

Electron-conductivity high- T_c superconductor with cubic symmetry

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Ceramic samples which exhibit a superconductivity with $T_c = 117$ K have been synthesized in the Tl-Pb-Sr-Ca-Ba-Cu-O-F system. According to x-ray diffraction, the symmetry of the samples is cubic, with a lattice constant $a = 6.04$ Å. At room temperature the conductivity is of the n type.

All the previously known high- T_c superconductors based on copper oxides have had a layered structure with prominent CuO_2 layers. In the present letter we are reporting the synthesis of some cubic copper-oxide-based compounds which exhibit a superconductivity with $T_c > 100$ K.

The synthesis of the thallium-containing copper oxides is carried out in two steps.¹⁻³ In the first step, the precursor material $\text{PbSr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ is prepared from the nitrates of strontium and calcium and from the oxides of lead and copper. A mixture

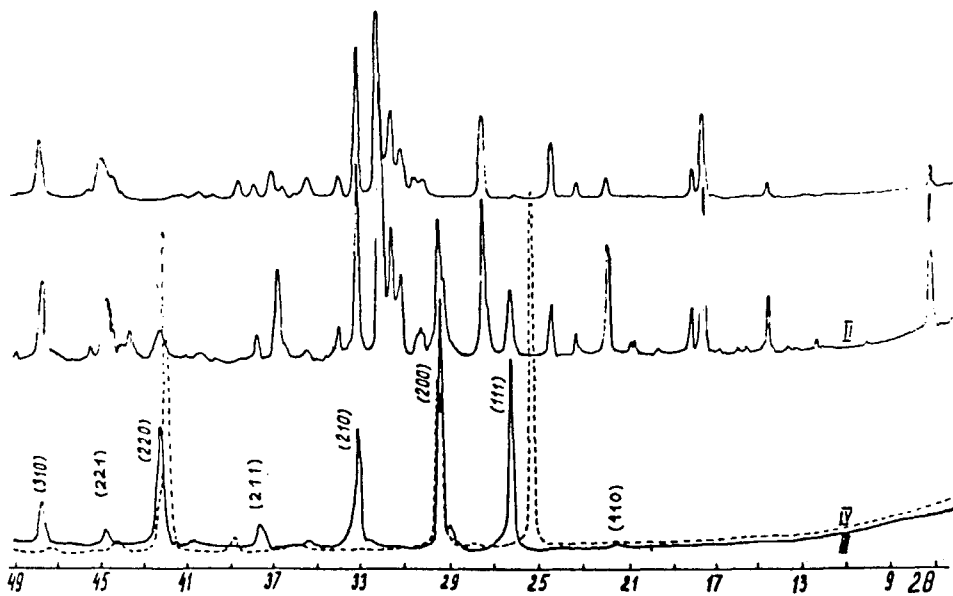


FIG. 1. Some powder x-ray diffraction patterns of samples I-IV at $T = 300$ K.

with the appropriate composition is heated at 720°C for 4–6 h. The material is re-ground in ethyl alcohol and annealed under the same conditions two or three times in order to improve the homogeneity of the samples. In the second step, compounds of barium, thallium, and fluorine are added in appropriate amounts to the material. The mixture is homogenized and dried at 105°C . The samples are synthesized by annealing pellets at $860\text{--}870^\circ\text{C}$ for 10–20 min and then quenching them to room temperature. The typical ceramic samples resulting from this synthesis have a density of 5.2 g/cm^3 .

The resulting samples correspond to the following chemical formulas:

I. $\text{Tl}_1\text{Pb}_1\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (this is the initial, control sample),

II. $\text{Tl}_1\text{Pb}_1\text{Sr}_2\text{Ba}_1\text{Ca}_2\text{Cu}_3\text{O}_x\text{F}_y$,

III. $\text{Tl}_1\text{Pb}_1\text{Sr}_2\text{Ba}_{2.5}\text{Ca}_2\text{Cu}_3\text{O}_x\text{F}_y$,

IV. $\text{Tl}_1\text{Pb}_1\text{Sr}_2\text{Ba}_{7.5}\text{Ca}_2\text{Cu}_3\text{O}_x\text{F}_y$,

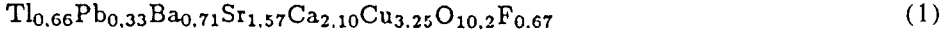
V. $\text{Tl}_1\text{Pb}_1\text{Sr}_2\text{Ba}_{10}\text{Ca}_2\text{Cu}_3\text{O}_x\text{F}_y$.

Figure 1 shows parts of the diffraction patterns of samples I–IV recorded at $T = 300$ K. The initial sample, I, is seen to have a layered structure of the 2223 type. Sample II contains, along with the 2223 phase, a new phase, of cubic symmetry. In sample III we find only the cubic phase. The small-angle reflections which are characteristic of layered structures with a long period in the direction transverse with respect to the layers are absent in the cases of samples III–V. With increasing barium content (samples IV and V), we find a splitting of the (200) reflection on the diffraction patterns and a shift of the (111) reflection to a smaller angle.

As the barium and fluorine contents are raised, the “impurity” lines of the initial

high- T_c superconductor of the 2223 type progressively fade away. When the ratio of the BaF_2 to the initial superconductor is 3:1, the pattern is approximately the same as that of a cubic structure with $a = 6.04 \text{ \AA}$ (for BaF_2 we have $a = 6.20 \text{ \AA}$). However, the unit cell of the product cannot be classified as face-centered, since (201), (301), etc., lines, which are forbidden in the face-centered cell of BaF_2 , are fairly intense here.

According to the results of the x-ray analysis carried out to identify the phases present and also the results of a chemical analysis (by fluorescence and electron microprobe analysis), sample III contains a superconducting phase with the composition



with a concentration by volume of about 70%. In addition to this superconducting phase, we found phases of the solid solutions $\text{Ba}_{1-x}\text{Sr}_x\text{F}_2$, BaPbO_3 , and Ca_2CuO_3 , with much smaller concentrations by volume. To determine specifically which phase was responsible for the superconductivity, we subjected the same sample to a prolonged annealing at a high temperature, $T = 900^\circ\text{C}$. This annealing destroyed the superconducting properties. All the phases listed above except phase I survived, and their concentrations by volume increased, according to the results of the same analysis. Phase I disappeared. These results are convincing proof that phase I is the superconducting phase.

One possible explanation for the structure of the high- T_c superconducting compound produced here is the ability of the fluorite structure to form "subtraction structures" (in the words of N. V. Belov) and nonstoichiometric solid solutions with heterovalent cations, e.g., $\text{Ba}_{1-x}\text{La}_x\text{F}_2$ with $x \approx 0.5$ (Ref. 4). (These properties of the fluorite structure are well known and indeed widely utilized.) Vacancies (fluorine vacancies) form in such systems, as do interstitial atoms; in some cases, clusters of various sizes also form.

On the other hand, when one of the cations is introduced, the extinction laws for

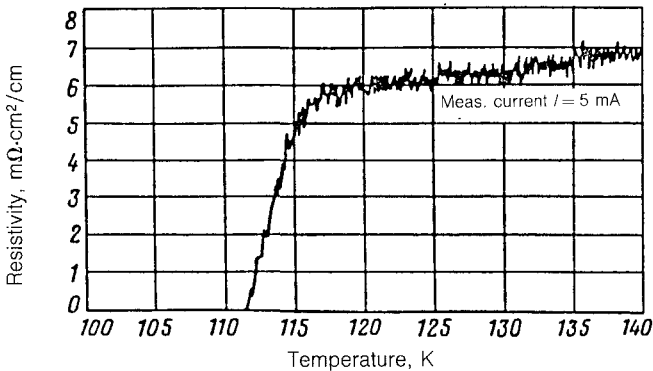


FIG. 2. Temperature dependence of the resistivity of sample III.

a face-centered cell usually remain in force. In our (much more complex) system, the atoms can be incorporated in the BaF_2 lattice in ways which lead to deviations from this rule. On the x-ray diffraction patterns of the cubic samples (curves III and IV in Fig. 1) we find nearly all the (hkl) lines of a cubic primitive cell except (100) . The relations among the intensities of the observed lines depend on the particular details of the preparation of the samples.

Figure 2 shows a temperature dependence of the resistivity of sample III, measured by a pulsed four-contact method with a measurement current of 5 mA. The initial and final temperatures of the transition are $T_{ci} = 117$ K and $T_{cf} = 112$ K. Above the transition point the resistivity is $\rho = 6$ m $\Omega \cdot \text{cm}$, low in comparison with that of layered thallium-containing superconducting copper oxides ($\rho \sim 10^2\text{--}10^3$ m $\Omega \cdot \text{cm}$). We also see a linear temperature dependence $\rho(T)$.

Measurements of the thermal emf at room temperature revealed that the current carriers are of the n type.

The magnetic susceptibility was measured by an inductive method with the help of a mutual-induction bridge and phase-sensitive detection at a frequency of 1.5 kHz. The samples were parallelepipeds with dimensions of $2 \times 3 \times 10$ mm. A sinusoidal magnetic field with an amplitude of 15 A/m was applied along the shortest dimension of the sample.

Figure 3 shows the temperature dependence of the real part (χ') and the imaginary part (χ'') of the magnetic susceptibility of sample III. The behavior here is typical of ceramic high- T_c superconductors. As the temperature is lowered below $T_c = 117$ K, the sample goes into a superconducting state, as can be seen from the appearance of a diamagnetic-response signal which corresponds to an intragrain superconductivity and to a superconductivity of grain boundaries. Below T_c we find a

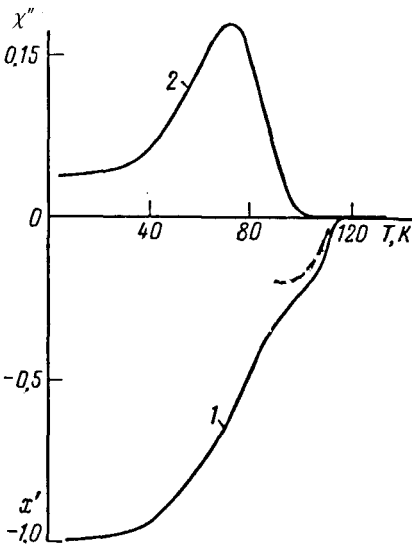


FIG. 3. Temperature dependence of (1) the real part and (2) the imaginary part of the magnetic susceptibility. The dashed line shows the shift of the $\chi'(T)$ curve in a magnetic field of 8×10^4 A/m.

peak in χ'' , which is due to magnetic losses. The dashed line in Fig. 3 shows $\chi'(T)$ in a field of 8×10^4 A/m at temperatures down to 77 K. The imposition of a static magnetic field also shifts the χ'' peak to a lower temperature.

The nonmonotonic temperature dependence $\chi'(T)$ is not a consequence of the presence of two superconducting phases [there is only a single peak on the $\chi''(T)$ curve]. It instead stems from the circumstance (typical of ceramic samples) that the ordering within grains and the ordering of the grain boundaries occur at different temperatures. In a magnetic field, the ordering in the grain boundaries shifts to a lower temperature.

A comparison of the susceptibilities of a lead powder in an insulating matrix with those of the ceramic under study here, with the same mass and volume, yields an estimate of the fraction of the volume represented by the superconducting material: 70% at 5 K.

Although the chemical composition and structure of these samples are still being refined, we can report some preliminary conclusions. First, all the previously known high- T_c superconductors with $T_c > 100$ K have had a p -type conductivity; the T_c 's of the n -type superconductors have been far lower. The samples produced in the present study constitute the first examples of n -type superconductors with $T_c > 100$ K. Second, since the cubic structure does not contain two-dimensional CuO_2 planes, many of the mechanisms for high- T_c superconductivity which make use of a two-dimensional topology apparently do not correspond to copper oxides. On the other hand, the local Cu-O environment may remain the same in the cubic lattice. Definitive conclusions will of course have to await a deciphering of the structure.

¹T. A. Bidman, V. E. Volkov, L. I. Verzhinina *et al.*, Sverkhprovodimost' (KIAE) 3(4), 625 (1990) [Superconductivity 3, 590 (1990)].

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³V. E. Volkov, T. A. Bidman, I. Yu. Danilov *et al.*, USSR Patent N 1628745, 3 April 1989.

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