formed at relatively low temperatures. Furthermore, the method of the present invention allows the superconductor to

be produced rapidly, in that it need only be heated for approximately 3 to about 5 minutes.

Accordingly, it is an advantage of the present invention to provide a new superconductor composition.

It is a further advantage of the present invention to provide a new method for making superconductors.

Additional advantages and features of the present invention are described in, 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 a graph of resistance verses temperature of two nominal  $Tl_{2.2}Ba_2CeCu_3O_{10.3}$  samples of the present invention.

FIG. 2 illustrates a graph of  $R(T)/R(200)$  as a function of temperature for nominal  $Tl_{2.2}Ba_2Ce_xCu_3O_y$  samples of the present invention, wherein  $x=0.1, 0.5, 1.0$  and  $1.5$ .

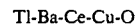
FIG. 3 illustrates a graph of the ac susceptibility as a function of temperature for two nominal  $Tl_{2.2}Ba_2CeCu_3O_{10.3}$  samples of the present invention.

FIG. 4 illustrates the powder x-ray diffraction patterns of nominal  $Tl_{2.2}Ba_2Ce_xCu_3O_y$  samples of the present invention, wherein  $x=0.1, 0.5, 1.0$  and  $1.5$ .

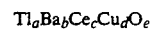
### DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENT

The present invention provides a new high temperature superconductor system and method of making same. As used herein, the term "high temperature" refers to a temperature above the boiling point of liquid nitrogen.

The superconductor system of the present invention has the following general formula:



In an preferred embodiment of the present invention, a superconductor constructed from the new superconductive system of the present invention has the following approximate stoichiometry:



wherein:

$$\begin{aligned} 1.1 &\leq a \leq 2.2; \\ 1.8 &\leq b \leq 2.2; \\ 0.5 &< c < 1.5 \\ 1.1 &\leq d \leq 4; \text{ and} \\ 5.55 &< e < 12.5. \end{aligned}$$

The  $TlBaCeCuO$  system is superconducting at 90 K.

In an embodiment, the superconductor composition of the present invention has a nominal composition  $Tl_{2.2}Ba_2CeCu_3O_{10.3}$ .

By the way of example and not limitation, examples of the new high temperature Tl-Ba-Ce-Cu-O superconductor of the present invention, and method of making same, will now be set forth.

### EXAMPLE

A. The following reagents were utilized:

1.  $Tl_2O_3$ ,
2.  $BaO_2$ ,
3.  $CeO_2$ ,
4.  $CuO$ .

B. The following procedure was followed:

1.  $Tl_2O_3$ ,  $BaO_2$ ,  $CeO_2$ , and  $CuO$  were completely mixed in a molar ratio of 1.1:2:1:3.
2. The mixture was then completely ground and pressed into a pellet having a diameter of 7 mm and a thickness of approximately 1 to about 2 mm.
3. The pellet was placed in an alumina crucible.
4. The crucible and its content were placed into a tube furnace which had been heated to a temperature of approximately  $900^\circ$  to about  $925^\circ$  C. The crucible and its content were then heated in flowing oxygen for approximately 3 to about 5 minutes.
5. The crucible and its content were then furnace cooled.

Nominal  $Tl_{2.2}Ba_2CeCu_3O_{10.3}$  samples prepared using this procedure, proved to be superconducting at 90 K. The samples had a dark grey color and were dense. The superconducting behavior of the samples was sensitive to both heating temperature and heating duration. Quenching of the samples depressed  $T_c$  only slightly.

FIG. 1 illustrates graphically resistance verses temperature for two nominal  $Tl_{2.2}Ba_2CeCu_3O_{10.3}$  samples made pursuant to the procedure of this example. The two samples were made in different batches. The resistance was measured by a standard four-probe technique with silver paste contacts. Both resistance and ac susceptibility data were taken in a commercial ADP closed-cycle refrigerator with computer-control and processing.

As illustrated in FIG. 1, sample A had an onset temperature of 95 K., a mid-point temperature of 88 K., and a zero resistance temperature of 83 K. Sample B had an onset temperature of 90 K., a mid-point temperature of 85 K. and a zero resistance temperature of 80 K.

FIG. 2 illustrates graphically  $R(T)/R(200)$  as a function of temperature for a series of samples with a starting composition of  $Tl_{2.2}Ba_2Ce_xCu_3O_y$ , where  $x=0.1, 0.5, 1.0$  and  $1.5$ . As illustrated in FIG. 2, the samples with a value of  $x=0.1, 0.5$ , and  $1.5$  all had a  $T_c$  of about 20 K. As illustrated, only the sample with the intermediate value of  $x=1.0$  was superconducting at 90 K. Therefore, the formation of a 90 K. superconducting phase of Tl-Ba-Ce-Cu-O has a strong dependence on the Ce concentration.

FIG. 3 illustrates graphically ac susceptibility verses temperature of the samples of FIG. 1. As the figure illustrates, the samples exhibit a diamagnetism onset at about 90 K., which is consistent with their superconducting transition temperatures measured resistively. The ac susceptibility signal decreases with decreasing temperature and does not saturate down to 15 K. In the present example, the signal at 15 K. was about 10-20% of that of a good quality Tl-Ba-Ca-Cu-O sample. Thermoelectric power determinations, from room temperature down to near the superconducting transition temperature, show n-type behavior for the sample of this example.

A powder x-ray diffraction analysis was used to attempt to identify the phase responsible for the 90 K. superconductivity. The powder x-ray diffraction was done for a number of Tl-Ba-Ce-Cu-O samples and a number of related samples. Powder x-ray diffraction studies were performed with  $Cu K\alpha$  and radiation with the use of a DIANO DTM 1057 diffractometer. FIG. 4 illustrates the powder x-ray diffraction patterns for the samples of FIG. 2.

In general, the diffraction patterns of the Tl-Ba-Ce-Cu-O samples can be assigned to one of three phases: unreacted  $CuO$ ; tetragonal  $Tl_2Ba_2CuO_6$ ; and an un-

known phase. In FIG. 4, the diffraction pattern of the unknown phase can be indexed to a cubic structure with lattice parameter of 4.400 A, which is very close to the lattice parameter of 4.386 A of the cubic  $BaCeO_3$ . This is omitting the  $2\theta=25^\circ$  peak in the figure.

If the  $28.7^\circ$  peak is assigned to the unidentified phase and assuming that the  $30.0^\circ$  peak represents the tetragonal,  $Tl_2Ba_2CuO_6$ , the ratios of the unidentified phase to the  $Tl_2Ba_2CuO_6$  phase are 0.5 for  $x=0.1$ , 1.5 for  $x=0.5$ , 5 for  $x=1.0$ , and 6 for  $x=1.5$ , respectively.

All four samples consist primarily of the two phases, but only the sample with  $x=1.0$  is superconducting at 90 K. The inventors believe that if the  $Tl_2Ba_2CuO_6$  phase is responsible for the 90K superconductivity, it, most probably, has been doped by Ce, and if the unidentified phase is responsible for the 90K superconductivity, it must consist of all four metallic elements, Tl, Ba, Ce, and Cu.

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 superconductor having the composition:



2. A superconductor having the following approximate stoichiometry:



wherein:

- $$1.1 \leq a \leq 2.2;$$
- $$1.8 \leq b \leq 2.2;$$
- $$0.5 < c < 1.5$$
- $$1.1 \leq d \leq 4; \text{ and}$$
- $$5.55 < e < 12.5.$$

3. A composition that is superconducting at 90 K. having the following approximate nominal stoichiometry:



4. A high temperature superconducting material including a  $Tl_2Ba_2CuO_6$  phase that has been doped by Ce.

5. A superconductor having the general formula  $TlBaCeCuO$  and a tetragonal  $Tl_2Ba_2CuO_6$  phase.

6. A method for making a high temperature superconductor comprising the steps of:

- a) mixing  $Tl_2O_3$ ,  $BaO_2$ ,  $CeO_2$ , and  $CuO$ ;
- b) heating the mixture in flowing  $O_2$ ; and
- c) cooling the mixture.

7. The method of claim 6 wherein  $Tl_2O_3$ ,  $BaO_2$ ,  $CeO_2$ , and  $CuO$  are mixed in a molar ratio of 1.1:2:1:3.

8. The method of claim 6 wherein the mixture is heated to a temperature of approximately  $900^\circ$  to about  $925^\circ$  C.

9. The method of claim 6 wherein the mixture, prior to being heated, is pressed into a pellet.

10. The method of claim 9 wherein the pellet is heated to a temperature of approximately  $900^\circ$  to about  $925^\circ$  C.

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11. The method of claim 8 wherein the pellet is heated in a tube furnace and flowing oxygen at a temperature of approximately 900° to about 925° C.

12. The method of claim 8 wherein the pellet is heated in flowing O<sub>2</sub> for approximately 3 to about 5 minutes.

13. The method of claim 8 wherein the pellet is furnace cooled.

14. A method for making a high temperature superconductor including a Tl<sub>2</sub>Ba<sub>2</sub>CuO<sub>6</sub> phase comprising the steps of:

heating a TlBaCeCuO mixture in flowing oxygen.

5 15. The method of claim 14 wherein the TlBaCeCuO mixture is created by mixing Tl<sub>2</sub>O<sub>3</sub>, BaO<sub>2</sub>, CeO<sub>2</sub>, and CuO.

16. The method of claim 14 wherein the mixture is heated to approximately 900° to about 925° C.

10 17. The product of the process of claim 6.

18. The product of the process of claim 14.

19. The product of the process of claim 15.

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