Temperature dependence of the lattice parameters in the 30-K superconductor $Ba_{0.6}K_{0.4}BiO_3$

R. M. Fleming, P. Marsh, R. J. Cava, and J. J. Krajewski

AT&T Bell Laboratories, Murray Hill, New Jersey 07974-2070

Using powder x-ray diffraction, we have measured the temperature dependence of the lattice parameters of the 30-K superconductor, $Ba_{0.6}K_{0.4}BiO_3$, in the range 14–300 K. We find that within the resolution of our measurement, $Ba_{0.6}K_{0.4}BiO_3$ remains cubic over the entire range of temperature with no peak splitting or additional peaks observed. This means that the compound maintains an undistorted, three-dimensional Bi-O array at the superconducting transition temperature.

The term "high-temperature superconductor" is used to describe materials that have a high superconducting transition temperature when compared with other materials with a similar density of states. Until recently, only copper-oxide-based superconductors have been unambiguously identified as being of this class, although it was also recognized that the 12-K superconductor, $Ba(Pb,Bi)O_3$ (Ref. 1) had an anomalously high T_c.[2-4] The recent discovery of the 30-K superconductor $Ba_{0.6}K_{0.4}BiO_3$ has emphasized that high-T_c superconductivity is not only confined to copper-oxide-based materials.[5-6] $Ba_{0.6}K_{0.4}BiO_3$ appears to be remarkable in that the material is a simple-cubic perovskite at room temperature,[6-7] unlike $Ba(Pb,Bi)O_3$, which shows an orthorhombic distortion from cubic symmetry.[1] Copper-oxide-based superconductors, such as a $La_{2-x}Sr_xCuO_4$ and $Ba_2YCu_3O_7$, also have phase transitions from tetragonal to orthorhombic symmetry at temperatures above the superconducting transition.[8,9] Given the presence of phase transitions to a lower symmetry in other oxide superconductors and the general tendency of perovskites to display structural distortions which relax bond angles or distances, the simple-cubic structure of $Ba_{0.6}K_{0.4}BiO_3$ is surprising. This comparison leads to the suggestion that $Ba_{0.6}K_{0.4}BiO_3$ may have a structural phase transition between room temperature and the superconducting transition at 30 K. The purpose of this study was to measure the lattice parameters of $Ba_{0.6}K_{0.4}BiO_3$ as a function of temperature to determine if the cubic symmetry remains in the superconducting state. We show that in the range 14–300 K, $Ba_{0.6}K_{0.4}BiO_3$ remains a simple-cubic perovskite with no observed evidence of a superlattice or other structural phase transition. The temperature dependence of the lattice parameter a_0 is approximately linear between 14 and 300 K.

A powdered sample of $Ba_{0.6}K_{0.4}BiO_3$ prepared as described earlier[6] was mounted with vacuum grease on a glass slide in a beryllium cell filled with He gas. (The superconducting properties of this sample are described in Ref. 6.) Temperature control was maintained by a closed-cycle refrigerator mounted on four-circle diffractometer. Copper $K\alpha$ x rays from a 15-kW rotating-anode source were focused in the vertical plane with a singly bent pyrolytic graphite monochromator. A flat pyrolytic graphite analyzer was used on the diffracted beam to maintain a symmetric resolution function and to minimize scattering from the cryostat windows. Two resolution configurations were used. The first configuration, called "low resolution," used only the monochromator and analyzer to define the resolution and produced a resolution function with a full width at half maximum (FWHM) of about 0.025 $Å^{-1}$ as measured with a $SrTiO_3$ powder. The second configuration, called "high resolution," used symmetric slits of 0.5 mm before the monochromator and before the analyzer. In the high-resolution mode the resolution linewidth was about 0.008 $Å^{-1}$.

A powder pattern of $Ba_{0.6}K_{0.4}BiO_3$ taken at 14 K with low resolution is shown in Fig. 1 where the log of the intensity from 25° to 120° 2θ is plotted. All peaks with the exception of the broad feature at about 27° (marked "IMP.") can be indexed with a cubic lattice parameter of 4.274 Å indicating that the sample is remarkably pure. (The impurity peak is from Bi_2O_3 and is less than 1% of the intensity of the strongest perovskite peak.) The calcu-
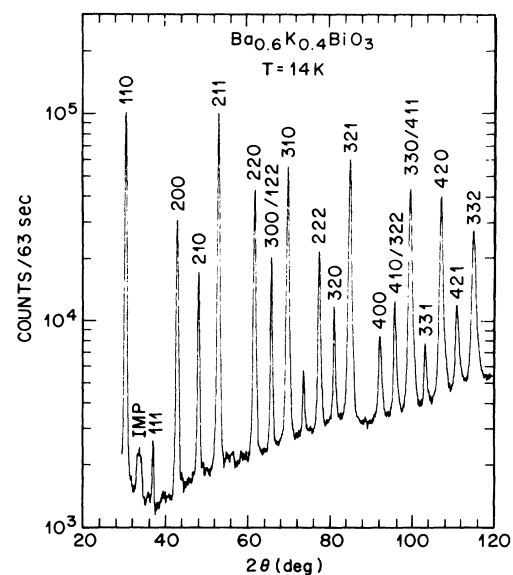

FIG. 1. Powder pattern obtained in the low-resolution configuration at a temperature of 14 K.

lated and the observed peak positions are summarized in Table I. Figure 2 shows high-angle peaks in the range $105°-120°$ 2θ taken in the high-resolution mode at 14 K. The shoulders visible on the high-angle side of the peaks are due to $K\alpha_1$-$K\alpha_2$ splitting. No detectable splitting from a lowering of the cubic symmetry can be observed. The measured linewidths have FWHM of 0.014 Å^{-1}, which is slightly broader than the resolution width of 0.008 Å; however, the observed linewidth does not change as a function of temperature.

The temperature dependence of the lattice parameter of $Ba_{0.6}K_{0.4}BiO_3$ is shown in Fig. 3. The solid line represents a linear expansion coefficient of about 10×10^{-6}/K, a number typical of metals. Within the resolution of this experiment, no change in the slope of the lattice parameters versus temperature could be detected at the superconducting transition temperature.

The undistorted perovskite structure is one of the simplest crystal structures formed by metal oxides of stoichiometry ABO_3. It is formed from an infinite array of corner-shared MO_6 octahedra; forming in this case, an infinite, three-dimensionally connected O-Bi-O array. The larger A atoms (Ba,K) are at the center of a twelve-coordinate cavity (see the inset to Fig. 3). As all atoms are in the special positions of the space group $Pmmm$, and we have observed no distortions from perfect cubic symmetry, we can estimate that at 14 K, Bi is at the center of an oxygen octahedron with six equally distant O neighbors with a Bi-O separation of 2.137 Å. The (Ba,K) atoms have twelve oxygen neighbors at 3.022 Å. Very small distortions from perfect coordination, such as those
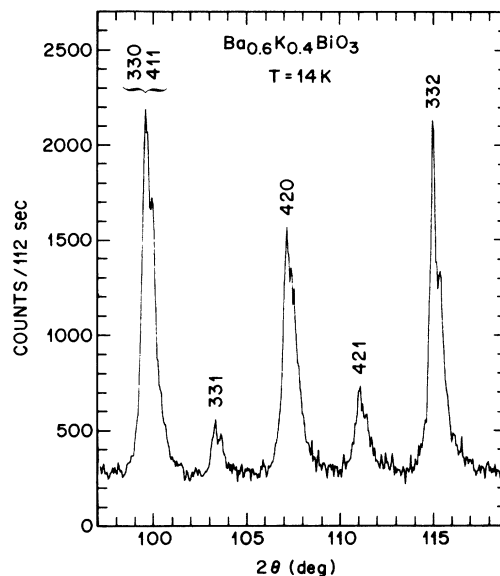

FIG. 2. Powder pattern obtained in the high-resolution configuration at a temperature of 14 K. No peak splitting characteristic of a phase transition to a lower symmetry is detected. The high-angle shoulders are due to $K\alpha_1$-$K\alpha_2$ splitting.

observed in materials with charge-density waves, typically result in superlattice peaks with intensities less than 10^{-2} of the main reflections; however, such reflections would only be marginally detectable in the present experiment.

The presence of lower symmetry in most copper oxide superconductors and the large anisotropy observed in the electronic properties have sometimes led to the suggestion that the lower symmetry and the quasi-two-dimensional character are required for "high-T_c" superconductivity. Theoretically, a requirement of lower symmetry is a function of the nature of the electron pairing mechanism as
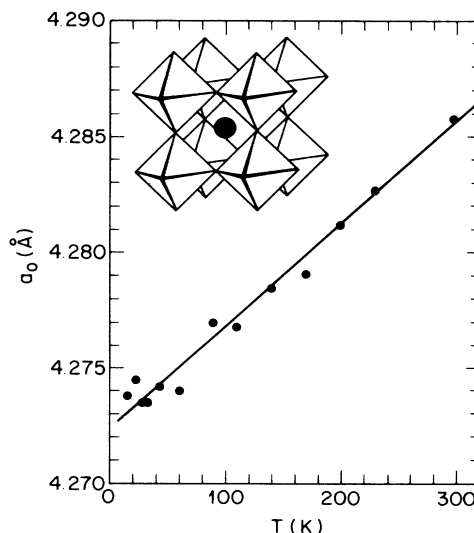
TABLE I. Observed and calculated powder-diffraction peaks of $Ba_{0.6}K_{0.4}BiO_3$ at 14 K. The peaks were indexed with a cubic cell, $a_0 = 4.2736$ Å.

h	k	l	$2\theta_{obs}$	$2\theta_{cal}$
1	1	0	29.492	29.485
1	1	1	36.292	36.319
2	0	0	42.172	42.185
2	1	0	47.472	47.451
2	1	1	52.292	52.305
2	2	0	61.212	61.187
3	0	0	65.362	65.342
1	2	2		
3	1	0	69.372	69.363
3	1	1	73.272	73.281
2	2	2	77.142	77.119
3	2	0	80.892	80.899
3	2	1	84.672	84.640
4	0	0	92.092	92.069
4	1	0	95.792	95.788
3	2	2		
3	3	0	99.512	99.533
4	1	1		
3	3	1	103.272	103.319
4	2	0	107.142	107.165
4	2	1	111.092	111.093
3	3	2	115.142	115.128

FIG. 3. The temperature dependence of the lattice parameters of $Ba_{0.6}K_{0.4}BiO_3$. The solid line is a guide to the eye.

well as the nature of the structural distortion. For the case of the bismuth-oxide-based superconductors, it has been suggested[5,10] that the superconductivity is related to the proximity of the compound to a breathing-mode distortion observed[11] in the parent compound $BaBiO_3$. $BaBiO_3$ is semiconducting with a gap that results from a commensurate charge-density wave producing an alternation of the Bi-O in-plane bond lengths. It is expected[5,10] that the maximum electron-phonon coupling and the maximum transition temperature occurs when one dopes the parent compound slightly into a metallic state, as in the case of $Ba_{0.6}K_{0.4}BiO_3$. A similar proposal has been made for the parent compound La_2CuO_4 as related to the superconductor $La_{2-x}Sr_xCuO_4$.[12,13] A complicating factor, however, is the presence of structural phase transitions that do not alter the in-plane bond distances and do not strongly couple to the conduction electrons. An example is the tetragonal-orthorhombic transition in $La_{2-x}Sr_xCuO_4$.[8] $BaPbO_3$ and $Ba(Pb,Bi)O_3$ also have similar distortions that do not involve the alternation of bond distances.[1,14] Within a model of electron-phonon coupling

induced by a breathing-mode distortion, one would not expect these phase transitions to affect the superconducting state; however, it was experimentally shown that superconductivity in $La_{2-x}Sr_xCuO_4$ only occurs in the orthorhombic state.[8]

Based on the above discussion, our observation that $Ba_{0.6}K_{0.4}BiO_3$ remains cubic above 14 K is not surprising and the lack of a static breathing-mode distortion gives some support to the model. However measurements of the oxygen thermal parameters[15] in $Ba_{0.87}K_{0.13}BiO_3$, a nonsuperconducting composition, show no evidence of an incipient breathing-mode distortion. We emphasize that in this powder-diffraction experiment we are only sensitive to static distortions of the lattice and the phonon structure of the material is not probed. Regardless of the validity of the breathing-mode hypothesis, $Ba_{0.6}K_{0.4}BiO_3$ appears to be unique among "high-T_c" oxides in that it maintains the simple-cubic perovskite symmetry in the superconducting state.

[1] A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, Solid State Commun. 17, 27 (1976).

[2] B. Batlogg, Physicia B 126, 275 (1984).

[3] L. F. Mattheiss, Jpn. J. Appl. Phys. 24, Suppl. B 24-2, 6 (1985).

[4] K. Kitazawa, S. Uchida, and S. Tanaka, Physica B 135, 505 (1985).

[5] L. F. Mattheiss, E. M. Gyorgy, and D. W. Johnson, Jr., Phys. Rev. B 37, 3745 (1988).

[6] R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp, Jr., A. E. White, K. Short, W. F. Peck, and T. Kometani, Nature (London) 332, 814 (1988).

[7] D. G. Hinks, B. Dabrowski, J. D. Jorgensen, A. W. Mitchell, D. R. Richards, Shiyou Pei, and Donglu Shi, Nature (London) 333, 836 (1988).

[8] R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, Phys. Rev. B 35, 7191 (1987).

[9] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. 58, 1676 (1987).

[10] L. F. Mattheiss and D. R. Hamann, Phys. Rev. Lett. 60, 2681 (1988).

[11] D. E. Cox and A. W. Sleight, Solid State Commun. 19, 969 (1976); Acta Crystallogr. Sect. B 35, 1 (1979).

[12] L. F. Mattheiss, Phys. Rev. Lett. 58, 1028 (1987).

[13] Werner Weber, Phys. Rev. Lett. 58, 1371 (1987); 58, 2154(E) (1987).

[14] R. D. Shannon and P. E. Bierstedt, J. Am. Ceram. Soc. 53, 635 (1970).

[15] J. P. Wigancourt, J. S. Swinnea, H. Steinfink, and J. B. Goodenough (unpublished).