JOURNAL OF SOLID STATE CHEMISTRY 75, 244–250 (1988)

Lanthanide Borogermanates $LnBGeO_5$: Synthesis and Structural Study by X-Ray Diffractometry and Vibrational Spectroscopy

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Received October 19, 1987

$LnBGeO_5$ borogermanates have been synthesized by solid-state reaction and investigated by powder X-ray diffractometry, infrared, and Raman spectroscopy. A hexagonal, stillwellite-like phase is obtained for Ln = La, Pr, and Nd (low-temperature phase). Smaller cations (Nd to Er and Y) lead to a monoclinic phase, $Z = 4$, with $a = 9.80$–10.03, $b = 7.42$–7.60, $c = 4.79$–4.96 Å, and $\beta = 91°14'$–$91°54'$, depending on the ionic radius of the rare earth. For the smallest lanthanides (Tm, Yb, Lu), no monoclinic phase is obtained: $Ln_2Ge_2O_7$ is eventually formed, with a total loss of B_2O_3. The vibrational spectrum of the monoclinic phase points to some analogies with the stillwellite structure, namely a tetrahedral coordination of boron, and an ordered distribution of the BO_4 and GeO_4 tetrahedra. © 1988 Academic Press, Inc.

Introduction

Until now, only two borogermanates have been reported and structurally investigated: $LiBGeO_4$, structurally similar to $BAsO_4$ (*1*, *2*), and the complex compound $Ca_3Er_3Ge_2BO_{13}$ with a sulfohalite-like structure (*3*). All attempts to synthesize borogermanates $M^1BGe_2O_6$ (similar to the pollucite-like borosilicates $M^1BSi_2O_6$) met no success (*4*). Among the number of well-known borosilicates, the lanthanide compounds $LnBSiO_5$ with a stillwellite structure have recently received some attention in connection with the hydrothermal crystallization of a radioactive waste storage glass (*5*).

We have accordingly investigated the possible existence of the corresponding borogermanates.

Experimental

$LnBGeO_5$ borogermanates have been synthesized by solid-state reaction between stoichiometric quantities of Ln_2O_3 (or commercially available oxides such as CeO_2, Tb_4O_7, and Pr_6O_{11}) of 99.9% purity, H_3BO_3, and GeO_2 (analytical purity). Some syntheses were also carried out with a 5 to 10% (mole) excess of H_3BO_3. In addition to compounds with B natural isotopic abundances (labeled ^nB), we used for vibrational studies compounds synthesized with boric acid highly enriched in ^{10}B, purchased from Oak Ridge National Laboratory.

The mixture is well ground and mixed under petroleum ether and progressively heated in covered platinum crucibles up to 850°C. After 1 day at this temperature, the mixture is reground, and the temperature is

0022-4596/88 $3.00

increased by steps of 50°C (up to a maximum of 1100°C) with intervening mixing and grinding.

The progress of the reaction is observed by IR spectroscopy and X-ray diffraction, and the thermal treatment is resumed so long as modifications are observed in the spectra.

The X-ray powder diagrams have been registered with a CGR diffractometer (Co$K\alpha$ monochromatized radiation). The IR spectra have been registered by the conventional pressed disk technique (Beckman 4250 spectrophotometer and KBr disks in the 2000–300 cm^{-1} region; Polytec FIR 30 interferometer and polyethylene disks in the 350–30 cm^{-1} region). The Raman spectra were obtained with a CODERG double monochromator equipped with a Spectra–Physics Ar$^+$ laser (5145 Å green line, 200 mW, spectral slit width of about 1.5 cm^{-1} for most spectra, increased to 3 cm^{-1} for the weak bands).

TABLE I

INDEXED X-RAY POWDER DIAGRAM OF LaBGeO$_5$ AND UNIT CELL PARAMETERS OF HEXAGONAL COMPOUNDS

I	$h\ k\ l$	d_{obs}	d_{calc}
7	1 0 0	6.0590	6.0555
14	1 0 1	4.5463	4.5407
88	1 1 0	3.4995	3.4962
6	1 1 1	3.1149	3.1153
65	2 0 0	3.0278	3.0278
100	1 0 2	2.9849	2.9855
4	2 0 1	2.7703	2.7702
18	1 1 2	2.4488	2.4490
25	2 1 0 0 0 3	2.2880	2.2888 2.2877
26	2 0 2	2.2708	2.2704
18	2 1 1	2.1717	2.1712
2	1 0 3	2.1404	2.1401
3	3 0 0	2.0174	2.0185
3	3 0 1	1.9372	1.9365
68	2 1 2	1.9035	1.9041
17	3 0 2	1.7400	1.7398
22	3 1 0	1.6797	1.6795
12	1 0 4	1.6506	1.6508
12	2 2 2	1.5578	1.5576
5	1 1 4	1.5403	1.5403
5	3 1 2	1.5093	1.5085
6	2 0 4	1.4925	1.4928

Note. LaBGeO$_5$, hexagonal $a = 6.9923(8)$, $c = 6.8631(17)$ Å; $V = 290.60(8)$ Å^3; $F_N = 45.30\ (0.014,25)$; $M_{14} = 75.6$. PrBGeO$_5$, hexagonal $a = 6.9352(11)$, $c = 6.8080(20)$ Å; $V = 283.57(10)$ Å^3; $F_N = 38.70\ (0.014,25)$; $M_{12} = 72.8$. F_N has been calculated for the Co$K\alpha$ radiation, taking into account the extinction rules of the $P3_1$ space group of stillwellite.

Results

X-Ray Diffraction

For Ln = La and Pr, the X-ray powder diagram is very similar to that of stillwellite LaBSiO$_5$ (ASTM cards No. 19-650, 25-1447, 26-349) and is easily indexed by comparison (Table I). The assignment to a stillwellite structure is supported by the very good agreement between observed and calculated d values. The behavior of the Nd$_2$O$_3$–GeO$_2$–B$_2$O$_3$ system is more complicated. In the temperature range just sufficient to start the reaction (850–900°C), both IR and X-ray data point to the formation of a stillwellite phase, but the reaction is too sluggish to go to completion. At the higher temperatures necessary to have a complete reaction, the stillwellite phase disappears and is replaced by a new single phase, which is also obtained directly (without the intermediate formation of a stillwellite) with the smaller cations Sm to Er and Y. However, the reaction, which is easy for Sm, Eu, and Gd, becomes more and more difficult when the ionic radius of the cation decreases, and the compounds with the small cations Ho, Er, and Y could not be obtained completely free from the corresponding pyrogermanate Ln_2Ge$_2$O$_7$, which is formed by the loss of B$_2$O$_3$. This could not be completely avoided by the addition of a small excess of H$_3$BO$_3$.

Finally, no definite borogermanate could be obtained with the smallest cations Tm,

TABLE II

INDEXED X-RAY POWDER DIAGRAM OF $EuBGeO_5$

I	$h\ k\ l$	d_{obs}	d_{calc}
30	1 1 0	6.0136	6.0115
9	2 0 0	5.0013	4.9959
17	$\bar{1}$ 1 1	3.8260	3.8239
30	1 1 1	3.7605	3.7596
30	$\bar{2}$ 0 1	3.5486	3.5443
29	1 2 0	3.5250	3.5215
67	2 0 1	3.4427	3.4437
100	$\bar{2}$ 1 1	3.2083	3.2065
70	2 1 1	3.1331	3.1315
8	3 1 0	3.0459	3.0457
8	2 2 0	3.0033	3.0057
55	0 2 1	2.9816	2.9812
82	$\bar{1}$ 2 1	2.8719	2.8706
67	1 2 1	2.8447	2.8431
37	$\bar{3}$ 1 1	2.6158	2.6157
33	3 1 1	2.5547	2.5546
5	4 0 0	2.4977	2.4980
25	0 0 2	2.4423	2.4427
43	4 1 0	2.3700	2.3708
10	$\bar{1}$ 1 2	2.2749	2.2768
42	2 3 0 $\bar{3}$ 2 1	2.2407	2.2419 2.2410
8	4 0 1	2.1998	2.1986
5	0 2 2	2.0492	2.0489
12	$\bar{1}$ 2 2	2.0167	2.0167
11	1 2 2 $\bar{3}$ 0 2	1.9977	1.9976 1.9974
15	5 1 0 $\bar{4}$ 2 1 $\bar{3}$ 1 2	1.9317	1.9314 1.9314 1.9305
2	$\bar{2}$ 2 2	1.9116	1.9119
14	3 1 2 0 4 0 2 2 2	1.8804	1.8815 1.8815 1.8798
4	$\bar{1}$ 4 0	1.8498	1.8490
6	$\bar{5}$ 1 1	1.8130	1.8135
2	5 1 1	1.7789	1.7793
2	4 3 0	1.7700	1.7701
20	0 4 1	1.7553	1.7558
11	$\bar{4}$ 1 2	1.7244	1.7250
19	$\bar{4}$ 3 1	1.6756	1.6752

Yb, and Lu: we obtained a mixture of unidentified phases which is progressively transformed into $Ln_2Ge_2O_7$ with a total loss of B_2O_3.

The X-ray powder diagram of the new phase (Nd to Er) has been indexed with the help of the Visser program (*6*): all reflections are satisfactorily accounted for by a monoclinic cell (Table II); the refinement of the unit cell parameters was carried out by a least-squares program. The measured density of the Nd compound is 5.40 g · cm^{-3}, against a calculated value of 5.417 g · cm^{-3} for $Z = 4$.

All data are collected in Table III, which also includes the values of M_{20} (*7*) and F_N (*8*), calculated for the Co$K\alpha$ radiation. Most of the parameters exhibit a nearly linear variation with the ionic radius of the rare earth (Fig. 1).

Vibrational Spectra

In view of the complexity of the spectra, we shall restrict the discussion to some essential features.

Hexagonal (*stillwellite*) *phases*. We can point out the following facts:

(i) All the observed frequencies are located below 1100 cm^{-1} (Figs. 2 and 3). The coordination of boron is thus tetrahedral, in agreement with the proposed stillwellite structure of these phases.

(ii) The strong IR bands of the 1000–900

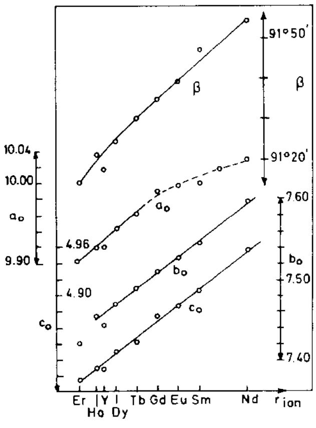

FIG. 1. Relationship between the unit cell parameters and the ionic radius of *Ln* for the monoclinic phases. The ionic radii are those of Shannon (*9*) for an eightfold coordination of *Ln*.

TABLE III

UNIT CELL PARAMETERS OF THE MONOCLINIC PHASES

Ln	a	b	c	β	M_{20}	F_N[a]
Nd	10.0292(28)	7.5957(13)	4.9568(12)	91°53.9′(1.5′)	21.8	18 (0.013, 84)
Sm	10.0032(22)	7.5446(24)	4.9065(11)	91°46.9′(0.7′)	18.4	15.2(0.016,100)
Eu	9.9960(10)	7.5260(14)	4.8874(9)	91°39.0′(0.6′)	26.4	19.4(0.015.126)
Gd	9.9897(20)	7.5103(14)	4.8741(8)	91°34.7′(1′)	18.1	16.2(0.018,111)
Tb	9.9620(20)	7.4903(20)	4.8433(12)	91°30.1′(1′)	26.5	14.5(0.022,105)
Dy	9.9443(14)	7.4698(16)	4.8295(8)	91°24.2′(0.8′)	23.3	20.2(0.017,110)
Ho	9.9204(21)	7.4543(16)	4.8107(10)	91°21.4′(1′)	18.6	16.0(0.02,104)
Er	9.9025(18)	7.4200(13)	4.7943(8)	91°14.3′(1′)	21.9	17.4(0.02,106)
Y	9.9213(15)	7.4431(12)	4.8093(7)	91°17.5′(0.7′)	21.8	20.9(0.015,112)

[a] No extinction rule has been used for calculating F_N; F_N has been calculated for the Co$K\alpha$ radiation.

cm^{-1} exhibit fairly large ^{10}B–^{n}B isotopic shifts (15 to 28 cm^{-1}: Table IV) and are thus predominantly stretching, antisymmetric motions of BO$_4$ tetrahedra. Bands with a similar isotopic behavior are observed at somewhat higher frequencies (between 1040 and 980 cm^{-1}) in the spectrum of the corresponding silicate LaBSiO$_5$ (Fig. 2).

This frequency increase may be due to the smaller unit cell parameters of the silicate, to interactions between BO$_4$ and SiO$_4$ vibrations, or both.

These bands are missing in the Raman spectrum, but even if they are allowed, they are expected to be weak because of their antisymmetric character and of the low polarizability of the BO$_4$ group. Conversely, the strong bands observed in the 900–800 (Ra) and 800–700 (IR) cm^{-1} region exhibit no or small ^{10}B–^{n}B isotopic shifts. Similar bands (by their intensity and their isotopic behavior) are observed at fairly higher frequencies in the spectrum of the silicate. The IR bands are thus assigned to vibrations which are essentially stretching motions of the GeO$_4$ (SiO$_4$) tetrahedra with

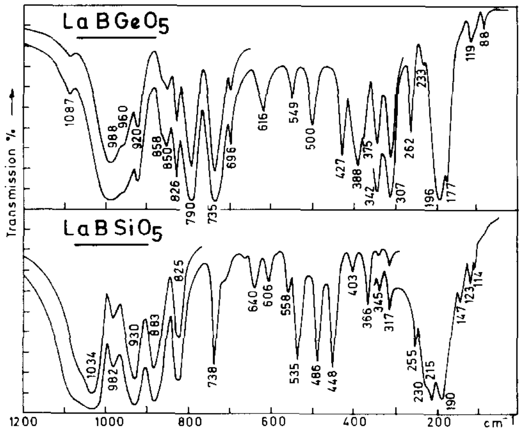

FIG. 2. IR spectra of LaBGeO$_5$ and LaBSiO$_5$.

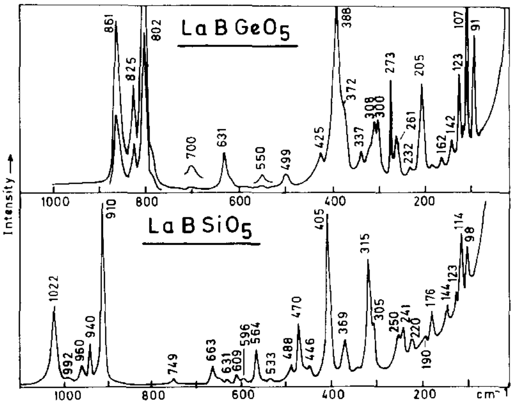

FIG. 3. Raman spectra of LaBGeO$_5$ and LaBSiO$_5$.

TABLE IV

VIBRATIONAL SPECTRUM OF $LaBGeO_5$

Infrared		Raman		Assignments (see text)
$^{10}B^a$	$^{n}B^a$	^{10}B	^{n}B	
1115	1087			ν_3 BO_4
1012	988			
975	960			
935	920			
875	858	863	861	
862	850			
828	826	828	825	Mainly $\nu_3 + \nu_1$ GeO_4 ν_1BO_4
		802	802	
792	790			
738	735			
700	696	703	700	
		632	631	
616	616			
553	549	555	550	
500	500	500	499	
427	427	425	425	
388	388	388	388	
≅375	≅375	≅372	≅372	
342	342			
		337	337	
307	307	308	308	
		300	300	
		273	273	
262	262	261	261	
232	233	232	232	
		205	205	
197	196			
177	177			
		162	162	
		142	142	
		123	123	
120	119			
		108	107	
		92	91	
88	88			

[a] ^{10}B stands for an isotopic composition with 92.4% ^{10}B. ^{n}B is the natural isotopic composition (81.17% ^{11}B).

a small contribution from the BO_4 tetrahedra, as indicated by the small (but quite reproducible) ^{10}B–^{n}B isotopic shifts.

The Raman peaks may be assigned partly to symmetric BO_4 vibrations, or to GeO_4 vibrations.

(iii) Only tentative assignments can be proposed for the lower frequency bands. The stillwellite structure is characterized by the existence of chains of BO_4 tetrahedra (*10*). The weak bands of the 700–500 cm^{-1} region may be assigned to chain vibrations which have a mixed stretching–bending character.

The stronger bands of the 450–300 cm^{-1} region are probably bending vibrations of the GeO_4 tetrahedra. This is supported by the existence of similar bands in the 550–450 cm^{-1} region of the spectrum of the silicate.

The lower frequency bands correspond to lattice modes, but we have been unable to find clear-cut mass effects which would identify the translations of the cation (La or Pr).

(iv) There are some IR–Ra coincidences, in agreement with the lack of a center of symmetry.

Monoclinic phases. We shall consider only those spectral features which can give structural information.

The high-frequency part of the IR spectrum is somewhat similar to that of the stillwellite phase, with a first group of strong bands (the higher frequency ones) characterized by large ^{10}B–^{n}B isotopic shifts, and a second group (800–700 cm^{-1}) with small to negligible isotopic shifts (Table V and Fig. 4). The highest frequency band is located near 1100 cm^{-1}, and it can be immediately inferred that, here also, the coordination of boron is tetrahedral. The sharpness of the bands (particularly striking in the low frequency part of the Raman spectrum) implies an ordered distribution of B and Ge over the tetrahedral sites. Finally, the existence of several IR–Ra coincidences suggests the lack of a center of symmetry (although the possibility of accidental coincidences cannot be totally ignored).

TABLE V

VIBRATIONAL SPECTRUM OF GdBGeO$_5$

Infrared		Raman		Assignments (see text)
^{10}B	^{n}B	^{10}B	^{n}B	
1155	1120			ν_3 BO$_4$
1021	1000			
		974	958	
	950			
943	939			Mainly $\nu_3 + \nu_1$ GeO$_4$ ν_1BO$_4$
		931	930	
		853	853	
806	804			
775	770	762	771	
	760			
694	689			
		675	675	
670	668			
568	567	567	567	
		513	509	
	505			
490	490	438	438	
431	430	426	426	
		404	403	
		393	392	
374	373			
350	350	335	336	
310	310	294	295	
	277	274	275	
			252	
			245	
	236			
	225		225	
			216	
	205		200	
			177	
			166	
	155		155	
			138	
	120		122	
			110	
			97	
			84	

Discussion

Compounds with the Stillwellite Structure

In addition to the mineral itself, which has a more or less complex composition (Ln, Ca)(Si, Al, P)B(O, OH, F)$_5$ (*11*), the stillwellite structure is now represented by four chemical families:

—The borosilicates LnBSiO$_5$ (Ln = La, Ce, Pr, Nd, Sm) obtained by hydrothermal synthesis (*12*).

—The borogermanates LnBGeO$_5$ (Ln = La, Pr, Nd) prepared by solid-state reaction and described in this paper. Since the stillwellite type Nd compound can be obtained only at relatively low temperature, it is reasonable to suppose that this structural family can be extended toward smaller rare earths by hydrothermal synthesis. We intend to carry out research in this direction.

—The borophosphates M^{II}BPO$_5$, with M^{II} = Ca, Sr, Ba (*13*) or Pb (*14*).

—The corresponding boroarsenates M^{II}BAsO$_5$ (*13*, *14*).

In his study of borophosphates and -arsenates (*13*), Bauer did not realize the structural analogy of these compounds with stillwellite and, for some unknown reason, he proposed for the c axis a value which is twice the value observed in the stillwellite family. We have shown (*14*) that this leads systematically to even values of l and that, consequently, the c axis must be halved. In this way, the indexed powder diagram is very similar to that of stillwellite.

So far, the stillwellite structure is re-

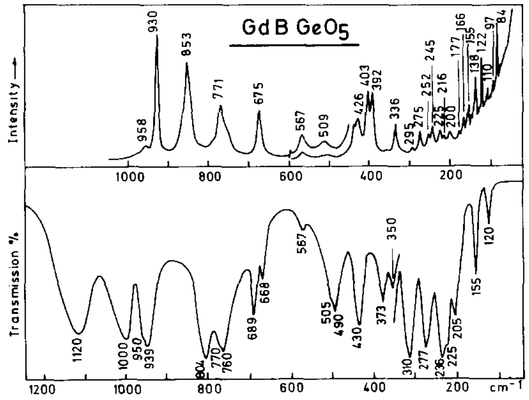

FIG. 4. Raman and IR spectra of GdBGeO$_5$.

stricted to borocompounds in which boron is associated to a high-valency element with a rather small ionic radius (Si, Ge, P, As) and to another element with a large ionic radius and a moderate valency.

The Monoclinic Phase

The detailed structure of this phase is unknown, but the existing structural information is in agreement with solid-state chemistry predictions:

—The fourfold coordination of boron may be related to the presence of the high-valency cation Ge.

—The ordered distribution of the BO_4 and GeO_4 tetrahedra is probably imposed by the large difference between the sizes of the BO_4 and GeO_4 groups, which precludes a statistical distribution of B and Ge over equivalent tetrahedral sites. This is a first confirmation of our prediction that, whenever borogermanates do exist, their structure must be characterized, either by different coordinations of B and Ge, or by an ordered distribution of BO_4 and GeO_4 tetrahedra (*2*). By the way, this prediction is also verified by the structure of the complex borogermanate $Ca_3Er_3Ge_2BO_{13}$ (*3*).

Presently, we do not know to what extent the structure of the monoclinic phase is different from that of stillwellite. The molecular volumes of hexagonal La and $PrBGeO_5$ lead by extrapolation to an approximate value of 93.3 Å^3 for hexagonal $NdBGeO_5$, to be compared with the 94.35 Å^3 figure for the monoclinic phase of the same compound. The fact that both structures exist for the Nd compound with similar values of the molecular volume suggests that the structures are not too different. A chain arrangement of the BO_4 tetrahedra (as in stillwellite) cannot be excluded. The possible existence of the corresponding silicates is still to be investigated. An attempt to synthesize $GdBSiO_5$ by solid-state reaction was unsuccessful, but more systematic work, including the use of hydrothermal reactions, is needed. It is also hoped that hydrothermal reactions, with either silicates or germanates, will provide small crystals suitable for a full structure determination.

Acknowledgments

The authors gratefully acknowledge the financial support of the Fonds National de la Recherche Scientifique.

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