

Effect of yttrium on the increase in T_c of Bi(2212) crystals

N. V. Zavaritskiĭ, V. N. Zavaritskiĭ, and Yu. F. Orekhov

P. L. Kapitza Institute of Physics Problems, 117334 Moscow, Russia

A. P. Mackenzie

Interdisciplinary Research Centre in Superconductivity, Cambridge CB3 0HE, UK

(Submitted 2 June 1994; resubmitted 28 June 1994)

Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 3, 188–192 (10 August 1994)

The incorporation of an yttrium dopant in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystals raises T_c from 86 K all the way to 95 K at $x \approx 0.1-0.15$. Chemical analysis shows that yttrium replaces Ca atoms in the lattice. The increase in T_c is attributed to a binding of excess holes in CuO_2 planes by the yttrium. This binding leads to an optimization of the carrier density. © 1994 American Institute of Physics.

The positions occupied by various elements in the lattices of the high T_c superconducting cuprates have attracted interest because of the possibility in principle of altering the carrier density in the system and altering the transport mechanisms in the normal and superconducting states. In a departure from the usual approach to the problem, we have grown some Bi–Sr–Ca–Cu crystals with the nominal 2-2-1-2 composition and have attempted to determine why these samples have superconducting transition temperatures (up to 95 K), which are higher than the customary ≈ 86 K. We have attempted to synthesize the results of a study of the characteristics of single crystals by both microscopic and macroscopic methods. The results show that there is a partial dissolution of the crucible in the course of the solid-phase synthesis. The crucible material changes the chemical composition of the material and can be the source of an uncontrollable doping of the crystal. The results indicate that a doping of a BSCCO crystal with yttrium leads to an increase in $T_c \geq 92$ K at $x \approx 0.1-0.15$.

The single crystals were grown in a two-step, solid-phase growth process.¹ In the first step, the compound $\text{Sr}_2\text{CaCu}_2\text{O}_x$ was synthesized from corresponding amounts of chemically pure, powdered SrCO_3 , CuO , and CaO . The powders were dried beforehand by baking at $\sim 400^\circ\text{C}$ for 4–24 h. Portions of the powders with masses corresponding to the stoichiometry were thoroughly mixed in a ball mill, pressed into pellets, and annealed in oxygen at $T \approx 1020^\circ\text{C}$ for $\sim 10-12$ h. The resulting $\text{Sr}_2\text{CaCu}_2\text{O}_x$ was ground and mixed in a ball mill with a stoichiometric amount of dry Bi_2O_3 . The resulting powder was packed densely in a cylindrical crucible of yttrium-stabilized zirconium oxide and placed in a vertical furnace with a gradient $\approx 3-7$ deg/cm. In the course of the synthesis, the furnace temperature was held at $\sim 970-1010^\circ\text{C}$ for 2–3 h in order to completely melt the material. It was then cooled rapidly, at $\sim 30-50$ deg/h, to $\sim 890^\circ\text{C}$. The crystals were grown in the course of a subsequent slow cooling at a rate of 0.5–10 deg/h to $\sim 770^\circ\text{C}$. This process occurred in air. The typical amount of starting material was about 200 g.

We made attempts to qualitatively determine the effect of the crucible material and the proportions of the starting components. In none of the melts carried out in corundum crucibles were we able to find crystals with $T_c > 86$ K. All the samples exhibited a broad superconducting transition with $\Delta T_c \sim 2-5$ K. Regardless of the crucible material, the effect of varying the amount of Bi in the starting mixture, between 2.0 and 2.2, on the characteristics of the crystals was negligible.

Test samples were prepared by splitting the crystals along a (0,0,1) cleavage plane. The samples had a lustrous surface with typical dimensions $\sim 5 \times 3$ mm in the plane at a thickness $\sim 5-20$ μm . The thickness was determined with the help of an optical microscope. The crystallographic structure of the test samples was monitored by x -ray diffraction using Cu $K\alpha$ radiation. The lattice constant c was determined from the position of the (0,0,30) reflections.

A first characterization of the superconducting properties of the crystals was carried out by a contactless method, involving inductive measurements at a frequency ~ 30 MHz. The temperature T_c was found through a linear extrapolation of the curve of the superconducting transition to $R=0$. The transition temperature found in this manner lay in the range $\approx 75-93$ K for most of the crystals which had not been subjected to an additional annealing (the as-grown crystals). Some of the samples had substantially lower transition temperatures, $T_c \geq 15$ K, but in most cases a brief annealing ($\sim 5-7$ min) in oxygen at $\sim 500^\circ\text{C}$ was sufficient to raise the transition temperature rapidly into the specified range.¹⁾ The wide range of T_c values observed indicates that some of the crystals are not saturated with oxygen; it may also be a consequence of a nonuniform distribution of the elements in the crucible.

The properties of Bi-2212 crystals are known²⁾ to depend on the deviation of the oxygen concentration from stoichiometry, δ . To reduce the effect of this factor, we subjected the test samples to an "optimizing" annealing, whose characteristics were tailored to each melt. In the course of these experiments the crystals were placed in a Pt crucible, annealed in flowing oxygen at $T_{\text{ann}} \approx (450-750)^\circ\text{C}$, and then quenched. The interval between successive values of T_{ann} was $20-50^\circ\text{C}$. The duration of the annealing was typically ≈ 15 min (this duration ranged up to 20 h in some control experiments). In the intervals between annealing steps, the lattice constant and T_c were determined for each crystal. Figure 1 shows experimental curves of $T_c(T_{\text{ann}})$ for several melts. Annealing in flowing O_2 leads primarily to a reversible shift of the superconducting transition in the interval $\sim 5-7$ K; for some of the samples, this shift was accompanied by some change in the width of the transition. Only a small fraction of the crystals (see the dashed curve in Fig. 1) required annealing at $T_{\text{ann}} > 750^\circ\text{C}$; this temperature was cited in Ref. 2 as the optimum temperature for annealing Bi(2212) crystals. For most of the test crystals the maximum value of T_c was reached as the result of annealing at a much lower temperature, $T_{\text{ann}} \approx 500-550^\circ\text{C}$. In the course of these annealings the lattice constant remained fixed within a relative error of 10^{-4} .

The chemical composition of the BSCCO crystals (like that of other cuprates) may differ from the composition of the starting material, since all these compounds are non-eutectic. Furthermore, the composition of the material may vary from point to point in the crucible and even within an individual crystal, not to mention subtler effects of a substitution of the constituent elements in the lattice, e.g., $\text{Ca} \rightleftharpoons \text{Sr}$ (Ref. 3). The wide range of

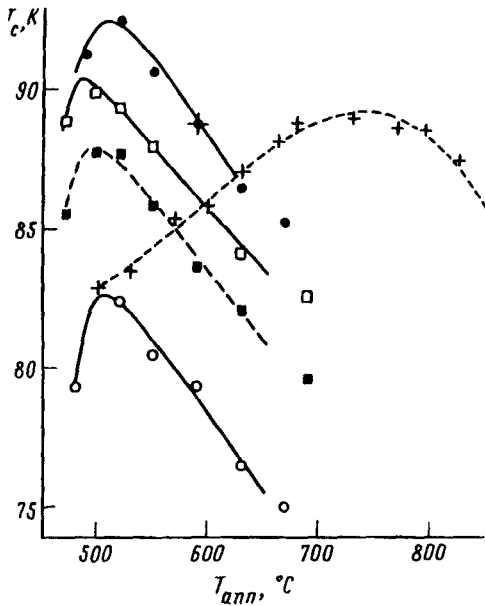


FIG. 1. Experimental plots of $T_c(T_{ann})$ for several Bi(2212) crystals.

T_c 's of the crystals extracted from different places in the crucible supports this suggestion. For this reason it was necessary to determine the chemical composition for each crystal studied. In the present experiments we used the method of electron microprobe analysis, which is based on comparative measurements of the energies of γ rays emitted by inner-shell electrons as they relax to the ground state. These measurements were carried out on a Cameca SX-50 apparatus, which is described in detail in Ref. 3. Since the γ 's which were analyzed were emitted from a volume of a few cubic microns, the analysis can be regarded as a point analysis. In a first step, the chemical composition was determined at two well-separated points on the surface of each crystal. A comparison of these results led to a zeroth-approximation conclusion regarding the homogeneity of the samples. It was observed that most of the samples contained an yttrium impurity, and that their composition (except for one sample with a 2201 composition) differed only slightly from the 2212 composition. Figure 2 shows the results of a determination of the local atomic content of calcium as a function of the content of the yttrium impurity, according to calculations from the measured weight concentrations, under the assumption that the sum of the cations is 15. It follows from the slope of the linear approximation that the yttrium impurity, x , replaces calcium in the lattice for the most part. At the same time, we see a weaker but systematic change in Bi with x , which is not shown in this figure. The concentrations of the other elements remained unchanged. A comparative analysis showed that the differences in composition were greatest for the samples having a significant amount of yttrium.

Transport properties of the crystals were determined through resistance measurements in a zero field. Two current contacts, with dimensions $\sim 0.3 \times 0.1$ mm, and four to eight potential contacts ($\sim 0.03 \times 0.05$ mm) were applied to each of the freshly cleaved (0,0,1) surfaces of a sample. Particular care was taken to ensure that the contacts were

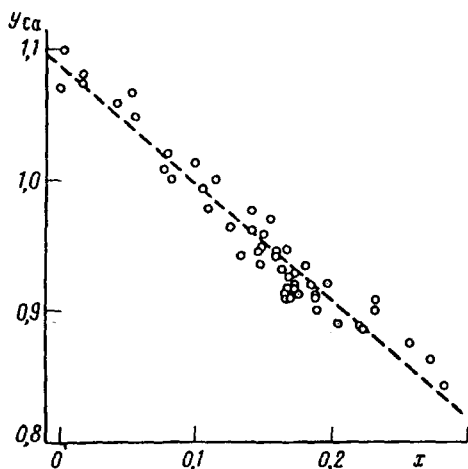


FIG. 2. The calcium atomic content y versus the yttrium impurity content x as calculated from the results of electron microprobe analysis of the chemical composition of 57 crystals with the nominal composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

arranged symmetrically. The typical deviation of the contacts on opposite sides of the sample from geometric superposition did not exceed ~ 0.01 mm. Brazing a conducting composite at $500\text{--}520^\circ\text{C}$ gave the contacts a resistance of $0.5\text{--}5\ \Omega$. Gold wire $5\text{--}10\ \mu\text{m}$ in diameter was used for the leads. In several of the experiments we used an additional mechanical attachment of the sample to the quartz substrate by means of cement. The best results were obtained with BF-2 cement. The multiple-contact geometry used in these experiments made it possible to select samples on the basis of their macroscopic homogeneity (through a method of comparing transition curves found from different pairs of contacts). The transition temperature T_c was found through a linear extrapolation of the curve of the superconducting transition from the level $\approx 10^{-2}R_n$ to $R=0$; here R_n is the resistance just before the beginning of the transition. Crystals for which the scatter in transition temperatures at any pair of contacts did not exceed the width of the transition in a zero field were selected for further study.

The chemical composition was analyzed for 14 of the selected crystals, with transition widths $\Delta T_c \leq 1.5$ K. To determine the distributions of the elements we analyzed various points (up to ten) on the surface of a crystal. Only six of the crystals exhibited a uniform distribution of yttrium (within 0.01). The other crystals had a cluster distribution of yttrium, possibly because of a segregation of elements. The basic conclusions of this study are based on the results found for the uniform samples. While using these results as a basis, we also drew on data for the "cluster samples" in cases in which a correlation was found between structural features on the transition curves and the macroscopic distribution of yttrium.

The chemical analysis reveals the composition at a depth $\sim 2\ \mu\text{m}$, so even in the case of an apparently uniform sample we cannot immediately rule out a possible nonuniformity along depth. To clarify this question, we subjected two samples, one uniform sample (with an yttrium concentration of 0.1) and one cluster sample (0.05 and 0.2), to an additional splitting along (0,0,1) planes into three parts. For each piece we measured maps of the chemical composition. Working on the basis of the quantitative agreement

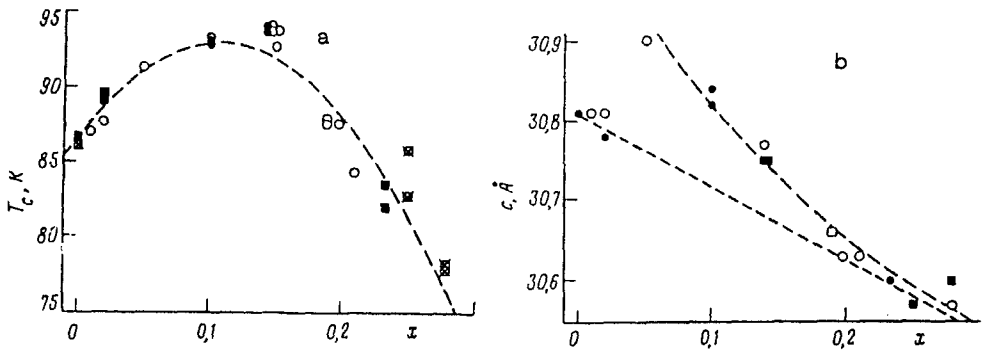


FIG. 3. Behavior of T_c (a) and of the lattice constant along the c axis (b) as functions of the yttrium impurity content in the crystal, x .

which was found (within 0.01 in terms of Y), we attempted to compare the values of T_c with the concentration of the yttrium impurity in the crystal (Fig. 3a). The data referring to the “uniform” samples are shown by filled symbols.

The curve of $T_c(x)$ is bell-shaped with a maximum at $x \approx 0.1-0.15$. A similar bell-shaped $T_c(x)$ curve had been observed previously by Srikanth *et al.*,⁴ but with a lower T_c^{\max} and with a maximum shifted to $x \approx 0.25-0.35$. We believe that the use of corundum crucibles in Ref. 4 may have led to a substantial contamination of the crystals with an Al impurity, which would reduce the positive effect of Y on T_c , and which could therefore be the reason for the quantitative discrepancy that is observed. The data of Ref. 5, like the results of our experiments with Al_2O_3 crucibles, support this interpretation.

Figure 3b shows the results of x -ray-diffraction measurements²⁾ of the $c(x)$ dependence. These results agree well with the data of Ref. 3 at $x > 0.03$. The obvious discrepancies with a linear approximation of $c(x)$ are probably due to contamination of the crystals with an Al impurity, as mentioned above, according to the data of a corresponding study⁵ (shown by the short-dash line in Fig. 3b). We see that the plot of $c(x)$ is not monotonic at $x \approx 0.05$. A possible reason is the formation of a second orthorhombic phase (the so-called D phase), with a different symmetry group.³ Since it was not possible to determine the lattice constants a and b in our experiments, we were unable to reliably test that suggestion.

The increase in the T_c of the Bi(2212) crystal upon doping with yttrium can be interpreted at a qualitative level by working from the assumption that the as-grown crystals are supersaturated with oxygen. In this case, the substitution $\text{Y}^{3+} \rightarrow \text{Ca}^{2+}$ compensates for excess holes in the CuO_2 planes, driving the carrier density toward its optimum value at $x \approx 0.1-0.15$. The circumstance that the temperature of the optimizing annealing (Fig. 1) is substantially lower than that for pure Bi(2212) is evidence in favor of this interpretation.

We wish to thank V. Hnatowicz (Prague, Czech Republic) for analyzing one of the crystals by Rutherford backscattering. We also thank I. Kosheleva (Kamerling-Onnes

Laboratory, Leiden) for studying another pair of crystals by ESCA. We thank the American Physical Society and the Council on Superconductivity for partial financial support. One of us (V.N.Z.) is sincerely indebted to the British Royal Society for a P. L. Kapitza Stipend, and to the team of the IRC in Superconductivity, Cambridge, for hospitality and substantial assistance.

¹In this case, in contrast with the "optimizing" annealing in O₂, described below, we observed a substantial decrease in the lattice constant *c*.

²Analysis of *x*-ray diffraction patterns did not confirm the earlier suggestion ¹ that the increase in *T_c* is related to a change in the symmetry group of the lattice, which is manifested in the onset of (0, 0, 2*n* + 1) peaks. N.

¹V. Zavaritsky *et al.*, *Physica C* **169**, 174 (1990); **180**, 417 (1991).

²M. R. Presland *et al.*, *Physica C* **176**, 95 (1991).

³X. F. Zhang *et al.*, *Physica C* **215**, 39 (1993).

⁴A. P. Mackenzie, *Physica C* **178**, 365 (1991).

⁵H. Srikanth *et al.*, *Physica C* **200**, 372 (1992).

⁶C. Kendziora *et al.*, *Phys. Rev. B* **45**, 13025 (1992).

Translated by D. Parsons