

Trigonal Phases in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$

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Trigonal ordering is evident from electron microscopy of quenched powders of composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. The powders are a mixture of phases, some of which are based upon two trigonal phases with $a = 0.54$ and $c = 0.66$ nm. In the first the yttrium and barium atoms order on the (111) planes of the parent perovskite structure rather than the (001) while in the second stacking sequence the yttrium layer of this structure is interchanged with one of the copper layers. © 1989 Academic Press, Inc.

Introduction

Since the discovery by Wu *et al.* (1) of a superconductor with $T_c = 93$ K in a Y–Ba–Cu–O mixed-phase sample, many groups have characterized the superconducting phase by X-ray and neutron diffraction (2–4). Although some of the details of their results differ, there is agreement upon the major characteristics of the material which are:

(1) The metal–ion stoichiometry is Y : Ba : Cu = 1 : 2 : 3.

(2) The superconducting structure is a variant of a triple perovskite based upon (001) stacking of Ba–O, Y–O, and Cu–O layers, and oxygen deficiency occurs in the Y–O and some Cu–O layers.

(3) The yttrium and barium atoms occupy the icosahedral sites whereas the copper atoms are in the center of octahedra.

In our early electron microscopy studies (5, 6) of the superconductor we detected evidence for some disorder of the heavy metal atoms in a few grains. This has led

us to suspect that, although the triple perovskite cell is the stable phase, there may be other phases where the metal atoms are in a different order, which may be metastable in nature. In this work we describe two new structures found in quenched $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, which are based on a stacking of (111) perovskite planes with a trigonal unit cell of $a = 0.54$ nm and $c = 0.66$ nm, and space groups of $P\bar{3}m1$ and $P3m1$. The existence of trigonal structures indicates that the perovskite frame structure is retained at high temperatures (950°C), but that the yttrium and copper layers are exchangeable.

Experimental Procedure

$\text{YBa}_2\text{Cu}_3\text{O}_7$ was prepared by the usual method of heating and grinding of CuO , Y_2O_3 , and BaCO_3 and confirmed by X-ray diffraction. The $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound was heated at 950°C for 24 hr in air and then allowed to cool in air. After this procedure, the resulting powder specimen was sintered at 950°C for 12 hr and then quenched in

vacuum quench oil. Acetone was used to remove the oil on the specimen. The inner part of the pellet was brown, while the outer part was black. We will only consider this inner brown material which was protected from being reduced by the oil. Susceptibility measurements indicated that the brown powder was paramagnetic, and its oxygen content was 6.5 as measured by thermogravimetric analysis on a DuPont 910 TGA. This is greater than the equilibrium oxygen content of 123 in air at 950°C which is slightly less than 6.2. The sample was examined in a Hitachi-700 at 200 kV for electron diffraction patterns. High-resolution images were obtained in a Hitachi-9000 electron microscope equipped with ultra high-resolution pole-pieces having a C_s of 0.9 mm operated at 300 kV. For image interpretation, images were simulated using the NUMIS computer programs which are interfaced to SEMPER routines operating on Apollo workstations.

Results

After fast quenching the 123 material is a brown powder from which a series of electron diffraction patterns, presented in Fig. 1, was obtained when the crystal was rotated along [100]. These patterns indicate a reciprocal lattice of a primitive trigonal or hexagonal structure, in which the sixfold and the twofold symmetry can be seen in the [001] and [010] zones, respectively. The dimensions of the unit cell were measured as $a = 0.54$, $c = 0.66$ nm. Since the heavy metal atoms (Ba, Y, and Cu) dominate the HREM images, matching high-resolution images to calculated images enables the positions of the heavy metal atoms to be determined. The anions are generally far more mobile than the metals which are reordering. We have not attempted to determine the oxygen sites and have assumed random occupancy of oxygen site in perovskite for the purpose of calculations. This is particu-

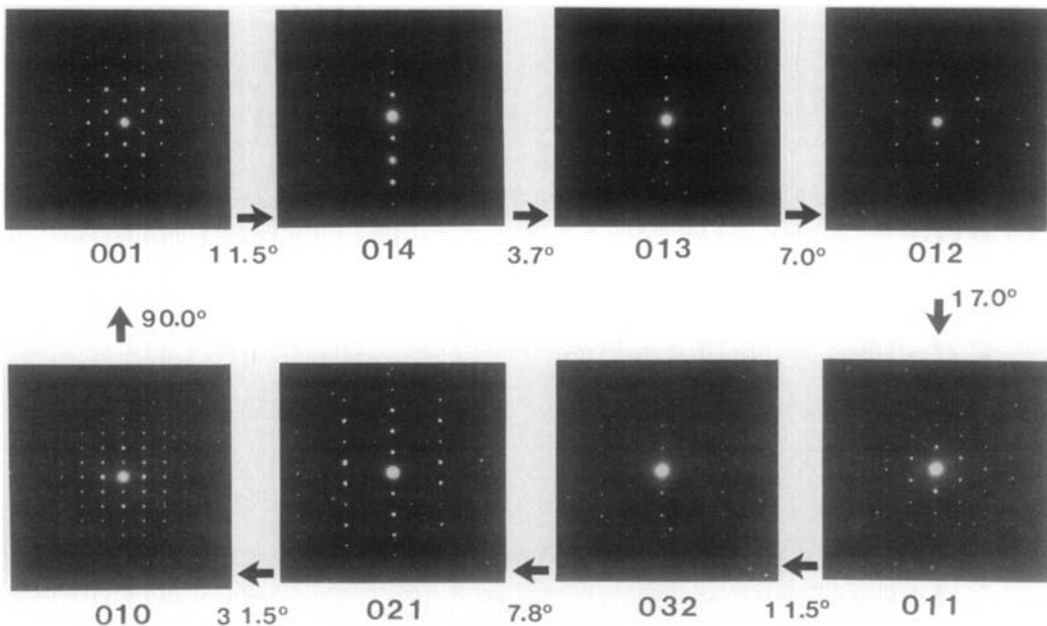


FIG. 1. The series of electron diffraction patterns of the trigonal phase in Y-Ba-Cu-O brown powder, rotating along [100].

larly unlikely for B2 where, given the normal coordination requirements of yttrium and copper, the distortions in the oxygen lattice should be large enough that the analogy to perovskite is of little chemical value. The experimental images for the [001] direction are shown in the upper portion of Fig. 2 where there are two types of hexagons: one has an edge of 0.54 nm, marked by the white lines, another has an edge of 0.39 nm. If we calculate the simulated images using an atomic model with space group $P\bar{3}m1$, as shown in Fig. 3 and Table I, we obtain a good match between the experimental and calculated images (see Fig. 2). In Fig. 3, the larger hexagon and its center are composed of Y–O columns and the inner smaller one is a Ba–O column. This structure, named B1, was identified in brown Y–Ba–Cu–O powder by electron diffraction and high-resolution imaging.

In the brown Y–Ba–Cu–O powder we found another trigonal phase, named B2. In its [001] images, shown in the lower portion of Fig. 2, a larger hexagon of 0.54 nm was retained but within this there is a smaller one of 0.39 nm broken into two triangles staggering with respect to each other. This indicates site exchange between yttrium and one copper relative to B1 (see Fig. 4).

TABLE I
POSITIONS OF THE ATOMS IN B1 TRIGONAL PHASE

$P\bar{3}m1$					
Atoms	Sites	X	Y	Z	Occupancy
Y	1(a)	0	0	0	1
Ba	2(d)	1/3	2/3	1/3	1
Cu	1(b)	0	0	1/2	1
Cu	2(d)	1/3	2/3	5/6	1
O	3(e)	0	1/2	0	0.7
O	6(i)	1/3	1/6	1/3	0.7

Note. The oxygen atom positions are assumed based upon the perovskite unit cell and the oxygen composition is taken such as to give a total content of 6.5 atoms.

TABLE II
POSITIONS OF THE ATOMS IN B2 TRIGONAL PHASE

$P\bar{3}m1$					
Atoms	Sites	X	Y	Z	Occupancy
Y	1(b)	1/3	2/3	5/6	1
Ba	1(b)	1/3	2/3	1/3	1
Ba	1(c)	2/3	1/3	2/3	1
Cu	1(a)	0	0	0	1
Cu	1(a)	0	0	1/2	1
Cu	1(c)	2/3	1/3	1/6	1
O	3(d)	0	1/2	0	0.7
O	3(d)	1/3	1/6	1/3	0.7
O	3(d)	1/6	1/3	2/3	0.7

Note. The oxygen positions were derived by the same approach as described in Table I.

With this model we calculated images and obtained a good match (see Fig. 2). The atomic positions for the space group $P3m1$ are indicated in Table II. The simulated images of B1 and B2, viewed along the [001] axis, were calculated under the same condition with 16 nm of thickness and -10 to -90 nm defocus and inserted into Fig. 2, from which we can see that the calculated pictures of both phases match well with the experimental images.

Comparing B2 with B1, both have the same unit cell size and the same atomic positions except for the Cu–Y exchange. As a result, [001] images of B1 show sixfold symmetry, while B2 shows threefold symmetry. The two trigonal phases can be distinguished easily from images along [001] (see Fig. 2) but not from electron diffraction patterns. A high-resolution image of B1 or B2 and its electron diffraction pattern along [211] direction are shown in Fig. 5. (Along this direction, there is no difference between B1 and B2.)

When the trigonal phases were damaged by the electron beam at 300 kV, it was found that DIET (desorption induced by electronic transitions) appeared to lead to some oxygen loss and chemical disordering

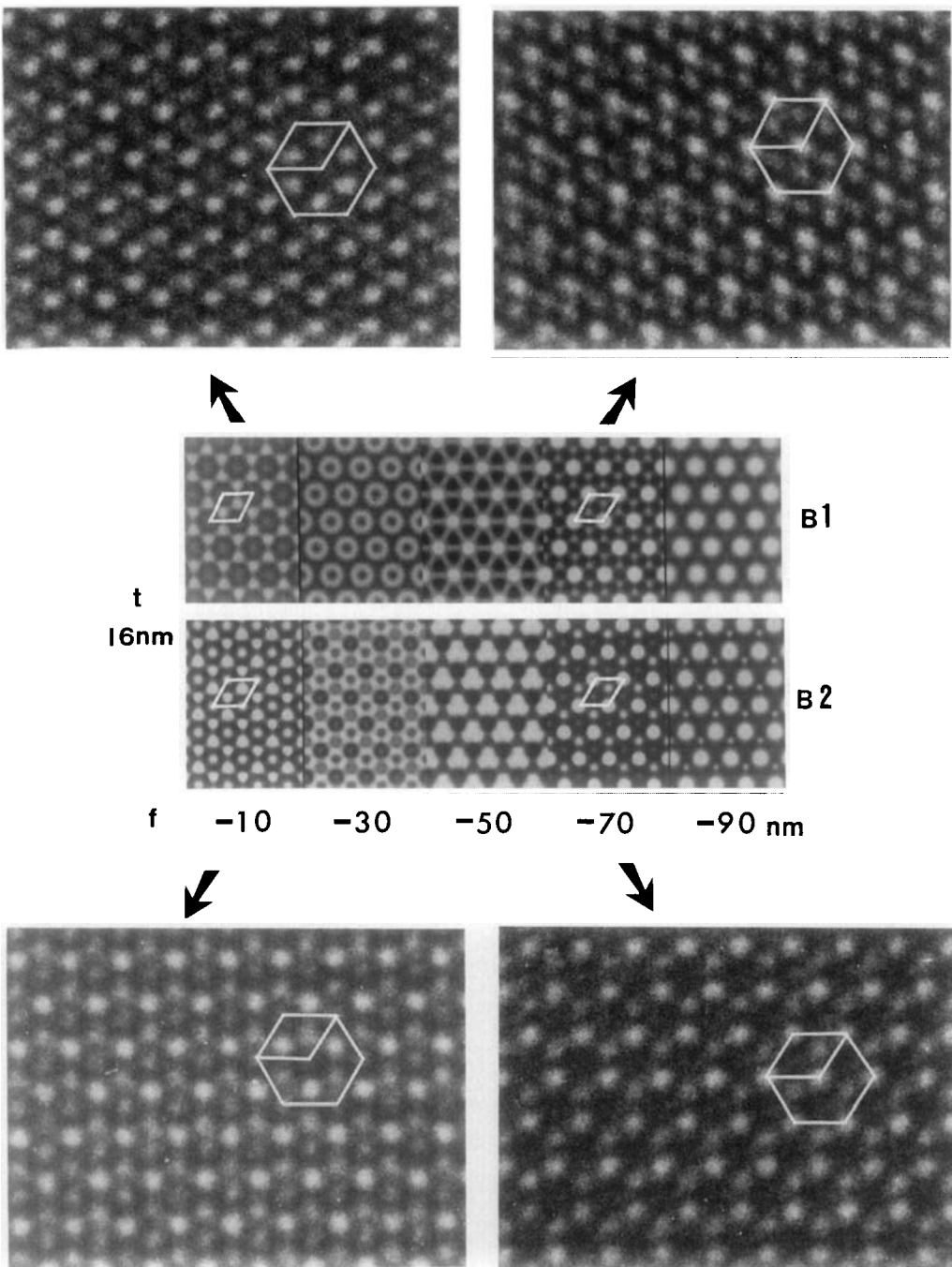


FIG. 2. The high-resolution images of B1 and B2 with their simulated pictures calculated under the same condition. The agreement between the experiment and calculated images is excellent within the limits of the signal to noise of the instrument. (Shot noise eliminates some of the finer details apparent in the calculated images.)

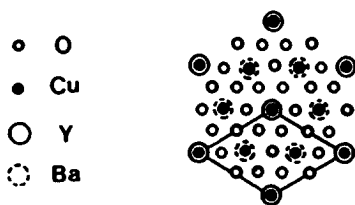


FIG. 3. Atomic model of B1.

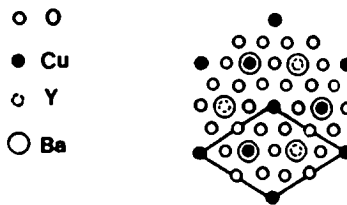


FIG. 4. Atomic model of B2.

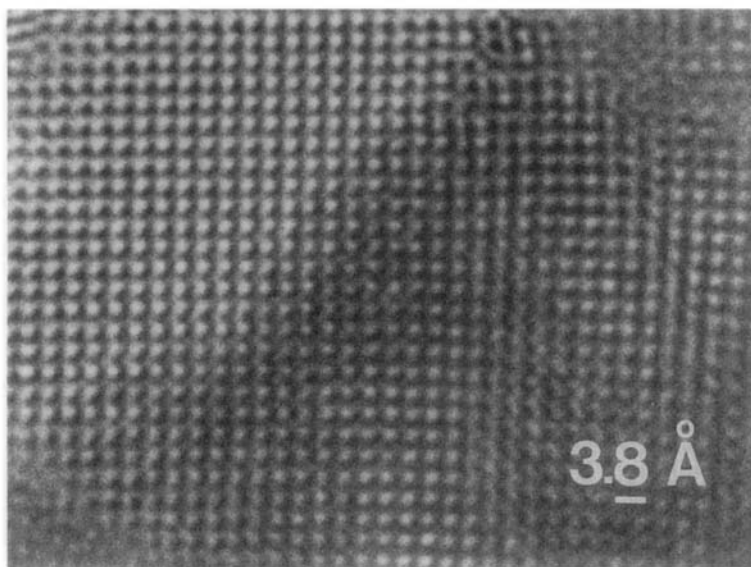
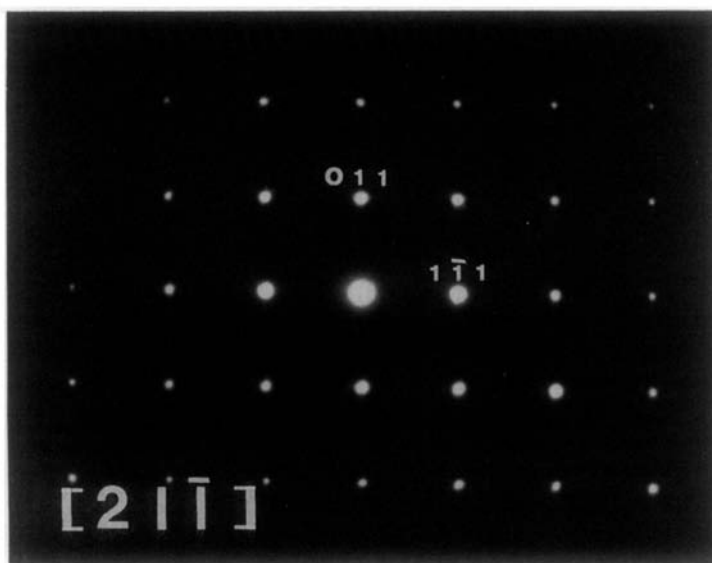


FIG. 5. High-resolution image and diffraction pattern taken along the $[2\bar{1}\bar{1}]$ direction, which corresponds to the $[001]$ direction of perovskite. Both the electron diffraction pattern and the high-resolution image show cubic structures.

even at very low flux (6). Figure 6 shows the initial stage of damage. The trigonal structure is orthogonally deformed where there exists a 120° relation as indicated by arrows due to the loss of the threefold axis during the transformation. Theoretically this phenomena supports the interpretation that the basic structure of the brown powder is trigonal, even though the transformation is not displacive (7).

Discussion

The two trigonal phases, as well as the Y-Ba-Cu-O superconducting phase, are

based on a perovskite structure which, with the formula ABO_3 , contains one metal atom A , at the corner; another metal atom B , in the center; and three oxygen atoms on the faces (see Fig. 7a). Considered in terms of close packing of perovskite, there exist two types of (111) layers and their formulas are AO_3 and B , as shown in Fig. 7b. The layers, similar to a fcc structure, are packed in an **ABC** sequence as **A**(AO_3)–**B**(B)–**B**(AO_3)–**C**(B)–**C**(AO_3)–**A**(B).

At high temperature, for the 123 Y-Ba-Cu-O compound, the A sites are probably occupied by Y and Ba randomly, so the so-

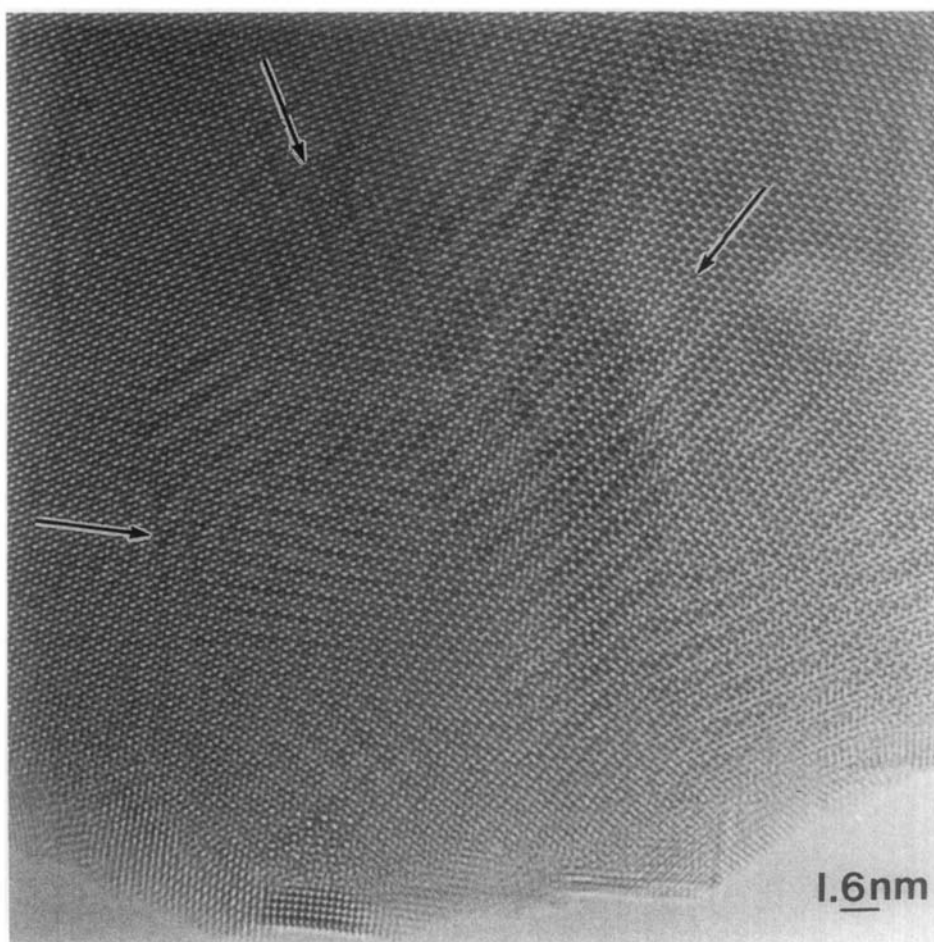


FIG. 6. Structure deformation induced by electron beam shows a 120° rotated relation indicating the trigonal character of the brown matrix.

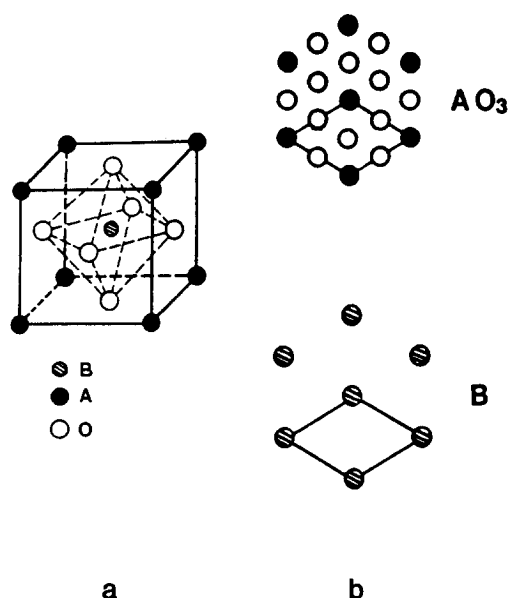


FIG. 7. Perovskite frame structure: (a) three-dimensional model and (b) projected model viewed along the $[111]$ zone.

lution is a disordering cubic structure based on the $[111]$ stacking of $(\text{Y}, \text{Ba})\text{O}_3$ and Cu layers. We believe that during slow cooling an order-disorder transformation takes place (5) with the yttrium and barium taking A sites in a sequence of Ba-Y-Ba along $[001]$ while the copper occupies B sites, and the ordering shows each (001) plane contains one species. The orthorhombic and tetragonal 123 structures are constructed by six (001) layers in a sequence of Cu-O, Ba-O, Cu-O, Y-O, Cu-O, and Ba-O.

Our results indicated that, in B1, the (111) layers are arranged in a sequence of $\text{A}(\text{YO}_3)\text{-A}(\text{Cu})\text{-B}(\text{BaO}_3)\text{-B}(\text{Cu})\text{-C}(\text{BaO}_3)\text{-C}(\text{Cu})$. Viewed along $[211]$ (equivalent to $[001]$ of perovskite) the cubic structure with an apparent lattice parameter of 0.38 nm is apparent. This means the perovskite frame exists in trigonal phases for the same oxygen frame and A and B sites are taken by metals. But now the species habit plane is (111) perovskite, i.e., each (111) perovskite contains one species

of metal atoms rather than (001) in the superconducting 123 structure. The fast cool is a nonequilibrium procedure, so B1 and B2 are presumably metastable. The brown powder is a mixture and some phases arise from B1 or B2 by change of the composition or size, so we can identify B1 and B2 from the SAED (selected area electron diffraction pattern) rather than the multiphase X-ray diffraction pattern. It should be noted that we did not find any grains of the normal 123 superconducting phase in brown powder, but after annealing the 123 phase appeared. We suspect that thin films of Y-Ba-Cu-O before annealing may have the same structure as the brown powder because they are quenched when deposited on the substrate, and their color is also brown (8). We have been able to synthesize materials with excess yttrium and copper by quenching from 950°C and then annealing. These results have been presented elsewhere (9) and, combined with the occurrence of the brown phases, indicate that a major part for slow cooling of the superconductors, which is known to be crucial in producing "good" superconductors, is the establishment of the metal superstructure in addition to the correct oxygen stoichiometry. Indeed, the two are unavoidably linked. In the perovskite $\text{Ba}_2\text{Bi}_{2-x}\text{La}_x\text{O}_{3-y}$, the ordering of the B cations has been shown to be directly related to the oxygen content and thermal history (10).

Acknowledgments

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