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(19) (CA) **CANADIAN PATENT** (12)

(54) Metal Oxide Material

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1 ABSTRACT OF THE DISCLOSURE

A metal oxide material is provided which is represented by the composition formula:



5 wherein  $2 \leq x \leq 3.5$ ,  $2 \leq y \leq 3.5$ ,  $x+y > 4$ , and  $4 < z$ ;

A is an element or a group of elements selected from alkaline earth metal elements; and B is an element or a group of elements selected from the group of elements consisting of bismuth, lead and thallium.

10 The material has a superconductivity transition temperature of from 4.2K to 12K.

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1 TITLE OF THE INVENTION

Metal Oxide Material

BACKGROUND OF THE INVENTION

5 Field of the invention

The present invention relates to a copper oxide material, and particularly to a copper oxide material useful as a superconductive material.

Related Background Art

10 Hitherto known as copper oxides are  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ , as well as  $\text{CuGeO}_3$ ,  $\text{CuNbO}_3$ ,  $\text{CuVO}_3$ ,  $\text{Bi}_2\text{CuO}_4$ ,  $\text{Cr}_2\text{CuO}_4$ ,  $\text{La}_2\text{CuO}_4$ , etc. Of these,  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$  (A = Ca, Sr or Ba) and  $\text{LnBa}_2\text{Cu}_3\text{O}_y$  (Ln = Y or lanthanoids) are known as superconductive materials.

15 However, in the conventional superconductive materials comprising copper oxides, the yttrium and lanthanoids that are component elements of the materials have been expensive materials because of  
20 their small amounts of the resource. In instances in which these copper oxides are formed into sinters or thin films depending on what they are used for, high temperatures of about  $1,000^\circ\text{C}$  are required as reaction temperature, bringing about the problems that a high production cost results and there are considerable  
25 limitations on substrates to be used. Moreover, they also can be formed into single crystals with

1 difficulty, and with restricted reaction conditions,  
so that no large single crystal has ever been  
obtained. Furthermore, deviation in compositional  
ratios may greatly affect the superconductivity  
5 transition temperature (hereinafter "Tc"), having  
brought about the problem that the materials exhibit  
no superconductivity within the range of  $x \geq 0.2$  in,  
for example,  $Y_{1+x}Ba_{2-x}Cu_3O_7$ . This is particularly a  
great problem since the compositional deviation  
10 becomes liable to occur when thin films are prepared.

Z. Phys. B-Condensed Matter 68, 421-423 (1987)  
discloses a novel Bi-based superconductive material,  
having its composition of  $Sr_2Bi_2Cu_2O_{7+\delta}$ , Tc of 7 to 22  
K in the midpoint. This Bi-based superconductive  
15 material does not employ any expensive raw materials  
such as Y and lanthanoids as its component elements,  
can be formed using reaction temperatures of not  
higher than 900°C, can be inexpensive when compared  
with conventional  $La_{2-x}A_xCuO_4$  and  $LnBa_2Cu_3O_y$ , and can  
20 afford to accept a broader scope of selection in  
respect of the materials for substrates when thin  
films are formed, and thus can be said to be superior  
materials in these respects. They, however, have the  
problems such that the Tc tends to be extremely  
25 lowered because of inclusion of impurities and it is  
difficult to obtain a superconductive material having

1 a stable Tc.

SUMMARY OF THE INVENTION

An object of the present invention is to  
5 provide a novel copper oxide material useful as a  
superconductive material that does not require any  
expensive raw materials such as Y and lanthanoid  
elements and can be readily cooled by liquid helium.

Another object of the present invention is to  
10 provide a novel superconductive copper oxide material  
that can be formed at a low reacting temperature and  
enables easy preparation of single crystals.

Still another object of the present invention  
is to provide a copper oxide material useful as a  
15 superconductive material whose Tc can be less affected  
even by the compositional deviation and presence of a  
small amount of impurities.

The above objects can be achieved by the  
present invention described below.

20 The present invention is a metal oxide  
material represented by the compositional formula:



wherein  $2 \leq x \leq 3.5$ ,  $2 \leq y \leq 3.5$ ,  $x+y > 4$ , and  $4 < z$ ;

A is an element or a group of elements selected from  
25 alkaline earth metal elements; and B is an element or  
a group of elements selected from the group of elements

1 consisting of bismuth, lead and thallium.

In a preferred embodiment of the present invention, the above metal oxide material has a superconductivity transition temperature of from 4.2 K  
5 to 12 K.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, the copper oxide material particularly suitable for the objects of the  
10 present invention is a material represented by the compositional formula:



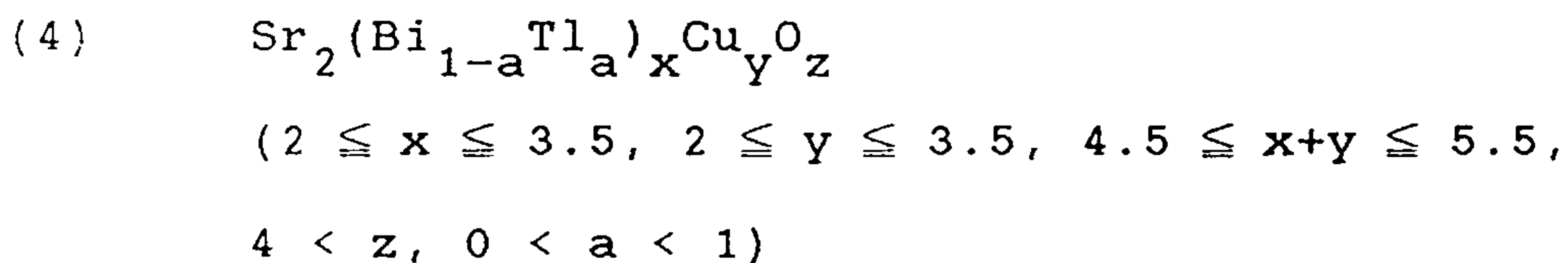
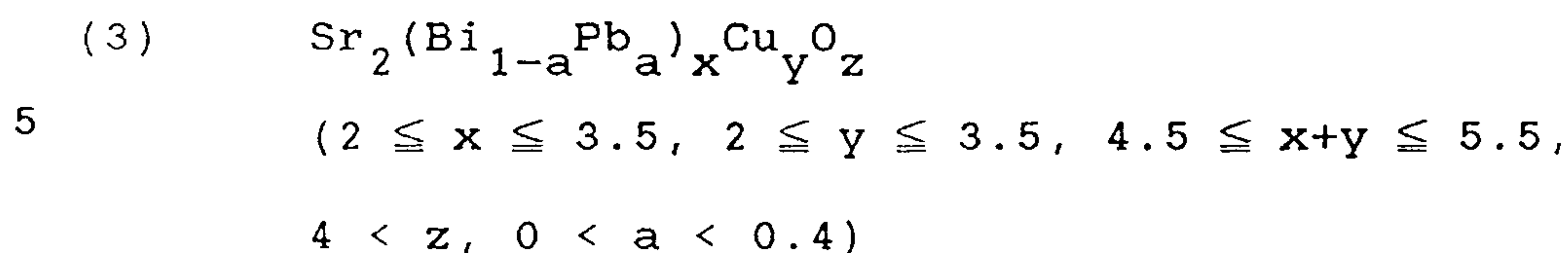
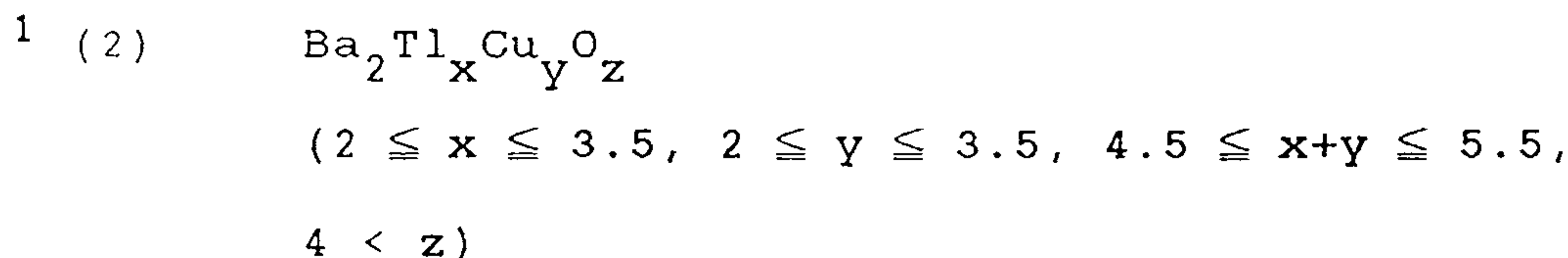
wherein  $2 \leq x \leq 3.5$ ,  $2 \leq y \leq 3.5$ ,  $x+y > 4$ , and  $4 < z$ ;

A is an element or a group of elements selected from  
15 alkaline earth metal elements; and B is an element or a group of elements selected from the group of elements consisting of bismuth, lead and thallium.

Preferably used as the alkaline earth metal  
are calcium, strontium and barium.

20 In the above composition, preferred combination of the element or the group of elements includes:

- (1)  $Sr_2 Bi_x Cu_y O_z$   
 $(2 \leq x \leq 3.5, 2 \leq y \leq 3.5, 4.5 \leq x+y \leq 5.5,$   
25  $4 < z)$



10 Of the copper oxide materials represented by  
the above compositional formulas (1) to (4), a  
material  $Sr_2Bi_{3-x}Cu_{2+x}O_z$ , where  $0 < x < 1$ , in the  
compositional formula (1) is superior from the view  
point of practical use because of its good  
15 crystallinity and less possibility for the Tc to be  
affected by the compositional deviation, particularly  
when a thin film thereof is prepared.

Of the materials having the composition of the  
above (1) to (4), those having an ortho-rhombic  
20 crystalline structure and having a lattice constant of  
 $a = 24$  to  $25 \text{ \AA}$ ,  $b = c = 5.3$  to  $5.4 \text{ \AA}$  are preferred  
because of their relatively high Tc.

As methods of preparing the above oxide  
materials of the present invention, it is possible in  
25 the present invention to use any of reaction and  
sintering methods utilizing the heating of raw

1 material powders generally used in ceramic materials.

Examples of such methods are disclosed in  
Material Research Bulletin, Vol. 8, p.777 (1973);  
Solid State Communication, Vol. 17, p.27 (1975);  
5 Zeitschrift für Physik, Vol. B-64, p.189 (1986);  
Physical Review Letters, Vol. 58, No. 9, p.908 (1987);  
etc., and these methods are presently known as  
qualitatively very common methods.

A method of effecting single-crystal growth  
10 after a raw material powder has been melted at a high  
temperature is also useful in the present invention.  
Still also, the material of the present invention may  
be formed on a substrate in the form of a thin film by  
means of sputtering such as radio frequency sputtering  
15 or magnetron sputtering, using a target containing raw  
materials, electron beam vapor deposition, or other  
vacuum vapor deposition, as well as a cluster ion beam  
method, or CVD or plasma CVD employing gaseous  
20 materials as raw materials. In such instances, it is  
often effective to feed gaseous oxygen to the  
apparatus to carry out oxidation therein. More  
specific examples of conditions for the preparation  
will be described in Examples herein set out below.

The thus obtained oxide material of the  
25 present invention, which is mainly composed of copper

1 oxide does not exhibit any metal-nonmetal transition,  
has an electrical resistivity of about  $10^{-4}$  to  $10^{-1}$   
 $\Omega \cdot \text{cm}$  at room temperature, and exhibits a  
superconductivity at temperatures of from several K to  
5 about 10 K.

A preferable superconductivity can be obtained  
when x, y and z are respectively within the above  
range in the above compositional formula. No  
preferable superconductivity can result outside the  
10 above range.

The raw materials used in the present  
invention are all inexpensive, promising a low raw  
material cost, so that the oxide material of the  
present invention can be provided through an  
15 inexpensive route. For example, the oxide material of  
the present invention can be provided through an  
inexpensive route even when compared with a series of  
the compounds represented by  $\text{YBa}_2\text{Cu}_3\text{O}_{7-z}$ . Also, the  
oxide material of the present invention is relatively  
20 stable with less deterioration in the air as compared  
with the above compounds, and may suffer less  
deterioration by moisture. Since in addition the  $T_c$   
of the resulting oxide material is higher than the  
liquid helium temperature (4.2 K), it can be  
25 relatively easily used as the superconductive  
material.

1           It is also possible to control the reacting  
temperature in preparing the material, to as low as  
900°C or lower, and also achieve good crystallinity.

          A practically useful copper oxide material can  
5 also be obtained whose superconducting transition  
temperature is less affected by the compositional  
deviation.

#### EXAMPLES

10           The present invention will be described below  
in greater detail by giving Examples. The Tc shown in  
the following indicates the zero resistance  
temperature in every instance.

#### Examples 1 to 5, Comparative Examples 1 to 4

15           Bi<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub> and CuO as raw materials were  
weighed to give the compositional ratios as shown in  
Table 1 below, followed by dry mixing. The resulting  
mixtures were each press-molded into a pellet of 10 mm  
in diameter and 1 mm in thickness, and the molded  
20 products were each reacted and sintered on an alumina  
boat at 900°C in the air, thus preparing copper oxide  
materials of the present invention and those of  
Comparative Examples.

          The superconductivity of each oxide thus  
25 prepared was measured in a temperature range of from 3  
K to 50 K. Results obtained are shown in Table 1

<sup>1</sup> below.

As will be evident from Table 1, the oxide materials of the present invention exhibit the superconductivity, while the oxide materials of  
<sup>5</sup> Comparative Examples exhibited no satisfactory superconductivity within the range of the measurement temperatures.

X-ray diffraction of the samples of Examples 1, 2 and 3, having particularly good characteristics,  
<sup>10</sup> was also made to find that the unit cell was orthorhombic, and  $a = 24.6 \text{ \AA}$ ,  $b = 5.38 \text{ \AA}$  and  $c = 5.38 \text{ \AA}$ .

15

<sup>20</sup>

25

1

Table 1

<u>Samples</u>	<u>Components (molar ratio)</u>				<u>Tc</u>
	<u>Sr</u>	<u>Bi</u>	<u>Cu</u>	<u>O</u>	
5 Example:					
1	2	3	2	8.5	9
2	2	2.5	2.5	8.3	10
3	2	2	3	8	9
4	2	3	3	9	7
10 5	2	2.5	3.5	9	6
Comparative Example:					
1	2	2	4	9	3
2	2	1	2	5.5	-
3	2	2	2	7	4
15 4	2	4	1	9	-

The mark "-" in the column for Tc indicates that no superconductivity transition took place at 3 K or higher.

20

Examples 6 and 7, Comparative Examples 5 and 6

Using  $Tl_2O_3$ , BaO and CuO as raw materials, pellets were prepared in the same manner as in the above Examples, encapsulated into Ag pipes, and  
 25 reacted at 900°C. Results obtained are shown in Table  
 2.

1

Table 2

<u>Samples</u>	<u>Ba</u>	<u>Tl</u>	<u>Cu</u>	<u>Tc (K)</u>
5 Example:				
6	2	2.5	2.5	12
7	2	3	2	8
Comparative Example:				
5	2	2	2	-
10 6	2	1	2	-

Example 8, Comparative Example 7

In instances in which a thin film comprising  
 15 the oxide materials of the present invention is formed  
 on a substrate, three sets of crucibles and electron  
 sources are first disposed in a vapor deposition  
 apparatus, and bismuth, strontium and copper are  
 20 introduced into three the crucibles. Using magnesium  
 oxide (MgO) as a substrate, the inside of a vacuum  
 chamber is exhausted to  $2 \times 10^{-7}$  Torr, and thereafter  
 the substrate is heated to 600°C using a substrate  
 heater. Next, while introducing oxygen (O<sub>2</sub>) into the  
 vacuum chamber at a flow rate of 1 SCCM, vapor  
 25 deposition is started. Following the procedures known  
 in general in the art, deposition rate of the bismuth,

1 strontium and copper is monitored and feed back is  
 effected on electron beams to make control so that the  
 ratio of strontium : bismuth : copper may be 2 : 2.5 :  
 2.5 or 2 : 2 : 2. After deposition to give a  
 5 thickness of about 5,000 Å has been completed, the  
 substrate temperature is sufficiently dropped, and the  
 products are taken out in the air, followed by  
 annealing in the air at 800°C for several hours to  
 about 10 hours. The superconductivity of the thin-  
 10 filmy oxide materials thus obtained was measured in a  
 temperature range of from 3 K to 50 K. Results  
 obtained are shown below.

	<u>Samples</u>	<u>Sr</u>	<u>Bi</u>	<u>Cu</u>	<u>Tc (K)</u>
15	Example 8	2	2.5	2.5	7
	Comparative				
	Example 7	2	2	2	3

Examples 9 to 12, Comparative Examples 8 to 10

20 Using  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{PbO}_2$ ,  $\text{Tl}_2\text{O}_3$  as raw  
 materials, mixing and press-molding were carried out  
 in the same manner as in Example 1, followed by  
 reaction and sintering on alumina boat at 800°C, to  
 obtain four kinds of copper oxides  $\text{Sr}_2\text{Bi}_2\text{PbCu}_2\text{O}_y$ ,  
 25  $\text{Sr}_2\text{Tl}_3\text{Cu}_2\text{O}_y$ ,  $\text{Sr}_2\text{Bi}_2\text{TlCu}_2\text{O}_y$  and  $\text{Sr}_2\text{Bi}_{2.5}\text{Pb}_{0.5}\text{Cu}_3\text{O}_y$ .  
 Resistance measurement was effected at 4.2 K or higher

<sup>1</sup> to find that all the four kinds exhibited superconductivity at near 9 K.

For comparison, three kinds of copper oxides  $\text{Sr}_2\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Cu}_2\text{O}_y$ ,  $\text{Sr}_2\text{Tl}_2\text{Cu}_2\text{O}_y$  and  $\text{Sr}_2\text{Bi}_{1.5}\text{Tl}_{0.5}\text{Cu}_2\text{O}_y$   
<sup>5</sup> were prepared under the same conditions, but resulting in no exhibition of superconductivity at 4.2 K or higher.

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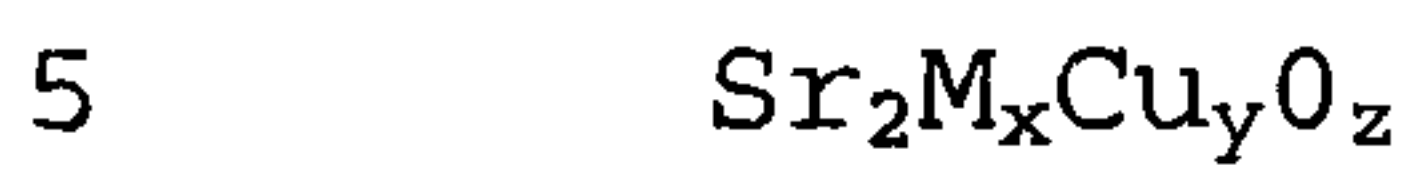
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CLAIMS

1. A metal oxide material represented by the  
compositional formula



wherein  $2 \leq x \leq 3.5$ ,  $2 \leq y \leq 3.5$ ,  $4.5 \leq x+y \leq 5.5$ , and  $4 < z$ ;

M is an element or a group of elements selected from  
the group of elements consisting of bismuth, lead and  
thallium.

10

2. The metal oxide material of claim 1, wherein M is  
bismuth.

3. The metal oxide material of claim 1, wherein said  
15 compositional formula is represented by  $Sr_2(Bi_{1-a}Pb_a)_xCu_yO_z$   
where  $0 < a < 0.4$ .

4. The metal oxide material of claim 1, wherein said  
compositional formula is represented by  $Sr_2(Bi_{1-a}Tl_a)_xCu_yO_z$   
20 where  $0 < a < 1$ .

5. The metal oxide material of claim 1, wherein said  
compositional formula is represented by  $Sr_2Bi_{3-w}Cu_{2+w}O_z$   
where  $0 < w < 1$ .

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