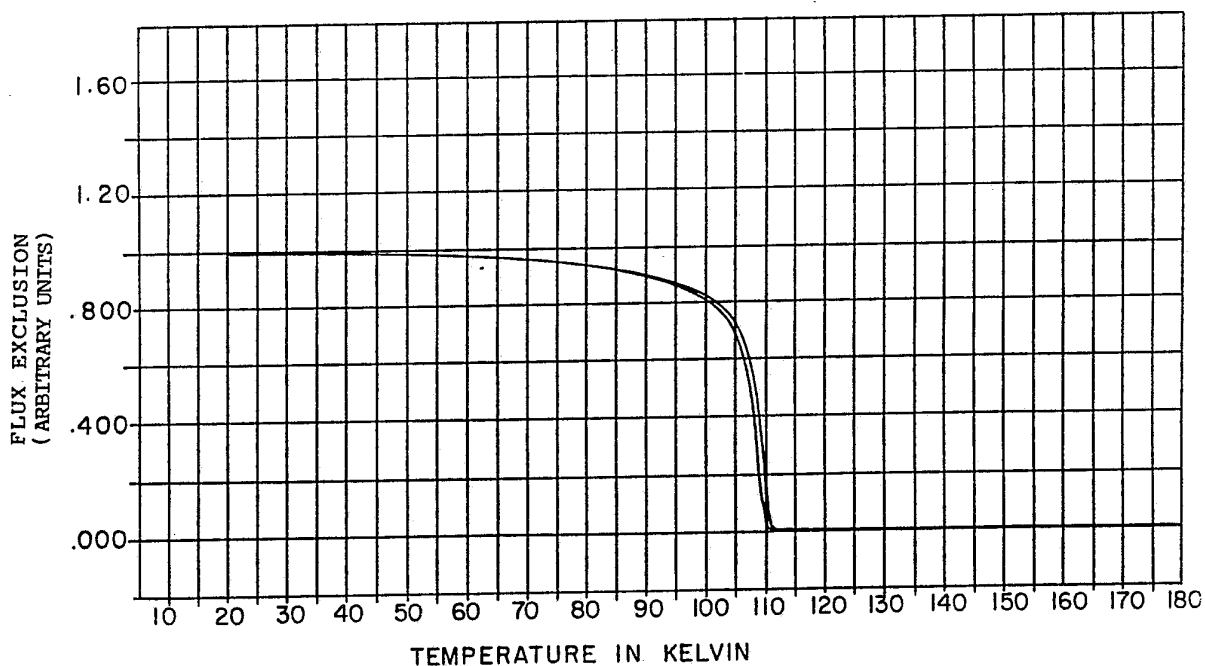




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(54) Title: SUPERCONDUCTING METAL OXIDE COMPOSITIONS AND PROCESSES FOR MANUFACTURE AND USE

**(57) Abstract**

Compositions having the nominal formula $T_e Pb_a Ca_b Sr_c Cu_d O_x$ wherein a is from about 1/10 to 3/2, b is from about 1 to 4, c is from about 1 to 3, d is from about 1 to 5, e is from about 3/10 to 1, $x = (a + b + c + d + e + y)$ where y is from about 1/2 to 3, are superconducting. Processes for manufacturing such compositions and for using them are disclosed.

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TITLESUPERCONDUCTING METAL OXIDE COMPOSITIONS
AND PROCESSES FOR MANUFACTURE AND USEBACKGROUND OF THE INVENTIONCross Reference to Related Application

This application is a continuation-in-part of U. S. Patent Application Serial No. 07/230,631 (Docket No. CR-8679) filed August 10, 1988.

Field of the Invention

This invention relates to novel Tl-Pb-Ca-Sr-Cu-O compositions which are superconducting.

References

Bednorz and Muller, Z. Phys. B64, 189 (1986), disclose a superconducting phase in the La-Ba-Cu-O system with a superconducting transition temperature of about 35 K. This disclosure was subsequently confirmed by a number of investigators [see, for example, Rao and Ganguly, Current Science, 56, 47 (1987), Chu et al., Science 235, 567 (1987), Chu et al., Phys. Rev. Lett. 58, 405 (1987), Cava et al., Phys. Rev. Lett. 58, 408 (1987), Bednorz et al., Europhys. Lett. 3, 379 (1987)]. The superconducting phase has been identified as the composition $\text{La}_{1-x}(\text{Ba}, \text{Sr}, \text{Ca})_x \text{CuO}_{4-y}$ with the tetragonal K_2NiF_4 -type structure and with x typically about 0.15 and y indicating oxygen vacancies.

Wu et al., Phys. Rev. Lett. 58, 908 (1987), disclose a superconducting phase in the Y-Ba-Cu-O system with a superconducting transition temperature of about 90 K. Cava et al., Phys. Rev. Lett. 58, 1676 (1987), have identified this superconducting Y-Ba-Cu-O phase to be orthorhombic, distorted, oxygen-deficient perovskite $YBa_2Cu_3O_{9-\delta}$, where δ is about 2.1 and present the powder x-ray diffraction pattern and lattice parameters.

C. Michel et al., Z. Phys. B - Condensed Matter 68, 421 (1987), disclose a novel family of superconducting oxides in the Bi-Sr-Cu-O system with composition close to $Bi_2Sr_2Cu_2O_{7+\delta}$. A pure phase was isolated for the composition $Bi_2Sr_2Cu_2O_{7+\delta}$. The X-ray diffraction pattern for this material exhibits some similarity with that of perovskite and the electron diffraction pattern shows the perovskite subcell with the orthorhombic cell parameters of $a = 5.32 \text{ \AA}$ (0.532 nm), $b = 26.6 \text{ \AA}$ (2.66 nm) and $c = 48.8 \text{ \AA}$ (4.88 nm). The material made from ultrapure oxides has a superconducting transition with a midpoint of 22 K as determined from resistivity measurements and zero resistance below 14 K. The material made from commercial grade oxides has a superconducting transition with a midpoint of 7 K.

H. Maeda et al., Jpn. J. Appl. Phys. 27, L209 (1988), disclose a superconducting oxide in the Bi-Sr-Ca-Cu-O system with the composition near $BiSrCaCu_2O_x$ and a superconducting transition temperature of about 105 K.

The commonly assigned application, "Superconducting Metal Oxide Compositions and Process For Making Them", S. N. 153,107, filed

Feb. 8, 1988, a continuation-in-part of S. N. 152,186, filed Feb. 4, 1988, disclose superconducting compositions having the nominal formula $\text{Bi}_a\text{Sr}_b\text{Ca}_c\text{Cu}_3\text{O}_x$ wherein a is from about 1 to about 3, b is from about $3/8$ to about 4, c is from about $3/16$ to about 2 and $x = (1.5a + b + c + y)$ where y is from about 2 to about 5, with the proviso that $b + c$ is from about $3/2$ to about 5, said compositions having superconducting transition temperatures of about 70 K or higher. It also discloses the superconducting metal oxide phase having the formula $\text{Bi}_2\text{Sr}_{3-z}\text{Ca}_z\text{Cu}_2\text{O}_{8+w}$ wherein z is from about 0.1 to about 0.9, preferably 0.4 to 0.8 and w is greater than zero but less than about 1. M. A. Subramanian et al., Science 239, 1015 (1988) also disclose the $\text{Bi}_2\text{Sr}_{3-z}\text{Ca}_z\text{Cu}_2\text{O}_{8+w}$ superconductor.

Y. Yumada et al., Jpn. J. Appl. Phys. 27, L996 (1988), disclose the substitution of Pb for Bi in the series $\text{Bi}_{1-x}\text{Pb}_x\text{SrCaCu}_2\text{O}_y$ where $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1.0. The T_c increases from 75.5 K for $x = 0$, no Pb present, to a maximum of 85.5 K for $x = 0.5$. T_c decreases for higher Pb content to 76 K for $x = 0.7$. No superconductivity was observed for the samples with $x = 0.9$ and $x = 1$.

M. Takano et al., Jpn. J. Appl. Phys. 27, L1041 (1988), disclose that partial substitution of Pb for Bi in the Bi-Sr-Ca-Cu-O system results in an increase in the volume fraction of the high T_c phase. Coprecipitated oxalates containing the relevant ions in various ratios underwent thermal decomposition below 773 K. The samples in powder form were then heated in air to 1073 K for 12 hours and, after being formed into pellets, at 1118 K for various

periods which extended to more than 240 hours in some cases. A starting composition of Bi:Pb:Sr:Ca:Cu = 0.7:0.3:1:1:1:8 was heated at 1118 K for 244 hours. The high- T_c phase shows an onset of superconductivity at around 115 K. This phase forms plate-like crystals and analysis of these crystals indicates that the cationic ratio is Bi:Pb:Sr:Ca:Cu = 67:5:100:85:180 so that there is considerably less Pb in the high- T_c than in the starting material.

M. Mizuno et al., Jpn. J. Appl. Phys. 27, L1225 (1988), also disclose that the addition of Pb to the Bi-Sr-Ca-Cu-O system results in an increase in the volume fraction of the high- T_c phase and a lowering of the optimum temperature to obtain this phase to about 855°C.

E. V. Sampathkumaran et al., J. Phys. F: Met. Phys. 18, L163 (1988) disclose that the partial substitution of K or Pb for Bi in the $\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_4$ results in an enhancement of the fraction of the phase superconducting at about 110 K.

Z. Z. Sheng et al., Nature 332, 55 (1988) disclose superconductivity in the Tl-Ba-Cu-O system in samples which have nominal compositions $\text{Tl}_2\text{Ba}_2\text{Cu}_3\text{O}_{8+x}$ and $\text{TlBaCu}_3\text{O}_{5.5+x}$. Both samples are reported to have onset temperatures above 90 K and zero resistance at 81 K. The samples were prepared by mixing and grinding appropriate amounts of BaCO_3 and CuO with an agate mortar and pestle. This mixture was heated in air at 925°C for more than 24 hours with several intermediate grindings to obtain a uniform black oxide Ba-Cu oxide powder which was mixed with an appropriate amount of Tl_2O_3 , completely ground and pressed into a pellet with

a diameter of 7 mm and a thickness of 1-2 mm. The pellet was then put into a tube furnace which had been heated to 880-910°C and was heated for 2-5 minutes in flowing oxygen. As soon as it had slightly melted, the sample was taken from the furnace and quenched in air to room temperature. It was noted by visual inspection that Tl_2O_3 had partially volatilized as black smoke, part had become a light yellow liquid, and part had reacted with Ba-Cu oxide forming a black, partially melted, porous material.

Z. Z. Sheng et al., Nature 332, 138 (1988) disclose superconductivity in the Tl-Ca-Ba-Cu-O system in samples which have nominal compositions $Tl_2Ca_2BaCu_3O_{9+x}$.

R. M. Hazen et al., Phys. Rev. Lett. 60, 1657 (1988), disclose two superconducting phases in the Tl-Ba-Ca-Cu-O system, $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Tl_2Ba_2CaCu_2O_8$.

SUMMARY OF THE INVENTION

This invention provides novel superconducting compositions having the nominal formula $Tl_aPb_bCa_cSr_dCu_eO_x$ wherein a is from about 1/10 to about 3/2, b is from about 1 to about 4, c is from about 1 to about 3, d is from about 1 to about 5, e is from about 3/10 to about 1 and $x = (a + b + c + d + e + y)$ where y is from about 1/2 to about 3. Preferably, the sum of a+e is about 1, b is about 2, c is about 2, d is from about 3 to about 4 and y is from about 1/2 to about 2. The onset of superconductivity for these compositions is at least 70 K.

This invention includes novel superconducting compositions having the nominal formula $TlPb_aCa_bSr_cCu_dO_x$ wherein a is from about

1/2 to about 3/2, b is from about 1 to about 4, c is from about 1 to about 3, d is from about 1 to about 5 and $x = (a + b + c + d + y)$ where y is from about 1/2 to about 3. Preferably, a is about 1, b is from about 1 to about 2, c is about 1, d is from about 3 to about 4 and y is from about 1/2 to about 2. The onset of superconductivity for these compositions is at least 70 K.

These superconducting compositions are prepared by heating a mixture of the Tl, Pb, Ca, Sr and Cu oxides, the relative amounts chosen so that the atomic ratio Tl:Pb:Ca:Sr:Cu is e:a:b:c:d, at a temperature of about 850°C to about 940°C, preferably about 860°C to about 925°C, for about 3 to 12 hours in a confined atmosphere, e. g., in a sealed tube made of a non-reacting metal such as gold which prevents any of the reactants including the metals and oxygen from escaping.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a plot of the flux excluded by a composition of this invention as a function of temperature.

DETAILED DESCRIPTION OF THE INVENTION

The superconducting compositions of this invention are prepared by the following process. Quantities of the oxide reactants Tl_2O_3 , PbO_2 , CaO_2 , SrO_2 , and CuO are chosen with the atomic ratio of Tl:Pb:Ca:Sr:Cu of e:a:b:c:d wherein a is from about 1/10 to about 3/2, b is from about 1 to about 4, c is from about 1 to about 3, d is from about 1 to about 5, e is from about 3/10 to about 1, and mixed, for example, by

grinding them together in a mortar. The mixed powder may then be heated directly or it can be first formed into a pellet or other shaped object and then heated. The superconducting composition of this invention is produced only when the atmosphere in which the reactants are heated is carefully controlled. One way to accomplish this controlled atmosphere is to place the reactants in a tube made of a non-reacting metal such as gold and then sealing the tube by welding. The sealed tube is then placed in a furnace and heated to about 850°C to about 940°C for about 3 to 12 hours. The power to the furnace is then turned off and the tube is furnace-cooled to ambient temperature, about 20°C, and then removed from the furnace. The tube is then opened and the black product recovered. The compositions prepared in this manner exhibit the onset of superconductivity above 70 K.

Two superconducting phases have been identified in these superconducting compositions. One phase, the "12 Angstrom phase", has an onset of superconductivity of about 85 K and lattice parameters of $a = 0.380$ nm and $c = 1.21$ nm as determined from X-ray powder diffraction results indexed on a tetragonal cell and the other phase, the "15 Angstrom phase", has an onset of superconductivity of about 120 K and lattice parameters of $a = 0.380$ nm and $c = 1.52$ nm as determined from X-ray powder diffraction results indexed on a tetragonal cell.

Superconductivity can be confirmed by observing magnetic flux exclusion, i.e., the Meissner effect. This effect can be measured by the method described in an article by E. Polturak

and B. Fisher in Physical Review B, 36, 5586(1987).

The superconducting compositions of this invention can be used to conduct current extremely efficiently or to provide a magnetic field for magnetic imaging for medical purposes. Thus, by cooling the composition in the form of a wire or bar to a temperature below the superconducting transition temperature, (T_c) by exposing the material to liquid nitrogen if T_c is above 77K or to liquid helium if T_c is below 77K in a manner well known to those in this field; and initiating a flow of electrical current, one can obtain such flow without any electrical resistive losses. To provide exceptionally high magnetic fields with minimal power losses, the wire mentioned previously could be wound to form a coil which would be exposed to liquid helium or liquid nitrogen, depending on T_c before inducing any current into the coil. Such fields can be used to levitate objects as large as railroad cars. These superconducting compositions are also useful in Josephson devices such as SQUIDS (superconducting quantum interference devices) and in instruments that are based on the Josephson effect such as high speed sampling circuits and voltage standards.

EXAMPLES OF THE INVENTION

EXAMPLE 1

2.2837 g of Tl_2O_3 , 2.3919 g of PbO_2 , 0.7208 g of CaO_2 , 1.1962 g of SrO_2 and 0.7954 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1:1:1:1:1, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed

from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 875°C and then held at 875°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 75 K.

EXAMPLE 2

Two other pellets of the mixed powder of Example 1 were treated as described in Example 1 except that the temperature to which they were heated and held was 925°C.

Meissner effect measurements showed the onset of superconductivity at about 70 K.

EXAMPLE 3

2.2837 g of Tl_2O_3 , 2.3919 g of PbO_2 , 1.1416 g of CaO_2 , 1.1962 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1:1:2:1:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 875°C and then held at 875°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then

removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 80 K.

EXAMPLE 4

Two other pellets of the mixed powder of Example 3 were treated as described in Example 3 except that the temperature to which they were heated and held was 925°C.

Meissner effect measurements were carried out and the results are shown in Fig. 1 where the flux exclusion is plotted as a function of temperature. The plot shows the onset of superconductivity at about 110 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 15 Angstrom phase.

EXAMPLE 5

2.2837 g of Tl_2O_3 , 2.3919 g of PbO_2 , 0.7208 g of CaO_2 , 1.1962 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1:1:1:1:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 875°C and then held at 875°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 85 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 12 Angstrom phase.

EXAMPLE 6

Two other pellets of the mixed powder of Example 5 were treated as described in Example 5 except that the temperature to which they were heated and held was 925°C.

Meissner effect measurements showed the onset of superconductivity at about 120 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 15 Angstrom phase.

EXAMPLE 7

2.2837 g of Tl_2O_3 , 2.3919 g of PbO_2 , 0.7208 g of CaO_2 , 1.1962 g of SrO_2 and 1.5908 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1:1:1:1:2, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 875°C and then held at 875°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 80 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 12 Angstrom phase.

EXAMPLE 8

Two other pellets of the mixed powder of Example 7 were treated as described in Example 7 except that the temperature to which they were heated and held was 925°C.

Meissner effect measurements showed the onset of superconductivity at about 85 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 12 Angstrom phase.

EXAMPLE 9

2.2837 g of Tl_2O_3 , 2.3919 g of PbO_2 , 0.7208 g of CaO_2 , 2.3924 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1:1:1:2:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 860°C and then held at 860°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 80 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 12 Angstrom phase.

EXAMPLE 10

Two other pellets of the mixed powder of Example 9 were treated as described in Example 9 except that the temperature to which they were heated and held was 890°C.

Meissner effect measurements showed the onset of superconductivity at about 80 K.

The X-ray powder diffraction of the product shows that the dominant phase is the 12 Angstrom phase.

EXAMPLES 11

0.6851 g of Tl_2O_3 , 1.6743 g of PbO_2 , 1.4416 g of CaO_2 , 2.3924 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 3/10:7/10:2:2:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 900°C and then held at 900°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 120 K.

The X-ray powder diffraction of the product is essentially the same as that shown in Example 12.

EXAMPLES 12

1.1419 g of Tl_2O_3 , 1.1960 g of PbO_2 , 1.4416 g of CaO_2 , 2.3924 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1/2:1/2:2:2:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long)

and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 900°C and then held at 900°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 120 K.

The d-spacings, the relative intensities and the indices of the observed reflections of the X-ray powder diffraction pattern of the product, which was essentially single phase, is shown in Table I. This is the characteristic pattern of the 15 Angstrom phase.

<u>d-spacing, nm</u>	<u>Intensity</u>	<u>hkl</u>
1.530	s	001
0.760	m	002
0.5097	m	003
0.3811	m	004
		100
0.3704	w	101
0.3400	m	102
0.3049	m	103
0.2698	vs	104
		110
2.652	w	111
2.541	m	006
2.178	w	007
2.022	w	115
1.907	m	200
1.852	w	116
1.707	w	108
1.694	m	117
1.618	w	213
1.558	m	218

w - weak

m - medium

s - strong

EXAMPLES 13

1.5986 g of Tl_2O_3 , 0.6696 g of PbO_2 , 1.4416 g of CaO_2 , 2.3924 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 7/10:3/10:2:2:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 900°C and then held at 900°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of superconductivity at about 110 K.

The X-ray powder diffraction of the product is essentially the same as that shown in Example 12.

EXAMPLES 14

2.0553 g of Tl_2O_3 , 0.22319 g of PbO_2 , 1.4416 g of CaO_2 , 2.3924 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 9/10:1/10:2:2:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 900°C and then held at 900°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room

temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed the onset of weak superconductivity at about 85 K.

The X-ray powder diffraction of the product showed the presence of a minor amount of the 12 Angstrom phase.

EXAMPLES 15

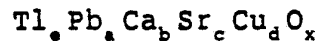
2.2838 g of Tl_2O_3 , 1.1960 g of PbO_2 , 1.1412 g of CaO_2 , 2.3924 g of SrO_2 and 2.3862 g of CuO , corresponding to a Tl:Pb:Ca:Sr:Cu atomic ratio of 1:1/2:3/2:2:3, were ground together in an agate mortar for about 30 minutes. Pellets, 10 mm in diameter and about 3 mm thick, were pressed from this mixed powder. Two pellets were loaded into a gold tube (3/8" dia and 4" long) and the tube was sealed by welding both ends. The tube was placed in a furnace and heated at a rate of 5°C per minute to 900°C and then held at 900°C for 6 hours. Power to the furnace was then shut off and the tube was allowed to cool to room temperature in the furnace. The tube was then removed from the furnace and cut open. The black product was recovered.

Meissner effect measurements showed two superconductivity transitions, one at about 116 K and one at about 80 K.

The X-ray powder diffraction pattern of the product showed the presence of both the 12 and the 15 Angstrom phases.

CLAIMSThe Invention Being Claimed is:

1. A superconducting composition having the nominal formula



wherein a is from about 1/10 to 3/2,

b is from about 1 to 4,

c is from about 1 to 3

d is from about 1 to 5

e is from about 3/10 to 1

x = (a + b + c + d + e + y) where

y is from about 1/2 to 3,

said composition having a superconducting transition temperature of at least 70 K.

2. A superconducting composition as in Claim 1 wherein "a" is about 1/2, "b" is about 2, "c" is about 2, "d" is from about 3 to 4, "e" is about 1/2 and "y" is from about 1/2 to 2.

3. A superconducting composition as in Claim 1 wherein "a" is about 7/10, "b" and "c" are each equal to 2, "d" is about 3, "e" is about 3/10 and "y" is from about 1/2 to 2.

4. A process for making superconducting compositions consisting essentially of mixing stoichiometric quantities of oxides of Tl, Pb, Ca, Sr and Cu to provide the composition of Claim 1; heating the mixture in a confined atmosphere to a temperature of about 850°C to 940°C and maintaining said temperature for about 3 to 12 hours to form said composition; and cooling said composition.

5. A process as in Claim 4 wherein the stoichiometric quantities of the oxides or oxide precursors are selected to provide the composition of Claim 2.

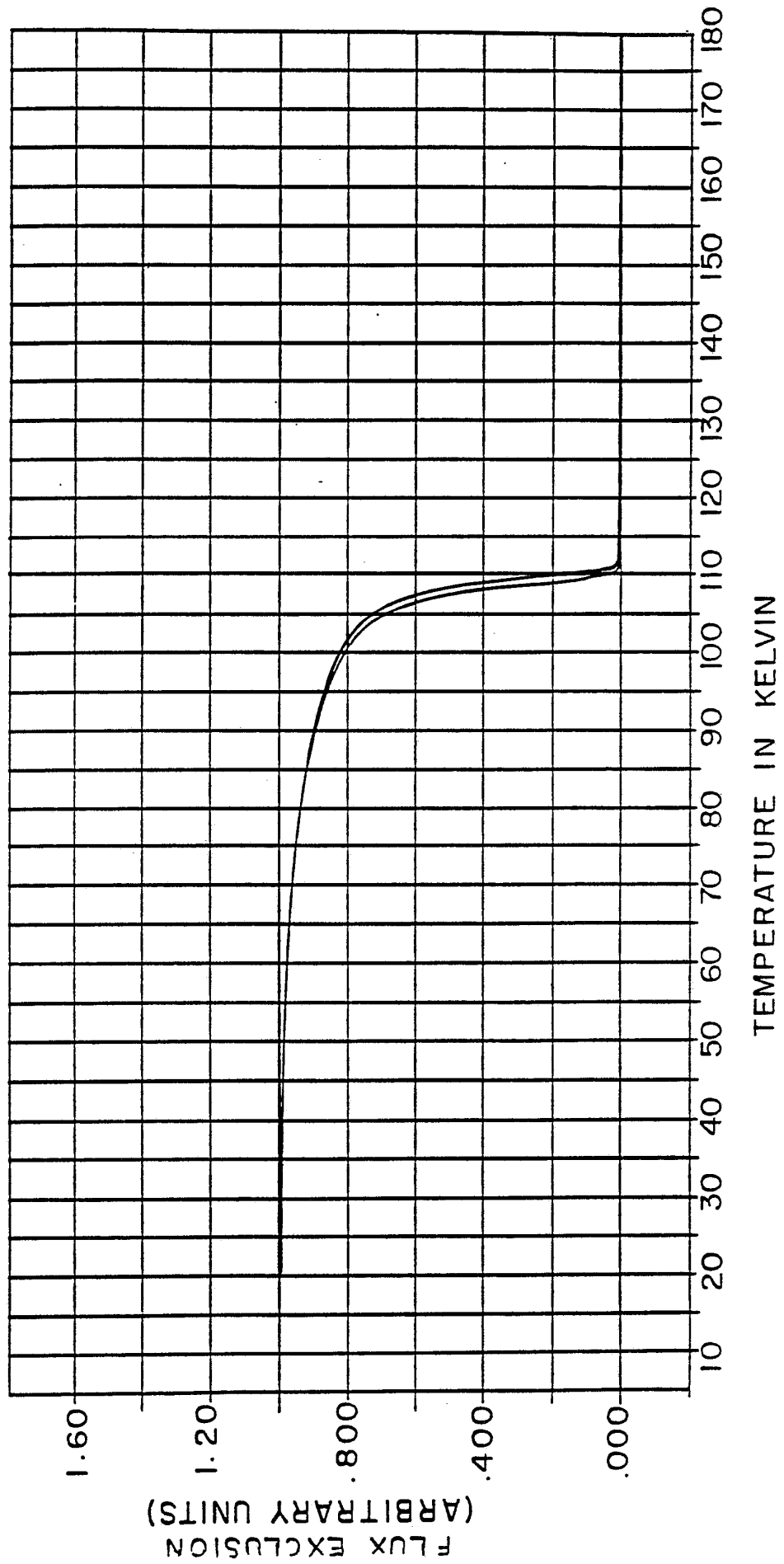
6. A method for conducting an electrical current within a conductor material without electrical resistive losses comprising the steps of:

cooling a conductor material composed of a composition of Claim 1 to a temperature below the T_c of said composition;

initiating a flow of electrical current within said conductor material while maintaining said material below said temperature.

7. An improved Josephson-effect device wherein the superconductive material comprises the composition of Claim 1.

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/03017

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4): C01F 11/02; C01G 3/02; C01G 21/00; H01L 39/12		
U.S. Cl. 423/624; 502/341, 346, 354; 505/T.		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	423/624; 502/341, 346, 354; 505/1	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Japanese Journal of Applied Physics, Volume 27, Number 5, June 1988, Yumada Et al., "Pb Introduction to the High-Tc Superconductor Bi-Sr-Ca-CuO", page L996-L998.	1-6
A	Physical Review B, Volume 35, Number 10, 01 April 1987, Gubser Et al., "Superconducting phase transitions in La-M-Cu-O layered perovskite system, M= La, Ba, Sr and Pb", pages 5350.	1-6
A	US, A, 3,932,315 (SLEIGHT), 13 January 1976, see entire document.	1
A	American Vacuum Society : Series 3, 06 November 1987, Richert et al., "Atomic Substitution in YBa ₂ Cu ₃ O ₇ " Modification of Structure', pages 277-283.	1
Y	US, A, 4,412,902 (MICHIKAMI ET AL) 01 November 1983, see entire document.	7
<p>¹⁰ Special categories of cited documents: ¹³</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Making of this International Search Report	
12 October 1989	30 OCT 1989	
International Searching Authority	Signature of Authorized Officer	
ISA/US	John Boyd <i>[Signature]</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE PREVIOUS SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Nature, volume 332, 10 March 1988, Sheng et al., "Bulk superconductivity at 120K in the Tl-Ca/Ba-Cu-O System", pages 138-139.	1-3
Y,P	Japanese Journal of Applied Physics, Volume 27, Number 11, November 1988, Itoh et al., "Preparation and Properties of Bulk Superconductors in the Tl-Pb-Sr-Ca-Cu-O system", pages L2052-L2054.	1-7
Y,P	Japanese Journal of Applied Physics, Volume 27, Number 12, December 1988, Tai et al., "Bulk Superconductivity in the New Orthorhombic (Tl, Pb)-Ca-Sr-Cu-O System", pages 12287-L2288:	1-7