

Crystal Structure of the $(\text{K}_{0.87}\text{Bi}_{0.13})\text{BiO}_3$ Superconductor

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The structure of a superconducting oxide $(\text{K}_{0.87}\text{Bi}_{0.13})\text{BiO}_3$ ($T_c \approx 10.2$ K) prepared under high pressure was analyzed by time-of-flight neutron powder diffraction. Rietveld refinement showed this compound to be a cubic perovskite ABO_3 with space group $Pm\bar{3}m$ (No. 221) and lattice parameter $a = 4.23377(3)$ Å. Refinement of occupation factors revealed the absence of oxygen vacancies and the substitution of Bi^{3+} ions for 13% of K^+ ions at the *A* site, presenting evidence for electron doping in this superconductor. Extraordinarily large atomic displacement parameters for the *A* and O sites are believed to reflect pronounced positional disorder mainly arising from the large difference in size between the K^+ and Bi^{3+} ions. © 1999 Academic Press

A series of perovskite-type oxides ABO_3 ($A = \text{Ba}, \text{Sr},$ and K ; $B = \text{Bi}, \text{Pb},$ and Sb) has superconducting transition temperatures, T_c , ranging from 3.5 K in $\text{Ba}(\text{Pb}_{0.75}\text{Sb}_{0.25})\text{O}_3$ to 30 K in $(\text{Ba}_{0.6}\text{K}_{0.4})\text{BiO}_3$ (1–5). Despite the relatively low density of states at the Fermi level, the T_c of 30 K holds the record for Cu-free superconductors. In contrast to high- T_c copper oxides, they contain a three-dimensional network of (Bi, Pb)–O bonds and only nonmagnetic metals. In the insulating phases of these perovskites, lattice distortion due to charge density waves was observed, which suggests that strong electron–phonon coupling is responsible for the Cooper-pair attractive interaction. The considerable contribution of phonons to the superconductivity in these materials was also confirmed by tunneling spectroscopy (6). However, it remains unclear whether they are conventional superconductors or whether a special charge-fluctuation mechanism is at work (7). Another question is concerned with the possibility of raising T_c further in bismuth oxides since the upper limit of T_c for BCS superconductors is theoretically predicted to be about 40 K (8). Answers to these questions can be obtained by investigating the essential electronic

characteristics influencing T_c in these materials and by searching for new bismuth oxides other than solid solutions based on BaBiO_3 .

Recently, we have discovered a new superconducting compound in the K–Bi–O system (9). Bulk superconductivity with the highest T_c of 10.2 K was observed in solid solutions, $\text{K}_{1-x}\text{Bi}_{1+x}\text{O}_3$ ($x = 0$ –0.1), with a cubic perovskite structure, which was confirmed by X-ray and electron diffraction. T_c hardly changed within this region, but a sample with a nominal composition $\text{K}_{0.9}\text{Bi}_{1.1}\text{O}_3$ had a superconducting volume fraction larger than and a T_c onset sharper than those of any other samples. Energy-dispersive spectroscopy revealed a decrease in its K content in comparison with the starting composition.

In superconductors based on bismuth oxides, the conduction band σ^* is derived from an antibonding mixture of $\text{Bi}(6s)$ – $\text{O}(2p)$ states. We suggested that, in the $(\text{K}_{1-x}\text{Bi}_x)\text{BiO}_{3-\delta}$ system, electron doping to the conduction band, which is empty for $x = 0$ and $\delta = 0$, results from partial occupation of the *A* site by Bi^{3+} ($x > 0$) and/or from oxygen vacancies ($\delta > 0$) (9). Though the existence of oxygen deficiencies could not be completely ruled out, we attributed the lower oxidation state of Bi at the *B* site to the former reason. Thus, determination of the chemical composition and crystal structure of the new superconducting phase is indispensable for clarifying the doping mechanism at work in this system. Then, we applied neutron diffraction to the present superconductor. This technique is very suitable for determining the occupancies of K, Bi, and O because of the large difference in the coherent scattering length, b_c , between K (3.71 fm) and Bi (8.5307 fm), and the relatively large b_c of O (5.803 fm) (10).

A sample with a nominal composition $\text{K}_{0.9}\text{Bi}_{1.1}\text{O}_3$ was prepared from KO_2 (96%) and Bi_2O_3 (99.99%). The starting mixture was ground and pressed into a pill shape in a glove box filled with Ar. It was then placed in gold capsules 30 mm³ in volume and pressed up to 5 GPa with a cubic-anvil-type high-pressure apparatus. The temperature was raised up to 1000°C in 7 min, held constant for 1 h, and finally dropped down to room temperature in a few

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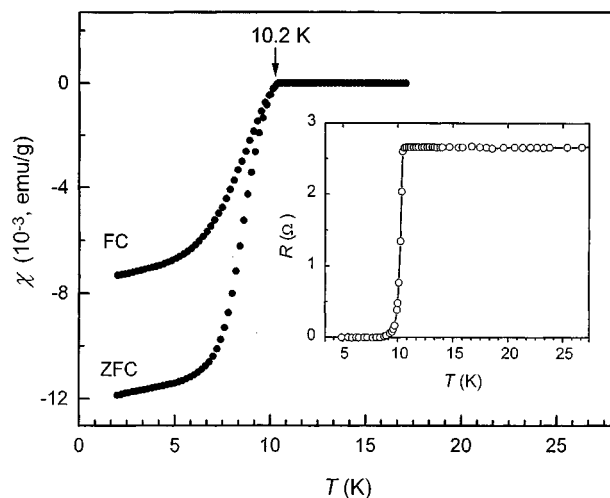


FIG. 1. Temperature dependence of the DC magnetic susceptibility, χ , and the electric resistance (inset), R , for $(\text{K}_{0.87}\text{Bi}_{0.13})\text{BiO}_3$. The ZFC curve was obtained in a magnetic field of 30 Oe after zero-field cooling, and the FC curve was obtained on cooling in the same field.

seconds. X-ray powder diffraction showed the resulting blue-black sample to be apparently single phase and cubic with $a = 4.2331(2) \text{ \AA}$ (throughout this paper numbers in parentheses denote the estimated standard deviation of the last significant digit). Superconducting properties of the sample were measured magnetically with a DC SQUID magnetometer and resistively using the conventional four-probe technique. The T_c onset was 10.2 K in both types of measurements (Fig. 1). The superconducting volume fraction corresponding to ca. 55% of the ideal diamagnet confirmed the bulk nature of its superconductivity.

Neutron diffraction data were measured at room temperature for ca. 70 h on the time-of-flight neutron powder diffraction Vega at the KENS pulsed neutron source. About 50 mg of the sample was charged in a V holder 2 mm in diameter, 11 mm in length, and 25 μm in thickness. Part of the holder was covered with Cd to avoid unnecessary scattering of neutrons.

The neutron diffraction data were analyzed by the Rietveld method with RIETAN-96T (11, 12). No reflections due to superstructure were observed, in agreement with electron diffraction patterns (9). In addition to the reflections of the superconductor, weak reflections assigned to $\text{KOH} \cdot \text{H}_2\text{O}$ and Cd (shielding material) appeared in the diffraction pattern. These additional phases were included in the Rietveld refinement with only their scale factors and lattice parameters varied and their structure parameters fixed at those reported in Refs. (13) and (14). At the final stage of the refinement, partial profile relaxation was applied to four reflections in the large d region to improve fits between their observed and calculated profiles (12).

Our structural model was based on the cubic perovskite structure (space group $Pm\bar{3}m$, No. 221) with $1b$, $1a$, and $3c$

TABLE 1
Crystallographic Data of $(\text{K}_{0.87}\text{Bi}_{0.13})\text{BiO}_3^a$

Atom Site	x	y	z	$B (\text{\AA}^2)$	g	U_{11}^b	U_{22}^b	U_{33}^b
K	$1b$	1/2	1/2	1/2	3.91(8)	0.87(1)		
Bi1	$1b$	1/2	1/2	1/2	$= B(\text{K})$	$1 - g(\text{K})$		
Bi2	$1a$	0	0	0	0.91(2)	1		
O	$3c$	1/2	0	0	2.99 ^c	1	1.18(6)	5.10(5) = U_{22}

^a Space group $Pm\bar{3}m$ (No. 221); $a = 4.23377(3) \text{ \AA}$; $Z = 1$; $R_{wp} = 6.04\%$, $R_p = 4.66\%$, $R_B = 4.62\%$, and $R_F = 3.11\%$.

^b U_{ii} 's ($i = 1-3$) are anisotropic atomic displacement parameters (10^{-2} \AA^2) when the displacement factor is represented as $\exp[-2\pi^2(h^2 U_{11} + k^2 U_{22} + l^2 U_{33})/a^2]$.

^c Equivalent isotropic atomic displacement parameter, B_{eq} .

sites fully occupied by (K, Bi), Bi, and O, respectively. All the fractional coordinates were fixed according to the symmetries of these sites. Only occupation factors, g , and atomic displacement parameters, isotropic ones B for the metal sites and anisotropic ones U_{ii} for the O site, were allowed to vary. Because the refined value of $g(\text{O})$ was very close to unity, i.e., 1.01(1), it was fixed at 1 in the final refinement. The occupancies of K and Bi1 at the $1b$ site were refined under a linear constraint of $g(\text{K}) + g(\text{Bi1}) = 1$. Table 1 lists the results of the Rietveld refinement, and Fig. 2 gives observed, calculated, and difference patterns, where background intensities were subtracted.

Our structure refinement gave unambiguous evidence for full occupation of the oxygen site in accordance with the synthetic conditions, viz., a closed system at very high pressure in the presence of the oxidizing agent KO_2 . The $g(\text{K})$ value of 0.87(1) corresponds to a chemical composition $(\text{K}_{0.87}\text{Bi}_{0.13})\text{BiO}_3$. The K:Bi ratio of 0.87:0.13 shows the K content to be lower than that in the starting mixture. This finding is consistent with inclusion of $\text{KOH} \cdot \text{H}_2\text{O}$ (ca. 2 mass%), which may be caused by the low purity of KO_2 .

In the average structure analyzed in this study, each A site metal is surrounded by 12 oxygen atoms to form a regular cuboctahedron with a metal–oxygen distance of 2.994 \AA . Such coordination behavior is unusual for the Bi^{3+} cation, which has a $6s^2$ lone electron pair and prefers structures other than the perovskite. Only one compound, BiFeO_3 , exists as a stable phase at ambient pressure (15). On the other hand, several magnetic perovskites (BiMnO_3 , BiCrO_3 , BiNiO_3 , and BiCoO_3) have been obtained under high pressure, which reduces the polarization energy of cations with ns^2 electronic configurations and favors tightly packed structures (16).

BiO_6 octahedra in the present compound are regular with a Bi–O distance of 2.117 \AA . This forms a striking contrast to semiconducting BaBiO_3 , where disproportionation of Bi into Bi^{3+} and Bi^{5+} manifests itself by the presence of two distinct octahedral sites for Bi (17). The oxidation state of

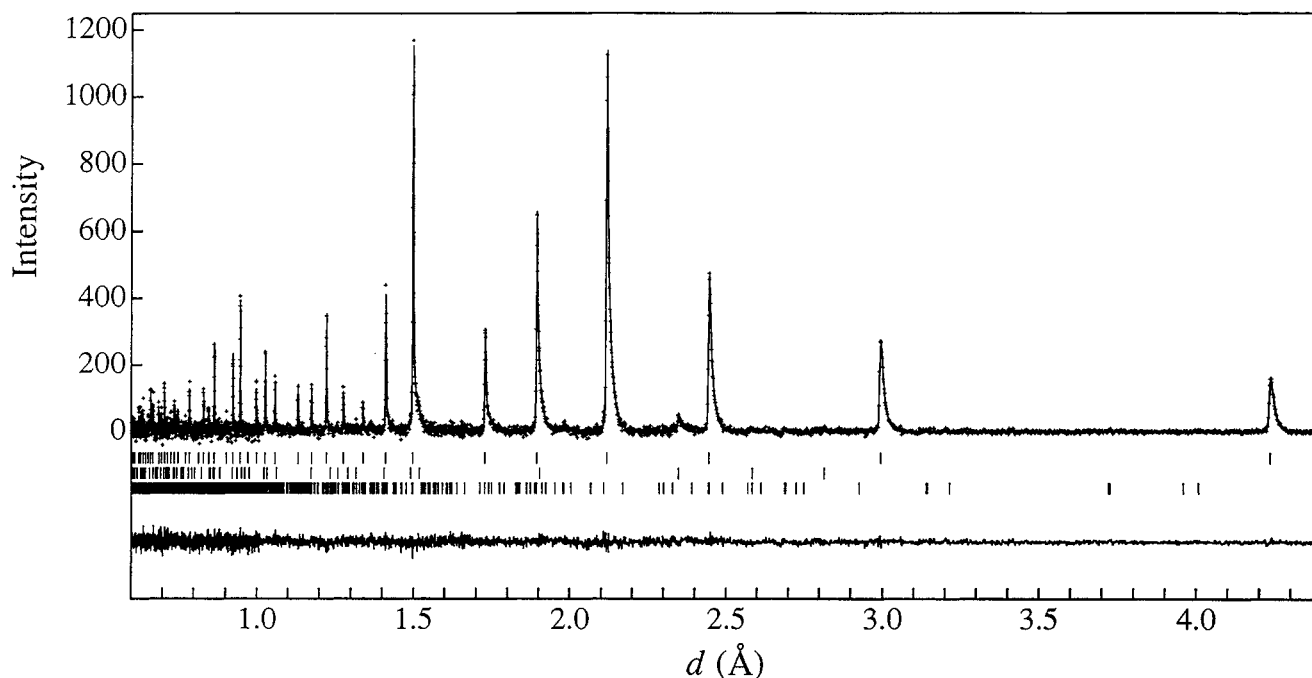


FIG. 2. Rietveld refinement profiles for $(K_{0.87}Bi_{0.13})BiO_3$. Plus marks (+) are observed neutron diffraction data, and the solid line is the calculated pattern. Tick marks below the profile mark the peak positions of allowed Bragg reflections for $(K_{0.87}Bi_{0.13})BiO_3$ (top), Cd (middle), and $KOH \cdot H_2O$ (bottom).

Bi2 estimated from the composition $(K_{0.87}Bi_{0.13})BiO_3$ is +4.74 if the oxidation state of Bi1 is assumed to be +3. Mattheiss *et al.* (2) proposed that to achieve a higher T_c in this system the conduction band should be close to a half-filled state, i.e., Bi^{4+} , where electron-phonon interaction is a maximum. The doping level in the present oxide is far from this condition in view of the oxidation state of Bi2, which may be a reason for the low T_c . So far, the highest band-filling level in a metallic phase has been realized in $(Ba_{0.6}K_{0.4})BiO_3$ with the highest T_c of 30 K (3).

The $(K_{1-x}Bi_x)BiO_3$ system resembles two other superconducting perovskites: $Ba(Pb_{1-x}Bi_x)O_3$ (1) and $(Ba_{1-x}K_x)BiO_3$ (3). As in $Ba(Pb_{1-x}Bi_x)O_3$, substitutional doping in the present oxide provides electrons to the σ^* conduction band, which is empty for $x = 0$. On the other hand, in both $(K_{1-x}Bi_x)BiO_3$ and $(Ba_{1-x}K_x)BiO_3$, the filling of the conduction band is varied by substitutional doping at the electronically inactive A site, while the conducting Bi-O network remains intact. Both systems have cubic perovskite-type structure in the superconducting state, but differ from each other in that atomic displacement parameters in $(K_{1-x}Bi_x)BiO_3$ are much larger than those in $(Ba_{1-x}K_x)BiO_3$ (18).

$B(K)$ and $B(Bi1)$ are as large as 3.91 \AA^2 , whereas $B(Bi2)$ is normal: 0.91 \AA^2 . The refined $U_{ii}(O)$ parameters revealed apparent anisotropy in thermal motion of oxygen with the largest displacement perpendicular to the Bi2-O-Bi2

bonds. The extraordinarily large displacement parameters for the A and O sites are believed to reflect the positional disorder of the (K, Bi) and O atoms, which is mainly ascribed to substitution of smaller Bi^{3+} for larger K^+ : the ionic radius $r = 1.17 \text{ \AA}$ for Bi^{3+} and $r = 1.51 \text{ \AA}$ for K^+ with both cations in 8-fold coordination (no ionic radius was given for Bi^{3+} in 12-fold coordination) (19). Such static disorder arising from the large mismatch between two kinds of A site cations is very common in perovskite-type oxides. In $(K_{1-x}Bi_x)BiO_3$, the displacements from the ideal positions seem to be also enhanced by the special electronic configuration of the Bi^{3+} ion. The $6s^2$ lone electron pair of Bi^{3+} is *stereochemically active* in that these electrons are not in a spherically symmetrical orbital but stick out to one side of cation (probably in some kind of $s-p$ hybridized orbital). This fact, coupled with the small ionic radius of Bi^{3+} , implies that each Bi^{3+} ion at the A site is locally coordinated to fewer than 12 oxide ions.

If the steric effect inherent in Bi^{3+} were remarkable in comparison with the effect of the size misfit, T_c would be raised by doping La^{3+} instead of Bi^{3+} , since these two cations are of comparable ionic radii (19). Moreover, La^{3+} is similar to Ba^{2+} in electropositive character, which favors the formation of superconducting oxides. Solid solutions, $(K_{1-x}La_x)BiO_3$ ($x = 0.1, 0.2, \text{ and } 0.3$), were prepared at a lower temperature of 900°C with a synthetic procedure similar to that used for $(K_{1-x}Bi_x)BiO_3$. A T_c of ca. 12 K and

a superconducting volume fraction of ca. 21% were observed in the best sample with $x = 0.2$. The slight rise in T_c suggests that the positional disorder due to the size misfit may be one reason for the T_c lower than that of $(\text{Ba}_{0.6}\text{K}_{0.4})\text{BiO}_3$, where the K^+ ion is an optimal dopant because of the ionic radius of K^+ ($r = 1.64 \text{ \AA}$) comparable to that of Ba^{2+} ($r = 1.61 \text{ \AA}$) (19) and a smaller difference in valence between these cations. Though superconducting properties in the bismuth oxides are more or less influenced by other factors, including the filling of the σ^* band described above, we believe that the local distortions, even without lowering the average crystal symmetry, affect the state of the conduction band and suppress T_c 's in $(\text{K}_{1-x}\text{Bi}_x)\text{BiO}_3$ and $(\text{K}_{1-x}\text{La}_x)\text{BiO}_3$.

The present study confirmed partial substitution of Bi^{3+} ions for K^+ ions in the $(\text{K}_{1-x}\text{Bi}_x)\text{BiO}_3$ system, which introduces electrons to the σ^* conduction band and gives rise to the superconductivity in this system. Oxygen deficiencies, which might also contribute to the superconductivity, were not detected. A further study where the physical and structural properties of the $(\text{K}_{1-x}\text{Bi}_x)\text{BiO}_3$ system are compared with those of other superconductors based on bismuth oxides would help to understand the role of phonon and electronic interactions in the microscopic pairing mechanism of this series of superconductors.

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