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Structure Determination of a New Perovskite Phase in the Ba–K–Bi–Na–O System

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During the synthesis by electrodeposition of $Ba_{1-x}K_xBiO_3$ superconducting crystals, black crystals of a new phase were grown at the anode. Chemical analysis (WDS) revealed the presence of sodium in these crystals. The chemical formula, $Ba_{3.12}K_{0.66}Bi_{3.37}Na_{0.63}O_{12}$, and the structure have been determined from single crystal X-ray diffraction. The structure is perovskite-like with a = 8.54 Å = $2a_p$, a_p being the lattice parameter of the perovskite cell. The doubling is due to a $1(B'):3(B)$ ordering on the octahedral sites. The B sites are occupied by Bi^{5+} cations whereas the B' sites are occupied by a mixture of Na and Bi cations. The latter should be disproportionated into Bi^{3+} and Bi^{5+}. No sign of diamagnetism has been detected in these crystals at low temperature. © 1991 Academic Press, Inc.

Introduction

Before the discovery of high T_c superconductivity by Bednorz and Müller in 1986 (*1*), $BaPb_{1-x}Bi_xO_3$ had the highest superconducting transition temperature among oxides ($T_c \approx 13$ K for $x \approx 0.25$) (*2*). The transport properties of this system change from metallic for $x < 0.3$ to semiconducting for $x \geq 0.3$. Over the entire range of composition the structure of these compounds is closely related to that of the perovskite (ABO_3). The Pb and Bi cations are disordered over the octahedral sites and the formal average valence of Bi cations is 4+.

In 1988, Mattheiss *et al.* (*3*), in analogy to $(La,Ba)_2CuO_4$, tried to dope the "A" site in $BaBiO_3$. They observed traces of superconductivity in multiphase samples of $(Ba,M)BiO_x$ (M = K,Rb) with magnetically determined onsets at 22 and 15 K, respectively. Monophasic powders of $Ba_{1-x}K_xBiO_3$ were obtained successively by Cava *et al.* (*4*) and Hinks *et al.* (*5*). These two groups used different, rather complicated synthesis techniques. The highest T_c for the A-doped $BaBiO_3$ is near 30 K ($x \approx 0.4$), more than twice that found for $BaPb_{1-x}Bi_xO_3$. A detailed structural phase diagram as a function of temperature and K content has been determined by Pei *et al.* (*6*) from powder neutron diffraction studies. At room temperature the structure of $Ba_{1-x}K_xBiO_3$ is monoclinic for $0 \leq x \leq 0.1$, orthorhombic for $0.1 \leq x < 0.35$, and cubic for $0.35 \leq x \leq 0.5$. It seems that the superconducting state

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is restricted to the cubic domain. As a function of x the average Bi formal valence changes from 4 for $x = 0$ to 4.45 for $x = 0.5$.

Several groups have tried to grow crystals, using flux methods (*7–9*) or, more recently, electrodeposition (*10*). X-ray characterization of the crystals obtained by the latter method indicated the presence of at least two perovskite phases having close cell parameters (4.29 and 4.27 Å).

Although the superconducting transition temperature of $Ba_{1-x}K_xBiO_3$ is lower than that of most of the superconducting copper oxides, this system is very interesting because the structure is cubic and consequently has no two-dimensional character.

As it is difficult to synthesize reproducibly powders with well-defined potassium stoichiometries we have prepared single crystals by electrodeposition following the procedure described by Norton (*10*). We obtained crystals of different colors (purple, blue, and black) which have been characterized by X-ray diffraction. One (black) of these crystals was found to be a new compound and we have undertaken the determination of the chemical formula and of its structure which are reported herein.

Experimental

1. Preparation

Single crystals were grown by electrolytic oxidation of a molten mixture of KOH, $Ba(OH)_2$, $8H_2O$, and Bi_2O_3 in the molar ratio 70 : 1 : 1. The starting materials were melted in a platinum crucible at 210°C using a vertical furnace. A current of 5 mA was maintained through the melt for about 6 hr by means of two platinum electrodes. The samples grown on the anode usually consisted of intergrown single crystals. Their color varied from purple to blue to black and their habit was cubic of maximum $0.5 \times 0.5 \times 0.5$ mm^3 size.

2. Preliminary X-Ray Characterization

The lattice parameters of the different crystals were determined from Gandolfi or Guinier diffraction patterns (λ Fe$K\alpha$ = 1.9373 Å). Single crystals were used with the Gandolfi camera while crushed crystals were used in the Guinier camera. In the case of the blue crystals the lattice parameters were in agreement with those given by Pei *et al.* (*6*) for $Ba_{0.6}K_{0.4}BiO_3$ ($a \approx 4.277$ Å). On the contrary, in the case of the black and the purple crystals, all reflections could be indexed on a cubic cell with $a \approx 2a_p = 8.54$ Å, where a_p is the parameter of the basic perovskite cell. Single crystal diffraction patterns obtained with a precession camera (λ Mo$K\alpha$ = 0.7107 Å) confirmed that the cell was body-centered cubic (extinctions for $h + k + l = 2n + 1$).

Among perovskite structures a doubling of the cell parameter a_p has already been observed, due to a 1–3 order over the A or B cation sites. For example in $(CaCu_3)Mn_4O_{12}$ (*11*) the order occurs over the A sites whereas in $Ba_4(LiBi_3)O_{12}$ (*12*) the order occurs over the B sites. The space group is $Im3$ in the former case, and $Im3m$ in the latter. Because of the high value of the absorption coefficient for the black crystal and the nonspherical shape of the samples, we were unable to determine from the examination of precession photographs whether or not hkl and khl reflections were equivalent, so that it remained undetermined at this point whether the space group was $Im3$ or $Im3m$.

3. X-Ray Data Collection

A black cubic-shaped crystal was selected and mounted on a Nonius CAD4 diffractometer. The wavelength was λ Ag$K\alpha$ (0.5608 Å) produced by a rotating anode. All reflections (7406) belonging to the reciprocal space between $\theta = 2°$ and $\theta = 30°$ and such that $h + k + l = 2n$ were collected by

TABLE I

Atomic Percentages of the Elements Present in the Crystal Used for Structure Determination (from WDS)

Element:	Ba	K	Bi	Na	O
Atomic %:	17.5(4)	3.4(1)	17.2(7)	3.5(2)	58.1(9)

ω-scans. Ten reflections (with CHI angles close to 90°) were also measured in ϕ-scan mode in order to apply an absorption correction. The lattice parameter of this crystal determined from a Gandolfi diffraction film was $a = 8.552(1)$ Å. Corrections for the Lorentz and polarization effects were applied along with the absorption correction using the SDP programs. The reflections were averaged in the *m*3 Laüe symmetry.

4. *Chemical Analysis*

Several black crystals (including the one used for intensity data collection) were studied by Energy Dispersive Spectroscopy (Kevex) and Wavelength Dispersive Spectroscopy (Cameca). The surface of the crystals had not been prepared for the chemical analysis because the crystals were too small.

Very surprisingly, the analysis revealed that there was as much *sodium* as potassium in our crystals. Likely the sodium was an "impurity" in the KOH which we used. An analysis of the starting KOH using atomic absorption spectroscopy indicated that 0.4 to 0.5% Na was present. The atomic percentages obtained for the crystal used for data collection are reported in Table I. They led to the chemical formula

$$Ba_{3.37(8)}K_{0.65(2)}Bi_{3.31(13)}Na_{0.67(4)}O_{11.2(2)}.$$

It should be noted that no trace of sodium was detected in the blue crystals belonging to the cubic perovskite phase $Ba_{1-x}K_xBiO_3$ ($x \approx 0.4$).

Structure Refinement

The refinements were carried out by the MXD program (*13*). The *Im*3 space group was used at the beginning. By taking into account the ionic radii of the different cations present in the crystal, Ba and K were positioned on the *A* sites (twelve-coordinated) whereas Bi and Na were located on the B sites (six-coordinated). We first tried the *A*-site ordering model, but it led to an unreasonable solution (negative temperature factors, etc.). The atomic positions used in the second model (with a 1–3 order on the *B* sites) are reported in Table II. The Ba and K cations were located on the same *A* site (8*c* positions). During the first cycles of the refinement, we did not take into account the presence of sodium and we positioned the Bi cations on the two different octahedral sites (2*a* position = *B'* site and 6*b* position = *B* site). We refined the scale factor, the position of the oxygen atoms, the anisotropic temperature factors for all atoms together with the percentage of barium and potassium on the *A* site. We noticed first that the *x* coordinate of the oxygen O2 (site 12*e*) was equal to $\frac{1}{4}$. This is the only coordinate which differentiates *m*3*m* from *m*3. It is therefore possible to describe the structure in the *Im*3*m* space group. The reflections were then averaged in the *m*3*m* Laüe symmetry and the atoms were positioned as reported in Table III. We noticed also that the values of the temperature factors of the Bi cations on the 2*a* site were

TABLE II

Special Positions Occupied in Space Group *Im*3

Ba, K	8*c* (3)	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$
Bi, Na	2*a* (*m*3)	0,0,0
Bi	6*b* (*mmm*)	$0,\frac{1}{2},\frac{1}{2}$
O1	12*d* (*mm*)	$x,0,0$
O2	12*e* (*mm*)	$x,0,\frac{1}{2}$

TABLE III

SPECIAL POSITIONS OCCUPIED IN SPACE GROUP *Im3m*

Ba, K	8*c* (3*m*)	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$
Bi, Na	2*a* (*m*3*m*)	0,0,0
Bi	6*b* (4/*mmm*)	$0,\frac{1}{2},\frac{1}{2},$
O1	12*e* (4*mm*)	*x*,0,0
O2	12d (42*m*)	$\frac{1}{4},0,\frac{1}{2}$

TABLE V

SELECTED INTERATOMIC DISTANCES

Bi–O1	2.011(4)	×2
Bi–O2	2.138(4)	×4
Bi,Na–O1	2.265(4)	×6
Ba,K–O1	3.026(1)	×6
Ba,K–O2	3.024(1)	×6

abnormally large. Consequently, in the next cycles a mixture of Bi and Na was introduced on this site and the percentage of Na was refined as an additional variable. The final values of the parameters are reported in Table IV, together with the *R*-factors. The interatomic distances are listed in Table V.

The chemical formula deduced from the refinement is

$$(Ba_{3.04}K_{0.96})Bi_3(Bi_{0.37}Na_{0.63})O_{12}.$$

The proportions of Bi and Na cations are in good agreement with those determined from chemical analysis. On the other hand, the Ba/K ratio determined from the structural refinement is smaller than that obtained from chemical analysis. Different reasons can be invoked to explain these discrepancies. First of all the crystal surface had not been prepared suitably for chemical analysis. Consequently, the results from the chemical analysis have to be considered only qualitatively. Another possibility could be that the *A* site is not fully occupied. In order to test this model the K percentage was fixed according to the chemical analysis and the Ba occupancy factor was refined. We found $p_{Ba} = 0.78$ (×4). Since $p_{Ba} + p_K = 0.78 + 0.16 < 1$. These results are in agreement with vacancies on the *A* site. The R-factors did not change significantly. The formula became

$$(Ba_{3.12}K_{0.66})Bi_3(Bi_{0.37}Na_{0.63})O_{12},$$

which is closer to that deduced from chemical analysis than the one obtained previously. It should be pointed out that it is not unusual in perovskite compounds to find vacancies on the *A* site. However, one cannot favor one formula or the other.

TABLE IV

POSITIONAL, THERMAL, AND OCCUPANCY PARAMETERS

O1	*x*	0.2648(4)
Na,Bi	*U*11 = 22 = 33	0.0039(3)
	p(Na)	0.631(3)
Ba,K	*U*11 = 22 = 33	0.0110(2)
	*U*12 = 13 = 23	0.00393(8)
	p(Ba)	0.760(4)
Bi	*U*11	0.00286(8)
	*U*22 = 33	0.00306(5)
O1	*U*11	0.006(1)
	*U*22 = 33	0.028(1)
O2	*U*11	0.004(1)
	*U*22 = 33	0.036(2)

Note: $R_w = 1.67\%$, $R_{uw} = 2.18\%$, $\chi^2 = 2.06$.

Discussion

The structure of $(Ba_{3.12}K_{0.66})Bi_3(Bi_{0.37}Na_{0.63})O_{12}$ is schematized in Fig. 1. The corner-sharing octahedral network comprises two types of octahedra in a 1 : 3 ratio, ordered as shown in Fig. 1. The first type is regular and occupied disorderly by a mixture of Bi and Na cations. The six Na(Bi)–O distances are equal to 2.265 Å. These octahedra are isolated from each other. The second type of octahedra is exclusively occupied by Bi cations. They share four corners

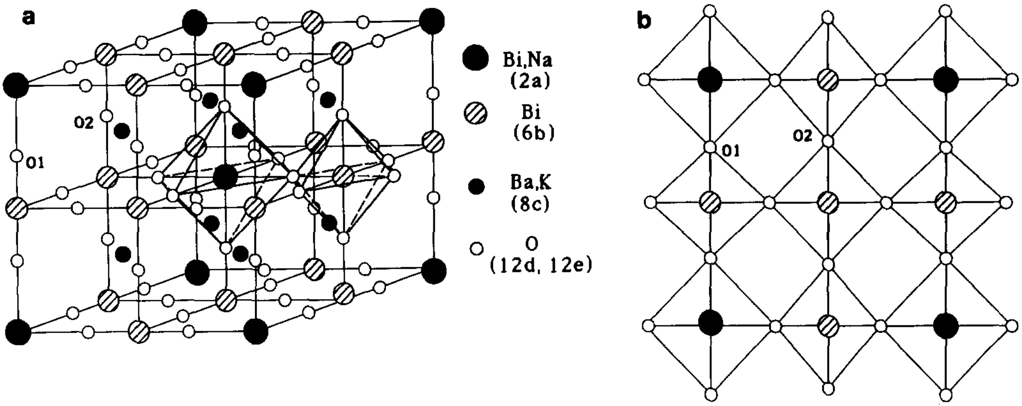

FIG. 1. (a) Schematic representation of the crystal structure of $(Ba_{3.12}K_{0.66})Bi_3(Bi_{0.37}Na_{0.63})O_{12}$ (b) $z = 0$ plane of the structure showing the arrangement of the octahedra.

with octahedra of the same type and two with octahedra of the first type. These two corners are opposite to each other. The Bi octahedra which are compressed along this direction form a tridimensional array. The Ba and K cations are disordered over the cuboctahedral sites.

From the Bi–O distances, using the Brown and Altermatt formula (*14*), we calculated the valence of the Bi cations located on the octahedral sites of the second type (*B*). We obtained $v_{Bi} = 4.96$, which indicates that these sites are occupied by Bi^{5+}. The same calculation cannot be applied to the *B'* site because it is only partially occupied by Bi cations. The average valence of the Bi cations on these sites as deduced from the chemical formula is equal to 4+. Since 4+ is not a stable valence for Bi cations, these cations are probably disproportionated into a mixture of Bi^{3+} and Bi^{5+}. The differentiation of the oxygen octahedra into two inequivalent sites is probably due to the rather large difference in average charge between the cations located on *B* and *B'* sites, respectively.

The a.c. susceptibility of several crystals including the one used for the structure determination was studied as a function of temperature. No sign of diamagnetism has been detected so far. This is not really surprising since the charges are localized (as Bi^{5+}) on the sites which form the 3-D arrangement. The other octahedral sites are isolated from each other and cannot therefore be considered as active sites for superconductivity. Studies are now in progress in order to retain the "double perovskite" structure and to cause charge delocalization on the *B* site at the same time.

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