Origin of the 110-K superconducting transition in the Bi-Sr-Ca-Cu-O system

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Superconducting critical transitions with an onset at 112 K and zero resistance at 107 K are obtained within the Bi-Sr-Ca-Cu-O system. The synthesis and formation of the 110-K superconducting phase using the 85-K material as a precursor is explained. The 110-K phase grows from the 85-K phase such that the resulting faceted crystal (a pseudomorph) can contain some of the 85-K phase in the core. With such a microstructure our magnetic data can be simply explained. A major structural difference between the 85- and 110-K materials is that the 85-K material can grow (relatively) large single crystals having long-range order whereas the 110-K material has only intermediate-range order (cryptocrystalline) of about 100–200 Å.

Obtaining new high-T_c materials among the cuprate oxide phases has been the objective of much research since the discovery of superconductivity at 40 K in the La-Cu-Sr-O system by Bednorz and Müller.[1] Superconductivity at 90 K was observed by Wu *et al.*[2] in the Y-Ba-Cu-O system and this temperature, until recently, had not been exceeded reproducibly. Superconductivity at 20 K was reported in another cuprate system containing bismuth[3] instead of yttrium, and recently superconductivity at 85 and 105 K (extrapolated zero resistance) was reported by Maeda, Tanaka, Fukutomi, and Asano[4] in a Bi-Sr-Ca-Cu-O system. The superconducting transition at 110 K (transition midpoint) determined resistively always had a resistive tail such that zero resistance was obtained only at 80 K. These results were confirmed by several workers[5] and the $Bi_4Sr_4Ca_2Cu_4O_{16+x}$ phase was found[6] to be responsible for superconductivity at 85 K and its crystal substructure established.[7] We previously have shown that single-phase material was obtained from mixtures of nominal composition $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ (we denote compositions by cation stoichiometry, here 4:3:3:4) and that processing this precursor compound by heating to temperatures near its melting point produces a sharp resistivity drop near 110 K that was unambiguously ascribed to a superconducting transition because of the diamagnetic shift observed in the magnetic measurements. However, isolating and characterizing the 110-K phase was a remaining objective. Although we cannot unambiguously ascribe here a composition to the "110-K phase," we have better characterized the origin and formation of the superconducting phase such that we are able to produce "crystals" and measure zero resistance at temperatures greater than 100 K. We report here our results.

A material having a large fraction of superconductivity at 110 K (20%–25%), as determined by the Meissner effect, was prepared using a 4:3:3:4 or 4:3:3:5 reacted powder as the precursor. The Meissner values reported herein were not corrected for the diamagnetism factor and therefore might be overestimated. The powders were annealed for several days in air very close to, but not above, the melting point (885 °C) and furnace cooled, taking 6 h, to room temperature. The difficulty encountered in preparing the 110-K phase indicates that it may be process dependent and therefore our results pertain to this preparative procedure. It is also conceivable that different regions of the same compact could produce, locally, a different processing history. The x-ray powder pattern of the resulting material was weak, having Bragg peaks for the 4:3:3:4 phase, a small amount of diffuse scattering, and weak peaks indicative of an impurity phase Ca_2CuO_3. The resistivity behavior of these ceramics show a sharp drop at 110 K but with zero resistance not reached until 80 K. Magnetic measurements on these powdered samples evidenced a 50% Meissner effect shared equally between 85- and 110-K superconducting transitions. Thus, one would expect this material to contain crystals corresponding to each of the superconducting phases.

Examination of the 4:3:3:4 preparation with a binocular microscope showed large (0.5 mm), roughly equidimensional black "crystals" having metallic luster. Some of these had large shiny growth facets which contrasted with the thin, micaceous crystals of the 85-K superconductor

$Bi_2Sr_2CaCu_2O_8$. Those from the 4:3:3:5 preparation were inhomogeneous, containing unidentified reddish-brown inclusions; thus we concentrated on the 4:3:3:4 preparation for which the crystals appeared to be homogeneous under a microscope at a magnification of 50×. Several "crystals" from this batch were selected for structural studies.

Transmission x-ray Laue diffraction patterns of these crystals unexpectedly showed three components to the diffraction instead of the intense sharp reflections expected: (1) An intense broad continuous diffraction indicating the presence of cryptocrystalline (very fine-grained polycrystalline) material with a crystalline size (coherent scattering region) of 200 Å or less; (2) a few weak spots superimposed on continuous streaks that radiated from the origin of the reciprocal lattice, indicating platelet-shaped oriented crystallites probably having stacking disorder; (3) weak powder lines indicating the presence of randomly-oriented crystallites. The spots of (2) do not occur on the powder circles of (3). When no sharp crystal edge is in the x-ray beam, feature (1) is dominant whereas features (2) and (3) become important for wedges or splinters.

As the absorption coefficient for Mo K radiation is of about 500 cm^{-1}, the x-ray beam effectively samples a 50-μm-deep thickness. Thus, from the above observations we derive the following conclusions. (a) Single crystals, of an unknown phase which is closely related to that of the 4:3:3:4 phase but of undetermined composition, grow at elevated temperatures (well-developed morphology leaves little doubt on this point). (b) At room temperature, these crystals become pseudomorphs and correspond to a minimum of three phases while retaining the morphology of a single crystal: a cryptocrystalline shell about 50 μm thick (the thickness is probably a function of time at the elevated temperature) and a core with both platelet-shaped crystals and randomly oriented crystallites. After crushing the pseudomorphs, their powder pattern corresponds to a mixture of 2:2:1:2 (the 85-K superconductor) and Ca_2CuO_3. As we know that 2:2:1:2 grows as thin plates, it seems likely that the above platelets are the 85-K superconductor while the randomly oriented grains are Ca_2CuO_3. Analytical electron microscopic studies confirm that the microstructure of the pseudomorph is polycrystalline containing both large crystals (tens of microns) and microcrystallites (hundreds of Å).

The high temperatures and long times required to convert 85-K material to 110-K material clearly indicate slow kinetics, probably involving the long-range diffusion of one at the cations. Thus the core has the microstructure of an 85-K material that has gone through the high-temperature thermal cycle but, because of a kinetically limited diffusion to the crystal-free surface, has not converted to 110-K material. The shell, on the other hand, has been transformed to 110-K material caused, and limited, by the diffusion to the free surface of one, or more of the constituents; calcium and/or bismuth are the most likely diffusing species (concomitant changes in oxygen content will, of course, accompany changes in cation concentration), since changes in oxygen alone do not seem to significantly affect T_c in the material precursor. In an attempt to identify the high-temperature phase, we performed morphological measurements with an optical goniometer in the hope of getting axial ratios for identification of the structure type using crystal data.[8] The seven face normals we measured on a pseudomorph (Fig. 1) were not sufficient to select a plausible set of crystal axes because no zones were observed.

Magnetic measurements were performed on crystals (weighing about 0.1 mg) by means of a SQUID magnetometer and the results are shown in Fig. 2. Note that most of the crystals reflect the property of the bulk and have two T_c's of 85 and 110 K. The magnitude of the 85- and 110-K superconducting transitions is different from crystal to crystal with some of them showing very little of the 85-K transition (crystals D and E), whereas others show an equal amount of 85 and 110 K (crystal C). Based on the mass of sample D (0.5 mg) and a rough estimate of the density as 7 g/cm^3, the Meissner signal is 63% of that expected for complete bulk superconductivity. If there were a perfect 110-K shell around each grain one should not observe the 85-K transition by magnetic measurements, contrary to what we observe. We believe that the 85-K transition is observable because of discontinuities in the shell which allows the penetration of magnetic flux. This is also consistent with the x-ray characterization described above. Thus we conclude that each crystal contains the recrystallized 85-K phase imbedded in a highly defective 110-K phase. To examine this possibility we simply removed the outside shell by etching the sample for several hours in an nitric acid solution (0.03N) and then remeasured the diamagnetic signal. Results of these measurements are shown in Fig. 2. Prior to the acid treatment (A) the magnitude of the 110-K transition was about 3 times larger than that of the 85 K. After etching, the diamagnetic signal at 110 K is completely gone such that we only have superconductivity at 85 K in our sample (B). An unexpected result is that the shielding curve superimposes the Meissner one for the sample treated in acid. Such a situation usually occurs when the supercon-

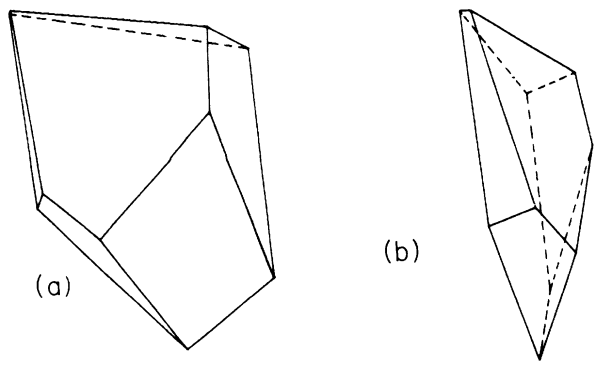

FIG. 1. Two stero views from optical goniometer measurements taken on a pseudomorph. When the x-ray beam axis is down, the viewing direction at the top, the Laue pattern is very diffuse indicating a cryptocrystalline material. When the x-ray beam axis is down, the viewing direction at the bottom, radial steaks indicative of oriented platelets, and concentric circles indicative of randomly oriented powder at the core of the crystal are seen. The largest dimension is about 0.6 mm.

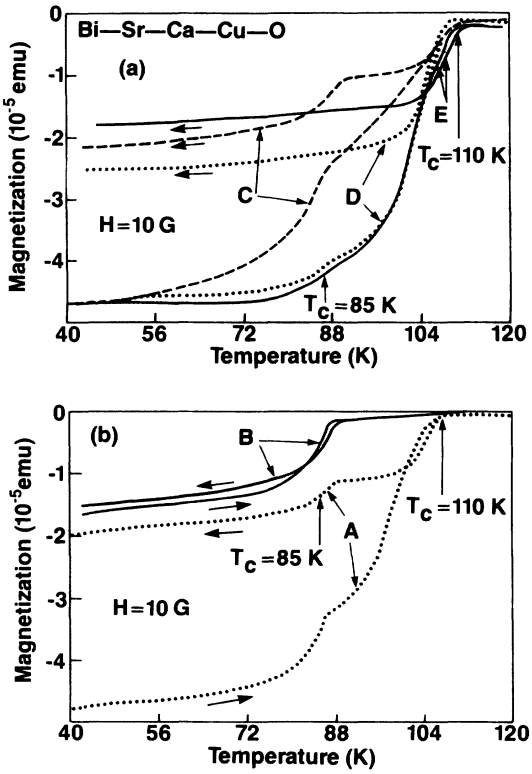

FIG. 2. Magnetization vs temperature for several crystals are shown. For each sample the upper curves are for cooling in a field of 10 G (Meissner) and the lower curves are for warming in a field of 10 G (shielding). (a) The Meissner and shielding curves are shown for three samples denoted *C*, *D*, *E*. The same set of crystals were used for resistivity measurements as well. (b) The Meissner and shielding curves are shown for a crystal as-grown (*A*) and after acid etching (*B*). For *B* Meissner and shielding superimpose.

ducting phase is free of defects or impurities or if H_{appl} is greater than H_{c1} (which is unlikely here). We conclude that the quality of the 85-K phase has been much improved. This can be explained by recalling that the 110-K phase grows from the 85-K phase at a temperature close to the material melting point. Thus that 85-K material which survives the heat treatment without transforming to the 110-K material has had a long time at a high temperature which would allow for rejection of impurities and the elimination of defects. The 85-K phase therefore shows a similar shielding and Meissner whereas a large difference is observed for the 110-K phase. We also note that the 110-K phase is not sensitive to moisture since no change in the magnitude of the diamagnetic signal was observed before and after a very small crystal was submerged in water for 12 h.

With our proposed sample microstructure, a remaining question is why resistivity measurements on such a material would show only zero resistance at 80 K whereas for the 25% Meissner, greater than the ideal percolation limit, one would expect zero resistance at 105 instead of 80 K (in the Y-Ba-Cu-O system zero resistance at 85 K was observed on samples which had only 2% Meissner effect). There are two possible explanations to account for such a behavior. (1) The shell is thin so that it cannot accomodate large currents and thus the resistivity foot down to 80 K appears. (2) Although each grain is surrounded by the 110-K phase material these grains are not themselves perfectly connected to each other but distributed in such a way that the current probes some of the 85-K material. This second possibility would suggest that resistivity measurements on the crystals should show zero resistance near the T_c onset. Temperature-dependent dc resistance was successfully measured on three separate very small crystals by the standard four-probe method in an exchange gas cryostat with a Si-diode thermometer calibrated to 0.2 K. We find that the superconducting 85- and 110-K Bi-Sr-Ca-Cu-O materials have a high-resistance "skin" on the surface. The inability to produce low-resistance contacts with silver ink and the ease with which tunneling barriers are formed by pressing fresh-cut indium on the ceramic surface[9] support this observation. The lowest resistance contacts (400 Ω at 300 K) were achieved with In(Ag) solder. Untouched crystals from the furnace which were black and shiny with obvious facets were the easiest to contact. Once the surface had been exposed to solvents (e.g., acetone, alcohol), adhesion with the In(Ag) was poor or impossible. Plasma oxidation improved

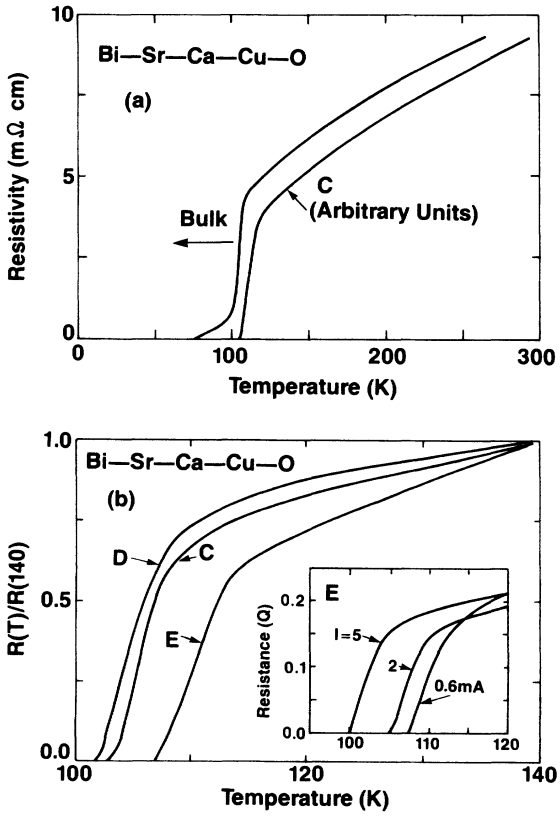

FIG. 3. Resistivity measurements are reported as a function of the temperature for several specimens. (a) Resistivity vs temperature from 0 to 300 K for the bulk ceramic and a crystal (*C*) picked from the bulk. (b) The resistivity normalized to the resistivity at 140 K is shown for several crystals picked from a bulk ceramic. The inset shows the changes in T_c with increasing measuring current for crystal *E*.

adhesion, but not to the level of the virgin crystal.

Figure 3(b) shows the normalized resistance of the three crystals (*C*, *D*, and *E*) from 100 to 140 K. Curves *C* and *D* were measured with currents of 2 and 0.3 mA, respectively. These crystals had been previously processed and exposed to solvent which resulted in their surfaces appearing more rough and solder adhesion was difficult. Curve *E* was measured with 0.6 mA on a shiny $0.73\times0.22\times0.13$ mm^3 faceted crystal upon removal from the compact, with no subsequent processing. Resistivity is not plotted because of the uncertainty in measuring crystal size, not knowing which points of the solder made connections, and what percentage of the material actually carried the current. Ignoring the last uncertainty, we can estimate the resistivity of *E* at room temperature to be between 2 and 25 mΩ cm. Comparing this value with that given by Sunshine *et al.*[10] for a crystal of the 85-K phase at room temperature (130 $\mu\Omega$ cm) we conclude that either the 110-K phase exhibits significantly higher resistivity than the 85-K phase, or that the last uncertainty mentioned (that only a small fraction of the material is carrying the current), is important. Because of the relatively high-contact resistance, low-current measurements were noisy. For this particular curve, the noise level was $\pm5\%$ of the signal above T_c. Our claim of 0 resistance at 107 K, determined by no change in the voltage characteristic with reversed current, is therefore quoted to a ±10 μV level, or 10 mΩ. At higher currents, the noise level dropped accordingly and $R=0$ was chosen within the 1 μV level giving upper bound resistances of 500 and 200 $\mu\Omega$ for 2 and 5 mA, respectively. The effect of increasing the current on the resistive superconducting transition is shown in the inset of Fig. 3(b). Increasing the current from 0.6 to 5 mA on crystal *E* monotonically reduced T_c from 107 to 100 K. The effect of T_c reduction with increasing current, observed in crystals *D* and *E*, does not clearly scale with the normal-state resistance as would be expected if it were due to heating at the contacts. Therefore, we believe this is predominantly a superconducting critical current effect, supporting our hypothesis that only a fraction of the material is superconducting above 100 K.

We have shown that the 110-K superconducting phase grows from the 85-K phase, and forms a shell around it. An important question is whether these two phases have identical structures but differ only by their oxygen content like the 60- and 90-K phases in the Y-Ba-Cu-O system. Except for a lower intensity, the x-ray powder patterns for the 85-K material and the mixed 105 and 85 K are identical, which suggests that there is a very subtle structural change upon going from the single-phase 85-K material to the mixed 85- and 110-K material. A detailed structural characterization of the 110-K phase is difficult because our preparation technique has produced a material with only intermediate range order of about 100–200 Å (cryptocrystalline). The process necessary to effect a grain coarsening in this very fine-grained material, or produce large crystals, has yet to be determined.

Electron diffraction patterns obtained with a 0.27-μm selected area aperture of different areas in one of the larger single crystals (likely an 85-K crystal) of a pseudomorph crystal shows an interesting result. Using the cell $5.41\times5.41\times30.64$ Å, one area of the crystal [Fig. 4(b)] shows a strong modulation along the b^* direction with repeat 25.4 Å (4.7 times the 5.41 Å repeat). In another area of the same crystal, the modulation is along a^* indicating that the crystallite is twinned with respect to the modulation. This observation is consistant with those made on crystals of the 85-K phase.[6,7] However, in an adjacent area of the same crystal [Fig. 4(a)], a simple square pattern with *h* and *k* even and no modulation is observed. This small area, tetragonal (within the accuracy of the measurement), with $a=5.41$ Å, may well be the 110-K material. The origin of the modulation observed within the 85-K phase is not clear but could be due to the ordering of the short Bi-O bonds. A Sr/Ca ordering at the Ca site may also be involved. Structural modulation can be suppressed by impurities, cation vacancies, or a change in the ordering between the Sr and Ca. Chemical analysis of three very small crystals (which showed almost pure 110-K material as determined by Meissner), revealed by

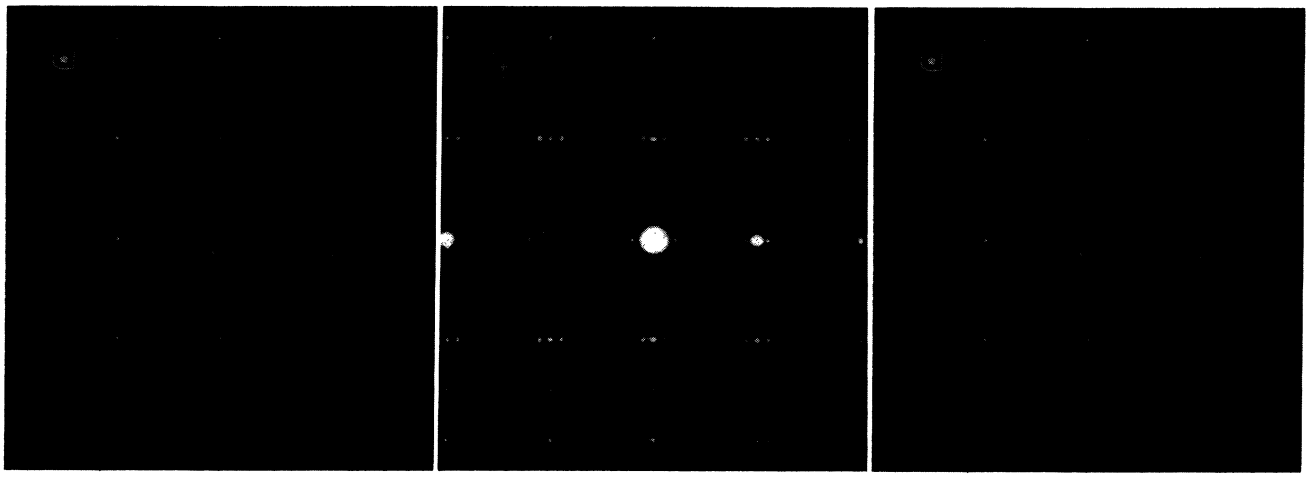

FIG. 4. Electron diffraction patterns (*a*, *b*, and *c*) obtained at different positions of the same crystal. The crystal was picked from a crushed crystal *E*.

inductively coupled plasma atomic-emission spectrometry, stoichiometries of 3:3:3:4 (two crystals) and 2:2:2:3 (one crystal). The alumina crucible was not a source of contamination as no aluminum was detected in the sample.

In summary, we have characterized the formation of the 110-K superconducting phase in the bismuth system. A major structural difference between the 85- and 110-K materials is that the 85-K material can grow (relatively) large single crystals having long-range order whereas the 110-K material, for the crystals we examined, has only intermediate range order of about 100–200 Å (cryptocrystalline). Like the $A15$ compounds, such as Nb_3Ge, it may be that this high-T_c material cannot easily be obtained as bulk form but may be more easily prepared using a thin-film deposition technique.[11]

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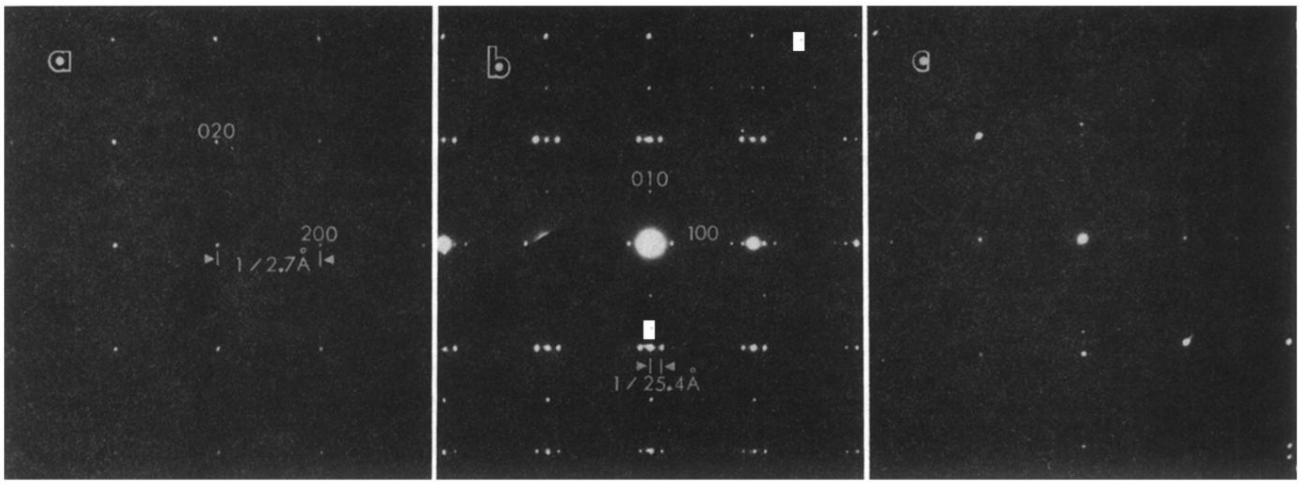

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