

Low-temperature structure of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$

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The newly discovered copper-free superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has the CaTiO_3 -type structure at room temperature, but its structure at or below T_c is not known. We report Rietveld refinements of the structures fit to neutron-powder-diffraction data taken at 297 and 10 K for a sample with $x=0.4$. We find that the structure remains cubic at 10 K, the dopant level remains close to that expected from the starting stoichiometry, the oxygen sites are essentially fully occupied, and the anisotropic thermal ellipsoids remain oblate with the unique axis along the Bi-O-Bi bonds.

The recent discovery of superconductivity in the K-doped barium bismuthates^{1,2} is remarkable in several respects: (1) The observed transition temperatures of approximately 30 K are the highest to date for an oxide superconductor that does not contain copper; and (2) the room-temperature structure is cubic, implying that the two-dimensional metal oxide sheets prevalent in the cuprate superconductors are now replaced by three-dimensional Bi-O arrays. However, given the widespread occurrence of structural instabilities in superconducting materials³⁻⁵ and in perovskites,⁶ it is important to know whether the cubic structure actually persists at temperatures below the superconducting transition temperature. In this Rapid Communication, we report the structures of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ at 10 and 297 K as determined from neutron powder-diffraction experiments. We find that the structure of this material remains cubic at low temperatures. The anisotropic thermal parameters for the bridging oxygen atoms are oblate along the Bi-O-Bi bonds indicating a rocking motion or possible disorder involving a tilting of the oxygen octahedra typical of the 2:1:4 cuprate superconductors⁷ and other perovskites.⁸

The $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ was prepared with a simplified synthetic route.⁹ We ground, pelletized, and baked overnight at 700°C stoichiometric amounts of BaNO_3 and Bi_2O_3 . This mixture was then added to the appropriate stoichiometric quantity of KNO_3 , pelletized, baked, and annealed following the procedures described by Hinks and co-workers.^{9,10} The pellets were first baked at 700°C for 1 h in flowing N_2 and then sequentially annealed at 450°C for 3 h and 375°C for 4 h, before furnace cooling, all in flowing O_2 . A room-temperature (297-K) x-ray-diffraction scan of the surface of one of the pellets showed the structure to be single phase and cubic with a lattice constant of 4.28686(4) Å. Bulk chemical analysis showed the overall cation stoichiometry for Ba:K:Bi to be 0.60(1):0.38(2):1.00(1). The onset of diamagnetism for a sample cut from one of the pellets occurred at 29 ± 1 K, with a midpoint of 26 K, with $\sim 98\%$ field exclusion.

Neutron-powder-diffraction data were taken at 297 K on the high intensity powder diffractometer (HIPD) and at 10 K on the neutron powder diffractometer (NPD) at the Los Alamos Neutron Scattering Center (LANSCE). HIPD has an incident-neutron flight path of 9.5 m and a resolution $\Delta d/d$ of 4×10^{-3} , while NPD has a flight path

of 32 m and a resolution of 1×10^{-3} . The higher resolution of NPD is important for the lower-temperature experiment because of our concern with the possible existence of a transformation to a lower-symmetry phase. A portion of the diffraction data at each temperature is shown in Fig. 1. These data were collected in four detector banks ($\pm 150^\circ$ and $\pm 90^\circ$) for approximately 5 h on HIPD and 20 h on NPD at average proton currents of approximately 25 μA .

The structural models were refined by the Rietveld refinement code developed by Larson and Von Dreele.¹¹ An inspection of both sets of data showed that in addition to the cubic superconducting phase, a small amount of a second monoclinic phase was present. From the stoichiometry and the synthetic procedure, it seemed reasonable that the second phase is a semiconducting oxygen-deficient Bi- or K-doped barium bismuthate; the former is known to be monoclinic, but the structure of the latter is not known. For an initial guess for the structure of the second phase, we used the structure of the monoclinic end member BaBiO_3 ,^{12,13} and later allowed dopant levels, oxygen stoichiometry, and structure to vary. Structural refinements with the data at the two temperatures with either a Bi- or K-doped second phase, gave slightly lower values of the weighted profile agreement factor R_{wp} when the former choice was made. In that case, the Bi dopant level at the Ba site refined to 0.0 within 3% for both sample temperatures. Refinement of the oxygen stoichiometry for the impurity BaBiO_{3-y} gave an approximate value of $y \approx 0.3$. The impurity phase appeared as small dense brown, presumably semiconducting, regions within the bluish-black pellets. These regions were probably formed by liquid-phase sintering of the nitrates within the pellets, and both K and O diffusion were probably very slow at these densities. Since the second phase is present at approximately 0.12 mol fraction, and since the intensity is spread over many lines for a monoclinic crystal system, the presence of the second phase did not strongly affect the structural refinement of the dominant phase. The results of two-phase Rietveld refinements are shown in Table I. In addition to the structural parameters shown, absorption and isotropic profile coefficients were also fitted. For the second phase, we fitted the lattice constants and atomic positions, dopant level, oxygen occupancy, isotropic thermal parameters, absorption, and anisotropic

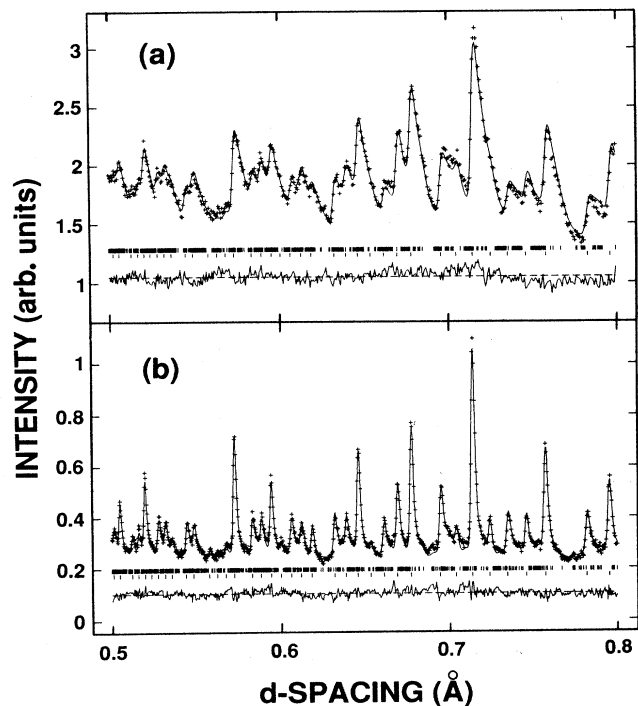


FIG. 1. Part of the neutron-diffraction data for cubic $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. Data shown by plus (+) marks in panel (a) represent data collected on the $+153^\circ$ detector bank of the HIPD for a sample temperature of 297 K, while the data shown in (b) are data taken on the $+148^\circ$ detector bank of the NPD for a sample temperature of 10 K. The continuous lines through the sets of points are the calculated profiles from two-phase Rietveld refinements of the structural models for the cubic superconductor ($Pm\bar{3}m$) and a second phase consisting of a monoclinic barium bismuthate ($I2/m$), presumably semiconducting oxygen-deficient $\text{BaBiO}_{3-\gamma}$. The sets of tick marks below the data indicate the positions for the allowed reflections for both cubic (lower set) and monoclinic (upper set) phases. The lower curve in each panel represents the difference between observed and calculated profiles. The higher resolution of NPD is readily evident.

profile coefficients. Determination of lattice constants with time-of-flight spectrometers is sensitive to sample position and absorption; since x-ray data were available at 297 K, the HIPD diffractometer constants were also varied to fit the lattice constant from x-ray powder data.

It is readily apparent from the data in Fig. 1, or from the fitted structures given in Table I, that the structure of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ remains cubic below its superconducting transition temperature. All previous cuprate and bismuthate¹⁴ superconductors have tetragonal or lower symmetry at or below their transition temperatures; the resulting lower dimensionality of the Cu-O arrays in the cuprates is now often thought to play a crucial role in their superconductivity. Thus the retention of cubic symmetry at low temperatures represents a marked departure from these other systems. The cubic structure of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is remarkably stable to changes in dopant stoichiometry⁹ and

TABLE I. Structural parameters for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ at 10 and 297 K. (The numbers in parentheses following refined parameters represent the estimated standard deviations in the last significant digit.) Space group $Pm\bar{3}m$: Ba/K(1/2,1/2,1/2), Bi(0,0,0), and O(1/2,0,0).

	10 K	297 K
$a(\text{\AA})$	4.2802(1)	4.28686(4) ^a
$n(\text{K})$	0.38(2)	0.46(1)
$n(\text{O})$	1.005(4)	1.010(3)
$U_{\text{iso}}(\text{Ba/K})(\text{\AA}^2)$	0.0073(2)	0.0129(3)
$U_{\text{iso}}(\text{Bi})(\text{\AA}^2)$	0.0044(1)	0.0054(1)
$U_{11}(\text{O}), U_{22}(\text{O})(\text{\AA}^2)$	0.0191(2)	0.0273(2)
$U_{33}(\text{O})(\text{\AA}^2)$	0.0045(3)	0.0046(2)
$R_{\text{wp}}(\%)$	6.75	3.51
$R_{\text{exp}}(\%)$	4.74	2.63

^aThe lattice constant for the 297-K structure was obtained from x-ray powder-diffraction data as discussed in the text. Corrections for refraction are not included; therefore, despite the high precision given by the refinement, we estimate the accuracy at five significant digits.

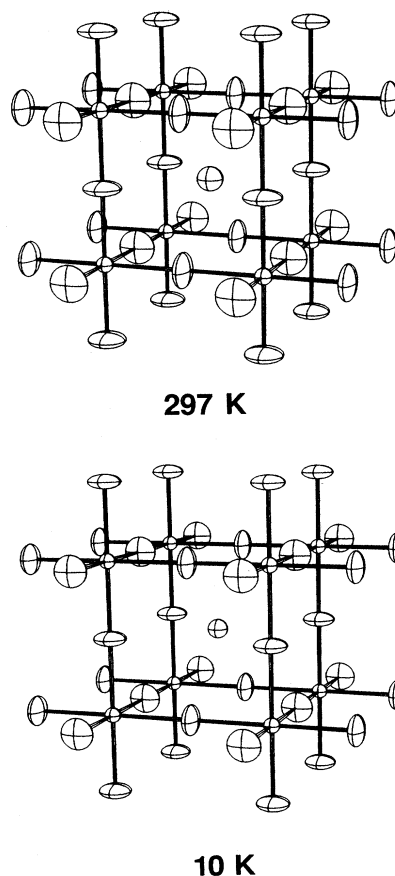


FIG. 2. The structure of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ at 297 and 10 K. The Ba and K atoms are located at the body centers of the cell, the Bi atoms at the corners, and the O atoms along the centers of the cell edges. Nearest-neighbor oxygen atoms from adjacent unit cells are included to show full Bi-O coordination. The thermal ellipsoids are drawn as 99% probability surfaces.

temperature. This is in contrast to its closely related superconducting bismuthate $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$, which goes through sequential orthorhombic, tetragonal, orthorhombic, and monoclinic phases as x is increased;¹⁵⁻¹⁷ and which, for the superconducting phase with $0.05 \leq x \leq 0.35$, changes symmetry from cubic to tetragonal, and perhaps monoclinic,¹⁵ as the temperature is lowered from above 620 K to below 160 K.^{16,17} The end member for both of the doped barium bismuthates BaBiO_3 also undergoes a number of phase transformations as the temperature is changed: It is monoclinic at room temperature, becoming rhombohedral at about 403 K, and cubic near 723 K. The observed room-temperature structures also provide implications for the oxidation state of bismuth in these systems. In semiconducting BaBiO_3 , the two inequivalent bismuth sites contain ordered disproportionated Bi^{III} and Bi^{V} species (e.g., $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$), bonded to their neighboring oxygen atoms with substantial covalent contributions.^{12,13} The two superconducting species, metallic in their normal state, have only a single bismuth site and, presumably a single oxidation state, to the extent that atoms in a metal can be assigned oxidation states.

The refined values of the site occupancies show that our sample is essentially at full oxygen stoichiometry and that the average K stoichiometry is at 0.42, close to the initial stoichiometry. The value of T_c appears high for the observed stoichiometry when compared to the values reported by Hinks *et al.*,⁹ but the correlation of T_c with lattice constant differs only slightly from their findings. The preservation of stoichiometry with the new synthetic route and the greater ease of handling KNO_3 vs KO_2 should make the synthesis of these materials substantially more easy and reliable. The second phase present in our sample can probably be eliminated by regrinding and pelletizing, followed by a second annealing cycle.

The thermal parameters for the cations are constrained

to be spherical by symmetry, but the anisotropic thermal parameters for the O atoms should provide information about the vibrational dynamics and/or possible disorder in this system. Recently, Wignacourt *et al.*¹⁸ determined the anisotropic thermal parameters for the O atoms by x-ray diffraction from a single crystal of semiconducting $\text{Ba}_{0.87}\text{K}_{0.13}\text{BiO}_3$. They found the anisotropic thermal ellipsoids for the O atoms to be oblate about the Bi—O—Bi bonds, indicating that the O atoms are locked between the Bi atoms with enhanced vibrations perpendicular to the bonds. As shown in Fig. 2, our results suggest that this qualitative picture also holds for both the higher K stoichiometries and the low temperatures at which $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is superconducting. The shapes of the thermal ellipsoids strongly resemble those for the 2:1:4 oxide superconductors⁷ and have been ascribed to a rocking motion of the oxygen octahedra. However, the large amplitude of the thermal motion of the O atoms for both cuprates and bismuthates at low temperatures suggests that a substantial amount of disorder may be present in the orientation of the oxygen octahedra. The structural instability and the thermal vibrations and disorder in the oxygen octahedra are common in the perovskites and occur because of mismatches in the ionic radii of the constituent atoms. For $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, the effect of K doping seems to be to stabilize the cubic structure and the single oxidation state for Bi, but the anisotropic vibrational motions and/or disorder in the oxygen octahedra still persist.

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