Electrosynthesis of $KBiO_3$: A Potassium Ion Conductor with the $KSbO_3$ Tunnel Structure

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Cubic, anhydrous $KBiO_3$ was synthesized by electrocrystallization from a KOH flux at 175 °C. $KBiO_3$ crystallizes in space group $Im\bar{3}$ (No. 204) with $Z = 12$. The room-temperature data were refined to $a = 10.0194(6)$ Å, $V = 1005.8(2)$ Å^3 and $R = 2.3\%$ for 576 unique reflections. The potassium ion partially occupies three sites in the tunnel structure and the activation energy for ionic conduction is 0.16 eV. The mobility of the potassium ion is low, however, presumably because of its role in stabilizing the Bi–O framework, resulting in an ionic conductivity of 10^{-5} S/cm at 300 °C. Thermogravimetric analysis shows that $KBiO_3$ is thermally unstable above 500 °C, decomposing into Bi_2O_3 and K_2O. The single-crystal structure, thermogravimetric data, and ionic conductivity of $KBiO_3$ are described.

Introduction

Low-temperature syntheses, especially flux syntheses, have been used successfully to prepare a large variety of interesting compounds with extended structures.[1-7] Often this low-temperature approach was motivated by the desire to avoid the thermodynamic limitations inherent in most high-temperature reactions and thereby to synthesize kinetic and metastable compounds. A modification of the flux technique involves the addition of an electrochemical potential as an active component for synthesis. Whereas flux synthesis relies on the creation of a temperature gradient and consequent changes in product solubility, electrocrystallization takes advantage of the solution properties of the flux and, in addition, employs a potential gradient to generate crystalline products at the electrodes. Highly oxidizing and reducing conditions can be created electrochemically in a single flux, leading to the preparation of materials containing elements in extreme oxidation states. Although there have been many reports of electrocrystallization reactions in the literature,[8-19] the use of this technique for the synthesis of oxides at very low temperatures has not been fully exhausted. Also, much of the work done previously has concentrated primarily on cathodic reactions and the synthesis of materials containing reduced early transition metals rather than on anodic reactions and the synthesis of oxidized materials.

Discussed in this paper is the low temperature, electrochemical synthesis of the highly oxidized phase $KBiO_3$. Unlike M^+NbO_3 and M^+TaO_3 (M = alkali metal),[20] $KBiO_3$ does not form the perovskite structure but rather forms a cubic tunnel structure first observed in $KSbO_3$.[21] Several compounds with the $KSbO_3$ skeleton structure have long been investigated for fast ion conductivity;[22,23] $KBiO_3$, although a member of this structural family, has not been tested for ionic transport.

Anhydrous $KBiO_3$ was first prepared by Jansen at 500–600 °C and 1000–2000 atm of oxygen pressure as a red powder and reported to be isostructural with $KSbO_3$.[24] There have been earlier reports[25,26] of the solution synthesis of $KBiO_3$ by the oxidation of bismuth nitrate in aqueous KOH or NaOH. The compound obtained from solution synthesis, $KBiO_3{\cdot}xH_2O$, contained waters of hydration, which apparently stabilized the structure and allowed formation under those conditions. This observation is consistent with Goodenough's finding that NaF stabilizes $NaSbO_3$,[22] which can be prepared as $NaSbO_3{\cdot}{}^1/_6NaF$ at

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atmospheric pressure. High-pressure synthesis, on the other hand, requires no stabilizing moiety and results in the formation of anhydrous $KBiO_3$.

In this paper we report the single-crystal electrochemical synthesis of anhydrous $KBiO_3$ at low temperature (175 °C) and atmospheric pressure. The single-crystal structure, thermogravimetric data, and ionic conductivity of $KBiO_3$ are described.

Experimental Section

Sample Preparation. Single crystals of $KBiO_3$ were grown electrochemically from a KOH flux in an alumina crucible. The reaction mixture consisted of 1 g of Bi_2O_3 (Cerac 99.9%), 2.5 g of $ZnCl_2$ (Cerac 99.5%), and 20 g of KOH (ACS grade). The filled crucible was placed into a closed Pyrex reaction vessel equipped with flowing, water-saturated air in order to prevent dehydration of the flux. The atmosphere was achieved by flowing air through a gas dispersion tube immersed in room temperature water. The reaction mixture was heated at 175 °C for 2 h, allowing the molten solution to equilibrate, before a potential was applied.

Synthesis was carried out by two-electrode constant-potential electrolysis. Zirconium wire (Aesar, 1.14-mm diameter, 99.2%) was used as the cathode and platinum wire (0.5 mm) or foil as the anode. The working potential for this reaction, 1.1 V, was determined to be the point at which the current increased sharply with changing potential on an i vs ν scan collected on a Pine Model AFRDE4 potentiostat. After electrolyzing overnight, the electrodes were removed and washed with water to remove any residual flux. $KBiO_3$ was deposited as red, well-faceted chunky crystals on the platinum anode and zinc metal was deposited on the zirconium cathode. Larger crystals can be grown by electrolyzing for up to 5 days.

$KBiO_3$ can be synthesized using $CuCl{\cdot}xH_2O$ as well as $ZnCl_2$. In this case, the working potential is 0.8 V and copper metal is deposited on the cathode. Attempts to make $KBiO_3$ using only KOH and Bi_2O_3 proved unsuccessful. The role of the metal deposited on the cathode, zinc or copper, is that of a sacrificial reductant, which balances the electron inventory of the redox processes. Under the reaction conditions described, a sacrificial reductant was found to be essential for product formation. Attempts to make the sodium and sodium/potassium analogs of $KBiO_3$ using NaOH and the NaOH/KOH eutectic, respectively, as well as ion-exchange experiments using molten $NaNO_3$ and $AgNO_3$ to make $NaBiO_3$ and $AgBiO_3$, respectively, from $KBiO_3$ were unsuccessful.

Physical Characterization. The crystals were analyzed by X-ray precession methods using a Charles Supper Co. precession camera mounted on an Enraf-Nonius 581 Diffractis X-ray generator. The diffraction patterns of the precession photos were consistent with a body-centered cubic structure. Energy-dispersive spectroscopy (EDS) was performed to confirm the presence of potassium and bismuth. Wavelength-dispersive spectroscopy (WDS) performed using a JEOL 781 microprobe on 20 representative crystals gave an average crystal composition of $K_{1.01(3)}Bi_{1.00(2)}O_{2.99(3)}$; the oxygen stoichiometry was determined by difference from WDS, as well as by thermogravimetric analysis. Copper and zinc impurities were not detected.

The ionic conductivity was measured by complex impedance spectroscopy using a Solartron 1260 frequency response analyzer. Crystals were crushed in an agate mortar and pelletized. Two stainless steel plungers (1.6-mm diameter), acting as blocking electrodes, compressed the sample inside an alumina tube. The stainless steel plungers were sandwiched by two platinum disks, which in turn were held in place by a spring-loaded alumina tube. The entire sample holder was contained inside a shielded nickel tube located inside a noninductively wound furnace. The furnace temperature was regulated using a programmable Eurotherm controller. Impedance measurements were performed at frequencies between 1 Hz and 5 MHz and temperatures ranging from 250 to 375 °C.

Thermogravimetric analysis was carried out using a CAHN-121 TGA system. Samples were heated at a rate of 5 °C/min in pure oxygen. Polycrystalline samples were structurally characterized by powder X-ray diffraction on a Rigaku RU300 diffractometer with Cu Kα radiation (λ = 1.5418 Å).

Table I. Crystallographic Data for $KBiO_3$ at 23 °C

chemical formula	$KBiO_3$
formula weight, g/mol	296.08
crystal color, habit	red, prismatic
crystal dimension, mm	0.06 × 0.04 × 0.05
crystal system	cubic
space group	$Im\bar{3}$ (No. 204)
lattice parameter, Å	a = 10.0194(6)
volume, Å^3	1005.8(2)
Z	12
D_{calc}, g/cm^3	5.865
radiation	λ = 0.7107 Å
μ (Mo Kα), cm^{-1}	534.8
secondary extinction	1.41×10^{-7}
octants	$+h+k+l$
R^a	0.023
$R_w{}^b$	0.021
GOF	1.10

[a] $R = \sum \||F_o| - |F_c\||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

Crystallographic Studies. A small, red, prismatic crystal of $KBiO_3$ with the approximate dimensions of 0.060 × 0.040 × 0.050 mm was used for the structure determination. Single-crystal diffraction studies of $KBiO_3$ were performed on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 69 Å). Unit-cell parameters were established by least-squares analysis of 25 reflections in the range $13.0 \leq 2\theta \leq 26.0°$, a = 10.0194(6) Å, V = 1005.8(2) Å^3. The space group was determined to be $Im\bar{3}$ (No. 204). Crystallographic data are summarized in Table I. Data were collected using the ω–2θ scan method to a maximum 2θ of 60.0°. A total of 1712 reflections were collected. The intensities of three representative reflections, measured after every 60 min of X-ray exposure time, remained constant throughout data collection indicating crystal and electronic stability. Data were corrected for Lorentz and polarization effects and secondary extinction. Initially data were corrected for absorption based on the azimuthal scans; an empirical correction was also applied.[27]

All calculations were carried out on a MicroVAX 3500 with the use of TEXSAN crystallographic software.[28] The position of the bismuth and potassium, K(1), were determined by direct methods.[29] The remaining potassium and oxygen positions were located from difference Fourier maps. Refinement was performed using a full-matrix least-squares calculation. The final values of the discrepancy factors were R = 0.023 and R_w = 0.021. The atomic scattering factors were those of Cromer and Waber,[30,31] and corrections for anomalous dispersion were from Cromer.

Results and Discussion

Anhydrous crystals of $KBiO_3$ were synthesized by two-electrode constant-potential electrolysis in molten KOH at 175 °C. This electrochemical approach generates a high oxygen activity at low temperature, making it possible to prepare highly oxidized species, such as Bi(V) oxides. Otherwise, such materials may be prepared only under highly oxidizing conditions, for example, at high oxygen pressures and elevated temperatures. Only relatively short electrolysis times are required and single crystals suitable for X-ray structure analysis can be obtained in times as

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Table II. Final Positional Parameters and Their Estimated Standard Deviations

atom	Wyckoff	x	y	z	B(eq)	percent site occupation	% total K
Bi1	12e	$^1/_2$	0	0.16004(6)	0.10(3)	100	
K1	16f	0.1571(5)	0.1571	0.1571	2.202(2)	60(1)	80(2)
K2	8c	$^1/_4$	$^1/_4$	$^1/_4$	2.258(7)	22(1)	14.4(8)
K3	2a	0	0	0	2.223(8)	34(2)	5.6(4)
O1	24g	0.3387(8)	0	0.2874(9)	0.7(2)	100	
O2	12d	0.363(1)	0	0	0.6(2)	100	

Table III. Anisotropic U_{ij} Coefficients for $KBiO_3$

atom	position	$u_{11}(U)^a$	u_{22}	u_{33}	$u_{12}{}^b$	u_{13}	u_{23}
Bi	12e	0.0031(3)	0.0019(3)	0.0007(3)	0	0	0
K(1)	16f	0.02601(2)	0.02601	0.02601	0.008(2)	0.008	0.008
K(2)	8c	0.0270(1)	0.0270	0.0270	0.033(9)	0.033	0.033
K(3)	2a	0.0270(1)					
O(1)	12d	0.012(4)					
O(2)	24g	0.004(6)					

^{a} $u_{11} = u_{22} = u_{33}$ for positions (f) and (c). ^{b} $u_{12} = u_{13} = u_{23}$ for positions (f) and (c). $u_{13} = u_{13} = u_{23} = 0$ for position (e).

Table IV

	(A) Selected Distances (Å)		
Bi–Bi	3.207(1)	Bi–O(2)	2.108(7)
Bi–K(1)	3.777(2)	K(1)–O(2)	3.039(8)
Bi–K(2)	3.6553(3)	K(1)–O(1)	2.735(7)
Bi–O(1)	2.136(9)	K(2)–O(1)	2.685(3)
Bi–O(1)	2.053(9)		
	(B) Selected Distances between Potassium Positions		
K(1)–K(1)	3.156(9)	K(1)–K(3)	2.733(8)
K(1)–K(2)	4.288(2)	K(2)–K(3)	4.3385(3)

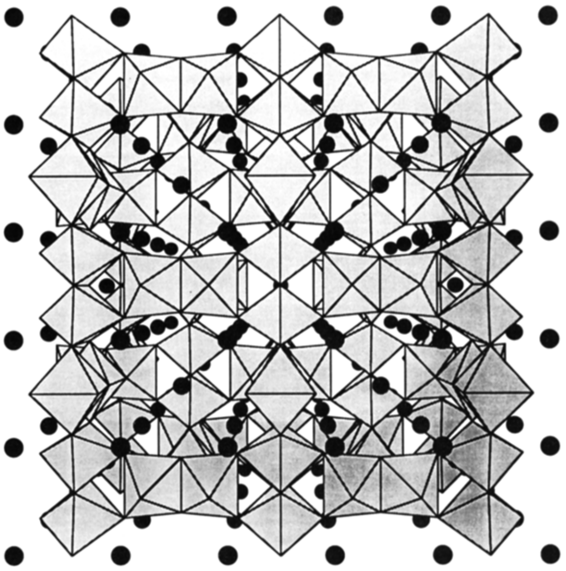

Figure 1. Drawing of the $KBiO_3$ structure showing the corner-sharing Bi_2O_{10} cluster. The shaded circles represent potassium atoms located along the [111] direction. For clarity, not all potassium atoms are shown.

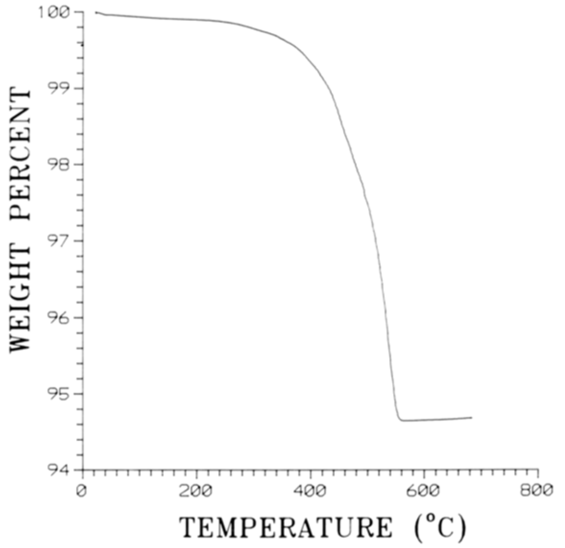

Figure 2. TGA of $KBiO_3$. The 5.4% weight loss at 500 °C corresponds to the loss of one oxygen atom.

short as 1 h. Red crystals of $KBiO_3$ grew as aggregated cubes on the anode and could easily be isolated for structural studies.

Unlike electrolytic reduction of oxides, where oxygen gas can be liberated at the anode to balance the redox process, electrolytic oxidation requires the reduction of a solution component at the cathode. Adding an easily reduced sacrificial reductant to the solution, *e.g.*, $ZnCl_2$ or $CuCl_2$, can lead to reactions taking place at lower operating potentials by providing an easy reduction reaction at the cathode. Under the described reaction conditions, the presence of $ZnCl_2$ or $CuCl_2$ in the reaction mixture was necessary for the formation of $KBiO_3$.

The final atomic positions, thermal parameters, and occupancies for the room temperature structure determination of $KBiO_3$ are listed in Table II. Anisotropic U values are listed in Table III, and selected interatomic bond distances are shown in Table IV. The $KBiO_3$ structure, isostructural with $KSbO_3$,[23] contains pairs of BiO_6 octahedra which are edge shared to form Bi_2O_{10} clusters. These clusters share corners to form the tunnel structure shown in Figure 1. The potassium atoms are located in three partially occupied crystallographic sites, two along the tunnels and one at the origin. Although Goodenough[23] does not report the presence of alkali-metal ions at the origin position of $KSbO_3$, our refinements of $KBiO_3$ show that electron density is clearly present at the origin. Furthermore, this electron density at the origin refined well as a potassium atom. One might consider refining the electron density at the origin as a water of hydration; however, this does not agree with the stoichiometry obtained from microprobe and thermogravimetric measurements, which gave no indication of any waters of hydration.

Figure 2 shows the TGA data for $KBiO_3$ heated in 1 atm of O_2. The thermogravimetric data displays a sudden weight loss near 500 °C. The total weight reduction of 5.4% corresponds to the loss of one oxygen atom from the sample and computes to an initial oxygen content of 2.99(0.02). There is no evidence of any water of hydration, which should result in a detectable weight loss at a temperature lower than the sample decomposition temperature of 500 °C. An X-ray analysis of the residual material shows that the $KBiO_3$ thermally decomposes into K_2O and Bi_2O_3. The thermal instability of this sample above 500 °C is consistent with the observation that $KBiO_3$ cannot be prepared by solid-state reactions at atmospheric pressure. High oxygen pressure stabilizes Bi(V), and consequently $KBiO_3$ can be prepared at 600 °C and several

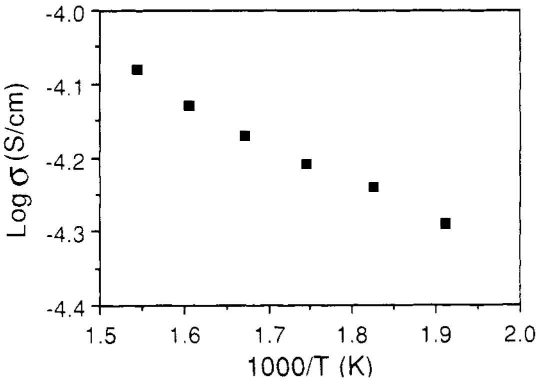

Figure 3. Temperature dependence of the ionic conductivity of $KBiO_3$.

thousand atmospheres of oxygen pressure. This instability also imposes an upper limit on the ionic conductivity measurements that can be carried out.

The partial occupancy of the three potassium sites suggests that this tunnel structure might exhibit good potassium ion conductivity and, consequently, also undergo alkali-metal-ion exchange. In the isostructural $KSbO_3$ material, Goodenough[23] found that it was possible to exchange the potassium for sodium to prepare $NaSbO_3$. We have attempted the ion exchange, albeit unsuccessfully. This behavior can be rationalized by considering that in other tunnel structures waters of hydration are required to stabilize the framework structure when trying to exchange potassium ions with smaller alkali-metal ions.[32] Interestingly, Goodenough, who used high-pressure synthesis to prepare $KSbO_3$, was unable to prepare the $NaSbO_3$ by this method, suggesting that the sodium ions are not large enough to stabilize the structure during synthesis. However, in the case of $KSbO_3$, ion exchange of alkali metals into the structure, once the antimony-oxygen framework has formed, was possible.

The potassium ion conductivity of $KBiO_3$ was measured as a function of temperature and is shown in Figure 3. The activation energy for potassium ion conduction is only 0.16 eV, which is comparable to that of sodium in β-alumina.[33] The potassium ions are located in tunnels along the [111] direction, which are made up to face-shared octahedral sites. The bottleneck for ionic conductivity is the passage through oxygen triangles which make up the octahedral faces. The oxygen triangles of the K(1) position are widened, making it easy for the potassium to hop through, while the oxygen triangles of the K(2) position are more restrictive. The conductivity of $KBiO_3$, 10^{-5} S/cm at 300 °C, is 3 orders of magnitude lower than the reported conductivity of $NaSbO_3\cdot{}^1/_6NaF$, 10^{-2} S/cm at 1 kHz and 300 °C.[22] A significant part of this difference may be due to the smaller size ratio of Na^+ and Sb^{5+}, compared to K^+ and Bi^{5+}, while the remainder can be explained by the lower mobility of the potassium ion compared to that of the sodium ion. The sodium ion in $NaSbO_3\cdot{}^1/_6NaF$ is relieved of its role of stabilizing the framework structure due to the presence of the additional NaF in the structure, enhancing its mobility. The potassium ion in $KBiO_3$, on the other hand, is needed to stabilize the Bi–O structure and, consequently, cannot be very mobile, which is consistent with the ion exchange results.

The potassium ion mobility might be enhanced if its structure-stabilizing role could be assumed by another species, such as H_2O, as is observed in the aqueous synthesis route. Water might act analogously to NaF in $NaSbO_3\cdot{}^1/_6NaF$, and stabilize the Bi–O framework in $KBiO_3$. Furthermore, it has been found that KF enhances the mobility of the sodium ions.[22] Introducing water of KF into $KBiO_3$, consequently, may free up the potassium ions for ion-exchange reactions with other alkali metals as well as enhance the potassium ion mobility for improved ionic conductivity.

Conclusion

Cubic, anhydrous $KBiO_3$ was synthesized by electrocrystallization from a KOH flux at 175 °C. The single-crystal structure was solved and found to be isostructural with $KSbO_3$. The potassium ion partially occupies three sites in the structure and has a low activation energy for ionic conduction, 0.16 eV. The mobility of the potassium ion is low, however, presumably because of its role in stabilizing the Bi–O framework structure, resulting in an ionic conductivity at 300 °C of 10^{-5} S/cm. Thermogravimetric analysis shows that $KBiO_3$ is thermally unstable above 500 °C and decomposes into Bi_2O_3 and K_2O.

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Note Added in Proof. Since submission of this paper, we have become aware that Sleight *et al.*[34] have reported on the synthesis and crystal structure of hydrated $KBiO_3$. They report the presence of a water molecule at the origin.

Supplementary Material Available: Structure factor table for room-tempeature $KBiO_3$ (3 pages). Ordering information is given on any current masthead page.

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