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COPPER OXIDE SUPERCONDUCTING COMPOUNDS

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(57) Claim

1. Superconductor compounds of the RE AE_{1+x} Cu_{2+x} O_{7-y} type, with RE standing for a rare earth metal or a rare earth-like metal, AE standing for an alkaline earth metal, and having a transition temperature above 90 K, characterized in that x = 2, 3, 4, such that the stoichiometric relations between the rare earth metal, or the rare earth-like metal (RE), the alkaline earth metal (AE) and copper are respectively 1:3:4, 1:4:5 or 1:5:6, that the copper coordination is made by six and four oxygen atoms, and that the oxygen content, in which y is less than or equal to one, is adjusted such that the resulting crystal structure has perovskite layers.

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Complete Specification for the invention entitled:

New Layered Copper Oxide Superconductor Compounds

The following statement is a full description of this invention, including the
best method of performing it known to me/us

5845/3

NEW LAYERED COPPER OXIDE SUPERCONDUCTOR COMPOUNDS

DESCRIPTION

The invention relates to new superconductors, in particular to compounds containing layers of corner-sharing copper oxygen octahedra having superconductor properties below a relatively high transition temperature.

Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials: About a quarter of the elements and over 1000 alloys and components have been found to be superconductors. Superconductivity is considered a property of the metallic state of the material, in that all known superconductors are metallic under the conditions that cause them to superconduct. A few normally non-metallic materials, for example, become superconductive under very high pressure, the pressure converting them to metals before they become superconductors.

Superconductors are very attractive for the generation and energy-saving transport of electrical power over long distances, as materials for forming the coils of strong magnets for use in plasma and nuclear physics, in nuclear resonance medical diagnosis, and in connection with the magnetic levitation of fast trains. Power generation by thermonuclear fusion, for example, will require very large magnetic fields which can only be provided by superconducting magnets. Certainly, superconductors will also find application in computers and high-speed signal processing and data communication.

While the advantages of superconductors are quite obvious, the common disadvantage of all superconductive materials so far known has been their

very low transition temperature (usually called the critical temperature T_c) which has until recently been around 23 degrees Kelvin. The use of superconductors at these temperatures requires liquid helium which is very expensive and not sufficiently abundant to justify industrial application.

To improve the situation, i.e., to raise the critical temperature T_c , Bednorz and Müller have introduced compounds of the Ba-La-Cu-O system, metallic oxides, which exhibit a critical temperature T_c of about 40 K (c.f. J.G. Bednorz and K.A. Müller, Possible High T_c Superconductivity in the Ba-La-Cu-O System, Z. Phys. B - Condensed Matter 64, 189-193 (1986); J.G. Bednorz, M. Takashige and K.A. Müller, Susceptibility Measurements Support High - T_c Superconductivity in the Ba-La-Cu-O System, Europhys. Lett., 3(3), 379-385 (1987); ~~EP-A-87100961-9~~ Australian Patent Application No. 10699/88).

These compounds consist of copper oxygen octahedra having corners at which oxygen atoms are located, and in between layers of LaO. The base formula of these compounds is La_2CuO_4 in which the lanthanum is partially substituted by alkali earth ions, such as Ca^{2+} , Sr^{2+} or Ba^{2+} . The critical temperature of these substituted compounds is in the 40 K range, i.e., with these materials, cooling with liquid neon becomes possible.

The work of Bednorz and Müller has attracted the interest of numerous groups of scientists who all concentrate on compounds of the Ba-La-Cu-O system and their equivalents, i.e. those compounds which consist of a rare earth element partially substituted by an element of the alkaline earth group, and combined with a copper oxide, of the general formula $\text{AE}_x\text{RE}_{2-x}\text{CuO}_{4-y}$, where AE stands for the group of alkaline earth elements, and RE stands for the group of rare earth elements. Of course, also compounds of the AE-RE-Cu-O system not meeting the x:2-x:1 relation have been investigated.

As a result of all of these efforts, several new materials have been found which exhibit a critical temperature above the boiling point of nitrogen. One paper recently published is of particular interest in this connection: M.K. Wu et al., Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure, Phys. Rev. Lett. 58(9) (1987) pp. 908-910. Herein,



the rare earth lanthanum, use of which was proposed by Bednorz and Müller in their first paper cited above, is replaced by its closest relative yttrium, a rare earth-like metal of the same IIIB group of the periodic table of elements as lanthanum.

5 The composition of the compound proposed in this reference has been determined to be the single-phase $\text{Y Ba}_2\text{Cu}_3\text{O}_7$ (cf. M.A. Beno et al, Structure of the Single Phase High Temperature Superconductor $\text{Y Ba}_2\text{Cu}_3\text{O}_7$, submitted in March 1987 to Appl. Phys. Lett.; J.J. Capponi et al., Structure of the 100K Superconductor $\text{Ba}_2\text{YCu}_3\text{O}_7$ between 5 & 300 K by Neutron Powder Diffraction, submitted in March 1987 to Europhys. Lett.). This compound is reported to have a critical temperature above 90 K. i.e. cooling is considerably facilitated, not only because less energy is required, but also because liquid nitrogen can be used for cooling, and there is a virtually unlimited supply.

10 The x-ray and diffraction patterns so far published for this compound have been indexed on the basis of the perovskite lattice where, along a particular [100] direction, i.e. along the quasi-tetragonal c-axis of the crystal, a layer of oxygen atoms is missing. In addition, stoichiometry requires that still further oxygen atoms should be missing. The structure proposed by these references thus requires layers of copper atoms with five-fold coordination not otherwise known to exist in ordered layers in oxides. It is, hence, not clear whether these compounds are stable.

20 It is therefore, an object of the present invention to propose new compositions for high- T_c superconductors comprising layered copper oxide in which the copper coordination is by six and four oxygen atoms, these coordinations being generally known in inorganic chemistry.

25 In accordance with the present invention there is disclosed superconductor compounds of the $\text{RE AE}_{1+x}\text{Cu}_{2+x}\text{O}_{7-y}$ type, with RE standing for a rare earth metal or a rare earth-like metal, AE standing for an alkaline earth metal, and having a transition temperature above 90 K, characterized in that $x = 2, 3, 4$, such that the stoichiometric relations between the rare earth metal, or the rare earth-like metal (RE), the alkaline earth metal (AE) and copper are respectively 1:3:4, 1:4:5 or 1:5:6, that the copper coordination is made by six and four oxygen atoms, and that the oxygen content, in which y is less than or equal to one, is adjusted such that the resulting crystal structure has perovskite layers



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preferably compounds having a layer-type structure of corner-sharing copper oxygen octahedra are proposed. This structure is in particular present in oxides of the general composition $RE AE_{1+x} Cu_{2+x} O_{7-y}$, wherein RE stands for rare earth metals, including rare earth-like metals, AE stands

5 for the group of alkaline earth elements. In this general formula, x may take the values 2, 3, or 4. It is a characteristic of the present invention that in the



compounds in question the stoichiometry is preserved at relative ratios of 1:3:4, 1:4:5, or 1:5:6, resulting in an octahedral and square-planar structure.

The oxygen content of the compounds in accordance with the present invention actually depends on the heat treatment the compounds undergo during fabrication. This is best described by y having a value of unity or slightly smaller.

For example, compounds that meet the description given above include lanthanum strontium copper oxide $\text{LaSr}_3\text{Cu}_4\text{O}_{7-y}$, yttrium barium copper oxide $\text{YBa}_3\text{Cu}_4\text{O}_{7-y}$, and scandium calcium copper oxide $\text{ScCa}_3\text{Cu}_4\text{O}_{7-y}$. Lanthanum is, of course, a rare earth metal. It may be replaced by any one, or a mixture, of the other rare earth metals, generally called the lanthanides, and comprising the elements with the atomic numbers from 58 through 71. Accordingly, neodymium strontium copper oxide $\text{NdSr}_5\text{Cu}_6\text{O}_{7-y}$ also fits the description given above.

Yttrium and scandium are rare earth-like metals belonging to the same IIIB group of the periodic table of elements as lanthanum, and being chemically so similar to the 'genuine' rare earth elements, -associated with which they occur in nature-, that they are very hard to separate from those.

These compounds are all ceramic-metal oxides having a perovskite-like structure. They can be produced by conventional synthesis methods such as solid-state reactions of the individual binary metal oxides, or by calcination of the respective mixed hydroxides, carbonates, nitrates, etc.; cf. A. Reller, Reversible Reduktions- und Reoxidationsprozesse des Typs $\text{ABO}_3 \rightleftharpoons \text{ABO}_{3-x}$ an Perovskitischen Metalloxiden, Berichte Bunsenges. Phys. Chem. 90, 742-745 (1986). In order to obtain stable compounds, their production should preferably occur at a temperature below 950°C .

The compounds in accordance with the present invention consist of corner-sharing copper oxide (CuO_6) octahedral layers, the same as in LaCuO_4 , interlinked by two or more corner-sharing square-planar copper oxide CuO_4

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The claims defining the invention are as follows:

1. Superconductor compounds of the RE $AE_{1+x}Cu_{2+x}O_{7-y}$ type, with RE standing for a rare earth metal or a rare earth-like metal, AE standing for an alkaline earth metal, and having a transition temperature above 90 K, characterized in that $x = 2, 3, 4$, such that the stoichiometric relations between the rare earth metal, or the rare earth-like metal (RE), the alkaline earth metal (AE) and copper are respectively 1:3:4, 1:4:5 or 1:5:6, that the copper coordination is made by six and four oxygen atoms, and that the oxygen content, in which y is less than or equal to one, is adjusted such that the resulting crystal structure has perovskite layers.
2. Compounds in accordance with claim 1, characterized in that they consist of corner-sharing copper oxide octahedral layers (CuO_6) interlinked by at least two corner-sharing square-planar copper oxide units (CuO_4).
3. Compounds in accordance with claim 1, characterized in that the rare earth metal (RE) is lanthanum, with the structural formula being $La AE_3Cu_4O_{7-y}$.
4. Compounds in accordance with claim 1, characterized in that the rare earth metal (RE) is scandium, with the structural formula being $Sc AE_3Cu_4O_{7-y}$.
5. Compounds in accordance with claim 1, characterized in that the rare earth metal (RE) is yttrium, with the structural formula being $Y AE_3Cu_4O_{7-y}$.
6. Compounds in accordance with any one of claims 3 through 5, characterized in that the alkaline earth metal (AE) is barium, with the structural formula being $RE Ba_3Cu_4O_{7-y}$.
7. Compounds in accordance with any one of claims 3 through 5, characterized in that the alkaline earth metal (AE) is strontium, with the structural formula being $RE Sr_3Cu_4O_{7-y}$.
8. Compounds in accordance with any one of claims 3 through 5, characterized in that the alkaline earth metal (AE) is calcium, with the structural formula being $RE Ca_3Cu_4O_{7-y}$.
9. Superconductor compounds substantially as described herein with reference to any one of the examples.

DATED this TWENTY-EIGHTH day of AUGUST 1990
International Business Machines Corporation



IAD/10630

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