

A Study of the Structural Series in the Tl–Ca–Ba–Cu–O Superconducting System

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Three possible superconducting phases have been identified in the system Tl–Ca–Ba–Cu–O using a combination of energy dispersive X-ray emission spectroscopy (EDS) and high resolution electron microscopy (HREM). HREM image contrast confirms that a structural series exists in this system, all the members of which are superconducting, and that these share a basic structure related to that of the superconducting phase in the Bi–Sr–Ca–Cu–O system. © 1990 Academic Press, Inc.

Introduction

Recently two new types of high T_c superconductor have been reported which do not contain yttrium or rare earth elements, unlike $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ (1) or $\text{YBa}_2\text{Cu}_3\text{O}_7$ (2). Detailed structural investigations of the first of these, containing the phase designated as $\text{Bi}_2(\text{Ca},\text{Sr})_3\text{Cu}_2\text{O}_{8+x}$ (3–5), identified the basic arrangement as being related to the “Aurivillius” oxide structures (6), but with modifications which include oxygen vacancies within the perovskite blocks, strontium ions at the top and bottom of these blocks, and a very different configuration of bismuth and oxygen ions between them. There is still some uncertainty regarding the exact composition of the superconducting phase, and the origin of a reported superstructure (7). A second phase with much lower copper content has also been identified in analytical

electron microscopic studies (8), and intergrowths with varying periodicities have been reported in high resolution electron microscopic (HREM) studies (9, 10).

An X-ray structure determination of one phase in the second system, involving the mixed oxides of thallium, barium, calcium, and copper, has been reported (11), and found to be analogous to the bismuth system, while diffraction and electron microscopic evidence (12, 13) suggests the existence of a complete series of phases containing varying numbers of calcium and copper/oxygen layers in the perovskite blocks. In a series of this type, it is logical to suppose that structural intergrowths exist and a complete range of compositions may be prepared, and accordingly we have investigated specimens prepared with differing metal oxide ratios by a combination of techniques including HREM, selected area elec-

tron diffraction (SAED), energy dispersive X-ray spectroscopy (EDS), and image contrast simulation using the multislice method (14, 15) to investigate this hypothesis.

Experimental

Specimens were prepared by direct reaction of metal oxides at 900°C for 5 min, followed by slow cooling in the furnace to 350°C, then removed to cool directly to room temperature. The oxides were first crushed, mixed, and pressed into pellets before reaction, and three compositions were made according to different starting admixtures. The starting metal atom ratios Tl:Ca:Ba:Cu were (I) 2:1:2:2, (II) 1:1:1:2, and (III) 3:2:2:3. Except for (I), the main phase produced appeared to be of a different composition from the corresponding starting ratio, with other minority phases present in the specimens. X-ray powder diffraction provided the initial characterization, followed by compositional identification using EDS to determine the number of phases present in each specimen. SAED and HREM were carried out in a microscope which had been modified to produce an interpretable point resolution of 1.95 Å (16, 17), such that the basic cation arrangement and details of any structural irregularities could be imaged directly under favorable conditions. HREM micrographs were recorded at magnifications of ca. 475,000× and 750,000× after careful alignment to ensure that images were free from residual astigmatism and the effects of incident beam inclination (18), and to assess the validity of proposed model structures image simulations were carried out using the multislice method.

Results

As a series of standard compounds for EDS analysis using the ratio method (19) were not available, EDS was employed only

to check the homogeneity of the preparations and to compare relative compositions between the different preparations. In this way, (I) was found to be almost completely homogeneous, all crystal fragments examined having the same composition, and there was no evidence to suggest that this differed from that of the starting preparation. (III) showed a lesser compositional uniformity, but one phase clearly predominated, although minority species were present. Comparison of analyses with those of crystals in (I) suggested a cation ratio of 2:2:2:3 for this majority phase, in accordance with previous diffraction evidence, while most of the other fragments in (III) showed compositions very similar to those of specimen (I). Specimen (II), on the other hand, showed a very wide range of compositions, with only a few fragments having the composition of specimen (I), and none corresponding to the main phase of (III).

SAED examination reinforced the conclusions from the analytical results of specimens (I) and (III), indicating unit cell dimensions of $a = b = 5.45$, $c = 28.87$ Å for the former and $a = b = 5.45$, $c = 36.61$ Å for the main phase of the latter. The phase of specimen (I) was clearly that for the 2:1:2:2 material of which the structure had been published, although the overall c -repeat was somewhat reduced when compared with the published value of 29.31 Å. No tendency to develop a mica-like morphology was observed in these specimens, in contrast with the bismuth-containing compound, and consequently good HREM images in both [100] and [110] projections could be obtained. [110] images from crystals of (I) and (III) are shown in Figs. 1 and 2, respectively. In the former the arrangement of dark dots is in accordance with the cation positions in the published structure, and this was confirmed by image simulation (shown inset), although the value of objective lens defocus computed from the image match (-500 Å) was beyond the optimum

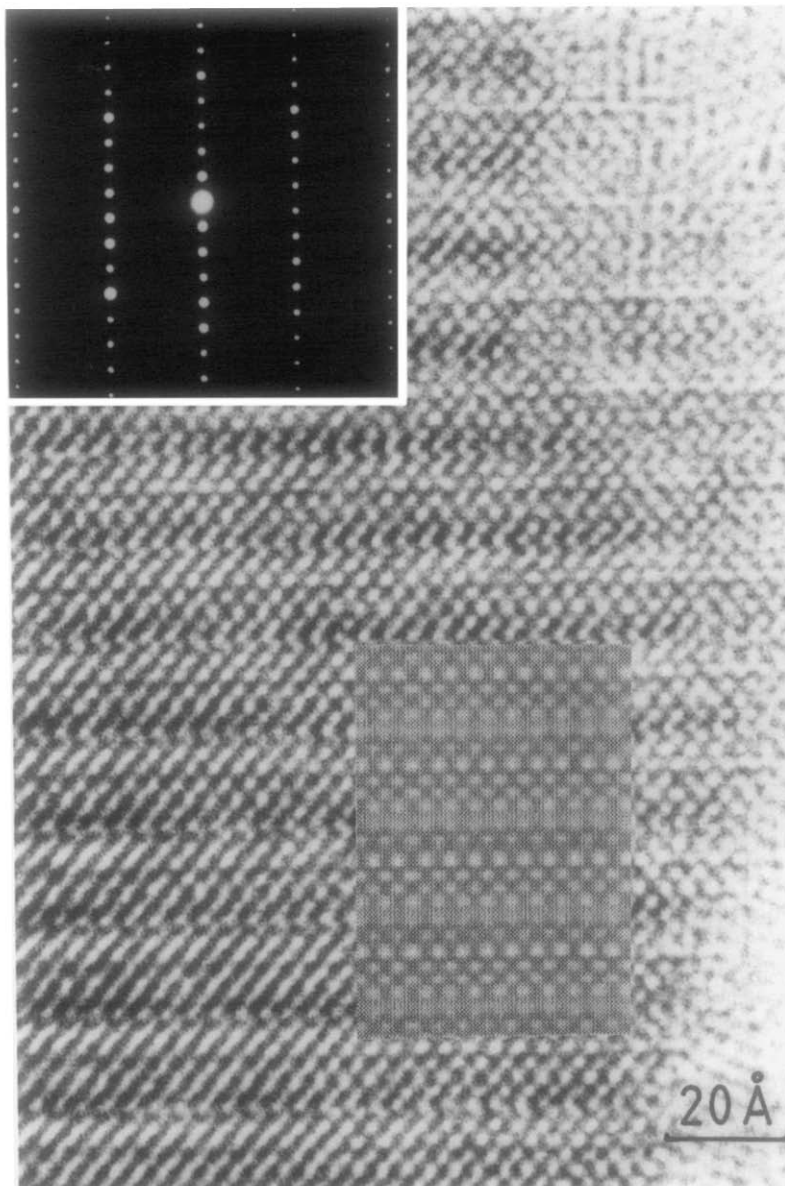


FIG. 1. HREM image of a crystal of assumed composition $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ from preparation 1 viewed down the $[110]$ direction. The insets show the SAED pattern and the simulated image which was computed from the structure model of Fig. 3b with the imaging conditions: specimen thickness, 2.0 nm, objective lens defocus, -500 \AA .

value or Scherzer focus (20) for the microscope used (ca. 430 \AA), indicating that considerable dynamical scattering occurred and therefore the dark dots could be displaced from the true cation positions. In

addition, the “zigzag” contrast at the position of the thallium cations was not as pronounced as might have been expected, but image simulation studies showed that this contrast was an exceptionally strong

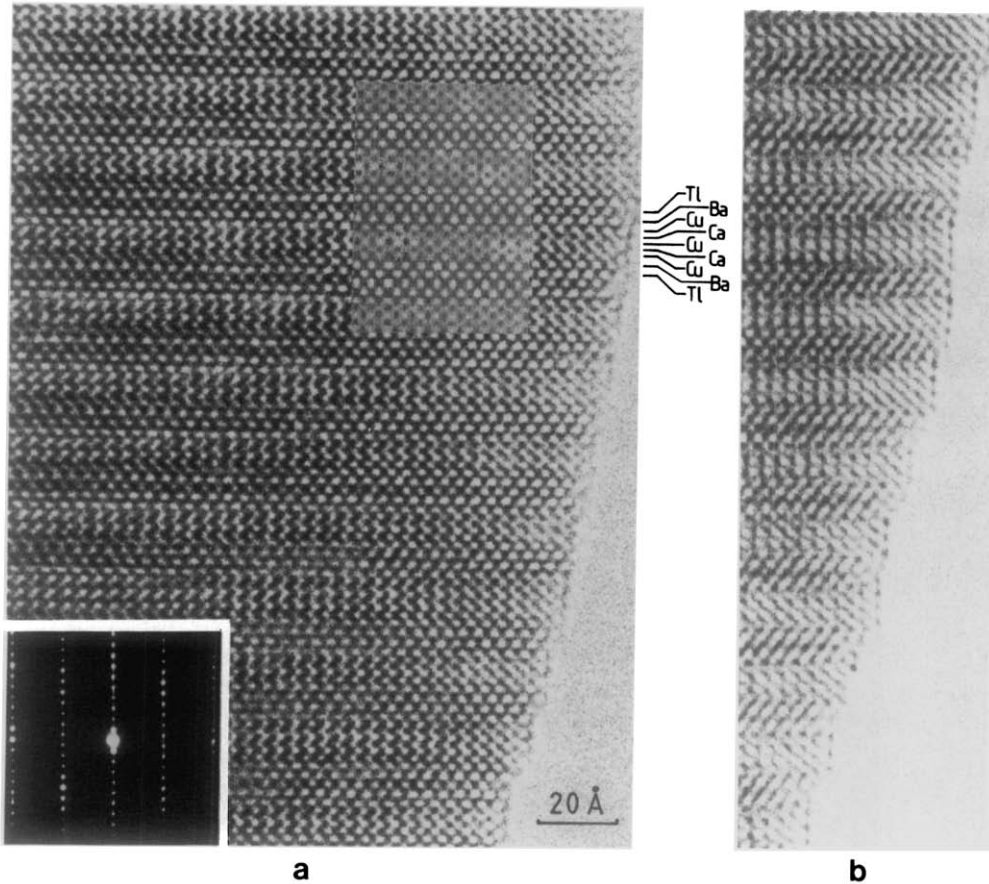


FIG. 2. (a) HREM image of a crystal of assumed composition $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (sample preparation (III)) also viewed down $[110]$, with SAED pattern and simulated image inset. The simulation used the model of Fig. 3a and the simulated conditions were specimen thickness, 20 Å, objective lens defocus, -550 Å. (b) The surface of the same crystal after exposure to the electron beam for approximately 30 min, showing surface reconstruction.

function of specimen thickness and defocus.

From the image of the main phase of specimen (III), shown in Fig. 2a, the arrangement of dark dots immediately suggests that this phase is the development of that in (I), namely 2 : 2 : 2 : 3 structure having an identical thallium and barium cation configuration, but with the extra layers of calcium and copper/oxygen inserted into the perovskite-like block. This is clearly shown by the enlargement of the portion of the HREM image

between the “zigzag” corresponding to the thallium/barium component, the latter being almost the same as the corresponding component in Fig. 1. As with the crystal of that figure, dynamical scattering in the image is pronounced and the positions of the dark dots almost certainly do not correspond exactly to the cation positions. This structure type was confirmed by image simulation, using the model structure of Fig. 3a. For comparison, the structure corresponding to the image of Fig. 1 is shown in Fig. 3b. No

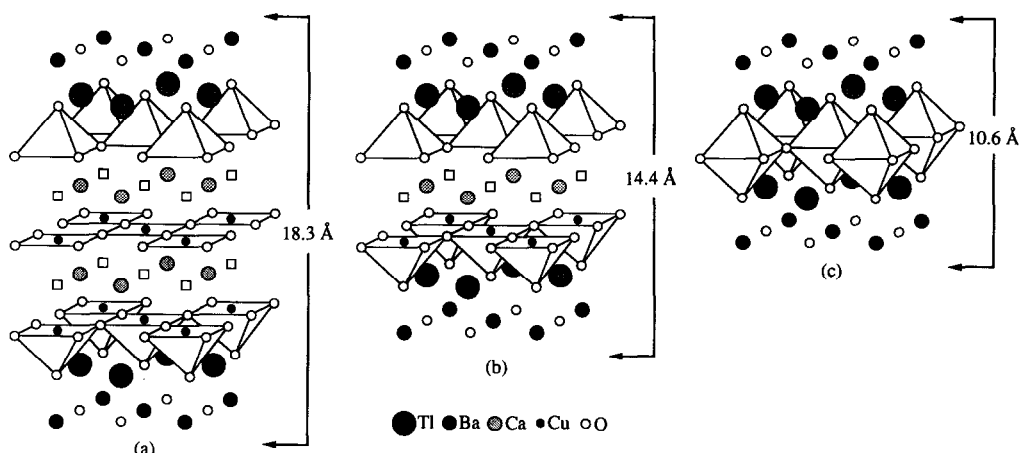


FIG. 3. Structure models for idealized atomic arrangements in the Tl-Ca-Ba-Cu-O system. (a) $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$, (b) $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$, (c) $\text{Tl}_2\text{Ba}_2\text{CuO}_6$. In each case the unit cell contains two layers in a body-centered tetragonal configuration with $a = b = 5.45 \text{ \AA}$ and $c/2$ as indicated. Additional oxygen atoms which would result from possible thallium substitution for calcium are shown as squares.

distinct intergrowths were noted in either this phase or the phase of specimen (I), nor were any superlattices observed, and although the two structures were obviously closely related it was apparent that, although the measured c -axis and layer spacings of the latter (28.87 and 14.44 \AA) were slightly lower than the values of the published structure (29.31 and 14.66 \AA), those for the main phase in (III) were slightly higher than the values which would be predicted from the atomic co-ordinates of the latter if extra layers of calcium and copper/oxygen were inserted (36.61 and 18.31 \AA observed as compared to 35.65 and 17.83 \AA calculated). This suggests that some relaxation of the perovskite blocks takes place when their thickness is increased, and consequently layers of the two structures may not fit together in an intergrowth as easily as might be imagined.

Both this phase and that of specimen (I) appeared to be stable to electron irradiation, but on prolonged exposure some surface reconstruction was noted in the 36.61 \AA phase, as shown in Fig. 2b. Whether this arises

from a simple relaxation of the surface or development of a surface metallic species, as noted in other oxides (21), could not be determined, although similar effects have been noted in lanthanum-copper oxides (22), where surface reconstruction involving a removal of some metal atoms and the outermost layer of oxygen atoms, accompanied by a shifting of the remaining metal atoms, is observed to occur. Unlike the case described above, the effect in La_2CuO_4 was not observed only as a result of exposure to the electron beam. For both materials, however, the effect on the superconducting properties remains unknown.

By comparison, crystals in preparation (II) showed frequent intergrowth structures, and the overall order of all crystals was much less than those of the previous two samples. Typical micrographs in [100] orientation are shown in Fig. 4. In the crystal shown in Fig. 4a, the predominant structure consists of 14.66 \AA layers, but intergrowths of layers of reduced spacing do occur, either singly or in pairs, the spacing of these layers being measured as 12.26 \AA . This would cor-

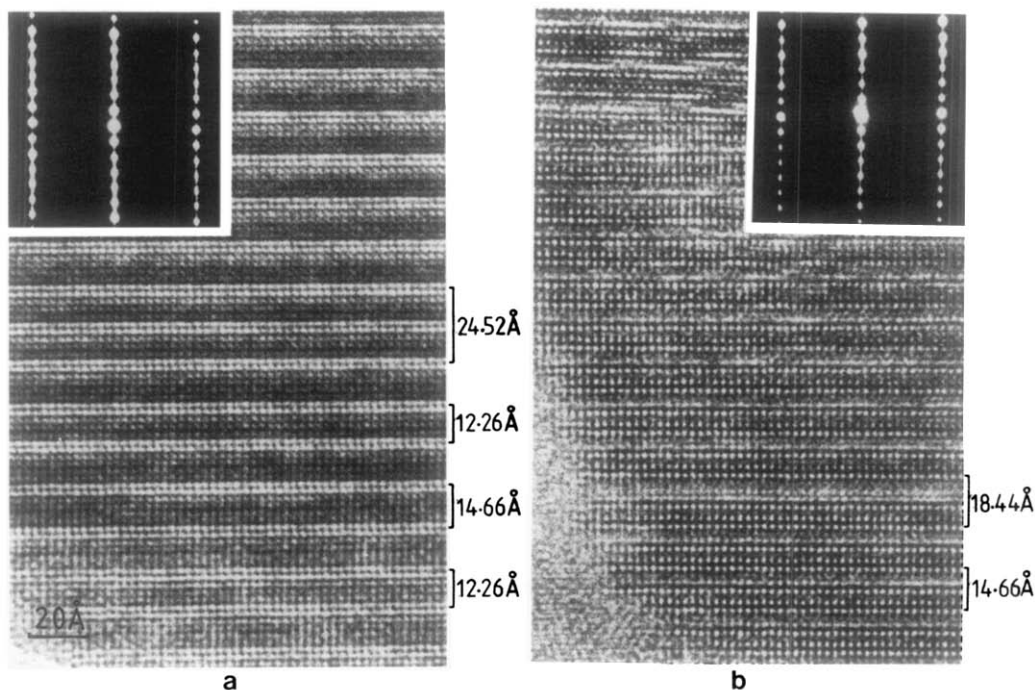


FIG. 4. HREM images, taken with the electron beam parallel to $[100]$, of two crystals from preparation (II). The bulk material in both is the same as that of Fig. 1, namely $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$, with a $c/2$ distance of 14.66 \AA , but intergrowths of two types are shown. (a) Single and double intergrowths of a 12.26 \AA layer. (b) A single intergrowth of a 18.44 \AA layer. SAED patterns are shown inset.

respond to a 24.52 \AA c -spacing, and the obvious structure for this intergrowth phase would be the one shown in Fig. 3c, which is derived from the published structure by removal of one layer of calcium and one copper/oxygen layer. Again, however, a predicted layer thickness for this phase using published co-ordinates would be much different, with a hypothetical calculated value of 11.49 \AA assuming no relaxation in the z -direction when the cation and cation/anion layers were removed. This difference is substantial, and indicates, if correct, that a considerable elongation parallel to the z -axis of the CuO_6 octahedra occurs, and that is may indeed be incorrect to think of the copper co-ordination polyhedra as octahedra in this phase. For the crystal shown in Fig. 4b, however, the main phase again has

the 14.66 \AA layers, but a single layer intergrowth of a thicker layer is indicated, and measurement yields a value of 18.44 \AA for this thickness. Once again this is not in agreement with either the value calculated from published atomic co-ordinates (17.83 \AA) or the value of 18.31 \AA calculated from the SAED pattern of Fig. 2a, although this latter discrepancy is probably within the errors of measurement. In addition, preliminary image simulation studies of intergrowths in these materials have revealed many difficulties in assigning periodicities to single or double layer intergrowth, and indeed to distinguishing between intergrowths between perovskite blocks of different sizes and modifications to the thallium-oxygen layers (12), and consequently all measured repeat distances can only be

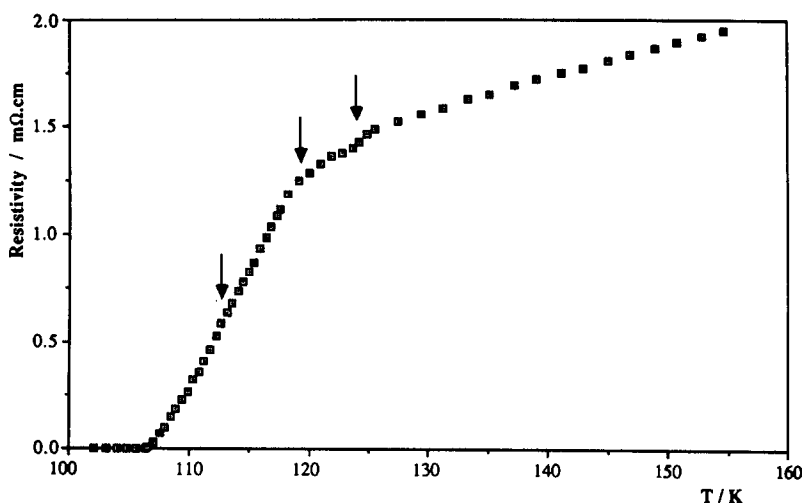


FIG. 5. Variations of resistivity with temperature for a pressed pellet specimen from preparation (III). The current used was 0.5 mA, and the onset temperatures for the various superconducting phases are indicated by arrows.

regarded as approximate. Only single-layer intergrowths of the larger phase were observed in specimen (III), and in no case was there any evidence of any intergrowth between appreciable regions of one distinct phase with another, suggesting that if a given structure once starts to develop in a crystal, that structure type will predominate.

Discussion

Evidence from the HREM investigation clearly supports the diffraction studies suggesting that a complete series of phases exists in the Tl-Ca-Ba-Cu-O system, and this series may well be responsible for the range of temperatures reported at which resistance vanishes. The width in temperature for the resistive transition is relatively broad, and the slope suggests a number of onset temperatures as indicated tentatively by the arrows in Fig. 5. In all of the structures shown in Fig. 3 the formal valence of the copper is 2.0, unlike the case of the

bismuth-containing superconductor, and some substitution of thallium by calcium or barium must occur if this to be increased, unless extra oxygens are introduced into the structures, possibly at the level of the calcium ions, as has been proposed for the bismuth compound (23). This latter process cannot, however, happen in the phase shown in Fig. 3c.

The lack of severely disordered intergrowths of the different structures is also surprising, and indicates that the two phases known to exist as distinct structures (that in specimen (I) and the main phase of specimen (III)) must occupy well-defined free energy minima, with possibly considerable differences between the detailed atomic positions and coordination polyhedra. From the results presented here, the separate existence of the 12.26 Å phase is in doubt, and no evidence has been found in these specimens for the formation of more complex phases with greater layer thicknesses. It remains to be seen if other chemical substitutions or varying conditions of preparations will alter

the structure types observed. The apparent discrepancies in the periodicities of intergrowth layers is also disturbing, and although this could arise from electronoptical artifacts the possibility of intergrowths with single layers of thallium atoms, as described by Ihara *et al.* (12) cannot be ruled out. However, a full analysis awaits more detailed image simulation studies of model intergrowth arrangements and this is proceeding.

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