

Preparation and Crystal Structure of a New Lithium Bismuth Oxide: LiBiO_3

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A new lithium bismuth oxide was discovered during the investigation of low-temperature hydrothermal reactions of the hydrated sodium bismuth oxide, $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$. This lithium bismuth oxide crystallizes in the orthorhombic system with the lattice parameters $a = 8.8278(3)$, $b = 4.9135(2)$, and $c = 10.6914(3)$ Å, space group $Pccn$, and $Z = 8$. The crystal structure was refined using neutron powder diffraction data giving final R factors of $R_{\text{WP}} = 10.04$, $R_{\text{p}} = 7.64$, $R_{\text{E}} = 3.88$, and $R_1 = 4.86\%$. The LiBiO_3 crystal structure is similar to that of LiSbO_3 . Both structures can be considered as based on an array of hexagonally closed packed oxygen atoms with cations occupying two-thirds of the octahedral sites. In both structures, the LiO_6 octahedra share faces to form a continuous string. However, in the LiSbO_3 structure SbO_6 octahedra each share two edges forming a continuous zigzag chain whereas in the LiBiO_3 structure BiO_6 octahedra each share one edge only. Thus, the LiBiO_3 structure also resembles the cubic KBiO_3 structure, both structures being based on a dimer unit of the type Bi_2O_{10} which shares corners forming a network having interstitial alkali cations. On heating to about 300°C , LiBiO_3 transforms to LiBiO_2 through evolution of oxygen and reduction of Bi^{5+} to Bi^{3+} . © 1996 Academic Press, Inc.

INTRODUCTION

We have previously reported several new bismuth oxides prepared by low-temperature hydrothermal reactions using hydrated sodium bismuth oxide, $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$, as a starting material (1–5). Some of these compounds contain pentavalent bismuth which is an unusual oxidation state for bismuth. There are three known lithium bismuth oxides containing pentavalent bismuth: Li_3BiO_4 (6), Li_7BiO_6 (7), and Li_5BiO_5 (8). However, LiBiO_3 has not been previously reported. An attempt to prepare LiBiO_3 with the ilmenite-type structure by an ion-exchange reaction using NaBi

$\text{O}_3 \cdot n\text{H}_2\text{O}$ was unsuccessful (9). We have now discovered a new lithium bismuth oxide, LiBiO_3 , prepared through a low-temperature hydrothermal reaction. The synthesis, crystal structure, and thermal stability of this new compound are described in this paper.

EXPERIMENTAL

1. Sample Preparation and Characterization

The starting material of $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ (Nacalai Tesque Inc.) was placed in a Teflon lined autoclave (70 ml) with LiOH and H_2O (30 ml) and was heated at 120 – 200°C for 4 days. The molar ratio of the starting material to lithium hydroxide was varied from 0.25 to 4. The solid products were separated by centrifuging, washed with distilled water, and dried at 50°C . The products were identified by X-ray powder diffraction using $\text{CuK}\alpha$ radiation. To determine chemical composition, the products were dissolved completely in concentrated HCl . The amount of sodium, lithium, and bismuth in the solution was analyzed by atomic absorption spectroscopy or induced coupled plasma spectroscopy. The specific gravity was measured with a picnometer. The valence of bismuth was determined by iodometric titrations. The thermal stability was investigated by TG-DTA with a heating rate of $10^\circ/\text{min}$. The gases evolved during TG-DTA measurements in flowing He were analyzed by mass spectrometry.

2. Crystal Structure Refinement

The structural refinement was carried out by neutron powder diffraction data collected at intervals of $0.05^\circ 2\theta$ from 10.00° to $120.00^\circ 2\theta$ using a wavelength of 1.8857 Å at 295 K on a high resolution powder diffractometer at the Brookhaven National Laboratory. As the sample used

data collection contained a small amount of unknown impurities, the peaks from them were excluded for the refinement. The data were refined using the Rietveld method with the program RIETAN (10).

RESULTS AND DISCUSSION

Preparation

Single phase LiBiO_3 was obtained after 2 days at 120°C using a molar ratio of $\text{Li/Bi} = 4$. The color of this product was brown. When the reaction temperature was 140°C , Bi_2O_4 (5) was obtained. The X-ray powder pattern of LiBiO_3 can be indexed (Table 1) as orthorhombic and the lattice parameters were determined to be $a = 8.8278(3)$, $b = 4.9135(2)$, and $c = 10.6914(3)$ Å on the course of the structural refinement. The results of the chemical analyses are listed in Table 2. No sodium was detected, and the mean valence of bismuth by iodometric titrations agreed with that estimated from weight loss caused by the reduc-

TABLE 1
X-Ray Powder Pattern for LiBiO_3

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (obs.)	<i>d</i> (calc)	<i>I</i> / <i>I</i> ₀
0	0	2	5.340	5.345	1.7
1	0	2	4.568	4.572	68.1
2	0	0	4.410	4.414	17.2
1	1	1	3.981	3.984	83.2
2	1	1	3.134	3.139	100.0
1	1	3	2.7412	2.7420	46.4
0	0	4	2.6728	2.6727	29.4
3	0	2	2.5780	2.5777	30.7
0	2	0	2.4573	2.4566	10.9
2	1	3	2.4149	2.4147	10.2
0	1	4	2.3477	2.3478	1.7
2	0	4	2.2864	2.2862	7.3
4	0	0	2.2069	2.2068	2.5
1	2	2	2.1657	2.1640	10.4
2	2	0	2.1469	2.1465	3.3
4	1	1	1.9785	1.9783	7.9
1	1	5	1.9205	1.9139	18.3
0	2	4	1.8103	1.8086	15.8
2	1	5	1.7932	1.7917	11.4
3	2	2	1.7801	1.7784	24.2
1	0	6	1.7495	1.7465	2.3
4	0	4	1.7028	1.7017	1.6
5	0	2	1.6760	1.6764	2.9
1	3	1	1.5938	1.5923	2.1
3	0	6	1.5257	1.5241	4.8
5	1	3	1.5067	1.5058	2.9
1	3	3	1.4674	1.4674	4.8
1	1	7	1.4403	1.4389	5.2
1	2	6	1.4251	1.4235	1.6
4	2	4	1.4002	1.3989	1.4
3	2	6	1.2968	1.2951	2.4
2	3	5	1.2465	1.2472	2.4

TABLE 2
Chemical Analysis for LiBiO_3

	Li_2O	Bi_2O_5	Total
Calc.(wt%)	5.66	94.34	100.0
Obs.(wt%)	5.33	94.64	99.97

tion of Bi^{5+} as described below. The calculated density (7.55 g/cm^3) for $Z = 8$ agreed with the measured value (7.39 g/cm^3). Electrical resistivity measured by the two probe method using a pressed compact showed a high resistivity of about $10^6 \Omega \cdot \text{cm}$ at room temperature.

Thermal Behavior

Figure 1 shows the TG-DTA curves and temperature dependence of gas evolution during TG-DTA measurements. The TG curve indicates weight loss in three steps, and only oxygen is evolved during the course of pyrolysis. The observed total weight loss (6.09 wt%) agrees well with the value (6.06 wt%) calculated on the assumption that LiBiO_3 converted to LiBiO_2 by release oxygen due to complete reduction of Bi^{5+} to Bi^{3+} . The X-ray powder pattern of the sample heated up to 600°C was identified with that of LiBiO_2 (11). The large endothermic peak observed at about 600°C in the DTA curve corresponds to melting of the sample.

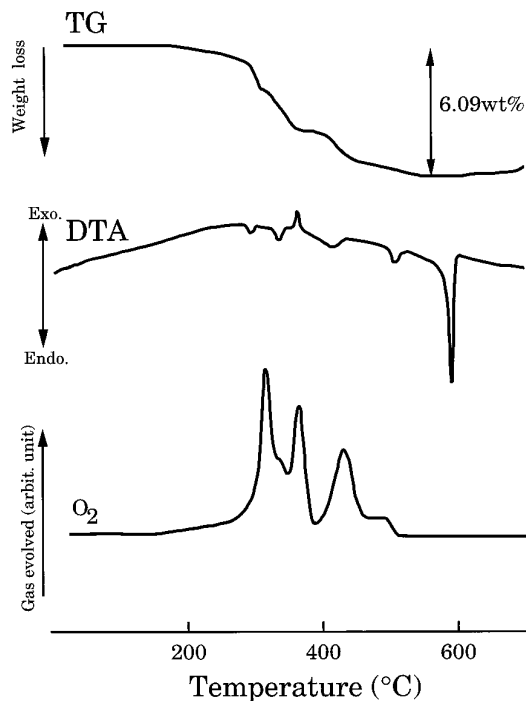


FIG. 1. TG-DTA curves and temperature dependence of gas evolution during TG-DTA measurement in a stream of He.

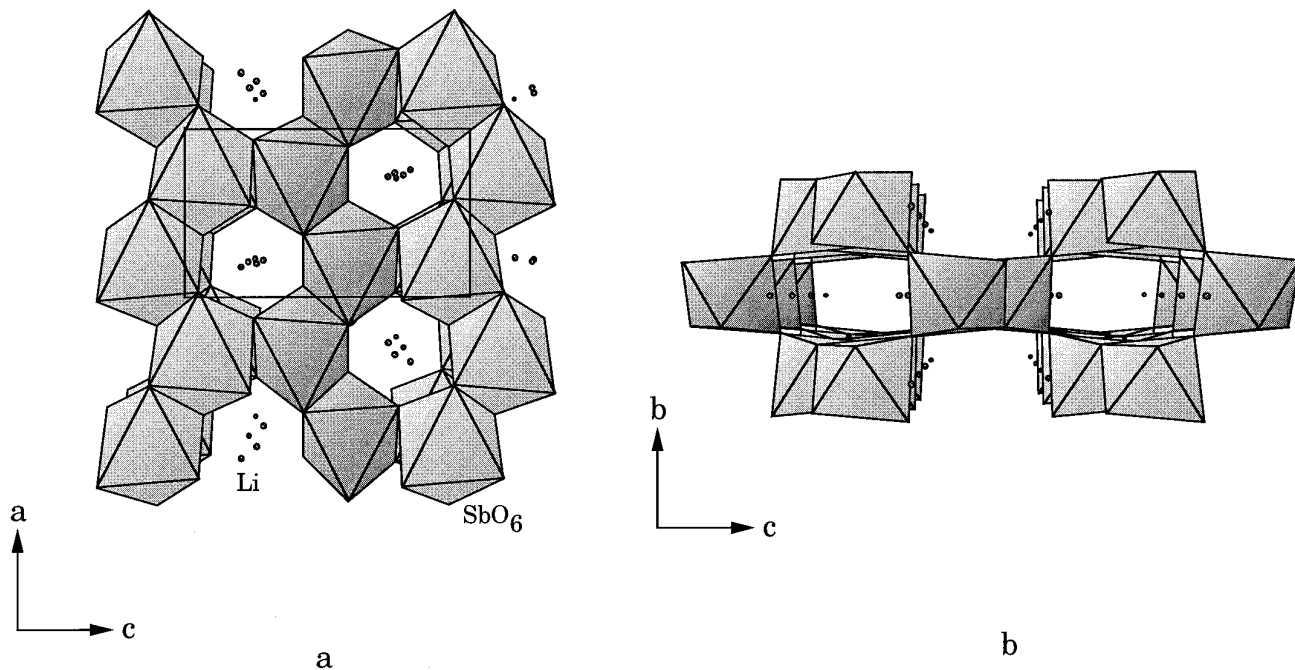


FIG. 2. Crystal structure of LiSbO_3 . (a) Projection along the b axis and SbO_6 octahedra. The rectangle denotes the unit cell. (b) Projection along the a axis.

Derivation and Description of the Structure

The lattice parameters of LiBiO_3 ($a_{\text{Bi}} = 8.828$, $b_{\text{Bi}} = 4.914$, and $c_{\text{Bi}} = 10.691 \text{ \AA}$) appeared related to those of LiSbO_3 ($a_{\text{Sb}} = 5.183$, $b_{\text{Sb}} = 4.893$, and $c_{\text{Sb}} = 8.491 \text{ \AA}$) with $a_{\text{Bi}} \approx c_{\text{Sb}}$, $b_{\text{Bi}} \approx b_{\text{Sb}}$, and $c_{\text{Bi}} \approx 2a_{\text{Sb}}$ (12). Diffraction peaks appear at similar d values for both compounds, but the intensities differ. The space group $Pccn$ (No. 56) for LiBiO_3 was deduced from the systematic absence of reflections with $l = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$, and $h + k = 2n + 1$ for $hk0$ as shown in Table 1. These extinction conditions differ from those of LiSbO_3 with space group

$Pnna$ (No. 52). Nevertheless, comparison of the lattice parameters of LiBiO_3 and LiSbO_3 suggested some similar structural features. The structure of LiSbO_3 is projected along the b_{Sb} axis in Fig. 2a and along the a_{Sb} axis in Fig. 2b. Using this structure as a guide, a structural model for LiBiO_3 was derived where two BiO_6 octahedra share edges in the ac plane. The problem of periodicity along the c axis was solved by connecting two edge-sharing octahedra at the same height along the b_{Bi} axis with another pair of edge-sharing octahedra at the different height along this axis. On the other hand, in the LiSbO_3 structure, pairs of octahedra are repeated at the same height along the b_{Sb}

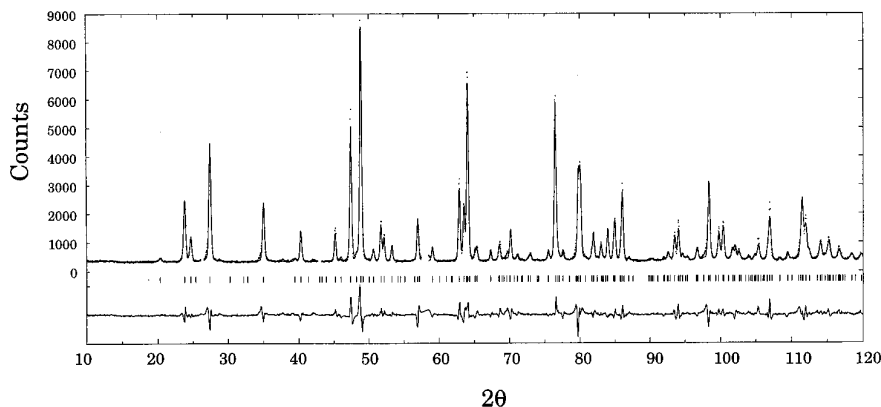


FIG. 3. Observed (dots), calculated (solid line), and difference (at the bottom) neutron diffraction profiles for LiBiO_3 .

TABLE 3
Crystal Data and Intensity Collection
for LiBiO₃

Color	Brown
Crystal system	Orthorhombic
Space group	<i>Pccn</i> (No. 56)
<i>Z</i>	8
Lattice parameters	$a = 8.8278(3)$, $b = 4.9135(2)$ $c = 10.6914(3)$ Å
Volume	463.74 Å ³
Formula weight	263.90
Calculated density	7.56 g/cm ³
Wavelength	$\lambda = 1.8857$ Å
Temperature	23°C
2 θ scan range	10.00–120.00°
R_{WP}	10.04%
R_P	7.64%
R_E	3.88%
R_I	4.86%

axis to form a continuous zigzag chain along the a_{Sb} axis. The structural model developed for LiBiO₃ is consistent with the space group *Pccn* (No. 56). The crystal structure of LiBiO₃ was refined based on this starting model, and the final agreement factors were $R_{WP} = 10.04$, $R_P = 7.64$, $R_E = 3.88$, and $R_I = 4.86\%$. Figure 3 shows observed and calculated neutron diffraction patterns. The crystallographic data are summarized in Table 3. Tables 4 and 5 show the atomic parameters and selected interatomic distances, respectively. The crystal structure of LiBiO₃ and the coordination environment around bismuth and lithium atoms are shown in Figs. 4 and 5. The bismuth atom is octahedrally coordinated by six oxygens at mean distances of 2.11, and these values agree well with the mean Bi⁵⁺–O distances of 2.10 Å in KBiO₃ (13) and 2.101 Å in Bi₂O₄ (5). In both the structures of LiBiO₃ and LiSbO₃, the LiO₆ octahedra share faces continuously along the b axis. The Li–O distances are ranged from 1.91(7) to 2.51(6) Å and the distances 2.34(5) and 2.5(6) Å for Li–O(3) and Li–O(2) are longer than those of the others. The position of the lithium atom is slightly deviated from the center of the octahedron.

TABLE 4
Positional and Thermal Parameters (Å²) for LiBiO₃

Atom	Site	x	y	z	B_{eq}
Bi	8e	0.414(1)	0.006(3)	0.3647(8)	0.4(2)
Li	8e	0.783(5)	–0.004(17)	0.402(4)	2(1)
O(1)	8e	0.406(2)	0.302(3)	0.043(2)	1.1(4)
O(2)	8e	0.420(2)	0.776(3)	0.200(2)	0.4(4)
O(3)	4c	1/4	1/4	0.285(3)	0.8(7)
O(4)	4d	1/4	3/4	0.952(3)	0.4(6)

TABLE 5
Selected Interatomic Distances (Å) for LiBiO₃

BiO ₆ octahedra		LiO ₆ octahedra	
Bi–O(1)	2.12(2)	Li–O(1)	1.91(7)
O(1)	2.12(2)	O(1)	2.01(6)
O(2)	2.09(2)	O(2)	1.98(7)
O(2)	2.09(2)	O(2)	2.51(6)
O(3)	2.07(2)	O(3)	2.34(6)
O(4)	2.14(2)	O(4)	2.02(7)
mean	2.11	mean	2.13
O(1)–O(1)	2.72(4)	O(1)–O(1)	2.80(4)
O(1)–O(2)	2.88(2)	O(1)–O(2)	2.88(2)
O(1)–O(2)	3.04(3)	O(1)–O(2)	3.09(2)
O(1)–O(2)	3.15(3)	O(1)–O(3)	2.95(3) × 2
O(1)–O(3)	3.09(3)	O(1)–O(4)	2.77(2)
O(1)–O(4)	2.77(2)	O(1)–O(4)	3.19(2)
O(1)–O(4)	3.05(2)	O(2)–O(2)	3.01(4)
O(2)–O(2)	3.03(2)	O(2)–O(3)	3.12(2)
O(2)–O(3)	2.91(2)	O(2)–O(3)	2.91(2)
O(2)–O(3)	2.92(2)	O(2)–O(4)	2.05(3) × 2
O(2)–O(4)	3.08(3)	mean	2.98
O(3)–O(4)	3.04(2)		
mean	2.97		
Bi–Bi	3.26(2)	Li–Li	2.5(2)

The difference in the crystal structures of LiBiO₃ and LiSbO₃ is seen by comparing Fig. 4 with Fig. 2. The pairs of edge-sharing BiO₆ octahedra at $y \approx 1/4$ and $3/4$ alternate along the c_{Bi} axis, and every adjacent pair is at different height in LiBiO₃. On the other hand, in LiSbO₃ edge-sharing SbO₆ octahedra at the same height form continuous zigzag chains along the a_{Sb} axis.

The structures of LiBiO₃ and cubic KBiO₃ may both be considered as based on edge-shared BiO₆ octahedra units which in turn share corners with each other. The geometry of the dimer unit is essentially the same in the two different structures. In both cases, the Bi atoms of the unit are displaced away from each other relative to ideal octahedra. Ideal octahedra with a Bi–O distance of 2.10 Å would give a Bi–Bi distance of 2.97 Å instead of the 3.26 and 3.21 Å Bi–Bi distances actually observed in both LiBiO₃ and KBiO₃. Although the same building blocks are used to form the covalent network of the structures, the KBiO₃ network is much more open. Comparing the unit cell volumes of LiBiO₃ and KBiO₃ shows that in fact the KBiO₃ network occupies 45% more space. The channels in the KBiO₃ structure can accommodate cations as large as Rb⁺ whereas those of LiBiO₃ may not be able to accommodate cations larger than Li⁺.

The lithium bismuth oxide LiBiO₃ obtained here is the only one which has not been prepared in $A^+ M^{5+} O_3$ compositions ($A = Li, Na, K; M = Nb, Ta, Sb, Bi$) (14). The

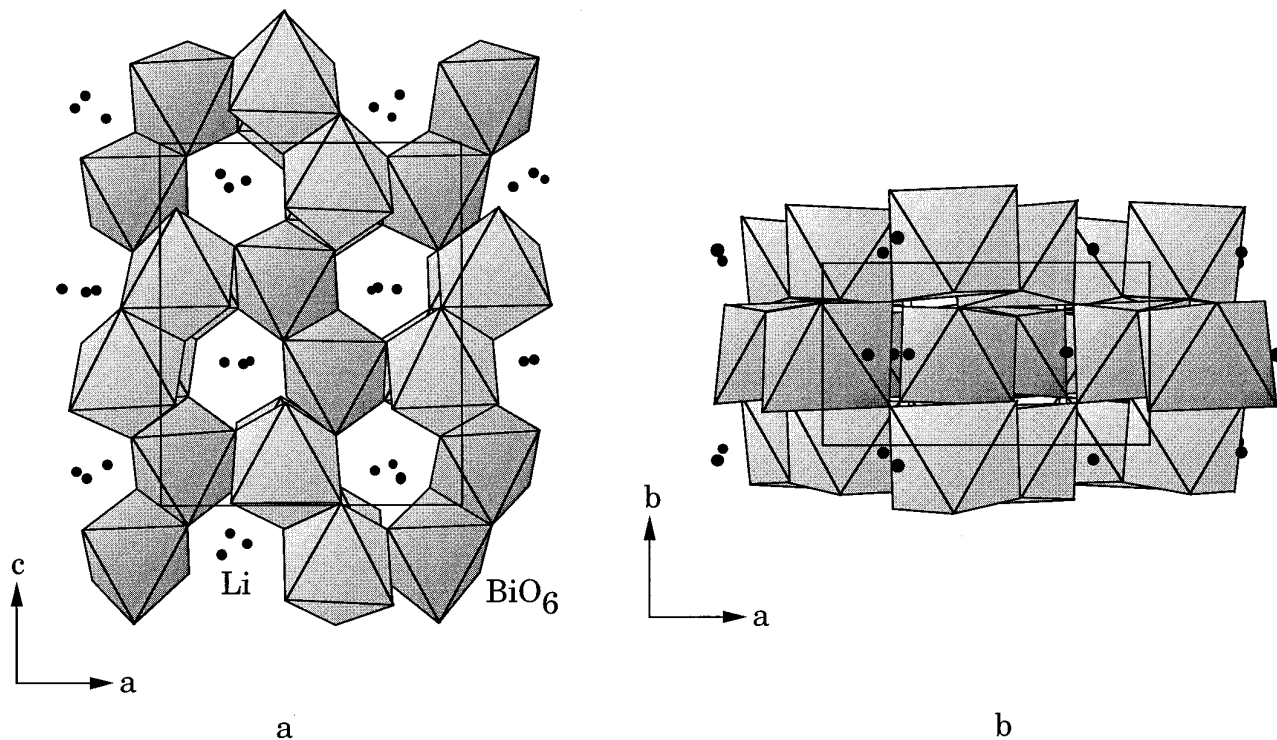


FIG. 4. Crystal structure of LiBiO_3 . (a) Projection along the b axis and BiO_6 octahedra. The rectangle denotes the unit cell. (b) Projection along the c axis.

crystal structures for $A^+ M^{5+} \text{O}_3$ compounds are listed in Table 6. The fact that the crystal structure of LiBiO_3 is closely related to that of LiSbO_3 but not to the LiNbO_3 -type structure is consistent with general features pointed out by Goodenough and Kafalas (14) of the crystal structures for $A^+ M^{5+} \text{O}_3$ compounds. We have reported the preparation of metastable ilmenite-type niobates which are in contrast to the general features of $A^+ M^{5+} \text{O}_3$ com-

pounds: NaNbO_3 by low-temperature hydrothermal reaction (15) and LiNbO_3 by ion-exchange reaction of the former (16). Metastable phases which are new in structure or composition have been prepared very often by low-temperature hydrothermal reactions or by ion-exchange reactions. The compound of LiBiO_3 might exist as a stable phase under sufficient oxygen pressure, as its structure follows the general features of $A^+ M^{5+} \text{O}_3$ compounds.

CONCLUSION

Using a low-temperature hydrothermal method, a new lithium bismuth oxide, LiBiO_3 , was prepared for the first

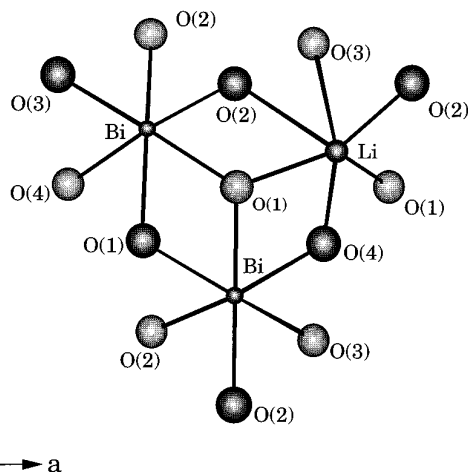


FIG. 5. Coordination environment around Bi and Li atoms.

TABLE 6
Crystal Structures of $A^+ M^{5+} \text{O}_3$ Compositions

A	M			
	Nb	Ta	Sb	Bi
Li	LiNbO_3 ilmenite (16)	LiNbO_3	LiSbO_3 ilmenite (9)	LiBiO_3 (this work)
Na	perovskite ilmenite (15)	perovskite	ilmenite	ilmenite
K	perovskite	perovskite	ilmenite	KBiO_3

time. This had been the only missing member of the $A^+M^{5+}O_3$ family where $A = \text{Li, Na, or K}$ and where $M = \text{Nb, Ta, Sb, or Bi}$. The crystal structure of LiBiO_3 has features in common with both LiSbO_3 and KBiO_3 . At temperatures higher than about 300°C , LiBiO_3 decomposes into LiBiO_2 by complete reduction of Bi^{5+} to Bi^{3+} .

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