



ELECTROCHEMICAL SYNTHESIS OF SINGLE-CRYSTAL (Ba_{0.05}K_{0.95})BiO₃·1/6H₂O WITH THE KSbO₃ STRUCTURE

D.-Y. Jung¹, P. Han², S.R. Wilson³, and D.A. Payne^{2*}

¹Department of Chemistry, SungKyunKwan University, Suwon 440–746, Korea

²Science and Technology Center for Superconductivity, Department of Materials Science and Engineering, Fredrick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Illinois 61801 USA

³School of Chemical Sciences, University of Illinois at Urbana-Champaign, Illinois 61801 USA

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ABSTRACT

A new compound with a cubic structure, (Ba_{0.05}K_{0.95})BiO₃·1/6H₂O (BKBO), was synthesized by electrochemical crystal growth using a rotating anode in molten KOH flux at 255°C. The BKBO crystal had the KSbO₃ structure and belonged to space group $Im\bar{3}$ (No. 204) with $Z = 12$. Refinement of X-ray diffraction data at room temperature gave $a = 10.0204(2)$ Å, $V = 1006.1(1)$ Å³, and $R = 2.4\%$ for 1465 unique reflections. Potassium, barium, and hydrated oxygen were found to occupy different sites in the tunnel structure. The electrical conductivity at room temperature was similar to the ionic conductor KBiO₃. BKBO decomposed to Bi₂O₃, K₂O, and BaO above 400°C.

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KEYWORDS: A. oxides, B. crystal growth, C. X-ray diffraction, D. crystal structure

INTRODUCTION

Mixed bismuth oxidation states have led to superconductivity in the perovskite structure for Ba(Pb,Bi)O₃ [1] and (Ba,K)BiO₃ [2]. For the (Ba_{1-x}K_x)BiO₃ crystalline solution series,

*To whom correspondence should be addressed.

superconductivity has been observed in the range $x = 0.30$ – 0.73 [3] with the highest T_c (38 K) at $x = 0.38$ [4–7]. This is the highest known transition temperature for an oxide that does not contain copper. In these bismuthates, the formal oxidation state of the bismuth ion is between III and V. Since Bi(IV) is postulated to disproportionate into Bi(III) and Bi(V) for BaBiO_3 , [8], it is important to synthesize and characterize compounds containing Bi(III) and Bi(V). Trivalent bismuth is the most stable oxidation state for bismuth in an oxygen-framework structure, and bismuth(V) has only been stabilized in sixfold coordination for a few compounds: BaLaMBiO_6 ($M = \text{Mg, Ca, Sr}$) with the perovskite structure [9], $(\text{Ba}_{1.7}\text{K}_{1.3})\text{Bi}_2\text{O}_7$ in a Ruddlesden-Popper series [10], $\text{Sr}_2\text{Bi}_2\text{O}_7$ of the weberite structure [1], alkali metal/alkaline earth metal bismuth oxides such as $\text{NaBa}_3\text{BiO}_6$ [12], and KBiO_3 with the KSbO_3 structure [13–18]. The oxidation state of Bi(V) is expected to be unstable and, therefore, difficult to stabilize in an oxide lattice without the use of applied oxygen pressure.

Norton [19] and other groups [20–23] have shown that crystals of $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ with superconducting properties can be grown by electrochemical methods [24–25]. Electrochemical synthesis is a low-temperature approach to the stabilization of compounds that are normally unstable at higher temperatures. The electrochemical potential is the driving force for the reduced-temperature synthesis. Unusual oxidation states of Bi can be obtained when reduced transition metals are used at the cathode and oxidized materials at the anode. In addition, experimental conditions (e.g., deposition temperature, electric potential, and concentration of reactants) play an important role on the synthesis products obtained (e.g., perovskite $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$; viz., the layered-structure $(\text{Ba}_{1-x}\text{K}_x)_3\text{Bi}_2\text{O}_7$).

The most homogeneous crystals grown to date have been obtained by top-seeded flux growth [5]. We have investigated the electrochemical synthesis of $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ with increasing values of x and determined their electric properties. However, the end member ($x = 1$) KBiO_3 , unlike ANbO_3 and ATaO_3 ($A = \text{alkaline metal}$) [26], did not have the perovskite structure, but had an open KSbO_3 cubic tunnel structure [27]. Several compounds with the KSbO_3 structure have been prepared and characterized for their properties [28,29].

In this paper we report the synthesis of a new compound in the BKBO system, which does not have the perovskite structure. The discovery originated from a systematic study of K incorporation into the perovskite structure at reduced temperatures by electrochemical synthesis. The intent was to study the effect of electronic structure and oxidation states (e.g., Bi(III) and Bi(V)) on superconducting properties, for both under-doped and over-doped compositions, and to extend the superconducting range to higher potassium contents than previously obtained. Data are reported for the single-crystal structure, thermogravimetric analysis (TGA), secondary ion mass spectrometry (SIMS), and electrical conductivity.

EXPERIMENTAL

Sample Preparation. Single crystals of BKBO were grown by an electrochemical method from KOH flux in a Teflon container. Top-seeded flux growth was used with a rotating anode in a three-electrode cell configuration [5]. The reactants, 1.5 g of Bi_2O_3 (Alfa, 99.999%), 1 g of BaO (Alfa, 99.99%), and 250 g KOH (Alfa, 99.999%), were placed in the Teflon container, which was positioned in a closed silica tube furnace equipped with flowing nitrogen (5 mL/min.). The nitrogen was saturated with water to prevent dehydration of the KOH flux. The reactants were equilibrated at 255°C for 1 h before crystal growth was started.

The electrodes in the electrochemical cell were bismuth-electroplated platinum wire (0.5 mm, 99.99%) i.e., for the anode, cathode, and reference electrodes. The working potential

between the anode and the cathode was 0.85 V. These conditions corresponded to when the current increased rapidly with increasing voltage. Current–voltage conditions were monitored by a potentiostat (EG&G Princeton Applied Research, Potentiostat/Galvanostat model 273A). After electrochemical crystal growth, the electrodes were removed from the cell, washed in deionized water to remove any residual flux, and then allowed to dry in air. BKBO was deposited at the anode as red, well-faceted crystals.

Crystallographic Analysis. Preliminary X-ray data were obtained for $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3$ crystals by a powder diffraction (Rigaku Geigerflex) method using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) monochromatized by graphite crystals. Analysis of the X-ray data indicated the KSbO_3 tunnel structure. The intensities of three representative reflections, measured over 60 min. of X-ray exposure time, remained constant, thus indicating the stability of the compound in air and in the X-ray beam. A small red crystal of $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3$, $0.05 \times 0.05 \times 0.05$ mm in size, was selected for further single crystal studies. X-ray data were obtained for BKBO on a X-ray diffractometer (Siemens SMART-CCD), using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) monochromatized by graphite crystals. Unit-cell parameters were calculated by a least-squares analysis of 1465 reflections and gave $a = 10.0204(2) \text{ \AA}$ and $V = 1006.1(1) \text{ \AA}^3$. The space group was determined to be $Im\bar{3}$ (No. 204), assuming an ideal cubic KSbO_3 structure for the BiO_3 framework. Data were collected, using the ω -scan method, to a maximum 2θ value of 57° . The data were corrected for Lorentz and polarization effects and secondary extinction. Data were corrected empirically for absorption. All calculations were performed through the use of Siemens crystallographic software [30]. The positions for barium, potassium, and bismuth were determined by direct methods. Refinement was carried out by a full-matrix least-squares refinement on F_o^2 calculations. The final values of the discrepancy factors were $R = 0.0242$ and $R_w = 0.0531$.

Physicochemical Characterization. Crystals were examined in a scanning electron microscope (Hitachi S800) equipped for energy-dispersive spectroscopy (EDS). The stoichiometric proportion of potassium, barium, and bismuth were determined for 30 representative crystals. The results gave an average composition of $(\text{K}_{0.95}\text{Ba}_{0.05})\text{Bi}_{1.00}$. The oxygen stoichiometry was determined by TGA. No impurities were detected by EDS.

Thermogravimetric data (TA Instruments, TGA 2950 system) were obtained at a heating rate of $1^\circ\text{C}/\text{min}$. Flowing oxygen was used to prevent the formation of any carbonate phase. Polycrystalline products were characterized by X-ray diffraction methods after TGA.

Electrical measurements were made using a Stanford SR350 lock-in amplifier at 15 Hz as a function of temperature. The temperature was controlled between 280 and 660 K, using a programmable controller (Eurotherm with S-type thermocouple). Crystal sections were cut in the (111) direction and electroded with sputtered gold. The specimen size was approximately $2 \times 2 \times 0.5$ mm.

RESULTS AND DISCUSSION

Synthesis. Figure 1 summarizes the reported [31] crystallographic data for $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ as a function of x . Superconductivity was determined for $0.3 \leq x \leq 0.72$, with the highest T_c at $x = 0.4$ [6]. Below $x = 0.72$, $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ had the perovskite structure with random occupancy of the 12-fold A sites by barium and potassium. The phase diagram (Fig. 1) gives the space groups as a function of temperature and K content. The end member ($x = 1$),

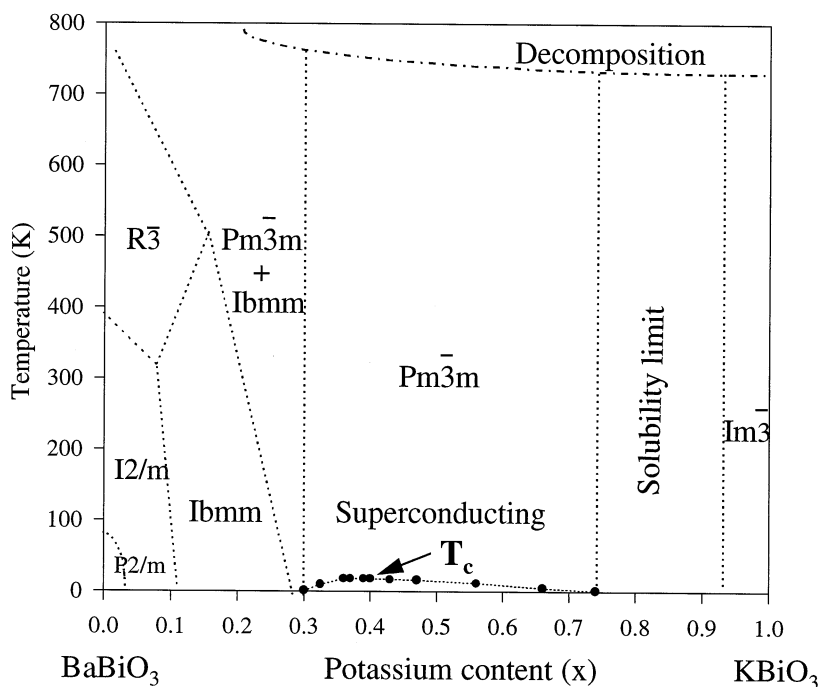


FIG. 1

Structures reported by neutron powder diffraction [31] and single crystal X-ray analysis in the $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ system. Superconducting transition temperatures of the perovskite phase are shown in the region $0.3 \leq x \leq 0.7$ for the perovskite structure [6].

KBiO₃ has the KSbO₃ structure. As far as we know, no phase has been reported for $0.72 < x < 1.0$. We obtained a new compound, $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$, with the KSbO₃ structure for $x \geq 0.95$, but were unable to synthesize single-phase material for $0.72 < x < 0.95$. Phase separation was attributed to a solubility limit, where $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ dissociated into both the perovskite and the KSbO₃ structures between $0.72 < x < 0.95$. The structures decomposed above ca. 400°C, especially for high potassium contents (Fig. 1).

In this study, new crystals of BKBO [$(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$] were grown by a rotating anode electrochemical method at constant potential. Seed rotation improved the chemical homogeneity of the crystals. Anodization gave high-oxidation states for bismuth at ambient pressure. Otherwise, Bi(V) could only be obtained by high oxygen applied pressures. In our method, red crystals of BKBO grew at the anode and could be isolated easily. The chemical substitution level for x was found to be experimentally dependent on the solute concentration in the flux, the electrochemical over-potential, the anode stirring rate, and the growth time. For example, Figure 2 gives a scanning electron photomicrograph of crystals grown in the range $0.72 < x < 0.95$. The red-colored crystals had the KSbO₃ structure, whereas the blue-colored crystals had the perovskite structure. Seed crystals were selected for further experimentation. Final BKBO crystals were grown on small red BKBO crystals deposited on electroplated platinum wire without sacrificial reduction of ZnCl_2 or CuCl_2 . The barium content (x) was determined as a function of depth by EDS, using ion-beam sputtering, and by SIMS.

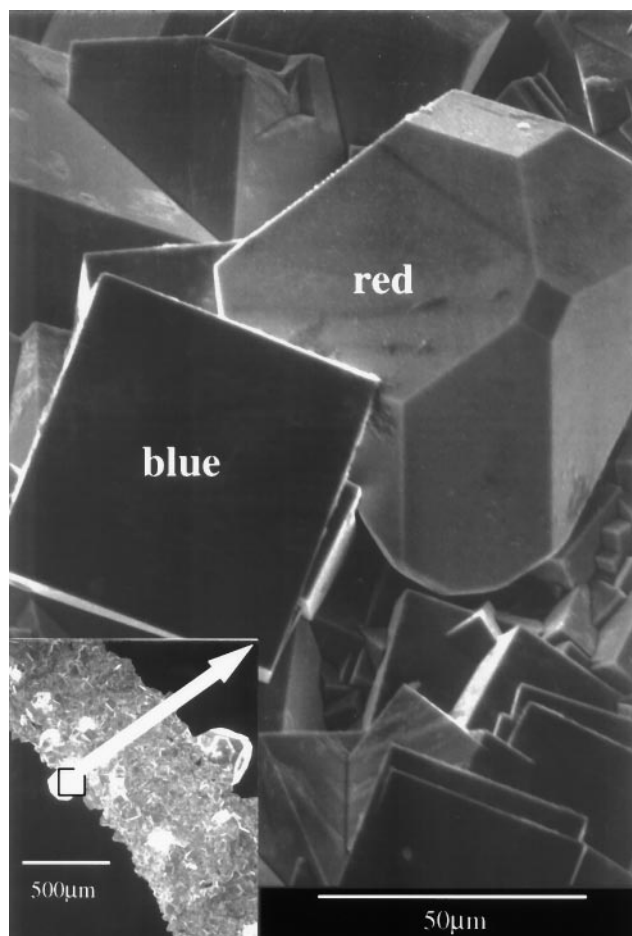


FIG. 2

Scanning electron photomicrograph of different BKBO crystals deposited at the anode.

Crystallography. After refining the parameters corresponding to Bi (12e), O1 (24g), and O2 (12d) and examining the Fourier transform electron density maps, the positions for Ba, K, and hydrated O3 were determined to be 8c ($1/4 \ 1/4 \ 1/4$), 16f ($x \ x \ x$), and 2a ($0 \ 0 \ 0$), respectively. $\text{KBiO}_3 \cdot y\text{H}_2\text{O}$ has been reported previously to have various degrees of hydration (y) and, therefore, correspondingly different cell parameters, depending upon the method of preparation [13–16]. Consequently, different potassium sites and waters of hydration have been reported in previous accounts [17,18].

Tables 1 and 2 list the crystallographic parameters determined in this study. The number in parentheses is the standard deviation for the last digit. Crystallographic data give a refined formula of $(\text{Ba}_{0.06}\text{K}_{0.94})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$, which is in acceptable agreement with the chemical analysis $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$ obtained by EDS. Anisotropic coefficients are summarized in Table 3, and selected inter-atomic distances and bond angles are given in Table 4. The BKBO structure, isostructural with KSbO_3 [29], contains pairs of BiO_6 octahedra that

TABLE 1
Crystallographic Data for BKBO at
Room Temperature

Chemical formula	(Ba _{0.05} K _{0.95})BiO ₃ ·1/6H ₂ O
Formula weight (g/mole)	303.99
Crystal system	Cubic
Space group	<i>Im</i> $\bar{3}$ (No. 204)
Lattice parameters (Å)	<i>a</i> = 10.0204(2)
Volume (Å ³)	<i>V</i> = 1006.1(1)
<i>Z</i>	12
λ (Å)	0.71073
<i>R</i> ^a	0.024
<i>R</i> _w ^b	0.053
Goodness of fit	1.207

$$^aR = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}}{1 + (0.0062P)^2 + 49.27P}, \text{ where } P = [\max(F_o^2, \phi) + 2(F_c^2)]/3.$$

share edges to form Bi₂O₁₀ dimers that share corners to form Bi–O linkages. The resulting tunnel structure is illustrated in Figure 3.

The Bi–Bi distance in BKBO is 3.208 Å (Table 4). Assuming a Bi₂O₆ dimer with two nondistorted octahedra and a Bi–O bond length of 2.118 Å, the calculated Bi–Bi distance would be 3.00 Å, which is smaller than the experimentally measured value of 3.208 Å. Figure 4 is a schematic for the proposed dimer, where the Bi–Bi distance is increased due to electrostatic repulsion. Table 4 indicates the Bi–O–Bi bond angles are 81.5° and 103.1°, suggesting the electrostatic repulsion of metal cations.

Potassium ions are located at 16f sites in the tunnel. Although the electron densities at sites 16f, 8c, and 2a were assigned differently in previous investigations, for differently prepared specimens of KBiO₃ (or KBiO₃(yH₂O) [17,18], the most probable refinement of our data is given in Table 2, based upon site occupancy. Tunnel oxygen (O3) was assigned to water, based upon excess electron density. SIMS measurements indicated comparable counts for

TABLE 2
The Final Refined Atomic Positions and Estimated Crystallographic Parameters for
BKBO at Room Temperature

Atom	Wyckoff	Coordinates			<i>U</i> _{eq}	% Occupancy
		<i>x</i>	<i>y</i>	<i>z</i>		
Ba	8c	0.2500	0.2500	0.2500	7(1)	8.84
K	16f	0.1574(4)	0.1574(4)	0.1574(4)	3.8(1)	70.64
Bi	12e	0.5000	0.16006(5)	0	0.89(3)	100
O1	24g	0.3384(8)	0.2884(8)	0	1.6(2)	100
O2	12d	0.362(1)	0	0	1.6(2)	100
O3 ^a	2a	0	0	0	3.0(7)	100

^aResults from hydrate water molecules.

TABLE 3
Anisotropic U_{ij} coefficients for **BKBO**

Atom	Position	U_1	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	8c	0.07(1)	0.07(1)	0.07(1)	0.05(1)	0.05(1)	0.05(1)
K	16f	0.038(1)	0.038(1)	0.038(1)	0.010(2)	0.010(2)	0.010(2)
Bi	12e	0.0098(3)	0.0079(3)	0.0088(3)	0	0	0
O1	24g	0.012(4)	0.010(4)	0.025(4)	0.003(3)	0	0
O2	12d	0.008(5)	0.013(5)	0.026(6)	0	0	0
O3	2a	0.030(8)	0.030(8)	0.030(8)	0	0	0

secondary hydrogen below 1000 Å. This hydrogen was attributed to crystalline water and could be detected up to 3000 Å in depth, where the experiment was terminated.

Previous investigators have obtained $\text{KBiO}_3 \cdot y\text{H}_2\text{O}$ from solution and oxidation of bismuth ion [13,14]. Goodenough et al. [28] reported NaF stabilized the NaSbO_3 structure. The present results for BKBO [$(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$] are consistent with those of previous reports. On the other hand, high-pressure synthesis [16] yields the formation of anhydrous KBiO_3 . Depending on whether the wet or dry method is chosen for preparation, KBiO_3 may or may not have water of hydration in the tunnel structure.

TGA. Figure 5 gives thermogravimetric data obtained for BKBO heated at 1°C/min. in flowing oxygen. The measured weight loss of 5.9% at 400°C is comparable to the theoretical value of 6.1% calculated from the proposed formula. X-ray diffraction indicated BKBO decomposed to K_2O , Bi_2O_3 , and BaO after heat treatment. The products were hygroscopic. Thermal decomposition of BKBO above 400°C is consistent with the need for reduced-temperature synthesis. This can be achieved in a closed system by high-pressure synthesis in oxygen or, in the present case, in an open system by electrochemical synthesis at 255°C [16].

Electrical Conductivity. Figure 6 gives the Arrhenius dependence of the low-frequency conductivity (σ) indicating two activated processes, with a transition temperature around 130°C. The calculated ($\sigma = \sigma_0 \exp(-\Delta E/kT)$) activation energies (ΔE) were 0.24 eV below 130°C and 0.35 eV above 130°C. These values are greater than the value reported for

TABLE 4
Selected Bond Distances (Å) and Angles (°)

Bond Distances			
Bi–O1	$2.068(8) \times 2$; $2.121(8) \times 2$	K–K	$3.153(8) \times 3$; $3.216(14)$
Bi–O2	$2.118(7) \times 2$	K–Ba	1.608(7)
K–O1	$2.739(7) \times 3$	K–Bi	3.778(2)
K–O2	$3.030(8) \times 3$	Ba–Bi	$3.656(1) \times 4$
K–O3	2.731(7)	Bi–Bi	3.208(1)
Ba–O1	$2.685(3) \times 6$		
Bond Angles			
O1–Bi–O1	103.1(4), 89.7(1), 179.2(9)		
O1–Bi–O2	87.7(3), 169.2(3)		
O2–Bi–O2	81.5(5)		

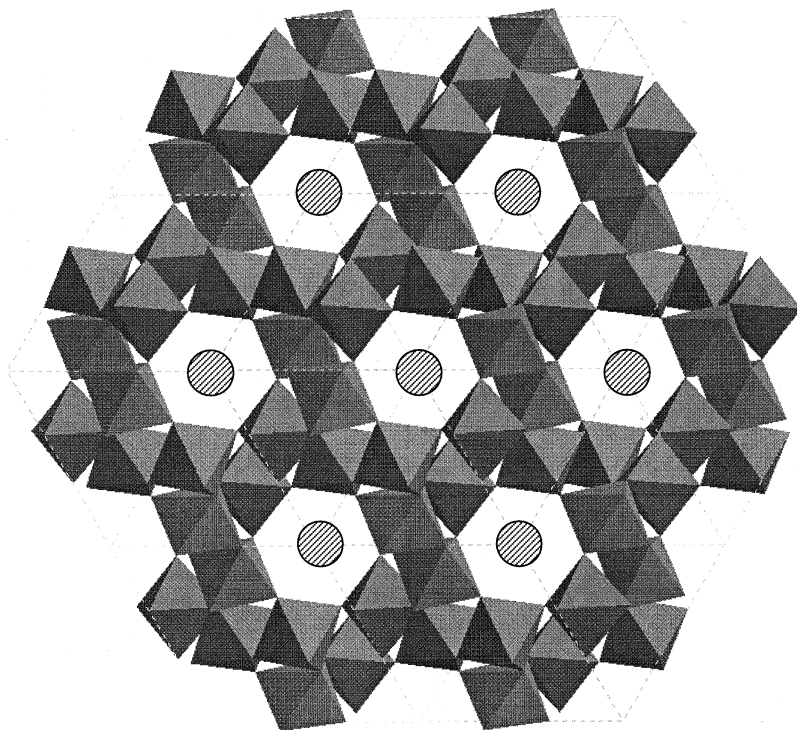


FIG. 3

Illustration of the proposed $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$ structure, indicating corner sharing of the Bi_2O_{10} clusters. The shaded circles represent potassium atoms located along the (111) direction.

potassium ion conductivity (0.16 eV) in anhydrous KBiO_3 [18]. The difference may be due to blocking effects of barium and water of hydration in the tunnel structure. The room temperature value of electrical conductivity for BKBO was 10^{-5}S/cm , which is comparable with that for KBiO_3 .

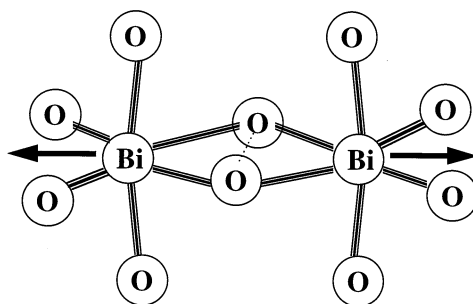


FIG. 4

Illustration of the octahedral dimer Bi_2O_{10} .

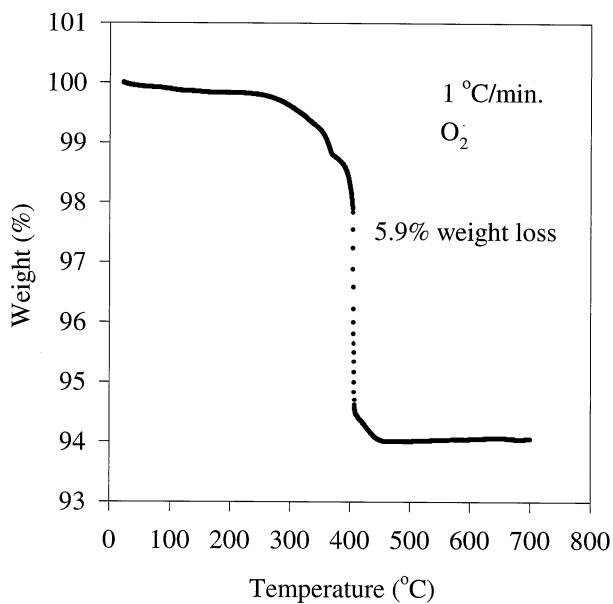


FIG. 5

TGA for $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$. The 5.9% weight loss at 500°C corresponds to the decomposition reaction to BaO, K₂O, Bi₂O₃, H₂O, and O₂.

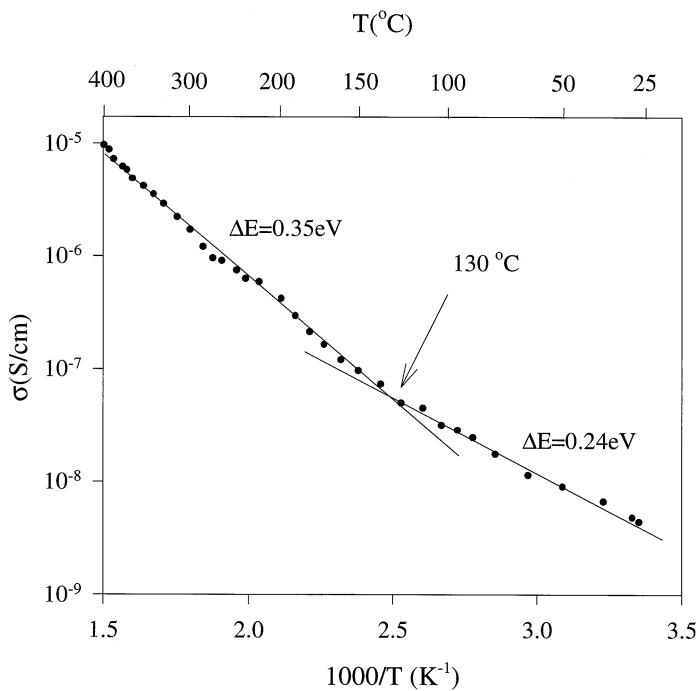


FIG. 6

Temperature dependence of the electrical conductivity for $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$.

CONCLUSION

Cubic crystals of hydrated BKBO, $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$, were grown by electrochemical synthesis from KOH flux at 255°C. The new compound had the KSbO_3 tunnel structure, not the perovskite structure of the lower potassium content containing crystalline solutions. Barium substitution for potassium was confirmed by XRD, EDS, and SIMS analyses. TGA determined that $(\text{Ba}_{0.05}\text{K}_{0.95})\text{BiO}_3 \cdot 1/6\text{H}_2\text{O}$ was thermally unstable above 400°C, with hydrate water release from the lattice. The products were hygroscopic. Refinement of atomic positions gave the best fit for the site occupancy of potassium, barium, and hydrated oxygen at different positions in the tunnel structure of KSbO_3 .

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