

ences in surface and bulk composition. Amorphous and spinel phase oxides in the Cu/Mn and Co/Mn systems have similar specific activities (i.e., activity per unit surface area), the slightly lower specific activity of the spinels possibly being due to a reduction of the oxidation state of the copper and cobalt suggested by EXAFS and XANES. For the CuCoMn oxides, the lower specific activity of the amorphous compared with the spinel oxide may be due to incomplete carbonate decomposition at the low temperature (325 °C) employed. Among the spinels, the CuCoMn spinel possesses much higher specific activity than the others. Direct comparison with the CuMn_2O_4 -spinel, where copper is also in both 1+ and 2+ oxidation states and manganese 3+ and 4+, suggests that the presence of Co^{3+} is responsible for the high activity. This is supported by the high specific activity of the spinel Co_3O_4 , where two-thirds of the cobalt is trivalent, and the comparatively low activity of CoMn_2O_4 , which contains a high proportion of cobalt as 2+ (tetrahedral). The specific activity of Co_3O_4 is around twice that of CuCoMnO_4 and can be explained by Co_3O_4 having, per unit cell, twice as much Co^{3+} as

CuCoMnO_4 . The 3-fold higher surface area of CuCoMnO_4 than Co_3O_4 makes it the most active of the catalysts examined. Manganese 3+/4+ is relatively inactive in the CoMn_2 , CuMn_2 , and MnO_x oxides. The higher activity of the $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ spinel compared to CuMn_2O_4 might be due to a higher proportion of copper being divalent (CuO is more active than the MnO_x oxide).

Of the various mixed metal oxide catalysts examined here for the low-temperature oxidation of CO to CO_2 , the best is undoubtedly the CuCoMnO_4 spinel: its intrinsic activity is high; it also has good thermal stability and may be readily prepared in a high area form.

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Hydrothermal Syntheses and Structural Refinements of Single Crystal LiBGeO_4 and LiBSiO_4

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The low-temperature form of LiBGeO_4 and the new composition LiBSiO_4 have been synthesized as single crystals for the first time by employing a hydrothermal recrystallization technique. They have been studied using single-crystal X-ray diffraction. These compounds possess the cristobalite structure, crystallizing in the tetragonal space group $I\bar{4}$ with $Z = 2$. The absence of a center of symmetry was confirmed by a second harmonic generation test. The cell parameters are $a = 4.5016$ (3), $c = 6.901$ (3) Å for LiBGeO_4 and $a = 4.3792$ (2), $c = 6.7784$ (3) Å for LiBSiO_4 . The lithium atoms are well ordered into sites with approximately tetrahedral geometry.

Introduction

The family of stuffed, ordered cristobalite structures (MABO_4) crystallize in the noncentrosymmetric space group $I\bar{4}$ and have therefore been considered as possible materials for nonlinear optical applications.¹ Lithium borogermanate, LiBGeO_4 , is believed to belong to this class of materials. It melts congruently at about 900 °C, and crystals have been grown by sufficiently slow cooling of the extremely viscous melt. However, differences of opinion persist concerning details of the structure of this material.¹⁻³ Specifically, Ihara² claims the structure is orthorhombic, pseudotetragonal, while more recent publications^{2,3} propose a tetragonal cell, space group $I\bar{4}$. Unfortunately, only twinned crystals have been obtained from slow cooling of the melt, and these are unsuitable for single-crystal diffraction measurements.

In the course of a general survey of the structure-property relationships of members of the cristobalite

family, we have grown crystals of LiBGeO_4 and LiBSiO_4 by hydrothermal techniques. The crystals of LiBGeO_4 were free of the twinning reported previously² and thereby provided an opportunity to accurately determine the crystal structure of this material. Further, for any potential optical applications untwinned single crystals are desirable; the hydrothermal technique provides a means of obtaining such materials.

The composition LiBSiO_4 is novel, and this material is expected to be isostructural with LiBGeO_4 ; the synthesis and structure of LiBSiO_4 are reported for the first time.

Experimental Section

Synthesis and Characterization. Small single crystals of LiBGeO_4 were grown hydrothermally in a sealed gold capsule containing appropriate quantities of preformed LiBGeO_4 powder (12 wt %) and 2 M H_3BO_3 (88 wt %). After the capsule was

*The Center for High Pressure Research: An NSF funded Science and Technology Center.

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Table I. Summary of X-ray Diffraction Data for LiBGeO₄ and LiBSiO₄

	LiBGeO ₄	LiBSiO ₄
color	colorless	
shape, size (mm)	euhedral capped prism, 0.08 × 0.12 × 0.18	anhedral prism, 0.05 × 0.05 × 0.10
crystal system	tetragonal	
space group	<i>I</i> $\bar{4}$ (No. 82)	
<i>a</i> , Å	4.5016 (3)	4.3792 (2)
<i>c</i> , Å	6.901 (3)	6.7784 (3)
temp, °C	20	
vol, Å ³	139.8	130.0
<i>Z</i>	2	
formula wt	154.34	109.84
calcd density, g/cm ³	3.66	2.81
μ (Mo), cm ⁻¹	106.1	6.694
diffractometer	Enraf-Nonius CAD4	Huber
radiation	Mo K α	
data collected	2652	700
min, max 2 θ , deg	6, 70	6, 70
max <i>h</i> , <i>k</i> , <i>l</i>	7 7 11	7 7 10
data octants	+++ , ++- , +-+ , +-+ , --- , -+- , -+- , ---	+++ , +-+
scan method	ω	$\omega/2\theta$
absorption method	analytical	none
transmission factors	0.26–0.45	
unique data (<i>I</i> > 3 σ (<i>I</i>))	295	289
merge <i>R</i>	1.55	1.00
refinement method	full-matrix least squares on <i>F</i>	
anomalous dispersion	Ge	none
weighting scheme	$\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$	
atoms refined	all anisotropic	
parameters varied	17	16
data/parameter ratio	17.35	18.06
<i>R</i>	0.014 (0.045) ^a	0.029 (0.032) ^a
<i>R</i> _w	0.015 (0.051) ^a	0.025 (0.029) ^a
error of fit	0.85 (2.80) ^a	1.60 (1.75) ^a
sec extinction, mm	0.22 (1) × 10 ⁻⁴	

^aNumbers in brackets refer to values for the alternative setting of the noncentrosymmetric structure.

heated to 600 °C at 3000 atm for 6 h, the sample was cooled at 10 °C/h to 300 °C and quenched. Beautiful, euhedral crystals from 0.1 to 0.5 mm were obtained. Optical examination of the crystals under a polarizing microscope showed no evidence of twinning. The crystals were found by the precession method to be tetragonal, with extinction symbol $I\bar{4}$. The photographic work also gave no evidence of twinning.

A DTA experiment on the crystals or preformed powder indicated a weak transition at about 885 °C, just below the melting point. This transition is probably the origin of the twinning observed by Liebertz and Stähr³ in crystals grown from the melt.

For the preparation of LiBSiO₄, 0.205 g of Li₂B₄O₇·H₂O (1 mmol), 0.108 g of SiO₂ (1.8 mmol), and 0.8 g of H₂O were encapsulated in a 1/4 × 3 in. gold tube. The capsule was heated to 750 °C at 2000 atm in a LECO Tempress apparatus for 20 h and then cooled at 10 °C/h to 350 °C. Recovery gave near to a quantitative yield of intergrown octahedra ranging in size from 0.1 to 2 mm. While the majority of the octahedra were multiply twinned, a fragment suitable for the collection of single-crystal diffraction data was cleaved from the clusters.

The second harmonic generation (SHG) properties of powdered LiBGeO₄ and LiBSiO₄ were examined using the technique of Kurtz and Perry.⁴ Both materials had SHG signals greater than 5 times that of quartz, confirming the absence of a center of symmetry in the structure.

Structure Refinement. *LiBGeO₄*. Data were collected on an Enraf-Nonius CAD-4 diffractometer using the experimental parameters given in Table I. The cell parameters reported in Table I were determined from 25 reflections with 6° < θ < 23°. Data were corrected for Lorentz, polarization, and absorption effects.

Structural refinement was initiated in space group *I* $\bar{4}$ with B, Ge, and O atoms close to the ideal positions expected for cristobalite. Refinement of positional and isotropic thermal param-

Table II. Fractional Coordinates and Isotropic Thermal Parameters for LiBGeO₄ and LiBSiO₄

atom	site ^a	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> , Å ²
LiBGeO ₄					
Ge(1)	2 <i>a</i>	0	0	0	0.3
O(1)	8 <i>g</i>	1691 (3)	2856 (2)	1321 (2)	0.5
B(1)	2 <i>c</i>	0	1/2	1/4	0.5
Li(1)	2 <i>d</i>	1/2	1/2	0	1.1
LiBSiO ₄					
Si(1)	2 <i>a</i>	0	0	0	0.3
O(1)	8 <i>g</i>	2699 (2)	1545 (2)	1285 (1)	0.5
B(1)	2 <i>c</i>	0	1/2	3/4	0.3
Li(1)	2 <i>b</i>	1/2	1/2	0	1.3

^aSpace group *I* $\bar{4}$ (No. 82). ^bAll atoms refined with anisotropic thermal parameters; *U*_{equiv} (Å² × 1000) is shown.

Table III. Anisotropic Thermal Parameters^a (Å² × 10³) for Atoms of LiBGeO₄ and LiBSiO₄

atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
LiBGeO ₄						
Ge(1)	4.2 (2)	4.2 (2)	4.5 (2)	0	0	0
O(1)	6.0 (4)	7.0 (4)	7.3 (4)	-0.4 (3)	0.9 (3)	-2.5 (3)
B(1)	5.7 (6)	5.7 (6)	5.9 (10)	0	0	0
Li(1)	11 (1)	11 (1)	20 (2)	0	0	0
LiBSiO ₄						
Si(1)	4.0 (2)	4.0 (2)	4.6 (3)	0	0	0
O(1)	6.6 (4)	5.3 (4)	7.4 (5)	0.0 (3)	-2.0 (3)	-0.4 (3)
B(1)	3.7 (6)	3.7 (6)	3.3 (10)	0	0	0
Li(1)	13 (1)	13 (1)	22 (2)	0	0	0

^aexp[-19.739(*U*₁₁*hha***a**... + 2(*U*₁₂*hka***b**...))].

eters quickly converged to a discrepancy index of 0.045. At this stage a Fourier difference map revealed the position of the Li atom. By employing anisotropic thermal parameters for all atoms, the final discrepancy indices reported in Table I were obtained. Values for the refinement of the structure of the enantiomorph are also given in Table I. Atomic parameters are given in Tables II and III.

LiBSiO₄. Data were collected on an Huber diffractometer using the experimental parameters given in Table I. The cell parameters reported in Table I were determined from 15 reflections with 13° < θ < 20° using an 8-beam centering technique. Data were corrected for Lorentz and polarization effects but not for absorption effects.

The structure of LiBSiO₄ was presumed to be isostructural with that of LiBGeO₄, and the initial refinements were carried out on that basis. However, the alternative setting of the noncentrosymmetric structure was found to give a better fit to the data (Table I) and was used for the final refinements. Anisotropic thermal parameters were employed for all atoms; results are summarized in Tables I–III.

Results and Discussion

Lithium borogermanate and lithium borosilicate, synthesized hydrothermally at 600 and 750 °C, respectively, belong to the family of ordered ABO₄ cristobalite structures¹ and are isostructural. These frameworks are composed of corner-linked BO₄ and GeO₄ or SiO₄ tetrahedra that are in strict alternation (Figures 1 and 2). As with any noncentrosymmetric crystalline material, the odds of mounting one of the two alternative settings for the unit cell are equal. In this study the crystals chosen are of the opposite setting (Table II, Figures 1 and 2).

Observations of low ionic conductivity² for lithium borogermanate are consistent with the position of the lithium ion. It appears tightly bound and lacks any significant disorder in the tetrahedral site (Figures 1 and 2). The thermal parameters for the Li site are larger than those of other cation sites in the BGeO₄ or BSiO₄ framework. This is anticipated for an ion occupying a site slightly larger than the ideal for four-coordinated Li⁺. On the basis

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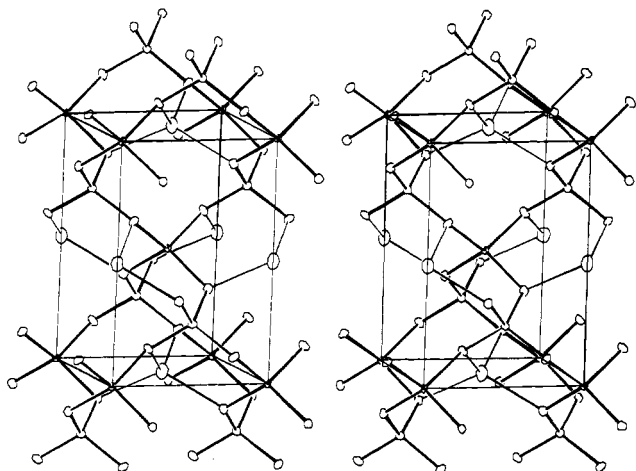


Figure 1. Stereorepresentation of the structure of LiBGeO₄ with atoms shown as 50% probability ellipsoids⁶ (Tables II and III).

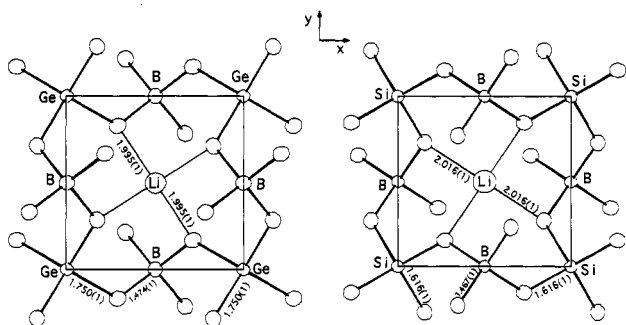


Figure 2. Coordination geometry about Li in LiBGeO₄ and LiBSiO₄ with atoms shown as 90% probability ellipsoids⁶ (Tables II and III).

of accepted ionic radii,⁵ this value is 1.950 Å, compared with the observed 1.995 Å in LiBGeO₄ and 2.016 Å in LiBSiO₄. The larger of the thermal parameters for Li is oriented along the *c* axial direction (Table III, Figures 1 and 2), or toward the more open part of the structure (Figures 1 and 2). The position and thermal parameters found for Li in the lithium borosilicate can be reconciled in a similar manner (Tables III and IV). Although no ionic conductivity data are available for this material, it is expected to be low.

The major differences between the two frameworks are related to the B–O–M (M = Si, Ge) angles. These angles

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for LiBGeO₄ and LiBSiO₄

LiBGeO ₄			
Ge(1)–O(1) × 4	1.750 (1)	B(1)–O(1)–Li(1)	108.73 (6)
O(1)–B(1) × 4	1.474 (1)	O(1)–B(1)–O(1) ^d	107.75 (4)
O(1)–Li(1) × 4	1.995 (1)	O(1)–B(1)–O(1) ^c	112.98 (9)
O(1)–Ge(1)–O(1) ^b	105.73 (4)	O(1)–Li(1)–O(1) ^f	102.04 (2)
O(1)–Ge(1)–O(1) ^a	117.24 (8)	O(1)–Li(1)–O(1) ^e	125.64 (7)
Ge(1)–O(1)–B(1)	122.94 (7)	Ge(1)–O(1)–Li(1)	116.24 (6)
Ge(1)–O(1)–Li(1)	116.24 (6)		
LiBSiO ₄			
Si(1)–O(1) × 4	1.616 (1)	B(1) ^g –O(1)–Li(1)	104.20 (6)
O(1)–B(1) × 4	1.467 (1)	O(1) ^h –B(1)–O(1) ⁱ	108.37 (4)
O(1)–Li(1) × 4	2.016 (1)	O(1) ^h –B(1)–O(1) ^j	111.69 (8)
O(1)–Si(1)–O(1) ^b	106.88 (3)	O(1)–Li(1)–O(1) ^g	100.76 (2)
O(1)–Si(1)–O(1) ^a	114.79 (7)	O(1)–Li(1)–O(1) ^e	128.80 (6)
Si(1)–O(1)–B(1) ^g	127.71 (7)	Si(1)–O(1)–Li(1)	116.54 (5)
Si(1)–O(1)–Li(1)	116.54 (5)		

^a Symmetry Operation Codes: *a*, *x*, *-y*, *z*; *b*, *-y*, *x*, *-z*; *c*, *-x*, *1 - y*, *z*; *d*, $1/2 - y$, $1/2 + x$, $1/2 - z$; *e*, *1 - x*, *1 - y*, *z*; *f*, *1 - y*, *x*, *-z*; *g*, *1 - y*, *x*, *1 - z*; *h*, *-y*, *x*, *1 - z*; *i*, $1/2 - y$, $1/2 + x$, $1/2 - z$; *j*, *y*, *1 - x*, *1 - z*.

increase with a decrease in the M–O distance, as Si replaces Ge in the cristobalite structure. A decrease in the Si–O distance with increasing Si–O–Si angle has been documented in the corner-connected tetrahedral frameworks, adopted by silicate materials; the theoretical basis for the phenomenon has been discussed by Gibbs and co-workers.⁷ As a consequence of this framework flexing, the Li–O bond length in LiBGeO₄ is shorter than in LiBSiO₄.

Conclusion

Single crystals of lithium borogermanate have been grown for the first time. A single-crystal X-ray diffraction study has confirmed that the symmetry for this material is $\bar{1}4$ and that the lithium is located in a tetrahedral site within a cristobalite framework composed of BGeO₄. The silicate analog, LiBSiO₄, has been synthesized for the first time. Its structure is similar to that of LiBGeO₄.

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Supplementary Material Available: Listing of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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