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

(54) Superconductor and Process for Its Preparation

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Abstract of the disclosure

Superconductor and process for its preparation

A description is given of superconducting substances having a content of Bi, Sr, Ca and Cu, and of processes for their preparation from the metal oxides within a range which is specified by the overall composition $Bi_a(Sr,Ca)_b$-Cu_6O_x, where a = 3 - 24 and b = 3.23 - 24, with an Sr/ Ca atomic ratio of 1:9 - 9:1 and a Bi:(Ca+Sr) atomic ratio of 0.3 - 1.5. The transition temperature is at least 60 K. The principal phase crystallizes in the orthorhombic system. The pure compounds $Bi_4(Sr,Ca)_4Cu_2O_{\approx 12}$ and $Bi_4(Sr,Ca)_6Cu_4O_{\approx 20}$.

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Description

Superconductor and process for its preparation

The present invention relates to high-temperature superconducting substances based on bismuth, strontium, calcium and copper.

While it was possible to use the conventional superconducting materials solely at very low temperatures which required the use of the very expensive coolant helium, the new superconducting oxidic substances operate at substantially higher temperatures which can be achieved with the comparatively cheap coolant nitrogen. This reduces the running costs of superconducting appliances and systems and opens up novel extensive application possibilities.

A substantial disadvantage of many novel oxidic superconductors is however that they contain, as a common component, La or Y or rare earth metals such as, for example, Sm, Lu, Ho or Eu. Some of these metals occur only in small quantities and are expensive owing to their complicated extraction. Disadvantages stemming from the high raw material prices and the limited reserves of the rare earth metals consequently arise for the production of large quantities of oxidic superconductors.

An oxidic superconductor having a transition temperature of 20 K is already known which contains in oxidic form the elements bismuth, strontium and copper in an atomic ratio of 1:1:1. (C. Michel et al., Z. Phys. B 68 (1987) 421). A transition temperature of about 20 K is, however, still not satisfactory for industrial purposes.

There was therefore the object of providing novel superconducting oxidic substances which do not contain any rare earth metals and do not contain lanthanum or yttrium and whose transition temperature is markedly above 20 K.

The invention is based on the discovery that the transition temperature in the system comprising the oxides of Bi, Sr, Ca and Cu is favorably influenced if calcium is also present in addition to strontium and a Bi:(Sr+Ca) atomic ratio of about 0.3 - 2.2, in particular 0.5 - 2.2, preferably 0.3 - 1.5 in the initial mixture of metal oxides is maintained. Particularly preferred is a ratio of 0.3 - 1.3.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a structural arrangement of atoms in one embodiment of a superconducting substance of the invention.

Figure 2 is a graph of the results of a critical temperature (T_c) experiment conducted in a SQUID magnetometer on a superconducting substance prepared according to Example 2.

DETAILED DESCRIPTION

Novel substances with superconductivity have now been found which contain the metal strontium, calcium, copper and bismuth in oxidic form. These are black crystalline substances with the overall composition

$Bi_a(Sr,Ca)_b Cu_6O_x$ where

a = 1.8 - 24, preferably 3 - 24

b = 3.23 - 24 and

x = about 1.5a+b+6

with a Ca/Sr atomic ratio of 9:1 - 1:9, in particular 9:1 - 1:3, preferably 3:1 - 1:3.

The substances have a critical temperature (transition temperature) T_c of at least 60 K and preferably of at least 70 K. They are black and their principal phases crystallize in the orthorhombic system.

Preferred are mixtures with a Bi/Cu atomic ratio of 0.5 - 2 (ie. a = 3 - 12) and a (Ca+Sr):Cu atomic ratio of 1 - 2 (ie. b = 6 - 12) and a Bi:(Ca+Sr) atomic ratio of 0.3 - 2, preferably 0.3 - 1.3, in particular 0.5 - 1.

In the substances, the oxygen content found to be somewhat higher than calculated for divalent copper and trivalent bismuth. They therefore probably contain also Cu^{+++} ions or Bi^{4+}/Bi^{5+} ions. For a given a, b and c, an oxygen content (x) which is as high as possible is advantageous for the superconductivity.

In one aspect the present invention provides a superconducting phase which cyrstallizes in the orthorhombic system, said phase being the main phase of a black superconducting substance having a transition temperature, T_c, of at least 70 K, comprising the elements bismuth, strontium, calcium and copper in oxidic form and having the overall composition $Bi_a(Ca,Sr)_bCu_6O_x$ wherein a is a number from 3 to 12, b is a number from 6 to 12, the Sr/Ca atomic ratio is from 1:9 to 9:1, the atomic ratio Bi:(Sr+Ca) is from 0.3:1 to 1.3:1, and x is sufficiently high that the black superconducting substance has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth, provided that if a = 3 then the atomic ratio Sr/Ca is not 1:1. In a preferred embodiment a is a number from >3 to 12, more preferably 4 to 12, more preferably >4 to 12, and more preferably still >6 to 12.

In another aspect the invention provides a superconducting compound having a transition temperature, T_c at least 70 K and having the overall formula $Bi_4(Ca,Sr)_8Cu_6O_{about20}$, wherein said compound comprises layers which are arranged in parallel, which alternate with one another,and which consist essentially of: (a) $[Bi_2O_4]^{2+}$ and (b) $[(Ca,Sr)_{2+n}Cu_{1+n}O_{4+2n}]^{2-}$ having a Perowskite structure with n = 2.

In a particular embodiment of the invention, the (Ca+Sr+Cu): Bi atomic ratio in the black crystalline substances is about 1.5. These substances have the general composition $Bi_2(Ca,Sr)_yCu_{3-y+k}O_f$, where k denotes a number between -0.05 and +0.05, preferably 0 and y denotes a number between 1 and 2.5, preferably 1.33 to 2.25, in particular 1.33 to 2.1, and f denotes about 6 + k. Here the range $y = 1.9 - 2.1$ is particularly preferred.

A black crystalline substance furthermore behaves advantageously which has the overall composition $Bi_a(Sr,Ca)_bCu_6O_x$, where $a = 3 - 24$ and $b = 3.23$ to 24, with a Sr/Ca atomic ratio of 1:9 to 9:1, a Bi:(Sr+Ca) atomic ratio of 0.45 to 1.5, preferably 0.5 - 1, a transition temperature T_c for the superconductivity of at least 60 K and a principal phase which crystallizes in the orthorhombic system. This also applies to mixtures in which $12 < a \leq 24$ and $b = 3.23 - 24$ or $a = 3 - 24$ and $3.23 \leq b < 6$ or $12 < b \leq 24$.

Preferred here are crystalline substances of the overall composition $Bi_a(Sr,Ca)_bCu_6O_x$ in which $a = 3 - 14$ and $b = 4$ to 18, in particular 4.9 to 14.

Particularly preferred are mixtures in which $a = 4$ to 14 and $b = 6$ to 14, with a Bi:(Sr+Ca) atomic ratio of 0.45 - 1.13, in particular 0.5 - 1.13.

One particularly preferred embodiment is a black compound which crystallizes in the orthorhombic system and has the overall composition $Bi_4(Sr,Ca)_6Cu_4O{=}_{20}$ with a Ca/Sr atomic ratio of 1:3.5 - 1:6.28 and a transition temperature T_c for the superconductivity of at least 60 K.

The index for the proportion of oxygen is about $x = 1.5a+b+6$. It is somewhat dependent on the annealing conditions. For high thermal post treatment temperatures, x is less than for low ones. Oxygen can probably be reversibly taken up at particular lattice sites.

Provided the black crystalline substance has an overall composition in the range $Bi_a(Sr,Ca)_bCu_6O_x$, where a = 9.8 to 14 and b = 9.8 to 14 and the Bi:(Sr+Ca) atomic ratio is 0.89 to 1.13, it contains as the principal component the superconducting phase of the composition $Bi_4(Sr,Ca)_4Cu_2O_x$. From the values of a and b it can readily be calculated that the value of x lies in the range 31.7 to 42.4. Further details of the preparation are to be found on page 7. In these mixtures too, the Ca:Sr atomic ratio is 9:1 - 1:9, in particular 3:1 - 1:3.

Particular mention is made of a black crystal mass containing as the main product $Bi_4(Sr,Ca)_6Cu_4O_{about20}$ with a Ca/Sr atomic ratio of 1:3.5 to 1:6.28, and which is prepared from oxides or oxide precursors of the elements Bi, Sr, Ca and Cu as starting components, and has a transition temperature T_c of at least 70 K.

Mention is further made of a black superconducting compound which crystallizes in the orthorhombic system having a transition temperature, T_c, of at least 70 K and having the overall formula $Bi_4(Ca,Sr)_{4+2n}Cu_{2+2n}O_{about12+4n}$ wherein n is 2, 3, 4 or 5, the Sr/Ca atomic ratio is of 1:9 to 9:1. In one preferred embodiment, the lattice constants are $a = 5.41 \times 10^{-8}$ cm, $b = 5.47 \times 10^{-8}$ cm and $c = (24.5 + (n \times 6.3)) \times 10^{-8}$ cm and in another preferred embodiment, the lattice constants are $a = 5.39 \times 10^{-8}$ cm, $b = 5.39 \times 10^{-8}$ cm and $c = (24.5 + (n \times 6.1)) \times 10^{-8}$ cm.

A further preferred embodiment is a superconducting compound, said compound being contained in a black superconductiong substance with the overall composition $Bi_a(Ca,Sr)_bCu_6O_x$ wherein a is a number from 3 to 12, b is a number from 6 to 12, the Sr/Ca atomic ratio is from 1:9 to 9:1, the atomic ratio Bi:(Sr+Ca) is from 0.3:1 to 1.3:1, and x is sufficiently high that the black superconducting substance has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth, provided that if a = 3 then the atomic ratio Sr/Ca is not 1:1.

Yet a further preferred embodiment is a black crystalline substance comprising $Bi_a(Ca,Sr)_bCu_6O_x$ wherein a is of from 3 to 12, b is of from 6 to 12, x is sufficiently high that the black crystalline substance has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth, with an Sr/Ca atomic ratio of from 1:9 to 9:1, a Bi:(Sr+Ca) atomic ratio of from 0.3 to 1.3, a critical temperature T_c for the superconductivity of at least 70 K, which substance crystallizes in the orthorhombic system, provided that if a = 3 then the atomic ratio Sr/Ca is not 1:1.

The novel substances can be prepared by mixing oxides or oxide precursors of the elements Bi, Sr, Ca and Cu thoroughly and heating the mixture to temperatures of at least 700°C.

During the reaction, the atomic ratio of the metals used does not change in a first approximation. The atomic ratio used therefore corresponds to the required oxide composition.

As oxide precursors, use may generally be made of compounds which react to form the corresponding oxides at the reaction temperature, in particular the hydroxides and nitrates. The acetates, formates, oxalates and carbonates of the said metals may also be used. For example, calcium oxide, strontium carbonate, bismuthic acid, bismuth (III) oxide, bismuth (V) oxide, Cu_2O and CuO may be used.

The reaction mixture does not have to, or only partially has to, melt. In this case, it is, however, necessary to keep it for a prolonged period at the reaction temperature.

The synthesis temperature is in this case preferably in the range between 700 and 900°C, preferably 750 - 850°C.

The reaction time should be at least 4 hours, still better, at least 8 hours. The reaction time is limited in the upward direction only by economic considerations. Reaction times of 100 or 120 hours are possible.

The mixture may also be heated so high that it is melted completely. In this case, cooling can be carried out rapidly to temperatures below the solidification point of the entire mixture, ie. 300 - 900°C, preferably 300 - 830°C, and the mixture may be kept in this range for a prolonged time (at least one hour, preferably 4 hours).

Advantageously, the melt can be deposited on a substrate and allowed to solidify there. In this manner, compact layers of the superconductor are obtained on a base after the subsequent temperature treatment at 300 -900°C. The substrate (base) should not react with the reaction mixture. Suitable as a material for the substrate are, for example, Al_2O_3, SiO_2 (quartz), ZrO_2, strontium titanate and barium titanate, and also metals such as steel and Cr/Ni alloys. In this manner, for example, fairly thin layers of 1 µm - 5 mm can be prepared.

The melt may also be spun. In this case, filaments or threads are produced which are also superconducting after annealing at 300 - 900°C, preferably 300-830°C.

The actual reaction should take place in a non-reducing atmosphere. Use may be made, for example, of air, pure oxygen, mixtures of O_2/Ar or O_2/N_2. It is preferable if the reaction of the oxides is carried out in an atmosphere containing oxygen.

After the reaction is complete, the sample is either removed from the furnace and slowly cooled to room temperature in air or oxygen, or is slowly cooled to room temperature in the furnace. Low cooling rates (not exceeding 100 K/h) have a favorable effect on the superconducting properties of the reaction product.

To make sure that the entire oxide mixture has reacted, it is advantageous to comminute the powder obtained further after cooling and to treat it again thermally. For this post treatment, the temperature is in the range from 300 to 900°C. The duration of the post treatment is at least 1 hour, preferably at least 4 hours. What has been stated for the reaction time applies to the upper limit of the post treatment time. Preferably the hot mixture is cooled to room temperature in an atmosph-ere containing oxygen.

Preferred lower limits of the post treatment temperature are at least 300°C, in particular 400°C, and a preferred upper limit is 750°C, better 600°C, in particular 550°C, and still better 500°C. The possible post reaction should be carried out in air, pure oxygen or in a gas mixture such as O_2/Ar or O_2/N_2. Commercially available crucibles or boats of inert materials such as, for example, aluminum oxide, zirconium, platinum and iridium may be used as reaction vessels. Suitable sources of heat are commercially available furnaces such as, for example, chamber, muffle or tubular furnaces.

A further process for preparing the superconducting substances is to mix salts of the said metals in the presence of an aqueous phase, evaporate down the water-containing salt mixture and heat at temperatures of at least 700°C. At least one of the salts used should be water-soluble and the salts should decompose to form oxides in the specified temperature range. The same applies in relation to the reaction time as when the oxides are used.

The salt mixture to be evaporated down can be prepared by dissolving metal oxides in nitric acid and fuming off the nitric acid.

Provided water-soluble salts are used, the metal hydroxides or at least one metal hydroxide can also be precipitated by adding a base, for example tetramethylammonium hydroxide. In this manner it is possible to achieve a particularly thorough mixing of the initial products. The precipitated hydroxides form, together with the undissolved constituent, the "insoluble constituent". This may be separated off, dried and then annealed as specified above. Preferably, no low-volatility cations are entrained by the base used and the salts used are derived from readily volatile acids. These are acids whose boiling point is below 150°C.

In this development of the process according to the invention, the atomic ratio of the metal salts used again corresponds to the required atomic ratio of the final product. The oxidic products prepared from the salts can also be thermally post treated as described above.

In the case of copper-rich formulations, crystals of Cu_2O (red) and CuO (needles) can be removed under the microscope from the black crystalline substance according to the invention after melting, cooling and comminuting. A black crystalline substance is left.

If a Bi:(Sr+Ca):Cu atomic ratio of 2:2:1 is maintained during the preparation, pure black crystals of the composition $Bi_4(Sr,Ca)_4Cu_2O_x$ can be obtained whose transition temperature T_c for the superconductivity is at least 60 - 85 K, generally 70 - 85 K. In this connection, Ca:Sr atomic ratios of 3:1 to 1:3, in particular 1.4:3 - 1.8:3 and particularly preferred, of about 1.6:3 are preferred. In superconducting crystals, the index for the oxygen content (x) is about between 12 and 14.

It has now been found that this compound has the lattice constants $a = 5.39 \times 10^{-8}$ cm, $b = 5.39 \times 10^{-8}$cm and $c = 24.53 \times 10^{-8}$ cm. This compound can be prepared from the required metal oxides, it being necessary to maintain the atomic ratios of the compound. It has further been found that the compound probably also contains pentavalent bismuth.

If the atomic ratio of the formulation is changed slightly, a compound with identical lattice constants and somewhat different composition is obtained. Use may be made, in particular, of formulations having a Cu:Bi atomic ratio of 1:1.9 - 1:2.1, a (Ca+Sr):Cu atomic ratio of 1.9:1 - 2.1:1, a (Ca+Sr):Bi atomic ratio of 0.9:1 - 1.1:1 and a Ca:Sr atomic ratio of 9:1 - 1:9, in particular 3:1 - 1:3, preferably 1:1 - 1:3.

It has further been found that, if the corresponding oxide ratios are maintained, a black crystalline substance of the overall composition $Bi_4(Ca,Sr)_6Cu_4O_{\approx 20}$ can be produced which also has a high transition temperature. It may also be obtained from the melt with subsequent thermal treatment with O_2. The crystalline substance so prepared is composed almost exclusively of a principal phase which crystallizes in the orthorhombic system and has the specified composition. Its transition temperature T_c is at least 70 K. The lattice constants of the compound which crystallizes in the orthorhombic system are $a = 5.395 \times 10^{-8}$ cm, $b = 5.393 \times 10^{-8}$ cm and $c = 30.628 \times 10^{-8}$ cm.

It has now been found that pure crystals with a somewhat higher transition temperature in which the Ca/Sr atomic ratio is 1:3.5 to 1:6.28, in particular 1:4.5 to 1:5.75, preferably 1:5, can be prepared from an initial mixture with somewhat higher Sr/Ca ratio. Reaction temperatures not exceeding 850°C, slow cooling and post annealing at 700°C are beneficial for the formation of the compound. Small excesses of CuO and also a higher Sr/Ca ratio are furthermore beneficial.

If the atomic ratios of the formulation are changed slightly, a compound with the lattice constants specified above and a somewhat different composition is again obtained. In particular, formulations having a Cu:Bi atomic ratio of 1:0.9 - 1.1:1, a (Ca+Sr):Cu atomic ratio of 3:1.9 - 3:2.1, a (Ca+Sr):Bi atomic ratio of 3:1.9 - 3:2.1 and a Ca:Sr atomic ratio of 1:1 - 1:9, in particular 1:3.5 - 1:6.28 may be used.

As an X-ray structural analysis has shown, the strontium-richer compound just mentioned is made up of layers which are arranged in parallel, which each alternate with one another and which are composed of

a) $[Bi_2O_4]^{2+}$ and

b) $[(Ca,Sr)_3Cu_2O_6]^{2-}$ with a Perowskite structure in which, in the layer, two planes of $[CuO_6]$ octahedra which join each other at the corners are present and, in the planes of oxygen atoms which are situated above and below in parallel with each of the two $[CuO_{4/2}]$ planes, the alkaline earth atoms are so arranged that they are each situated at the center of a smallest square composed of 4 oxygen atoms, and the two planes of $[CuO_6]$ octahedra have a layer of (Ca,Sr)O in common.

The oxygen positions between the two octahedral layers are (depending on the conditions of preparation of the superconductor), not occupied or only partially occupied. Prolonged heating at 900°C results in loss of oxygen, while prolonged heating at 400°C in an oxygen atmosphere results in a partial filling of said oxygen positions. The oxygen occupation in the $[Bi_2O_4]^{2+}$ layers is also altered by the thermal treatment. Up to two O atoms can be removed for each Bi_2O_4. Bismuth is then trivalent. At the same time the color of the crystals changes from black to brown. A high oxygen content (black mass) which can be established ideally at approx.~600°C is beneficial.

The X-ray structural analysis carried out on a single crystal having the Ca:Sr atomic ratio of 1:4 has revealed that only strontium atoms are present in the outer (Ca,Sr)O planes of the layer containing copper. On the other hand, the Ca/Sr atomic ratio in the inner (Ca,Sr)O plane of the layer containing copper is 1:1. Depending on the Ca/Sr ratio used in the formulation, this ratio may be 0.7:1 - 2.1:1, in particular 0.8:1 to 1.2:1. The structural arrangement of this compound is shown in Figure 1.

In addition to the compound just described and having a Perowskite structure in which, in the layer containing copper, 2 planes of $[CuO_6]$ octahedra which are joined to each other at the corners are present, and to the compound $Bi_4(Ca,Sr)_4Cu_2O_x$ having a Perowskite structure in which, in the layer containing copper, only one plane of $[CuO_6]$-octahedra joined to each other at the corners is present, compounds exist in which the layer containing Cu is made up of more than 2 planes of $[CuO_6]$ octahedra which join each other at the corners.

Using the generally specified processes, it is possible to prepare black superconducting compounds which crystallize in the orthorhombic system and have a transition temperature T_c of at least 70 K and a content of Bi, Ca, Sr and Cu, and which have an overall composition of $Bi_4(Ca,Sr)_{4+2n}-Cu_{2+2n}O$ about 16+4n, where n = 2, 3, 4 or 5. In these compounds, the Ca/Sr atomic ratio is 1:9 to 9:1. The lattice constants of the compounds are a = 5.39 x 10^{-8} cm, b = 5.39 x 10^{-8} cm and c = (24.5 + n x 6.1) x 10^{-8} cm.

X-Ray structural analyses indicate that the specified compounds are made up of layers which are arranged in parallel, which each alternate with one another and which are composed of

a) $[Bi_2O_4]^{2+}$ and
b) $[(Ca,Sr)_{2+n}Cu_{1+n}O_{4+2n}]^{-2}$ having a Perowskite structure in which, in this layer, 1 + n planes of $[CuO_6]$ octahedra which are joined to each other at the corners are present and the alkaline earth atoms in the 2 + n planes of the

oxygen positions, which are parallel to, but not in, the $[CuO_{4/2}]$ planes are so arranged that they are each situated at the center of a smallest square composed of 4 oxygen atoms and the planes of $[CuO_6]$ octahedra are joined by n common layers of (Ca,Sr)O.

Here, too, the oxygen positions between the two layers of octahedra, ie. in the (Ca,Sr)O plane are not occupied or only partially occupied. A corresponding remark applies to the $[Bi_2O_4]^{2+}$ layers. The degree of occupation also depends on the thermal treatment of the crystalline substance first produced and the reaction gas used. A post treatment as disclosed on page 6 is expedient.

The Sr/Ca atomic ratio in the two outer (Ca,Sr)O planes of the layer containing copper is at least 10. These planes are therefore very strontium-rich. On the other hand, the Ca/Sr atomic ratio in the n inner (Ca,Sr)O planes of the layer containing copper depends substantially on the initial Ca/Sr ratio and may therefore be 1:10 to 10:1, in particular 1:3 to 3:1, preferably 1:1. The Ca/Sr ratio in all n inner (Ca, Sr)O planes is probably the same.

Surprisingly, superconducting substances can be obtained in the process according to the invention from laboratory chemicals having a purity of only about 99.5 %.

If the atomic ratios of the formulation are changed slightly for the three-layer compound (n = 2), a substance is again obtained which has a very high proportion of the compound with the specified layer structure and the specified lattice constants, but somewhat different composition. For example, formulations having a Cu:Bi atomic ratio of 3:1.9 - 3:2.1, a (Ca+Sr):Cu atomic ratio of 8:5.8 - 8:6.2, a (Ca+Sr):Bi atomic ratio of 2.1:1 - 1.9:1 and a Ca:Sr atomic ratio of 1:1 - 1:5, in particular 1:1.9 - 1:2.1 may be used.

The superconducting substances obtained can be used in power engineering (for cables and wires, transformers, and energy storage devices in the form of coils with current flowing through them), in magnetic technology (for example, nuclear spin tomographs and to produce holding magnets for suspension railways), in computer technology (thin films, connections on printed circuit boards, Josephson switching devices) and for electronic components (detectors, antennas, transistors, electronic sensors, for example SQUIDs, galvanometers, modulators, bolometers and SLUGs). The use of superconduction in metrology is dealt with in a paper "Die Anwendung der Supraleitung in der Meßtechnik" by Prof. F. Baumann, Karlsruhe, published in a series of papers by the VDI-Bildungswert (1976).

It has further been found that several measures are advantageous for raising the proportion of a phase having $T_c \approx 110$ K.

A beneficial requirement is that the overall composition of the reaction mixture in the triangular coordinate system (ignoring the oxygen component) lies between four points ABCD which define a parallelogram, where

$A = Bi_{0.19}E_{0.35}Cu_{0.46}$,

$B = Bi_{0.14}E_{0.4}Cu_{0.46}$,

$C = Bi_{0.3}E_{0.38}Cu_{0.32}$,

$D = Bi_{0.25}E_{0.43}Cu_{0.32}$ and E denotes the sum of the alkaline earths Ca+Sr. The calcium/strontium atomic ratio is 0.85:1 - 1.2:1, in particular 0.95:1 - 1.1:1. Preferably it is 1:1. Preferably, the overall composition lies between the corner points $Bi_{0.2}E_{0.4}Cu_{0.4}$ and $Bi_{0.25}E_{0.4}Cu_{0.35}$ which define a straight line intersection. With a Ca/Sr atomic ratio of 1:1, this corresponds to the corner points $BiSrCaCu_2O_x$ and $BiSr_{0.8}Ca_{0.8}Cu_{1.4}O_x$.

It is furthermore advantageous to carry out the sintering process at as high temperatures as possible (for instance, above 860°C). However, in this process, the formulation should not melt. The duration of the sintering process is advantageously at least 50 hours, preferably at least 80 hours. It is beneficial to sinter in an oxygen-containing atmosphere, in particular air. If sintering is carried out in pure nitrogen, the formulation begins to melt about 40 K earlier.

A further advantageous measure is to cool down the formulation after sintering to temperatures of 550 - 650°C, preferably 580 - 620, in particular 590 - 610°C, to leave it for some time at this temperature (e.g., at least 20 minutes), to heat it up again to the sintering temperature and to repeat this process at least 2x. This process can be repeated 2 - 20 times. The proportion of the superconducting phase then decreases again. It is preferable to repeat the cycle 2 - 6 times, in particular 2 - 3 times. The time for cooling from the sintering temperature to 550 - 650°C, holding in the range 550 - 650°C and heating up again to the sintering temperature should be at least 30 minutes in each case, or better, at least 45 minutes. For the time of cooling to 550 - 650°C and holding at 550 - 650°C, a time is preferred of at least one hour, in particular 1 - 3 hours, in each case. A further increase in these times appears to offer no more advantages.

The invention further provides a black crystalline superconducting component which has been manufactured by preparing a mixture containing the oxides or corresponding oxide precursors of bismuth, strontium, calcium and copper, heating the mixture high enough for all the components of the mixture to be melted, cooling the mixture to a temperature of from 300 to 900°C, keeping the mixture in this temperature range for at least 1 hour and then cooling the mixture further, wherein the mixture has the overall composition $Bi_a(Ca,Sr)_bCu_6O_x$ wherein a is from 3 to 12, b is from 6 to 12, provided that if a = 3 and b = 6, the atomic ratio of Sr:Ca is other than 1:1, x is sufficiently high that the black superconducting component has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth, with a Sr/Ca atomic ratio of from 1:9 to 9:1, a Bi:(Sr+Ca) atomic ratio of from 0.3 to 1.3, a critical temperature T_c for the conductivity of at least 70 K and a main compound which crystallizes in the orthorhombic system.

The invention yet further provides a black substance whose principle phases crystallize in the orthorhombic system, said black substance having a transition temperature, T_c, of at least 70 K, comprising the elements bismuth, strontium, calcium and copper in oxidic form and having the overall composition $Bi_6Sr_6Ca_3Cu_6O_x$ where x is sufficiently high that the black superconducting substance has a transition temperature T_c, of at least 70 K, and whose principle phases show essentially the X-ray diffraction lines listed in Table 2, below, or in Table 3 below.

The invention is explained in more detail by the examples.

E

Example 1

1 mol of Bi_2O_3, 2 mol of SrO, 2 mol of CaO and 2 mol of CuO are comminuted in an agate mortar, very intimately mixed and transferred to an Al_2O_3 boat.

The specimen is rapidly heated in a suitable laboratory furnace to 950°C, and the specimen melts. Specimens quenched directly from 950°C to room temperature exhibit an X-ray diffraction diagram according to Table 1 and also do not exhibit any superconduction.

If the specimen is cooled from 950°C to 700°C and kept at this temperature for one hour and then rapidly cooled to room temperature, the fragments of the melt cake so obtained exhibit a critical temperature of T_c = 70 K with measurements in a SQUID magnetometer.

The X-ray diffraction diagram of this specimen exhibits the appearance of a further crystalline phase (Table 2).

If the specimen is cooled from 700°C to 500°C and again annealed there for one hour, the powder diagram exhibits the phase which appeared at 700°C as the main product (Table 3). This specimen also exhibits a critical temperature of approx. 70 K (SQUID magnetometer).

Example 2

3 mol of $SrCO_3$, 1.5 mol of Bi_2O_3, 3 mol of $CaCO_3$ and 6 mol of CuO are comminuted in an agate mortar, mixed thoroughly and transferred to an Al_2O_3 crucible.

The specimen is heated in air to 800°C in 6 hours in a suitable laboratory furnace and kept there for 6 hours. The specimen is then cooled to 400°C in 2 hours, kept at this temperature for a further 3 hours, then cooled to 100°C in 2 hours and removed from the furnace.

The black material so prepared exhibits a transition temperature of T_c = 75 K with measurements in a SQUID magnetometer (Figure 2).

Example 3

0.2 mol of Bi_2O_3, 0.6 mol of SrO, 0.2 mol of CaO and 0.6 mol of CuO are comminuted, mixed and rapidly heated to 830°C in a corundum crucible. This temperature is maintained for 2 hours and subsequent annealing is then carried out in air at 800°C for 3 hours. The formulation is quenched from 800°C to room temperature by removing it from the furnace and allowing it to cool in air.

A compound is obtained of the approximate composition

$Bi_4(Ca,Sr)_8Cu_6O_{20}$. The Sr/Ca atomic ratio is 4:1. The transition temperature T_c is 70 - 82 K.

Example 4

0.01 mol of CaO, 0.01 mol of Bi_2O_3, 0.01 mol of SrO and 0.01 mol of CuO are mixed in an agate mortar, comminuted and transferred to a corundum boat. The formulation is heated rapidly in air to 1000°C in a laboratory furnace and kept at this temperature for 30 minutes. The crystalline substance melts in this process. It is then allowed to cool in the furnace to room temperature. The black stalk-like solidified melt cake is comminuted in a mortar, heated again (to 800°C in 2 hours in an oxygen atmosphere), then kept for 3 hours at 800°C and cooled to room temperature in 3 hours.

A subsequent measurement of the susceptibility in a SQUID magnetometer reveals a transition temperature of 77 K. The compound has the overall composition $Bi_4(Ca,Sr)_4$-$Cu_2O_{\approx 14}$.

Example 5

0.02 mol of CaO, 0.01 mol of Bi_2O_3, 0.02 mol of SrO and 0.04 mol of CuO are mixed in an agate mortar, comminuted and transferred to a corundum boat. The formulation is heated in one hour to 1000°C in air in a laboratory furnace and kept at this temperature for 30 minutes. In this process a melt is formed. Cooling is then carried out to 500°C in 2 hours and the formulation is removed from the furnace at this temperature. A subsequent measurement of the susceptibility in a SQUID magnetometer reveals a transition temperature of about 80 K.

According to radiographic investigations, the main product is $Bi_4(Sr,Ca)_6Cu_4O_{\approx 20}$.

Example 6

2 mol of Bi_2O_3, 4 mol of $SrCO_3$, 4 mol of CaO and 8 mol of CuO are comminuted in an agate mortar, mixed thoroughly and transferred to an Al_2O_3 crucible. The specimen is rapidly heated in air to 800 - 820°C, kept there for 20 hours and rapidly cooled to room temperature. The annealed powder is comminuted and treated thermally and mechanically a further two times as described above.

The black powder is then pressed into tablets under a pressure of 300 MPa (3 kbar), these are placed on MgO sheets and variously treated thermally (in air) as described below:

a) Heating to 870°C for 3 hours
annealing at 870°C for 80 hours
cooling to room temperature (= RT) in 2 min ("quenching")
conductivity measurement: T_c (R=0)= 57 K
SQUID measurement: 12 % superconducting component at 4 K (measured at B = 100 gauss; 1 gauss = 10^{-4} Wb/m^2)

b) Heating to 870°C in 3 hours
annealing at 870°C for 80 hours
cooling to 600°C in 3 hours
quenching from 600°C to RT (2 min)
conductivity: T_c (R=0)= 63 K
SQUID measurement: -

c) Heating to 870°C in 3 hours
annealing at 870°C for 80 hours
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
heating to 870°C in 3 hours
annealing at 870°C for 3 hours
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours

heating to 870°C in 3 hours
annealing at 870°C for 3 hours
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
conductivity measurement: T_c (R=0)= 107 K
SQUID measurement: 30 % superconducting component at 4 K (measured at 100 gauss)

d) Heating to 864°C in 3 hours
annealing at 864°C for 50 hours

following temperature cycle run six times:
cooling to 600°C in 1 hour
annealing at 600°C for 1 hour
heating to 864°C in 1 hour
annealing at 864°C for 1 hour

then:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
conductivity measurement: T_c (R=0)= 102 K
SQUID measurement: 25 % superconducting component at 4 K (measured at B = 100 gauss)

e) Heating to 870°C in 3 hours
annealing at 870°C for 80 hours

following temperature cycle run twelve times:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
heating to 870°C in 3 hours
annealing at 870°C for 3 hours

then:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
conductivity: T_c (R=0)= 105 K

SQUID measurement: 26 % superconducting component at 4 K
(measured at B = 100 gauss)

f) Heating to 870°C in 3 hours
annealing at 870°C for 80 hours

following temperature cycle run three times:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
heating to 870°C in 3 hours
annealing at 870°C for 3 hours

then:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
conductivity: T_c (R=0)= 98 K
SQUID measurement: 35 % superconducting component at 4 K
measured with 100 gauss
50 % superconducting component measured with 10 gauss
1 gauss = 10^{-4} Wb/m^2.

Example 7

4.3 mol of Bi_2O_3, 7 mol of $SrCO_3$, 7 mol of CaO and 12 mol of CuO are comminuted in an agate mortar, mixed and transferred to an Al_2O_3 crucible. The specimen is rapidly heated in air to 800 - 820°C, kept there for 20 hours, rapidly cooled to RT and comminuted (agate mortar). The annealing comminuting is repeated a further two times. Then the powder is pressed into tablets under a pressure of 300 MPa (3 kbar) and treated thermally on MgO sheets as described below:

a) Heating to 866°C in 3 hours
annealing at 866°C for 65 hours

following temperature cycle traversed six times
cooling to 600°C in 3 hours

annealing at 600°C for 3 hours
heating to 866°C in 3 hours
annealing at 866°C for 3 hours

then:
cooling to 600°C for 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
T_c (R=0)= 66 K

b) Heating to 866°C in 3 hours
annealing at 866°C for 53 hours

following temperature cycle run six times:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
heating to 866°C in 3 hours
annealing at 866°C for 3 hours

then:
cooling to 600°C for 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
T_c (R=0)= 95 K
24 % superconducting component at 4 K
(measured with B = 100 gauss)

c) Heating to 868°C in 3 hours
annealing at 868°C for 34 hours

following temperature cycle run nine times:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
heating to 868°C in 3 hours
annealing at 868°C for 3 hours

then:
cooling to 600°C for 3 hours
annealing at 600°C for 3 hours

cooling to RT in 3 hours
T_c (R=0)= 60 K

Example 8

2 mol of Bi_2O_3, 4 mol of $SrCO_3$, 4 mol of CaO and 12 mol of CuO are processed into tablets by the method specified in Example 6. These are thermally treated in various ways (in air):

a) Heating to 863°C for 3 hours
annealing at 863°C for 50 hours

following cycle traversed six times:
cooling to 600°C in 1 hour
annealing at 600°C for 1 hour
heating to 863°C in 1 hour
annealing at 863°C for 1 hour

then:
cooling to 600°C in 1 hour
annealing at 600°C for 1 hour
cooling to RT in 1 hour
T_c (R=0)= 66 K

b) Heating to 868°C in 3 hours
annealing at 868°C for 34 hours

following cycle traversed eight times:
cooling to 600°C in 1 hour
annealing at 600°C for 1 hour
heating to 868°C in 1 hour
annealing at 868°C for 1 hour

then:
cooling to 600°C in 1 hour
annealing at 600°C for 1 hour
cooling to RT in 1 hour
T_c (R=0)= 64 K

Example 9

1 mol of Bi_2O_3, 2 mol of $SrCO_3$, 2 mol of CaO and 3 mol of CuO are processed into tablets by the method specified in Example 6. These are thermally treated in the following way (in air):

Heating to 870°C in 3 hours
annealing at 870°C for 80 hours

following cycle traversed twice
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
heating to 870°C in 3 hours
annealing at 870°C for 3 hours

then:
cooling to 600°C in 3 hours
annealing at 600°C for 3 hours
cooling to RT in 3 hours
T_c (R=0)= 65 K
20 % superconducting component at 4 K
(measured at 100 gauss)

Table 1

NO	2 THETA	D	INTEG.I (%)
1	7.125	12.4060	6.6
2	16.709	5.3057	0.5
3	21.674	4.1002	27.7
4	23.487	3.7877	0.7
5	25.718	3.4640	20.7
6	29.222	3.0560	100.0
7	29.600	3.0179	26.9
8	30.455	2.9351	3.9
9	31.937	2.8022	5.2
10	33.154	2.7021	14.8
11	34.884	2.5719	7.3
12	35.620	2.5204	0.6
13	36.532	2.4596	8.5
14	37.193	2.4173	6.2
15	37.854	2.3767	1.0
16	40.085	2.2494	1.1
17	41.047	2.1989	0.6
18	41.962	2.1530	15.4
19	44.368	2.0417	2.7
20	44.706	2.0270	8.9
21	50.234	1.8162	0.9
22	52.027	1.7577	16.8
23	53.693	1.7070	2.2
24	54.214	1.6919	1.3
25	54.972	1.6703	1.3
26	57.077	1.6136	9.0

Table 2

NO	2 THETA	D	INTEG.I (%)
1	4.122	21.4351	3.6
2	4.302	20.5386	2.3
3	5.698	15.5105	1.6
4	7.107	12.4381	4.3
5	7.682	11.5074	1.6
6	21.611	4.1121	29.5
7	22.809	3.8986	21.9
8	24.713	3.6025	8.3
9	25.713	3.4646	26.0
10	26.101	3.4140	1.5
11	27.278	3.2693	35.6
12	28.947	3.0844	100.0
13	29.637	3.0142	47.5
14	30.149	2.9642	2.1
15	30.676	2.9144	45.5
16	31.950	2.8011	17.4
17	33.057	2.7098	84.9
18	34.875	2.5728	38.7
19	35.781	2.5094	1.3
20	36.497	2.4618	9.8
21	37.210	2.4183	12.8
22	39.964	2.2559	1.8
23	42.093	2.1466	3.9
24	44.719	2.0265	99.4
25	46.642	1.9473	3.8
26	47.382	1.9186	31.6
27	50.234	1.8162	14.1
28	52.881	1.7313	1.5
29	53.697	1.7069	4.7
30	54.224	1.6916	2.4
31	54.917	1.6719	3.6
32	56.343	1.6329	1.9
33	56.797	1.6209	3.6
34	57.524	1.6021	0.9
35	58.423	1.5796	1.6

Table 3

NO	2 THETA	D-space	INTEG.I (%)
1	7.231	12.21443	6.1
2	14.363	6.16182	8.2
3	16.783	5.27810	8.3
4	19.324	4.58947	14.1
5	21.703	4.09147	8.5
6	23.570	3.77145	6.4
7	24.696	3.60198	6.1
8	25.753	3.45652	61.2
9	27.327	3.26082	6.2
10	28.700	3.10796	10.3
11	29.002	3.07624	48.6
12	29.675	3.00800	100.0
13	30.202	2.95671	9.6
14	30.553	2.92351	8.6
15	31.856	2.80687	13.6
16	32.057	2.78974	6.2
17	32.674	2.73843	6.3
18	32.917	2.71878	25.6
19	33.216	2.69494	53.0
20	34.491	2.59820	9.7
21	34.737	2.58039	8.7
22	35.681	2.51426	8.3
23	35.990	2.49334	7.9
24	36.376	2.46778	10.6
25	37.231	2.41303	7.2
26	42.002	2.14932	13.2
27	44.645	2.02803	14.2
28	47.340	1.91868	9.7
29	47.662	1.90646	19.7
30	51.393	1.77645	7.2
31	51.789	1.76380	12.6
32	52.047	1.75566	7.2
33	53.148	1.72185	6.8
34	54.943	1.66978	8.5
35	56.669	1.62296	6.3
36	56.861	1.61791	6.5
37	57.072	1.61243	10.5
38	57.408	1.60379	6.0
39	57.713	1.59604	6.6
40	60.004	1.54048	8.8

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A superconducting phase which crystallizes in the orthorhombic system, said phase being the main phase of a black superconducting substance having a transition temperature, T_c, of at least 70 K, comprising the elements bismuth, strontium, calcium and copper in oxidic form and having the overall composition

$$Bi_a(Ca,Sr)_bCu_6O_x$$

wherein

a is a number from 3 to 12,

b is a number from 6 to 12,

the Sr/Ca atomic ratio is from 1:9 to 9:1,

the atomic ratio Bi:(Sr+Ca) is from 0.3:1 to 1.3:1,

and x is sufficiently high that the black superconducting substance has a transition temperature, T_c, of at least 70 K

and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth, provided that if a = 3 then the atomic ratio Sr/Ca is not 1:1.

2. A superconducting phase as claimed in claim 1, having X-ray diffraction lines as shown in Table 2.

3. A superconducting phase as claimed in claim 1, having X-ray diffraction lines as shown in Table 3.

4. A superconducting phase as claimed in claim 1, having been obtained by preparing a mixture comprising the oxides or oxide precursors of the elements Bi, Sr, Ca and Cu in the ratios of the elements as claimed in claim 1, heating the mixture for at least 4 hours at a temperature of at least 700°C, at which the mixture does not melt or only partially melts, and cooling the mixture.

5. A superconducting phase as claimed in claim 1, having been obtained by preparing a mixture comprising the oxides or oxide precursors of the elements Bi, Sr, Ca and Cu in the ratios of the elements as claimed in claim 1, heating the mixture high enough for it to be melted completely and cooling the mixture.

6. A superconducting phase as claimed in claim 1, having been obtained by preparing an aqueous dispersion comprising a mixture of the salts of the elements Bi, Sr, Ca and Cu in the ratios of the elements as claimed in claim 1 of which at least one is water-soluble, and water; evaporating water from the dispersion; heating the resultant mixture at a temperature of at least 700°C; and cooling the mixture.

7. A superconducting phase as claimed in any one of claims 1 to 6 wherein a in the formula of the black superconducting substance is a number from > 3 to 12.

8. A superconducting phase as claimed in claim 7 wherein a is a number from 4 to 12.

9. A superconducting phase as claimed in claim 7 wherein a is a number from > 4 to 12.

10. A superconducting phase as claimed in claim 9, wherein a in the formula of the black superconducting substance is a number from > 6 to 12.

11. A superconducting phase as claimed in any one of claims 1 to 10, wherein in the formula of the black superconducting substance the Sr/Ca atomic ratio is 1:3 to 3:1.

12. A superconducting phase as claimed in claim 11, wherein in the formula of the black superconducting substance the Sr/Ca atomic ratio is 1:1.

13. A superconducting phase as claimed in any one of claims 1 to 12, wherein in the formula of the black superconducting substance the atomic ratio Bi:(Sr+Ca) is of from 0.5:1 to 1:1.

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14. A superconducting phase as claimed in claim 4, having been obtained by heating the mixture at a temperature within the range of from 700 to 900°C.

15. A superconducting phase as claimed in claim 6, having been obtained by heating the mixture at a temperature within the range of from 700 to 900°C.

16. A superconducting phase as claimed in claim 4, having been obtained by heating the mixture at a temperature of at least 700°C for at least 100 hours.

17. A superconducting phase as claimed in claim 6, having been obtained by heating the mixture at a temperature of at least 700°C for at least 100 hours.

18. A superconducting phase as claimed in claim 5, having been obtained by cooling the melted mixture rapidly to a temperature of 300 to 900°C, by keeping this temperature for at least one hour and by further cooling.

19. A superconducting phase as claimed in claim 5, wherein the black superconducting substance is in the form of a layer deposited on a substrate.

20. A superconducting phase as claimed in claim 5, wherein the black superconducting substance is in the form of a spun melt.

21. A superconducting phase as claimed in claim 1 which has the overall composition $Bi_4(Sr,Ca)_6Cu_4O_{about20}$.

22. A superconducting phase as claimed in any one of claims 1 to 21, wherein the atomic ratio Sr/Ca is from about 3.5:1 to about 6.28:1.

23. A superconducting phase as claimed in claim 22 wherein the atomic ratio Sr/Ca is in the range of about 4.5:1 to about 5.75:1.

24. A superconducting phase as claimed in claim 23, wherein the atomic ratio Sr/Ca is about 5:1.

25. A black crystal mass containing as the main product $Bi_4(Sr,Ca)_6Cu_4O_{about20}$ with a Ca/Sr atomic ratio of 1:3.5 to 1:6.28, and which is prepared from oxides or oxide precursors of the elements Bi, Sr, Ca and Cu as starting components, and has a transition temperature T_c of at least 70 K.

26. The black crystal mass as claimed in claim 25, wherein the Sr/Ca atomic ratio is 4.5:1 to 5.75:1.

27. The black crystal mass as claimed in claim 26, wherein the Sr/Ca atomic ratio is 5:1.

28. A superconducting phase as claimed in claim 21 which is made up of layers (a) and (b), which are arranged in parallel, which each alternate with one another and which are composed of:

(a) $[Bi_2O_4]^{2+}$ and

(b) $[(Ca,Sr)_3Cu_2O_6]^{2-}$ with a Perowskite structure having, in layer (b), two planes of $[CuO_6]$ octahedra which join each other at corners of the octahedra, and each octahedra having two $[CuO_{4/2}]$ planes and planes of oxygen atoms which are situated above and below and in parallel with each of the two $[CuO_{4/2}]$ planes, and wherein in the octahedra the Ca and Sr atoms are so arranged that they are each situated at the centre of a smallest square composed of 4 oxygen atoms, and the two planes of $[CuO_6]$ octahedra have a layer of (Ca,Sr)O in common.

29. A black superconducting compound which crystallizes in the orthorhombic system having a transition temperature, T_c, of at least 70 K and having the overall formula

$Bi_4(Ca,Sr)_{4+2n}Cu_{2+2n}O_{about12+4n}$

wherein

n is 2, 3, 4 or 5,

the Sr/Ca atomic ratio is of 1:9 to 9:1.

30. A superconducting compound as claimed in claim 29 wherein the lattice constants are $a = 5.41 \times 10^{-8}$ cm, $b = 5.47 \times 10^{-8}$ cm and $c = (24.5 + (n \times 6.3)) \times 10^{-8}$ cm.

31. A superconducting compound as claimed in claim 29 wherein the lattice constants are a = 5.39×10^{-8}cm, b = 5.39×10^{-8}cm and c = $(24.5 + (n \times 6.1)) \times 10^{-8}$cm.

32. A superconducting compound as claimed in claim 29 having a transition temperature, T_c, of at least 70 K and having the overall formula

$$Bi_4(Ca,Sr)_8Cu_6O_{about20}.$$

33. A superconducting compound as claimed in claim 32 wherein the lattice constants are a = 5.41×10^{-8}cm, b = 5.47×10^{-8}cm and c = 37.1×10^{-8}cm.

34. A superconducting compound as claimed in claim 32 wherein the lattice constants are a = 5.39×10^{-8}cm, b = 5.39×10^{-8}cm and c = 36.7×10^{-8}cm.

35. A superconducting compound, said compound being contained in a black superconducting substance with the overall composition

$$Bi_a(Ca,Sr)_bCu_6O_x$$

wherein

a is a number from 3 to 12,

b is a number from 6 to 12,

the Sr/Ca atomic ratio is from 1:9 to 9:1,

the atomic ratio Bi:(Sr+Ca) is from 0.3:1 to 1.3:1,

and x is sufficiently high that the black superconducting substance has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth, provided that if a = 3 then the atomic ratio Sr/Ca is not 1:1.

36. A superconducting compound as claimed in claim 35, wherein a = 4, b = 8 and x = about 20.

37. A superconducting compound as claimed in claim 29, having been obtained by preparing a mixture comprising the oxides or oxide precursors of the elements Bi, Sr, Ca and Cu in the ratios of the elements as claimed in claim 29 and heating the mixture for at least 4 hours at a temperature of at least 700°C, at which the mixture does not melt or only partially melts and cooling the mixture.

38. A superconducting compound as claimed in claim 29, having been obtained by preparing a mixture comprising the oxides or oxide precursors of the elements Bi, Sr, Ca and Cu in the ratios of the elements as claimed in claim 29 and heating the mixture high enough for it to be melted completely and cooling the mixture.

39. A superconducting compound as claimed in claim 29, having been obtained by preparing an aqueous dispersion comprising a mixture of the salts of the elements Bi, Sr, Ca and Cu in the ratios of the elements as claimed in claim 29, and water; evaporating water from the dispersion; heating the resultant mixture at a temperature of at least 700°C; and cooling the mixture.

40. A superconducting compound as claimed in claim 35 or 36 wherein for the black superconducting substance a is a number from >3 to 12.

41. A superconducting compound as claimed in claim 35 or 36 wherein for the black superconducting substance a is a number from 4 to 12.

42. A superconducting compound as claimed in claim 35 or 36 wherein for the black superconducting substance a is a number from >4 to 12.

43. A superconducting compound as claimed in claim 35 or 36, wherein for the black superconducting substance a is a number of from >6 to 12.

44. A superconducting compound as claimed in any one of claims 35 to 43, wherein the Sr/Ca atomic ratio of the black superconducting substance is 1:3 to 3:1.

45. A superconducting compound as claimed in claim 44, wherein the Sr/Ca atomic ratio of the black superconducting substance is 1:1.

46. A superconducting compound as claimed in claim 37, having been obtained by heating the mixture at a temperature within the range of from 700 to 900°C.

47. A superconducting compound as claimed in claim 37, having been obtained by heating the mixture at a temperature of at least 700°C for more than 100 hours.

48. A superconducting compound as claimed in claim 38, having been obtained by cooling the melted mixture rapidly to a temperature of 300 to 900°C, by keeping this temperature for at least one hour and by further cooling.

49. A superconducting compound as claimed in claim 38, wherein the superconducting substance is in the form of a layer deposited on a substrate.

50. A superconducting compound as claimed in claim 38, wherein the superconducting substance is in the form of a spun melt.

51. A superconducting compound having a transition temperature, T_c at least 70 K and having the overall formula $Bi_4(Ca,Sr)_8Cu_6O_{about 20}$,

wherein said compound comprises layers which are arranged in parallel, which alternate with one another, and which consist essentially of:

a) $[Bi_2O_4]^{2+}$ and

b) $[(Ca,Sr)_{2+n}Cu_{1+n}O_{4+2n}]^{2-}$ having a Perowskite structure with n = 2.

52. A superconducting compound as claimed in claim 51, wherein said layer (b) has 1 + n planes of $[CuO_6]$ octahedras which join each other at the corners of the octahedra, and each octahedra having two $[CuO_{4/2}]$ planes and 2 + n planes comprised of the positions for the oxygen atoms, which planes are parallel to, but not in, the $[CuO_{4/2}]$ planes, wherein the Ca and Sr atoms are in the 2 + n planes and are so arranged that they are each situated at the center of a smallest square comprised of 4 oxygen atoms and the planes of $[CuO_6]$ octahedras are joined by n common layers of (Ca,Sr)O.

53. A superconducting compound as claimed in claim 52, wherein in the (Ca,Sr)O layers, positions for the oxygen atoms are unoccupied or partially occupied.

54. A black crystalline substance comprising:

$Bi_a(Ca,Sr)_bCu_6O_x$

wherein

a is of from 3 to 12,

b is of from 6 to 12,

x is sufficiently high that the black crystalline substance has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth,

with an Sr/Ca atomic ratio of from 1:9 to 9:1,

a Bi:(Sr+Ca) atomic ratio of from 0.3 to 1.3,

a critical temperature T_c for the superconductivity of at least 70 K and

which substance crystallizes in the orthorhombic system, provided that if a = 3 then the atomic ratio Sr/Ca is not 1:1.

55. A crystalline substance as claimed in claim 54 wherein a is from >3 to 12.

56. A crystalline substance as claimed in claim 54 wherein a is from 4 to 12.

57. A crystalline substance as claimed in claim 54 wherein a is from >4 to 12.

58. A crystalline substance as claimed in claim 54, wherein a is from >6 to 12.

59. A crystalline substance as claimed in any one of claims 54 to 58, wherein the Sr/Ca atomic ratio is of from 1:3 to 3:1.

60. A crystalline substance as claimed in claim 59, wherein the Sr/Ca atomic ratio is 1:1.

61. A crystalline substance as claimed in any one of claims 54 to 60, wherein the Bi:(Sr+Ca) atomic ratio is of from 0.5:1 to 1:1.

62. A process for preparing a superconductor containing bismuth, calcium, strontium and copper, which comprises preparing a mixture of the oxides of bismuth, calcium, strontium and copper or corresponding oxide precursors having the atomic ratio stated in claim 54, heating the mixture to a temperature of at least 700°C so that the mixture is not melted or is only partially melted, keeping the mixture in this temperature range for a time of at least 4 hours and then cooling the mixture.

63. A process for preparing a superconductor as claimed in claim 62, wherein at least one oxide precursor is an acetate, formate, oxalate or carbonate.

64. A process for preparing a superconductor as claimed in claim 62 or 63, wherein the mixture is heated to a temperature within the range of from 700 to 900°C.

65. A process for preparing a superconductor as claimed in claim 62, 63 or 64, wherein the heating is carried out in an atmosphere which contains free oxygen.

66. A process for preparing a superconductor as claimed in any one of claims 62 to 65, wherein the superconductor is cooled to room temperature slowly enough to favourably affect the superconducting properties.

67. A process for preparing a superconductor as claimed in any one of claims 62 to 66, wherein the cooling is carried out in an atmosphere which contains oxygen.

68. A process for preparing a superconductor containing bismuth, calcium, strontium and copper, which comprises preparing a mixture of the oxides or corresponding oxide precursors of bismuth, calcium, strontium and copper having the atomic ratio stated in claim 54, heating the mixture high enough for all the components to be melted, cooling the mixture to a temperature of from 300 to 900°C, keeping the mixture in this temperature range for at least 1 hour and then further cooling the mixture.

69. A process for preparing a superconductor as claimed in claim 68, wherein at least one oxide precursor is an acetate, formate, oxalate or carbonate.

70. A process for preparing a superconductor as claimed in claim 68 or 69, wherein the melted and cooled mixture is kept in the temperature range of from 300 to 900°C for 4 hours.

71. A process for preparing a superconductor as claimed in claim 68, 69 or 70, wherein the melted mixture is deposited on a substrate and allowed to solidify, and wherein the solidified melt is heated at a temperature of from 300 to 900°C.

72. A process for preparing a superconductor as claimed in claim 71, wherein the melt is deposited in thin layers of 1 μm to 5 mm.

73. A process for preparing a superconductor as claimed in claim 68, 69 or 70, wherein the melt is spun to form filaments, and the filaments are allowed to solidify and are heated at a temperature of from 300 to 900°C.

74. A process for preparing a superconductor as claimed in any one of claims 68 to 73, which is carried out in an atmosphere which contains free oxygen.

75. A process for preparing a superconductor as claimed in any one of claims 68 to 74, wherein the further cooling is carried out to room temperature slowly enough to favourably affect the superconducting properties.

76. A process for preparing a superconductor as claimed in any one of claims 68 to 75, wherein the heating treatment, carried out in the temperature range of from 300 to 900°C, is maintained for 4 hours.

77. A process for preparing a superconductor containing bismuth, calcium, strontium and copper, which comprises preparing an aqueous dispersion of the salts of bismuth, calcium, strontium and copper, having the atomic ratio stated in claim 54 and of which at least one is water-soluble, and water; evaporating water; annealing the resultant mixture of salts by heating the mixture at a temperature of at least 700°C; and then cooling the mixture.

78. A process for preparing a superconductor as claimed in claim 77, wherein the water-soluble salt or salts are precipitated by adding a base prior to evaporating the water.

79. A process for preparing a superconductor as claimed in claim 78, wherein the precipitated water-soluble salt or salts are separated off prior to evaporating the water.

80. A process for preparing a superconductor as claimed in claim 77, 78 or 79, wherein the salt or salts are derived from readily volatile acids.

81. A process for preparing a superconductor as claimed in any one of claims 77 to 80, wherein oxidic products obtained by annealing the salts are thermally posttreated.

82. A process for preparing a superconducting material containing bismuth, strontium, calcium and copper, which comprises preparing a mixture of the oxides of bismuth, strontium, calcium and copper or the corresponding oxide precursors, wherein the composition of the initial mixture in the triangular coordinate system lies between the points ABCD which define a four sided figure where

A = $Bi_{0.19}E_{0.35}Cu_{0.46}$

B = $Bi_{0.14}E_{0.4}Cu_{0.46}$

C = $Bi_{0.3}E_{0.38}Cu_{0.32}$

D = $Bi_{0.25}E_{0.43}Cu_{0.32}$

and E denotes the sum of alkaline earths Ca+Sr, and the Sr/Ca atomic ratio is 1:0.85 to 1:1.2, heating the mixture high enough for all the components to be melted, cooling to a temperature in the range 300 - 900°C, keeping the material in this temperature range for at least one hour and then cooling further.

83. A process as claimed in claim 82 wherein the Sr/Ca atomic ratio is 1:0.95 to 1:1.1.

84. A process for preparing a superconducting material containing bismuth, strontium, calcium and copper, which comprises preparing a mixture of the oxides of bismuth, strontium, calcium and copper or the corresponding oxide precursors, wherein the composition of the initial mixture in the triangular coordinate system lies between the points ABCD which define a four sided figure where

$A = Bi_{0.19}E_{0.35}Cu_{0.46}$

$B = Bi_{0.14}E_{0.4}Cu_{0.46}$

$C = Bi_{0.3}E_{0.38}Cu_{0.32}$

$D = Bi_{0.25}E_{0.43}Cu_{0.32}$

and E denotes the sum of alkaline earths Ca+Sr, and the Sr/Ca atomic ratio is 1:0.85 to 1:1.2, heating the mixture to a sintering temperature, which temperature is above 860°C but below the melting point of the mixture in an atmosphere containing oxygen for a period of at least 50 hours, and then cooling the mixture.

85. A process as claimed in claim 84, wherein the mixture is heated for a period of at least 80 hours.

86. The process as claimed in claim 82 or 83, which is carried out in an oxygen-containing atmosphere.

87. The process as claimed in claim 84 or 85, wherein the cooling is carried out to a temperature in the range 550 - 650°C, the temperature in this range is maintained for at least 20 minutes and heating is then again carried out to the sintering temperature, and this process is repeated at least twice.

88. The process as claimed in claim 84 or 85, wherein the cooling is carried out to a temperature in the range 580 - 620°C, the temperature in this range is maintained for at least 20 minutes and heating is then again carried out to the sintering temperature, and this process is repeated at least twice.

89. The process as claimed in claim 84 or 85, wherein the cooling is carried out to a temperature in the range 590 - 610°C, the temperature in this range is maintained for at least 20 minutes and heating is then again carried out to the sintering temperature, and this process is repeated at least twice.

90. The process as claimed in claim 87, 88 or 89, wherein cooling and reheating is repeated up to 20 times.

91. The process as claimed in claim 87, wherein the time for cooling to 550 - 650°C, holding in the range 550 - 650°C and heating up again to the sintering temperature is each at least 30 minutes.

92. The process as claimed in claim 87, wherein the time for cooling to 550 - 650°C, holding in the range 550 - 650°C and heating up again to the sintering temperature is each at least 45 minutes.

93. The process as claimed in claim 87, wherein the time for cooling and holding at a temperature in the range 550 - 650°C is at least one hour in each case.

94. An electric power transmitting, storage or transforming component comprising a superconducting phase of any one of claims 1 to 24.

95. An electric power transmitting, storage or transforming component comprising a superconducting compound of any one of claims 29 to 53.

96. An electric power transmitting, storage or transforming component comprising a superconducting black crystalline substance of any one of claims 54 to 61.

97. A magnetized device comprising a superconducting phase of any one of claims 1 to 24.

98. A magnetized device comprising a superconducting compound of any one of claims 29 to 53.

99. A magnetized device comprising a superconducting black crystalline substance of any one of claims 54 to 61.

100. An electronic component comprising a superconducting phase of any one of claims 1 to 24.

101. An electronic component comprising a superconducting compound of any one of claims 29 to 53.

102. An electronic component comprising a superconducting black crystalline substance of any one of claims 54 to 61.

103. An electronic component as claimed in claim 100, 101 or 102, wherein said component is a computer component.

104. An electronic measurement device comprising a superconducting phase of any one of claims 1 to 24.

105. An electronic measurement device comprising a superconducting compound of any one of claims 29 to 53.

106. An electronic measurement device comprising a superconducting black crystalline substance of any one claims 54 to 61.

107. A black crystalline superconducting component which has been manufactured by preparing a mixture containing the oxides or corresponding oxide precursors of bismuth, strontium, calcium and copper, heating the mixture high enough for all the components of the mixture to be melted, cooling the mixture to a temperature of from 300 to 900°C, keeping the mixture in this temperature range for at least 1 hour and then cooling the mixture further, wherein the mixture has the overall composition

$$Bi_a(Ca,Sr)_bCu_6O_x$$

wherein

a is from 3 to 12,

b is from 6 to 12,

provided that if a = 3 and b = 6, the atomic ratio of Sr:Ca is other than 1:1,

x is sufficiently high that the black superconducting component has a transition temperature, T_c, of at least 70 K and wherein the oxygen content is higher than that calculated for divalent copper and trivalent bismuth,

with a Sr/Ca atomic ratio of from 1:9 to 9:1,

a Bi:(Sr+Ca) atomic ratio of from 0.3 to 1.3, a critical temperature T_c for the superconductivity of at least 70 K

and which crystallizes in the orthorhombic system.

108. A superconducting component as claimed in claim 107, wherein a is from >3 to 12.

109. A superconducting component as claimed in claim 107, wherein a is from 4 to 12.

110. A superconducting component as claimed in claim 107, wherein a is from >4 to 12.

111. A superconducting component as claimed in claim 107, wherein a is from >6 to 12.

112. A black substance whose principle phases crystallize in the orthorhombic system, said black substance having a transition temperature, T_c, of at least 70 K, comprising the elements bismuth, strontium, calcium and copper in oxidic form and having the overall composition

$Bi_6Sr_6Ca_3Cu_6O_x$

where x is sufficiently high that the black superconducting substance has a transition temperature T_c, of at least 70 K, and whose principle phases show essentially the X-ray diffraction lines listed in Table 2.

113. A black substance whose principle phases crystallize in the orthorhombic system, said black substance having a transition temperature, T_c, of at least 70 K, comprising the elements bismuth, strontium, calcium and copper in oxidic form and having the overall composition

$$Bi_6Sr_6Ca_3Cu_6O_x$$

where x is sufficiently high that the black superconducting substance has a transition temperature T_c, of at least 70 K, and whose principle phases show essentially the X-ray diffraction lines listed in Table 3.

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FIG. 2

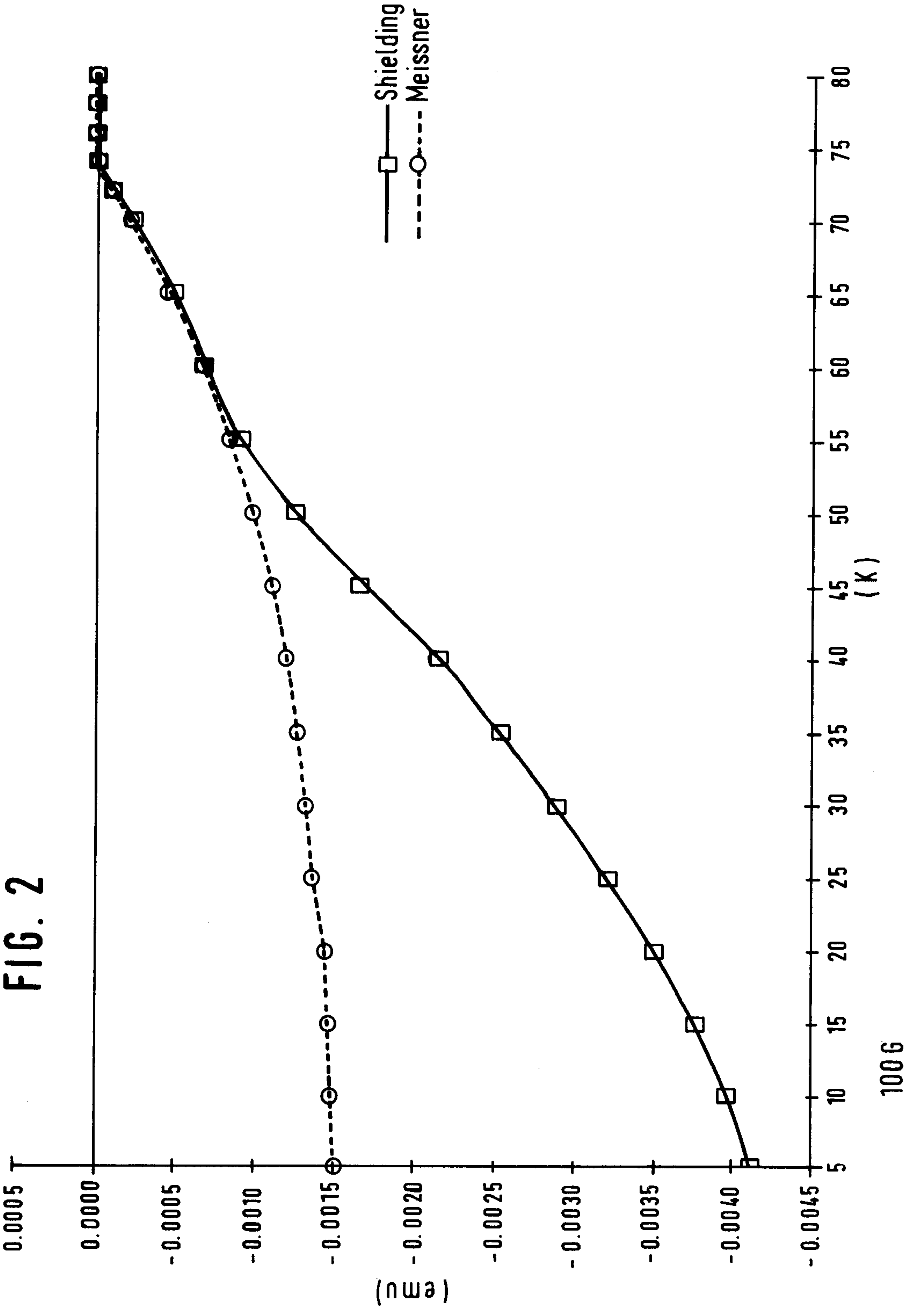

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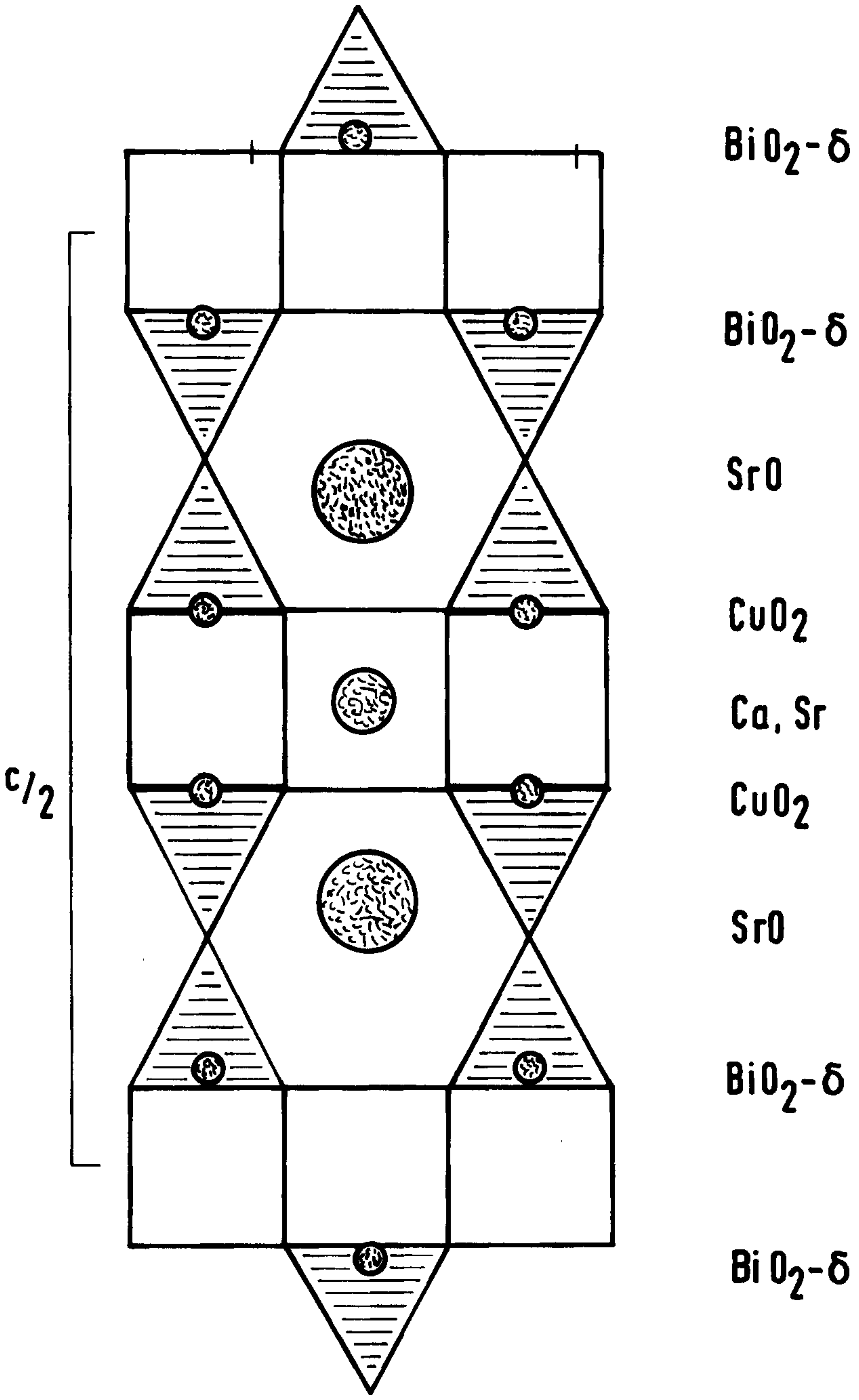
FIG. 1



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