High-temperature superconductivity of the system Bi–Sr–Ca–Cu–O

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A high-temperature superconductivity with $T_c = 60$–80 K has been detected in the Bi–Sr–Ca–Cu–O system over a broad temperature range. Samples of the composition $BiCaSr_2Cu_2O_y$ revealed the presence ($\sim 10\%$) of the superconducting phase with $T_c \gtrsim 110$ K.

Michel *et al.*[1] have recently reported the detection of superconductivity in the Bi–Sr–Cu–O system. The samples with $T_c = 7$–22 K were obtained for compositions of approximately orthorhombic phase $Bi_2Sr_2Cu_2O_{7+\delta}$. The discovery of a new family of superconducting cuprites, which do not contain a rare-earth ion, holds promise for further search for high-temperature superconductivity in perovskite-like structures. In this letter we report the results of an experimental study of the superconducting properties of the Bi–Sr–Ca–Cu–O system of various compositions.

The samples were synthesized by the solid-phase reaction method. The following oxides were used as the starting components: Bi_2O_3, SrO, CaO, and CuO. The synthesized samples were annealed in a O_2 stream at temperatures of 820–870 °C for several hours and then cooled in a O_2 atmosphere at the rate of 100 °C/h.

The samples of various compositions in the Bi–Sr–Cu–O system were found to be superconductors with a superconducting transition temperature $T_c = 7$–15 K, in agreement with the results of Ref. 1. On the other hand, no superconductivity was observed in the Bi–Ca–Cu–O system over the entire range of compositions.

High-temperature superconductivity with $T_c > 60$ K was detected in the mixed system Bi–Sr–Ca–Cu–O. Figure 1 is a plot of T_c as a function of x for the composition

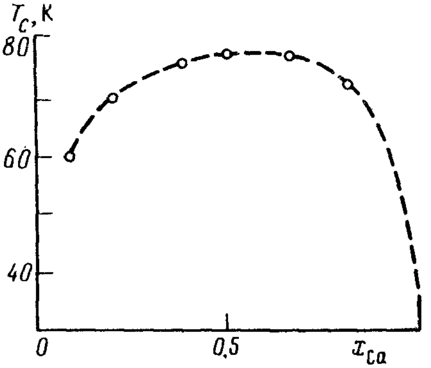

FIG. 1. T_c versus the concentration x of calcium in the system $Bi(Sr_{1-x}Ca_x)_2Cu_3O_y$.

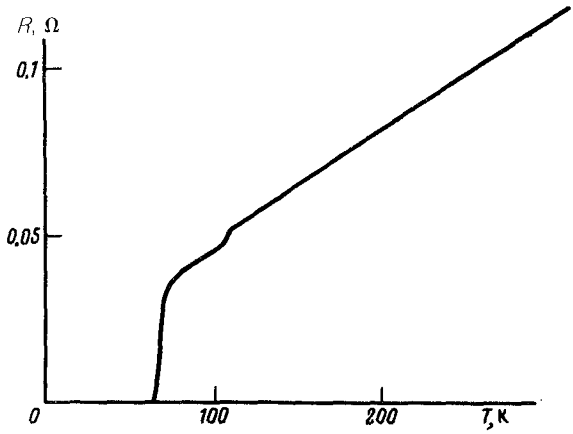

FIG. 2. Temperature dependence of the resistance for the sample of the composition $BiCaSr_2Cu_2O_y$.

$Bi(Sr_{1-x}Ca_x)_2Cu_3O_y$ with $0.1 < x < 0.9$ (the suggested 1–2–3 phase). The value of T_c was determined from the midpoint of the resistivity jump. At 300 K the resistivity of the samples $\rho_{300} = 4$–100 mΩ·cm (a relative decrease in Cu content leads to a certain decrease in ρ) decreases linearly with decreasing temperature. The resistivity ratio $\rho_{300}/\rho_{100} = 1.5$–2.2 has the maximum value for the composition $BiSr_{1.6}Ca_{0.4}Cu_3O_y$. The $R(T)$ curve no longer behaves linearly at $T = 130$–150 K (a relative deviation of 10% from linear behavior occurs at $T_{c0} \gtrsim 90$ K).

The principal x-dependent transitions were observed at $T_c = 60$–80 K. The transition width determined from the sharpest part of the curve is $\Delta T_c = 4$–10 K. The samples had multiple phases.[1] The susceptibility measurements showed that the Meissner phase accounted for up to 20%–25%.

In the case of certain samples of the composition $Bi(Sr_{1-x}Ca_x)_2Cu_3O_y$ the $R(T)$ curves had a second resistivity jump of 1%–2% near $T > 100$ K, suggesting that the test samples might have a small amount of the phase with $T_c > 100$ K. We studied a variety of compositions in order to increase the percentage of the high-temperature phase. The samples with the composition close to $BiCaSr_2Cu_2O_y$ yielded the best results. Figure 2 shows the $R(T)$ curve for the sample of the indicated composition. In comparison with the 1–2–3 phase the principal transition is shifted toward higher temperatures. We clearly see, however, a second transition, which begins at 115 K. The magnitude of the resistivity jump in this case is ~10%. The data obtained from an ESR analysis confirm that these samples have a superconducting phase at $T \lesssim 120$ K.

The results which we have obtained thus show that the Bi–Sr–Ca–Cu–O system has a high-temperature superconducting phase with $T_c \gtrsim 110$ K. Further experimental studies must, however, be carried out to determine the structure of this phase and to develop methods of synthesizing single-phase samples.

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[1]C. Michel, M. Hervieu, M. M. Borel *et al.*, Preprint, Caen University (CRISMAT), France, 1987.

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