

## Six New Bi(V) Materials: $\text{LiSr}_3\text{BiO}_6$ , $\text{NaSr}_3\text{BiO}_6$ , $\text{NaBa}_3\text{BiO}_6$ , $\text{Li}_6\text{KBiO}_6$ , $\text{Li}_6\text{RbBiO}_6$ , and $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$

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Received February 7, 1991; in revised form August 13, 1991

Large single crystals of  $\text{LiSr}_3\text{BiO}_6$ ,  $\text{NaSr}_3\text{BiO}_6$ ,  $\text{NaBa}_3\text{BiO}_6$ ,  $\text{Li}_6\text{KBiO}_6$ ,  $\text{Li}_6\text{RbBiO}_6$ , and  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$  were grown by precipitation from molten mixtures of alkali and/or alkaline earth metal hydroxides at 550°C. Single crystal X-ray methods were used to solve the structures of  $\text{NaBa}_3\text{BiO}_6$ ,  $\text{Li}_6\text{KBiO}_6$ , and  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ .  $\text{NaBa}_3\text{BiO}_6$  has trigonal Laue symmetry with unit cell dimensions  $a = 7.226(1)$  Å and  $\alpha = 91.79(3)^\circ$ . The structure was refined in the space group  $R\bar{3}c$  to an  $R$  value of 2.7%.  $\text{NaSr}_3\text{BiO}_6$  [ $a = 6.930(1)$  Å,  $\alpha = 92.26(1)^\circ$ ] is isostructural and  $\text{LiSr}_3\text{BiO}_6$  [ $a = 6.872(1)$  Å,  $b = 6.864(2)$  Å,  $c = 6.872(1)$  Å,  $\alpha = 92.31(2)^\circ$ ,  $\beta = 92.27(2)^\circ$ ,  $\gamma = 92.29(2)^\circ$ ] has a related structure.  $\text{Li}_6\text{KBiO}_6$  has trigonal Laue symmetry with unit cell dimensions  $a = 5.428(1)$  Å and  $\alpha = 101.49(1)^\circ$ . The structure was refined in the space group  $R\bar{3}m$  and was refined to an  $R$  value of 4.6%.  $\text{Li}_6\text{RbBiO}_6$  [ $a = 5.464(1)$  Å,  $\alpha = 101.46(1)^\circ$ ] is isostructural.  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$  has orthorhombic Laue symmetry with unit cell dimensions  $a = 14.593(5)$  Å,  $b = 5.989(1)$  Å, and  $c = 14.363(2)$  Å. The structure was refined in the space group  $Pnma$  to an  $R$  value of 3.6%. In all six materials the Bi(V) atoms are coordinated by an octahedron of oxygen atoms; the Bi(V)-O bond lengths range from 2.04 to 2.17 Å. These materials are hygroscopic, but are otherwise stable under ambient conditions. © 1992 Academic Press, Inc.

### Introduction

The structure and properties of alkali metal and alkaline earth metal bismuth oxides have attracted attention because of the discoveries of superconductivity in two materials derived from  $\text{BaBiO}_3$ :  $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$  (1) and  $\text{Ba}_{0.65}\text{K}_{0.35}\text{BiO}_3$  (2). The latter exhibits superconductivity near 30 K; 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 atoms is between  $3+$  and  $5+$ . Since it has been postulated that Bi(IV) disproportionates to Bi(III) and

Bi(V) in  $\text{BaBiO}_3$  (3), it is important to have good model compounds for Bi(III) and Bi(V). Although there are many Bi(III) materials that have been characterized structurally (4), to date the only well-refined structure of an oxide containing Bi(V) is that of  $\text{Na}_3\text{BiO}_4$  (5); the synthesis of several other lithium and sodium bismuth(V) oxides have been reported (6), but the crystals structures have not been refined. Our goal is to prepare and characterize new Bi(V) materials to determine the Bi(V)-O bond distances and possible coordination geometries of oxygen around Bi(V).

We have found that quaternary lithium bismuth(V) oxides are crystallized readily from mixtures of molten alkali and/or alka-

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TABLE I  
 REACTION MIXTURES

Material	Melt constituent (g, mmol)			
NaBa <sub>3</sub> BiO <sub>6</sub>	NaOH (10,40)	Ba(OH) <sub>2</sub> (5,30)	Bi <sub>2</sub> O <sub>3</sub> (0.4,0.8)	KOH <sup>a</sup> (5,90)
NaSr <sub>3</sub> BiO <sub>6</sub>	NaOH (10,40)	Sr(OH) <sub>2</sub> (5,30)	Bi <sub>2</sub> O <sub>3</sub> (0.4,0.8)	KOH <sup>a</sup> (5,90)
LiSr <sub>3</sub> BiO <sub>6</sub> <sup>b</sup>	LiOH (7,300)	Sr(OH) <sub>2</sub> (7,42)	Bi <sub>2</sub> O <sub>3</sub> (0.5,1.0)	
Li <sub>6</sub> KBiO <sub>6</sub>	LiOH (10,420)	KOH (10,180)	Bi <sub>2</sub> O <sub>3</sub> (0.7,1.5)	
Li <sub>6</sub> RbBiO <sub>6</sub>	LiOH (1,42)	RbOH (4,40)	Bi <sub>2</sub> O <sub>3</sub> (0.1,0.24)	
LiBa <sub>5</sub> Bi <sub>2</sub> O <sub>11</sub>	LiOH (5,209)	Ba(OH) <sub>2</sub> (5,30)	Bi <sub>2</sub> O <sub>3</sub> (0.4,0.8)	RbOH <sup>a</sup> (5,50)

<sup>a</sup> Addition of KOH/RbOH improved the quality of the crystals.

<sup>b</sup> A silver crucible was used for this reaction. All other reactions took place in Al<sub>2</sub>O<sub>3</sub> crucibles.

line earth hydroxides at 550°C. In this paper, we report the preparation of Li<sub>6</sub>KBiO<sub>6</sub>, Li<sub>6</sub>RbBiO<sub>6</sub>, LiSr<sub>3</sub>BiO<sub>6</sub>, and Li<sub>2</sub>Ba<sub>5</sub>Bi<sub>2</sub>O<sub>11</sub> by precipitation from molten LiOH mixed with KOH, RbOH, Sr(OH)<sub>2</sub>, or Ba(OH)<sub>2</sub>, respectively. In addition, the sodium analogs, NaSr<sub>3</sub>BiO<sub>6</sub> and NaBa<sub>3</sub>BiO<sub>6</sub>, have been synthesized. All the materials are stoichiometric except for Li<sub>2</sub>Ba<sub>5</sub>Bi<sub>2</sub>O<sub>11</sub>, which has fewer lithium and oxygen atoms than indicated by the nominal stoichiometry. The structures of NaBa<sub>3</sub>BiO<sub>6</sub>, Li<sub>6</sub>KBiO<sub>6</sub>, and Li<sub>2</sub>Ba<sub>5</sub>Bi<sub>2</sub>O<sub>11</sub> have been determined by single crystal X-ray diffraction methods as reported below; Li<sub>6</sub>RbBiO<sub>6</sub> is isostructural with Li<sub>6</sub>KBiO<sub>6</sub>, NaSr<sub>3</sub>BiO<sub>6</sub> is isostructural with NaBa<sub>3</sub>BiO<sub>6</sub>, and LiSr<sub>3</sub>BiO<sub>6</sub> has a structure related to NaBa<sub>3</sub>BiO<sub>6</sub>.

## Experimental

*General.* Reagents were used directly without further purification unless noted. KOH (ACS certified), NaOH (ACS certified), LiOH (purified, anhydrous powder), and anhydrous Ba(OH)<sub>2</sub> (reagent grade)

were obtained from Fisher Scientific. Bi<sub>2</sub>O<sub>3</sub> (99.9%) was purchased from Aldrich and RbOH (99%) was obtained from AESAR. Sr(OH)<sub>2</sub> · 8H<sub>2</sub>O was purchased from Alfa Chemical and was stored in a drying oven (125°C) prior to use. X-ray powder diffraction was performed on a Siemens D-500 automated X-ray powder diffractometer with a copper X-ray source.

*Synthesis.* The constituents of the individual reaction mixtures are listed in Table I. These reagents were placed (unmixed) into an alumina crucible which was then placed into a furnace that had been preheated to 550°C. The furnace was open to the ambient atmosphere at all times. Initially, a clear solution formed. The reaction was allowed to proceed for approximately 24 h, at which time transparent yellow crystals could be seen growing on the sides and bottom of the crucible. The crucible was pulled from the furnace and the excess solvent was decanted from the crucible. After the crucible had cooled to room temperature, methanol was added to dissolve the remaining hydroxide. The product was filtered and rinsed with

TABLE II  
CRYSTAL DATA FOR  $\text{Li}_6\text{KBiO}_6$ ,  $\text{NaBa}_3\text{BiO}_6$ , AND  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$

Material	$\text{NaBa}_3\text{BiO}_6$	$\text{Li}_6\text{KBiO}_6$	$\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$
Space group	$R\bar{3}c$	$R\bar{3}m$	$Pnma$
$a$ (Å)	7.226(1)	5.428(1)	14.592(2)
$b$ (Å)	—	—	5.9889(7)
$c$ (Å)	—	—	14.358(3)
$\alpha$ (deg)	91.79(3)	101.49(1)	—
volume (Å <sup>3</sup> )	376.8(3)	148.8(3)	1254.7(3)
$Z$	2	1	4
fw	730.97	385.72	1294.54
crystal size (mm)	0.17 × 0.17 × 0.17	0.17 × 0.22 × 0.20	.05 × .10 × .10
$\rho$ (calc) (g cm <sup>-3</sup> )	6.5	4.3	6.8
$\mu$ (calc) (cm <sup>-1</sup> )	387.09	301.87	433.6
temp (K)	298	298	170
$I_{\min}/I_{\max}$	0.73	0.30	0.56
$g$	$1.10(2) \times 10^{-6}$	$2.25(2) \times 10^{-5}$	$9.3(1) \times 10^{-8}$
$R(F^2)$	2.7	4.6	3.7
$R_w(F^2)$	3.7	5.8	4.2
GOF	1.242	2.613	1.382

methanol. As the crystals are hygroscopic, the material was stored in a desiccator containing  $\text{CaSO}_4$ .

### X-ray Structure Determination

*General.* Intensity data for single crystals of  $\text{NaBa}_3\text{BiO}_6$ ,  $\text{Li}_6\text{KBiO}_6$ , and  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$  were collected on an Enraf-Nonius CAD-4 diffractometer (7) using a  $\theta$ - $2\theta$  scan technique.  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) and a monochromator of highly oriented graphite ( $2\theta = 12.2^\circ$ ) were used. Unit cells for these three bismuthates were determined by automatic peak search and indexing procedures. Cell parameters and data collection parameters are summarized in Table II.

Measured intensities were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects (8). For  $\text{NaBa}_3\text{BiO}_6$  and  $\text{Li}_6\text{KBiO}_6$ , the data were corrected by a linear decay factor for the two-percent decrease measured in the magnitude of the intensity standards during the

period of data collection; no decay was observed in the intensity standards for  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ . Absorption corrections were based on azimuthal data (9) which showed a variation  $I_{\min}/I_{\max}$  for the average curves as given in Table II. In addition, spherical absorption corrections based on the calculated absorption coefficients were applied. Also given is the value of  $\mu$  used for the spherical absorption correction.

The structures were solved by using Patterson methods and refined via standard

TABLE III  
FINAL ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC DEBYE-WALLER FACTORS,  $\text{NaBa}_3\text{BiO}_6$

Atom	$x$	$y$	$z$	$B(\text{Å}^2)$
Bi	0.00	0.00	0.00	0.449(3)
Ba	0.39831(7)	0.102	0.75	0.772(9)
Na	0.25	0.25	0.25	0.90(4)
O	0.0816(8)	0.2769(9)	0.9471(9)	1.0(1) <sup>a</sup>

<sup>a</sup> Included with isotropic thermal parameters.

TABLE IV  
SELECTED BOND DISTANCES AND  
ANGLES,  $\text{NaBa}_3\text{BiO}_6$

Bi–O	2.109(2) Å	× 6
Na–O	2.485(2) Å	× 6
Ba–O	2.658(2) Å	× 2
	2.788(2) Å	× 2
	2.827(2) Å	× 2
	3.026(2) Å	× 2
O–Bi–O	180.0°	× 3
	89.44(9)°	× 2
	90.56(9)°	× 2
	89.43(9)°	× 4
	90.57(9)°	× 2
	89.45(9)°	× 2
O–Na–O	132.0(1)°	× 3
	147.6(1)°	× 3
	93.4(1)°	× 3
	73.35(8)°	× 3

least squares and Fourier techniques. All atoms except lithium and oxygen were refined using anisotropic thermal parameters. The quantity minimized by the least-squares routine was  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  is the weight of a given observation. The secondary extinction parameter  $g$  was refined also, and its value is given in Table II. The  $p$  factor used to reduce the weight of the intense reflections was set to 0.03 in the final stages of refinement. The analytical forms of the scattering factors of the neutral atoms were used (10), and all scattering factors were corrected for both the real and imaginary components of the anomalous dispersion (11). Lists of  $F_o$  and  $F_c$  are available as supplementary material.

Specific comments regarding the structure solutions for the three bismuthates are given below.

$\text{NaBa}_3\text{BiO}_6$ . Precession photos showed trigonal symmetry. Automatic peak searching and indexing gave a primitive rhombohedral cell. Inspection of the data indicated the presence of a  $c$ -glide which allowed for the possibility of two space groups:  $R\bar{3}c$  and

TABLE V  
FINAL ATOMIC POSITIONAL PARAMETERS AND  
EQUIVALENT ISOTROPIC DEBYE–WALLER FACTORS,  
 $\text{Li}_6\text{KBiO}_6$

Atom	$x$	$y$	$z$	$B(\text{Å}^2)$
Bi	0.00	0.00	0.00	0.865(5)
K	0.50	0.50	0.50	2.05(4)
Li	0.00	0.343(2)	–0.343	0.8(3) <sup>a</sup>
O	0.084(2)	0.719(2)	0.719	1.7(2) <sup>a</sup>

<sup>a</sup> Included with isotropic thermal parameters.

$R\bar{3}c$ . As data refinement was successful in  $R\bar{3}c$ ,  $R3c$  was not considered. Intensities for 1884 reflections were measured ( $\pm h, \pm k, +l, 0^\circ < 2\theta < 55^\circ$ ). Removal of the systematic absences and averaging the redundant data yielded 341 unique reflections. The  $R$  value of agreement based on  $F_{\text{obs}}$  was 2.9%. The final residuals for 15 variables refined against 283 independent reflections for which  $F^2 > 3\sigma(F^2)$  were  $R = 2.6\%$ ,  $R_w = 3.7\%$ , and  $\text{GOF} = 1.242$ . The  $R$  value for all 341 data was 3.1%. The final refinement cycle converged with a shift/error  $< 0.03$ , and the largest peak in the difference Fourier had an absolute value of electron density of 2.6 electrons/Å<sup>3</sup>. Positional parameters are listed in Table III, and selected bond distances and bond angles are given in Table IV.

TABLE VI  
SELECTED BOND DISTANCES AND  
ANGLES,  $\text{Li}_6\text{KBiO}_6$

Bi–O	2.115(6) Å	× 6
K–O	3.086(9) Å	× 6
	3.049(9) Å	× 6
Li–O	1.95(2) Å	× 2
	1.99(1) Å	× 2
O–Bi–O	180.0(0)°	× 3
	92.7(3)°	× 6
	87.3(3)°	× 6

TABLE VII  
FINAL ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC DEBYE-WALLER  
FACTORS,  $\text{LiBa}_5\text{Bi}_2\text{O}_{11}$

Atom	x	y	z	$B(\text{\AA}^2)$
Bi(1)	0.58525(5)	0.75	0.93262(5)	0.83(1)
Bi(2)	0.45043(5)	0.25	0.59264(5)	0.77(1)
Ba(1)	0.3293(1)	0.75	0.5338(1)	1.02(2)
Ba(2)	0.4954(1)	0.25	0.8323(1)	0.99(2)
Ba(3)	0.5726(1)	0.75	0.6577(1)	0.99(2)
Ba(4)	0.8362(1)	0.75	0.5359(1)	0.96(2)
Ba(5)	0.2492(1)	0.25	0.7427(1)	1.01(2)
Li(1)	0.114(3)	0.25	0.252(3)	1.8(6) <sup>a</sup>
O(1)	0.3363(9)	0.25	0.942(1)	1.2(2) <sup>a</sup>
O(2)	0.5	0	0	1.2(2) <sup>a</sup>
O(3)	0.5	0	0.5	1.2(2) <sup>a</sup>
O(4)	0.3399(6)	-0.002(2)	0.127(1)	1.4(2) <sup>a</sup>
O(5)	0.4024(6)	0.009(2)	0.680(1)	1.3(2) <sup>a</sup>
O(6)	0.245(1)	0.25	0.296(1)	1.3(3) <sup>a</sup>
O(7)	0.081(1)	0.25	0.846(1)	1.6(3) <sup>a</sup>
O(8)	0.013(1)	0.25	0.331(2)	1.3(2) <sup>a</sup>
O(9)	0.333(1)	0.25	0.509(1)	0.4(2) <sup>a,b</sup>

<sup>a</sup> Included with isotropic thermal parameters.

<sup>b</sup> Partially occupied; occupancy = 0.84(2).

$\text{Li}_6\text{KBiO}_6$ . Automatic peak search and indexing procedures yielded a primitive rhombohedral cell. No systematic absences were observed for  $\text{Li}_6\text{KBiO}_6$ , thus narrowing the choice of space groups to  $R\bar{3}m$ ,  $R3m$ , and  $R32$ . As refinement was successful in  $R\bar{3}m$ ,  $R3m$  and  $R32$  were not considered. Intensities for 732 reflections were measured ( $\pm h$ ,  $\pm k$ ,  $+l$ ,  $0^\circ < 2\theta < 55^\circ$ ). Averaging the redundant data yielded 137 unique reflections. The  $R$  value of agreement based on  $F_{\text{obs}}$  was 3.8%. The final residuals for 11 variables refined against the 137 independent reflections for which  $F^2 > 3\sigma(F^2)$  were  $R = 4.6\%$ ,  $R_w = 5.8\%$ , and  $\text{GOF} = 2.613$ . The  $R$  value for all 137 retained data was 4.6%. The final refinement cycle converged with a shift/error  $< 0.03$ . The three largest peaks in the difference Fourier were located within 1.5 Å of the bismuth atom. All remaining peaks in the difference Fourier had an absolute value of electron density less than 1.5 electrons/Å<sup>3</sup>. Positional parameters are listed in

Table V, and selected bond distances and bond angles are given in Table VI.

Note added in proof: Hubenthal and Hoppe (14) report the same structure for  $\text{Li}_6\text{KBiO}_6$ . All lattice parameters and atomic positions are consistent with our results.

$\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ . Precession photos showed  $mmm$  symmetry. Automatic peak search and indexing confirmed a primitive orthorhombic unit cell. Analysis of the data revealed systematic absences consistent with an  $n$ -glide perpendicular to  $a$  and an  $a$ -glide perpendicular to  $c$ . This narrowed the choice of space groups to  $Pnma$  and  $Pn2a$ . As the refinement was successful in  $Pnma$ ,  $Pn2a$  was not considered. Intensities for 2135 reflections were measured ( $+h$ ,  $+k$ ,  $+l$ ,  $0^\circ < 2\theta < 60^\circ$ ). Removal of the systematic absences yielded 1989 unique reflections. The final residuals for 73 variables refined against the 1499 independent reflections for which  $F^2 > 3\sigma(F^2)$  were  $R = 3.7\%$ ,  $R_w = 4.2\%$ , and  $\text{GOF} = 1.382$ . The  $R$  value

TABLE VIII  
SELECTED BOND DISTANCES AND  
ANGLES,  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$

Bi(1)–O(1)	2.13(2)	
–O(2)	2.17(1)	× 2
–O(4)	2.05(1)	× 2
–O(8)	2.05(2)	
		Avg. Distance = 2.10
Bi(2)–O(3)	2.129(1)	× 2
–O(5)	2.04(1)	× 2
–O(7)	2.10(2)	
–O(9)	2.09(1)	
		Avg. Distance = 2.09
Ba(1)–O(1)	2.75(1)	
–O(3)	2.946(1)	× 2
–O(4)	3.19(1)	× 2
–O(5)	2.82(1)	× 2
–O(7)	3.00(2)	
–O(9)	3.016(2)	× 2
Ba(2)–O(1)	2.81(2)	
–O(2)	2.836(1)	× 2
–O(4)	2.89(1)	× 2
–O(5)	2.95(1)	× 2
–O(7)	2.85(2)	
–O(8)	2.997(1)	× 2
Ba(3)–O(3)	2.915(1)	× 2
–O(5)	2.95(1)	× 2
–O(6)	2.74(1)	
–O(7)	2.997(1)	× 2
–O(8)	2.79(2)	
–O(9)	2.76(2)	
Ba(4)–O(1)	3.010(2)	× 2
–O(2)	2.867(1)	× 2
–O(4)	2.77(1)	× 2
–O(6)	2.69(2)	
–O(8)	2.91(2)	
–O(9)	2.55(1)	
Ba(5)–O(1)	3.14(2)	
–O(4)	2.58(1)	× 2
–O(5)	2.81(1)	× 2
–O(6)	3.09(4)	× 2
–O(7)	2.87(2)	
Li(1)–O(5)	1.88(3)	× 2
–O(6)	2.01(4)	
–O(8)	1.86(4)	
O(1)–Bi(1)–O(2)	86.1(3)	× 2
O(1)–Bi(1)–O(4)	93.7(4)	× 2
O(1)–Bi(1)–O(8)	167.9(6)	
O(2)–Bi(1)–O(2)	87.07(3)	
O(2)–Bi(1)–O(4)	89.0(3)	× 2
O(2)–Bi(1)–O(4)	176.1(3)	× 2
O(2)–Bi(1)–O(8)	85.1(3)	× 2
O(4)–Bi(1)–O(4)	94.9(6)	
O(4)–Bi(1)–O(8)	94.5(4)	× 2
O(3)–Bi(2)–O(3)	89.36(3)	
O(3)–Bi(2)–O(5)	90.2(3)	× 2
O(3)–Bi(2)–O(5)	179.4(3)	× 2
O(3)–Bi(2)–O(7)	87.4(3)	× 2
O(3)–Bi(2)–O(9)	85.4(3)	× 2
O(5)–Bi(2)–O(5)	90.2(6)	
O(5)–Bi(2)–O(7)	93.1(4)	× 2
O(5)–Bi(2)–O(9)	94.1(4)	× 2
O(7)–Bi(2)–O(9)	169.8(6)	

TABLE IX  
LATTICE PARAMETERS FOR  $\text{NaSr}_3\text{BiO}_6$ ,  $\text{LiSr}_3\text{BiO}_6$ ,  
AND  $\text{Li}_6\text{RbBiO}_6$

	$\text{NaSr}_3\text{BiO}_6$	$\text{LiSr}_3\text{BiO}_6$	$\text{Li}_6\text{RbBiO}_6$
Structure type	$\text{NaBa}_3\text{BiO}_6$	$\text{NaBa}_3\text{BiO}_6$	$\text{Li}_6\text{KBiO}_6$
$a$ (Å)	6.930(1)	6.872(1)	5.464(1)
$b$ (Å)	—	6.864(2)	—
$c$ (Å)	—	6.872(1)	—
$\alpha$ (°)	92.26(1)	92.31(2)	101.46(1)
$\beta$ (°)	—	92.27(2)	—
$\gamma$ (°)	—	92.29(2)	—
Volume	332.5(2)	323.2(2)	151.8(2)

for all 1989 data was 5.5%. The final refinement cycle converged with a shift/error < 0.03, and the largest peak in the difference Fourier had an absolute value of electron density of 2.82 electrons/Å<sup>3</sup>. Positional parameters are listed in Table VII, and selected bond distances and bond angles are given in Table VIII.

$\text{Li}_6\text{RbBiO}_6$ ,  $\text{NaSr}_3\text{BiO}_6$ , and  $\text{LiSr}_3\text{BiO}_6$ . By analysis of single crystal precession photographs and comparison of the powder X-ray diffraction patterns, it was determined that  $\text{Li}_6\text{RbBiO}_6$  is isostructural with  $\text{Li}_6\text{KBiO}_6$ ,  $\text{NaSr}_3\text{BiO}_6$  is isostructural with  $\text{NaBa}_3\text{BiO}_6$ , and  $\text{LiSr}_3\text{BiO}_6$  has a structure related to  $\text{NaBa}_3\text{BiO}_6$ . Although  $\text{LiSr}_3\text{BiO}_6$  does not have a rhombohedral lattice, we report the lattice parameters in terms of a triclinic unit cell chosen to show that it is a

TABLE X  
SUMMARY OF BISMUTHATES PREPARED IN MOLTEN  
HYDROXIDE MIXTURES

Hydroxide melt	Products formed upon addition of $\text{Bi}_2\text{O}_3$ and:	
	LiOH	NaOH
KOH	$\text{Li}_6\text{KBiO}_6$	$\text{Na}_3\text{BiO}_4$
RbOH	$\text{Li}_6\text{RbBiO}_6$	$\text{Na}_3\text{BiO}_4$
SrOH	$\text{LiSr}_3\text{BiO}_6$	$\text{NaSr}_3\text{BiO}_6$
BaOH	$\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$	$\text{NaBa}_3\text{BiO}_6$

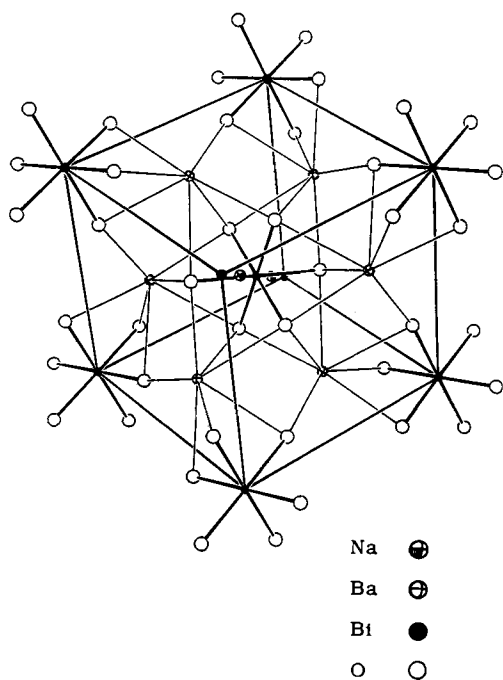


FIG. 1. ORTEP drawing of  $\text{NaBa}_3\text{BiO}_6$  viewed down the three-fold axis, showing 50% probability ellipsoids. The bismuth atoms are located at the origin and center of the unit cell. The sodium atoms are located above and below each bismuth atom and form a  $\text{NaBiO}_6^{6-}$  chain. The barium atoms are located between the  $\text{NaBiO}_6^{6-}$  chains.

distorted version of the unit cell of  $\text{NaBa}_3\text{BiO}_6$ . Lattice parameters for  $\text{NaSr}_3\text{BiO}_6$  and  $\text{LiSr}_3\text{BiO}_6$  were obtained through automatic peak search and indexing on an Enraf-Nonius CAD-4 diffractometer. For  $\text{Li}_6\text{RbBiO}_6$ , the lattice parameters were refined by full profile analysis of the X-ray powder diffraction pattern using the GSAS software package (12). The results are listed in Table IX.

## Results and Discussion

In our search for new Bi(V) materials, we have discovered that lithium bismuthates and sodium bismuthates are precipitated readily from mixtures of molten LiOH or

NaOH with either KOH, RbOH,  $\text{Sr}(\text{OH})_2$ , or  $\text{Ba}(\text{OH})_2$ . Seven different products were obtained from these eight hydroxide mixtures as summarized in Table X. The known material  $\text{Na}_3\text{BiO}_4$  (4) was isolated from NaOH/KOH, NaOH/RbOH, as well as from pure NaOH. In addition,  $\text{Li}_7\text{BiO}_6$  (5) was isolated from LiOH. However, crystals of  $\text{Na}_3\text{BiO}_4$  and  $\text{Li}_7\text{BiO}_6$  suitable for analysis by single crystal X-ray methods have not been obtained. In contrast, the six new quaternary bismuth(V) oxides crystallize as sizeable (up to 0.5 mm) single crystals that are transparent and yellow in color. It appears that the advantage of using mixed metal hydroxides as solvents is that the crystallinity of the products is better. We also note that addition of a third metal hydroxide such as KOH or RbOH (see Table I) often improved the quality of the crystals obtained.

Among the six new bismuthates prepared, there are three new structure types:  $\text{NaBa}_3\text{BiO}_6$ ,  $\text{Li}_6\text{KBiO}_6$ , and  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ . The crystal structures of these three materials are described below.

*NaBa<sub>3</sub>BiO<sub>6</sub>*. A view of the rhombohedral unit cell of  $\text{NaBa}_3\text{BiO}_6$  is shown in Fig. 1. The structure can be described in terms of parallel chains of alternating bismuth and sodium atoms, with the metal atoms connected to each other by three bridging oxygen atoms; an isolated chain is shown in Fig. 2. These  $\text{NaBiO}_6^{6-}$  chains extend along the three-fold axis of the rhombohedral unit cell and are packed in a hexagonal array. The barium atoms are located between these chains.

The bismuth atoms are located at the corners and center of the unit cell. Six oxygen atoms are coordinated in an octahedral array around each bismuth atom at a distance of 2.109(2) Å. The sodium atoms are positioned at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  and  $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$  between the faces of two  $\text{BiO}_6$  octahedra at a distance of 2.485(2) Å from the oxygen atoms. It is unusual that the six oxygen atoms are coor-

minated to the sodium atoms in an array that is approximately trigonal prismatic; trigonal prismatic coordination of sodium is found also in  $\text{Na}_{0.5}\text{CrO}_2$  (13). The trigonal prism is distorted by a twist of  $10.9^\circ$  about the threefold axis. Each oxygen atom bridges one bismuth atom and one sodium atom; in addition, there are four barium atoms in the coordination sphere of each oxygen atom.

The barium atoms are coordinated to eight oxygen atoms from three different  $\text{NaBiO}_6^{6-}$  chains at distances ranging from 2.658(2) to 3.026(2) Å. The geometry can be described best as a distorted polyhedron. Each barium atom is coordinated to three oxygen atoms from the faces of two  $\text{BiO}_6$  octahedra residing in two different chains, and to two oxygen atoms on the edge of a  $\text{NaO}_6$  trigonal prism from a third chain. We note that the eight faces of the  $\text{BiO}_6$  octahedra are capped by six barium atoms and two sodium atoms. The resulting  $\text{Na}_2\text{Ba}_6\text{BiO}_6$  unit is essentially the  $\text{Ba}_3\text{BiO}_6$  perovskite unit with two of the barium atoms replaced by sodium atoms.

The strontium analog,  $\text{NaSr}_3\text{BiO}_6$ , is isostructural with lattice parameters slightly smaller than those obtained for  $\text{NaBa}_3\text{BiO}_6$ . Since the alkali metal is coordinated to six oxygen atoms in a trigonal prismatic array, it is surprising that  $\text{LiSr}_3\text{BiO}_6$  also forms. However,  $\text{LiSr}_3\text{BiO}_6$  has a triclinic unit cell that is a distorted form of the rhombohedral unit cell of  $\text{NaBa}_3\text{BiO}_6$ ; presumably the trigonal prismatic site is too large for lithium. As given in Table IX, two axes of the triclinic cell of  $\text{LiSr}_3\text{BiO}_6$  are 6.872(1) Å, while the third is slightly smaller at 6.864(2) Å. We note that attempts to prepare  $\text{LiBa}_3\text{BiO}_6$  resulted in the formation of  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ .

$\text{Li}_6\text{KBiO}_6$ . A view of the rhombohedral unit cell of  $\text{Li}_6\text{KBiO}_6$  is shown in Fig. 3. The most striking structural feature is an icosahedral array of 12 oxygen atoms surrounding a potassium atom in the center of the cell. The lithium atoms cap twelve faces of the icosahedron around the three-fold

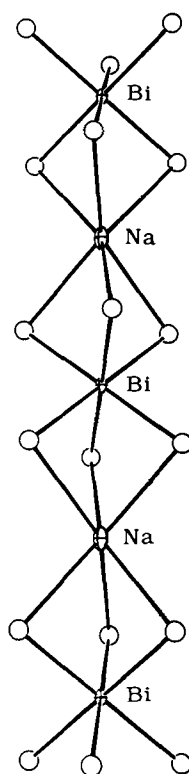


FIG. 2. View of a  $\text{NaBiO}_6^{6-}$  chain in  $\text{NaBa}_3\text{BiO}_6$ .

axis of the rhombohedral unit cell. These  $\text{K}[\text{Li}_{12}\text{O}_{12}]$  units are attached to six others by six of the twelve  $\text{Li}_2\text{O}_2$  faces as shown in Fig. 4. The bismuth atoms cap faces of the icosahedron along the three-fold axis; the three faces adjacent to these two bismuth atoms are not capped.

The bismuth atoms are located at the origin of the unit cell. Six oxygen atoms are coordinated in an octahedral array around each bismuth atom at a distance of 2.115(6) Å. The potassium atoms are located at the center of the unit cell. The twelve K–O distances range from 3.049(9) to 3.087(9) Å. The lithium atoms are coordinated to four oxygen atoms in an array that is approximately tetrahedral with Li–O distances of 1.945(2) and 1.992(1) Å. The oxygen atoms have a coordination number equal to seven;



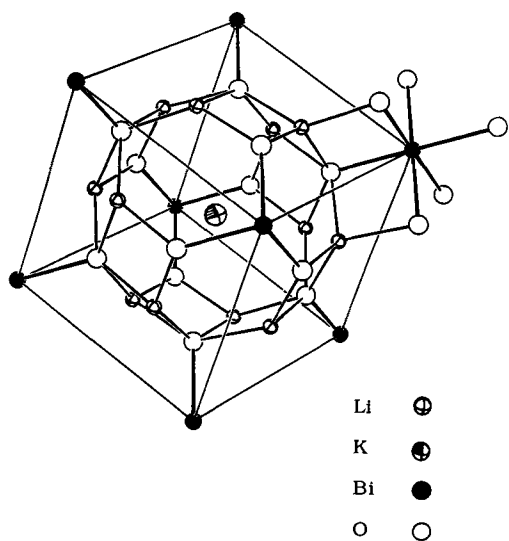


FIG. 3. ORTEP drawing of  $\text{Li}_6\text{KBiO}_6$  viewed down the three-fold axis, showing 50% probability ellipsoids. The bismuth atoms are located at the origin of the unit cell. The potassium atom is located at the center of the unit cell and is surrounded by an icosahedral array of twelve oxygen atoms. Twelve faces of the icosahedron are capped by lithium atoms while the two faces that are located along the three-fold axis are capped by bismuth atoms.

the coordination sphere is comprised of one bismuth atom, two potassium atoms, and four lithium atoms.

An alternative description of the structure of  $\text{Li}_6\text{KBiO}_6$  emphasizes the relationship between the structure of this material and that of  $\text{NaBa}_3\text{BiO}_6$ . Both consist of  $\text{BiO}_6$  octahedra alternating with either Na or K so as to form chains along the three-fold axis of the rhombohedral unit cell. In the case of  $\text{Li}_6\text{KBiO}_6$ , the potassium atoms in the  $\text{KBiO}_6^{6-}$  chains are coordinated to 12 oxygen atoms in an icosahedral array such that the various chains are linked by oxygen atoms. In  $\text{NaBa}_3\text{BiO}_6$ , the sodium atoms in the  $\text{NaBiO}_6^{6-}$  chains are in a trigonal prismatic array of six oxygen atoms such that the chains are not connected by oxygen atoms.

The rubidium analog of  $\text{Li}_6\text{KBiO}_6$  has lattice parameters that are slightly larger, as expected.

$\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ . A view of the orthorhombic unit cell of  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$  is shown in Fig. 5. The most important structural features are the zigzagged chains of corner shared  $\text{BiO}_6$  octahedra which extend parallel to the  $b$  axis. There are two crystallographically distinct chains and two distinct sites for the bismuth atoms in the unit cell, one in each chain. As shown in Fig. 6, the chains can be described in terms of a basic perovskite unit in which eight barium atoms form an array that is approximately a cube; each  $\text{Ba}_8$  cube shares a face with two other cubes. The  $\text{BiO}_6$  octahedra inside each cube are positioned such that the oxygen atoms are on the faces of the cube. These perovskite units are distorted since only seven faces of each  $\text{BiO}_6$

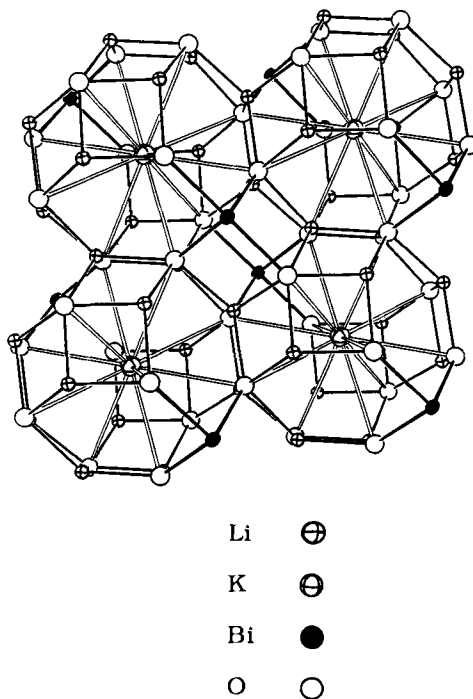


FIG. 4. Packing diagram of four  $\text{KO}_{12}$  icosahedra. Twelve lithium atoms and two bismuth atoms cap fourteen of the twenty faces of each icosahedron.

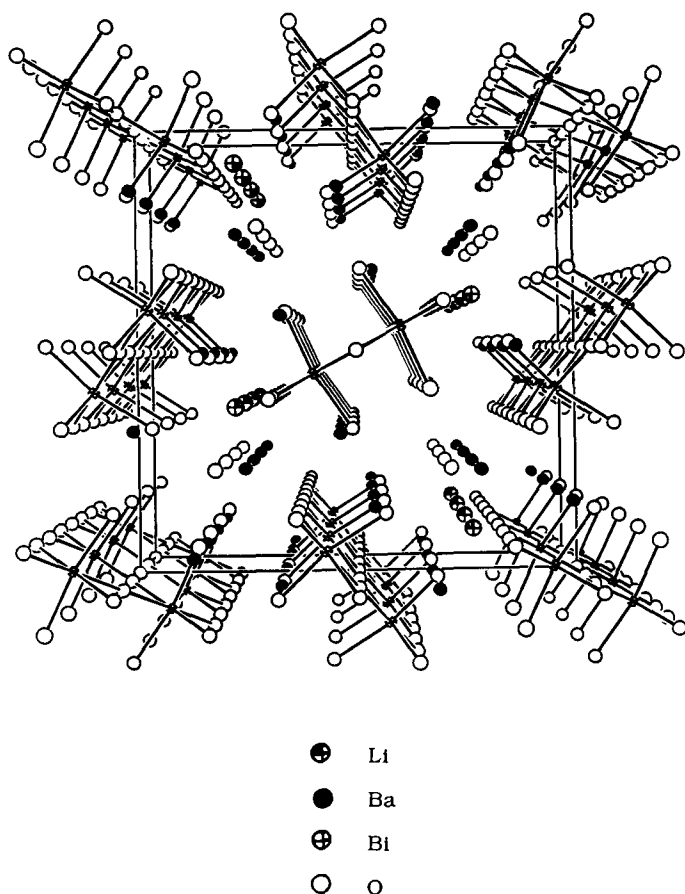


FIG. 5. ORTEP drawing of  $\text{Li}_2\text{Ba}_3\text{Bi}_2\text{O}_{11}$  viewed down the  $b$  axis, showing 50% probability ellipsoids. Four unit cells are shown. Note the chains of corner-shared  $\text{BiO}_6$  octahedra which are parallel to the  $b$  axis.

octahedra are capped by the barium atoms; the remaining barium atom of the Bi(1) perovskite unit shares only one oxygen atom with Bi(1), while the remaining barium atom of the Bi(2) perovskite unit shares two oxygen atoms with Bi(2). The lithium ions plus an additional oxygen atom are located between the perovskite chains.

The octahedral coordination of the oxygen atoms around the bismuth is distorted with Bi–O distances ranging from 2.04(1) to 2.17(1) Å. Ba–O distances range from 2.55(1) to 3.14(2) Å. The lithium atoms are in a site

that is approximately tetrahedral with Li–O distances ranging from 1.86(4) to 2.01(4) Å. Three of the oxygen atoms [O(4), O(6), O(9)] have a coordination number equal to five; the remaining six oxygen atoms have a coordination number equal to six. In addition, one oxygen site [O(9)] in the Bi(2) coordination sphere was found to be only partially occupied (84%, site multiplicity = 0.50).

We believe that we have not found all the lithium atoms. Based on the Li, Ba, Bi, and O stoichiometries determined from the single crystal structure, the stoichiometry of

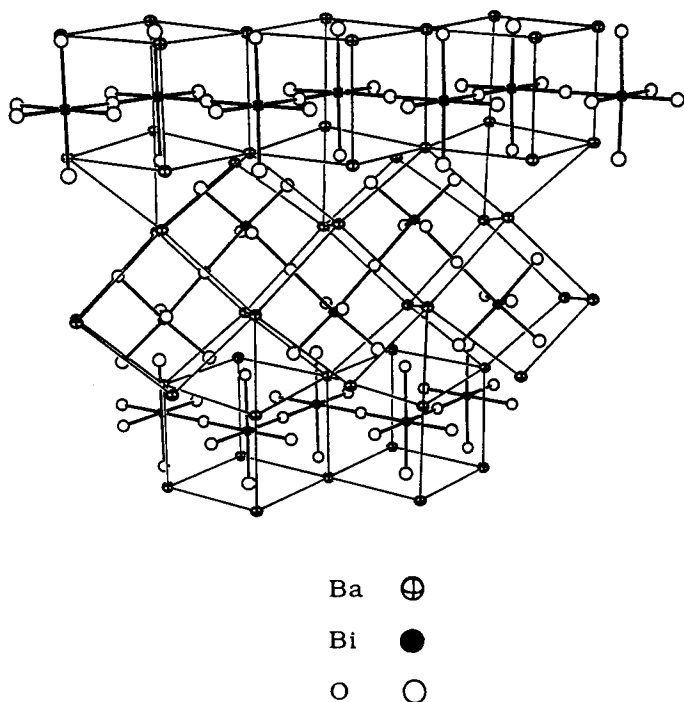


FIG. 6. View of three perovskite chains found in  $\text{Li}_2\text{Ba}_7\text{Bi}_2\text{O}_{11}$ . The perspective is perpendicular to the view in Fig. 5. Heavy lines denote Bi-O bonds, while the remaining lines represent the perovskite  $\text{Ba}_8\text{BiO}_6$  units.

the material is  $\text{LiBa}_5\text{Bi}_2\text{O}_{10.84}$ ; the formal oxidation state of the bismuth would be  $4.32+$ . Since the material is transparent and yellow in color, it is unlikely that the bismuth is reduced. If the bismuth oxidation state is assigned as  $5+$ , then the actual stoichiometry is  $\text{Li}_{1.68}\text{Ba}_5\text{Bi}_2\text{O}_{10.84}$  (weight% Li = 0.90). Elemental analysis for lithium (15) (weight% Li = 0.83) supports this calculated stoichiometry. We attempted to locate the missing lithium site by filling the coordination sphere of O(4), O(6), and O(9). One possible hole (coordination number = 3) was identified at (0.30, 0.25, 0.18). The location of a cation at this site would increase the coordination numbers of O(4) and O(6) to six. However, all attempts to refine this model were unsuccessful. It is hypothesized that the additional 0.68 lithium atoms are randomly positioned in interstitial holes in the lattice.

## Conclusions

Analysis of three new oxides which contain Bi(V) reveals that Bi(V) preferentially coordinates to six oxygen atoms in an octahedral array. A typical Bi(V)-O bond distance was found to be  $2.11 \text{ \AA}$ . These results are consistent with data obtained for other bismuthates such as  $\text{Na}_3\text{BiO}_4$  (5) in which the octahedrally coordinated bismuth has a Bi-O distance of  $2.13 \text{ \AA}$ . It is interesting to note that there is an exception to these observations; in  $\text{Li}_2\text{Ba}_5\text{Bi}_2\text{O}_{11}$ , the  $\text{BiO}_6$  octahedra are distorted, and one  $\text{BiO}_6$  octahedron is missing an oxygen atom 16% of the time.

## Acknowledgments

This work was supported by a Presidential Young Investigator Award from the National Science Founda-

tion (Grant CHE83-51881) to A.M.S. and matching funds from E. I. du Pont de Nemours and Co. V.A.C. thanks the NSF for a graduate student fellowship. A.M.S. thanks the Alfred P. Sloan Foundation and the Camille and the Henry Dreyfus Foundation for their support.

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