$(Ba,K)_3Bi_2O_7$: A layered bismuth oxide

R. J. Cava, T. Siegrist, W. F. Peck, Jr., J. J. Krajewski, B. Batlogg, and J. Rosamilia

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

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The synthesis and crystal structure of a new perovskite-based bismuth oxide are reported. The phase, of composition $Ba_{1.7}K_{1.3}Bi_2O_7$, is the $n=2$ member of the Ruddlesden-Popper series $A_{n+1}B_n$-O_{3n+1}. It has tetragonal symmetry, space group $I4/mmm$, with unit-cell dimensions $a=4.2477(6)$ Å, and $c=21.885(3)$ Å. The phase is synthesized for the alkali metals K and Rb from KOH (RbOH) + $Ba(OH)_2 \cdot H_2O$ melts. The stoichiometry is apparently not easily varied. The phase is not superconducting down to 2 kelvin.

The $BaPbO_3$-$BaBiO_3$ family of superconductors, with T_c's ranging from 3.5 K ($BaPb_{0.75}Sb_{0.25}O_3$) to 30 K ($Ba_{0.6}K_{0.4}BiO_3$) is an interesting and controversial class of materials.[1-3] The controversy, over whether they are conventional electron-phonon-coupled superconductors, or whether there may be a nonconventional charge-fluctuation-based mechanism at work, is not likely to be easily resolved.[4-6] These materials are fundamentally different from the copper-oxide-based superconductors due to both the absence of magnetic interactions and the fact that their crystal structures are three dimensionally rather then two dimensionally connected. For the copper oxides, the most effective argument against a conventional superconducting mechanism has been their high T_c. For the $BaPbO_3$-$BaBiO_3$ family, there remains the possibility that layered materials could also have high T_c's. The number of known layered Pb- or Bi-based perovskitelike oxides is however very small compared to the number based on Cu. They are Ba_2PbO_4 (Ref. 7) and $Ba_4Pb_3O_{10}$,[8] neither of which has been made superconducting. Here we report the synthesis and structural characterization of the layered bismuth-based oxide $(Ba,K)_3Bi_2O_7$. Our efforts to make it superconducting have not been successful.

SYNTHESIS

We could not find conditions by which the new phase could be synthesized through conventional ceramic processing. Rather, an electrochemical synthesis technique, similar to that which can be employed to synthesize $(Ba,K)BiO_3$, was used.[9,10] Starting materials were "KOH" (which is at least 10% water by weight as received from the manufacturer), $Ba(OH)_2 \cdot 8H_2O$, and Bi_2O_3. The best, single-phase $(Ba,K)_3Bi_2O_7$ was obtained from a melt which consisted of 40 g KOH, 6 g $Ba(OH)_2 \cdot 8H_2O$, and 3 g Bi_2O_3. Significant departures from this mixture resulted either in the formation of the $(Ba,K)BiO_3$ perovskite or the lack of an electrochemical deposit. Melting was in either nickel or carbon crucibles (placed within larger nickel crucibles) which acted as the electrochemical cathode. A rotating gold electrode was employed as the anode. The melt was held at 320 °C and was most stable under N_2-, O_2-, or CO_2-free air, which was necessary to prevent the formation of carbonates.

A small but satisfactory deposit could be obtained un-der constant current conditions, at anodic current densities of 10–20 mA/cm². It is common to obtain a deposit which is a mixture of $(Ba,K)BiO_3$ and $(Ba,K)_3Bi_2O_7$. The composition of the perovskite which forms under these conditions is approximately $Ba_{0.5}K_{0.5}BiO_3$, which has a T_c of 15 K, making the detection of small amounts of extrinsic superconductivity for "$(Ba,K)_3Bi_2O_7$" samples a common occurrence. To obtain high-purity $(Ba,K)_3Bi_2O_7$, the melt was allowed to evaporate part of its water by holding at 320 °C for 30 min before applying the current. For 2–3 h deposition times, microcrystalline deposits were obtained, but for longer times (5–16 h) small single crystals, suitable in size for x-ray-diffraction measurements, were obtained. Crystals of $(Ba,K)_3Bi_2O_7$ are distinguished from the cubes of the perovskite $(Ba,K)BiO_3$ by being tabular, and often are intergrown with the perovskite.

CRYSTAL STRUCTURE

The crystal structure of $(Ba,K)_3Bi_2O_7$ was determined by single-crystal x-ray diffraction using an Enraf-Nonius CAD-4 diffractometer (graphite monochromated $Cu K\alpha$ radiation) controlled by the NRCCAD program. The unit cell determined from single-crystal x-ray diffraction is body-centered tetragonal, with lattice parameters $a=4.2477(6)$ and $c=21.885(6)$ Å. The crystallographic data collection parameters are presented in Table I. The measured intensities were corrected for absorption using a Gaussian integration absorption correction based on the platelike shape of the crystal.

The data refined smoothly in space-group $I4/mmm$ to the $A_3B_2O_7$ structure of the $n=2$ member of the Ruddlesden-Popper series $A_{n+1}B_nO_{3n+1}$.[11] Positional and thermal parameters, which were determined to high precision, are presented in Table II. The crystal structure is shown in Fig. 1. There are two kinds of large-atom sites, those within the perovskite blocks which are 12 coordinated to oxygen, labeled Ba(1) in Table II, and those between the perovskite blocks, which are 9 coordinated to oxygen, labeled Ba(2) in Table II. Refinement of the ratio of Ba to K on the two types of sites found that the 12-coordinate site contained only Ba, and the 9-coordinate site a mixture of Ba and K in the ratio 0.348:0.652, refined to a high precision. The overall composition is therefore $(Ba_{0.565}K_{0.435})_3Bi_2O_7$ or $Ba_{1.7}K_{1.3}Bi_2O_7$. In

TABLE I. Data collection parameters of $(Ba_{0.565}K_{0.435})_3$-Bi_2O_7. Estimated standard deviations are given in parentheses.

Space group	$I4/mmm$
a (23.2 °C)	4.2477(6) Å
c	21.885(3) Å
Volume	394.87(8) Å^3
Z	2
Calc. density	6.85 g/cm^3
Absorption coeff. μ	52.9 mm^{-1}
Crystal size	0.15×0.11×0.01 mm^3
Min. transmission	0.0290
Max. transmission	0.5031
Scan mode	ω-2θ
$2\theta_{max}$	100°
Measured reflections	4956
Unique reflections	669
Observed reflections $[I_{net} > 2.5\sigma(I)]$	669
Parameters	86
R_f (obs)	0.024
R_w (obs)	0.033
Extinction length	0.139(8) μm

terms of the large-atom coordinations, it is Ba^{XII} $(Ba_{0.35}K_{0.65})_2^{IX}Bi_2O_7$. Powder x-ray-diffraction data on more than 50 electrochemical preparations showed that there was virtually no variation of lattice parameter with changes in synthetic conditions, suggesting that the composition of the electrochemically deposited material was not variable. None of the single phase preparations were superconducting. The powder x-ray-diffraction pattern for $Ba_{1.7}K_{1.3}Bi_2O_7$ is presented in Fig. 2, indexed for $I4/mmm$ symmetry with $a = 4.25$ and $c = 21.9$ Å.

Interatomic distances are presented in Table III. The 12-coordinated Ba is in a very regular perovskite A-atom site with Ba-O distances near 3.0 Å. The Ba and K in the sites between the perovskite blocks are in the standard ninefold coordination, with the bond length to the capping oxygen [O(2), 2.59 Å] somewhat shorter than those of the waist oxygens [O(3), 3.00 Å] or those in the BiO_2 planes [O(2), 3.02 Å], as is generally found. The octahedral BiO_6 coordination is relatively regular. The bismuth-oxygen bond distances in the BiO_2 planes perpendicular to c are 2.14 Å and the shared oxygen between planes is 2.17 Å from the bismuth atoms above and below it. The one short Bi-O distance, 2.04 Å, is to the oxygen at the edges of the double BiO_6 layers, in the Ba(2)-O plane. There is no structural signature to suggest the kind of Bi(4) ± δ

TABLE II: Atom positions of $(Ba_{0.565}K_{0.435})_3Bi_2O_7$. Estimated standard deviations are given in parentheses. Occ represents occupancy.

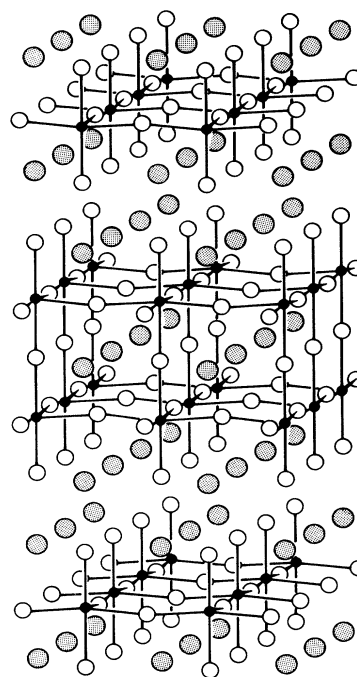| Atom	positions	x	y	z	B_{iso} [Å^2]	Occ
Ba(1)	2b	0	0	0.5	0.76(1)	
Ba(2)	4e	0	0	0.31077(5)	0.97(2)	0.348(6)
K	4e	0	0	0.31077(5)	0.97(2)	0.652(6)
Bi	4e	0	0	0.09934(2)	0.344(5)	
O(1)	2a	0	0	0	1.0(1)	
O(2)	8g	0	0.5	0.0914(3)	1.0(1)	
O(3)	4e	0	0	0.1923(3)	1.7(2)	

FIG. 1. The crystal structure of $Ba_{1.7}K_{1.3}Bi_2O_7$. Open circles: oxygen; closed circles: bismuth; larger-shaded circles: barium and potassium.
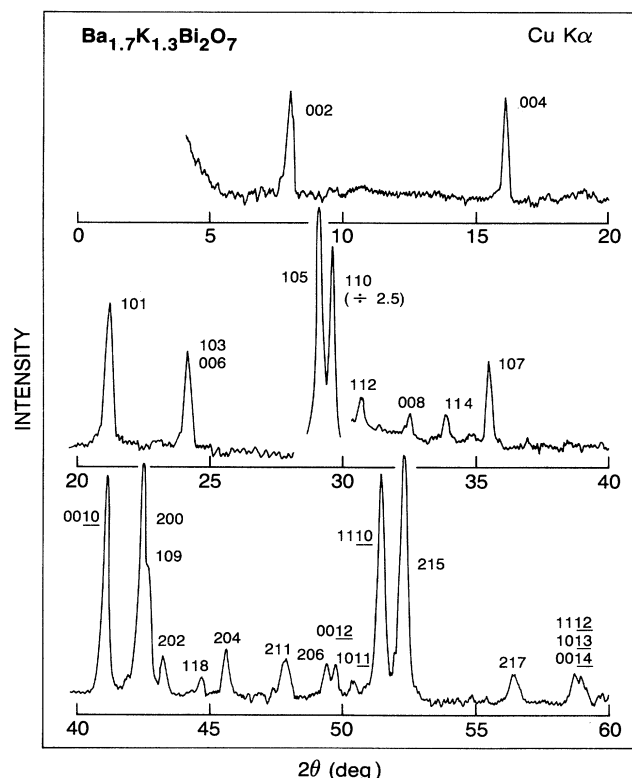

FIG. 2. Powder x-ray-diffraction pattern of $Ba_{1.7}K_{1.3}Bi_2O_7$, Cu $K\alpha$ radiation. The intensities of the two strongest peaks near $2\theta = 30°$ have been divided by 2.5 before plotting so that both strong and weak diffraction peaks would be visible.

TABLE III: Interatomic distances in $(Ba_{0.565}K_{0.435})_3Bi_2O_7$. Estimated standard deviations are given in parentheses.

Ba(1)	$\cdots$	O(1)	3.0036(4)	4×
	$\cdots$	O(2)	2.918(4)	8×
[Ba(2),K]	$\cdots$	O(2)	3.016(4)	4×
	$\cdots$	O(3)	2.592(8)	
	$\cdots$	O(3)	3.0043(5)	4×
Bi	$\cdots$	O(1)	2.1741(5)	
	$\cdots$	O(2)	2.1309(6)	4×
	$\cdots$	O(3)	2.035(8)	

charge disproportionation that is observed in $BaBiO_3$, where the highly charged Bi ($\sim Bi^{4.5+}$) has Bi-O distances of 2.13 ± 0.01 Å and the weakly charged Bi ($\sim Bi^{3.5+}$) has Bi-O distances of 2.26 ± 0.01 Å.[12] The short average Bi-O bond length in $Ba_{1.7}K_{1.3}Bi_2O_7$, 2.13 Å, is consistent with the relatively high charge on the Bi ($Bi^{4.65+}$) obtained by simple valence counting.

CONCLUSIONS

We have prepared single phase $(Ba,K)_3Bi_2O_7$ as powders and small single crystals by an electrochemical synthetic route. The phase was also observed to exist for $(Ba,Rb)_3Bi_2O_7$ prepared in the same manner, with $a \simeq 4.29$ Å and $c \simeq 22.0$ Å, but we did not refine the synthetic conditions sufficiently to prepare single phase materials. We could not find conditions under which the phase could be made for the alkali metals Li, Na, or Cs. With the discovery of $Ba_{1.7}K_{1.3}Bi_2O_7$, the $n = 1$, 2, 3, and ∞ members of the $A_{n+1}B_nO_{3n+1}$ series are now known for
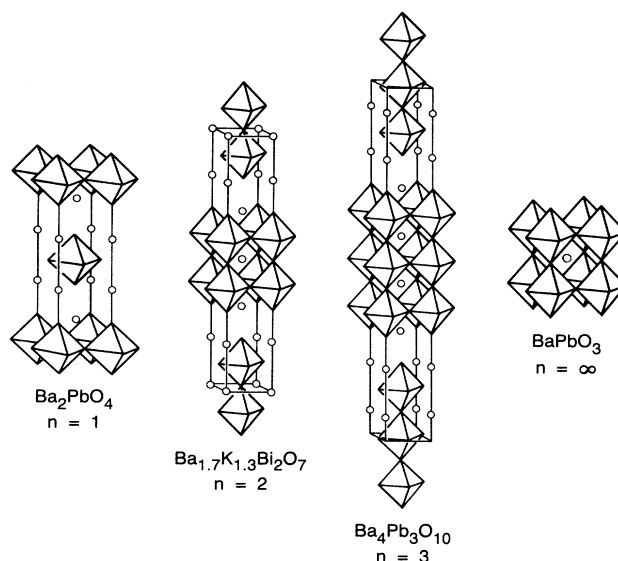

FIG. 3. The currently known members of the $A_{n+1}B_nO_{3n+1}$ series for lead and bismuth based oxides.

Pb(Bi)-based oxides (Fig. 3). Only the $n = \infty$ members, the perovskites, have been shown to be superconducting. This could be due to either intrinsic problems with the electronic structures of the layered materials, or to problems with attaining the appropriate band filling. Extreme caution must be exercised in investigating the physical properties of the layered materials as even small admixtures of the perovskite phases can give rise to the observation of spurious superconductivity.

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