HIGH PRESSURE SYNTHESES OF SmB_2 AND GdB_{12}

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Summary

High pressure, high temperature techniques have been used to synthesize SmB_2 and GdB_{12}. The diboride has a hexagonal AlB_2-type structure and the dodecaboride has a cubic UB_{12}-type structure. Lattice parameters are a = 3.310 Å, c = 4.019 Å and a = 7.524 Å, respectively. Intensity data from X-ray powder diffraction patterns indicate that the Sm atom in SmB_2 is flattened in the direction of the crystallographic c axis.

Introduction

Borides of composition LnB_2 and LnB_{12} have been reported [1, 2] for the smaller members of the lanthanide series. Diborides have been prepared [3 - 10] for Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc; dodecaborides are known [5, 6, 11 - 16] for Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc. The diborides are isomorphous and have the AlB_2-type (C32) structure. This structure is hexagonal (*P*6/*mmm*) and consists of alternating layers of metal atoms and boron atoms. The metal atoms form close-packed (3^6) layers and the boron atoms form hexagonal (6^3) layers. The layers are arranged in such a way that the boron atoms are positioned over the faces of the triangles formed by the metal atoms. The dodecaborides (except ScB_{12}) each assume the UB_{12}-type ($D2_f$) structure. This structure is cubic (*Fm*3*m*) with metal atoms at f.c.c. positions, and each metal atom is surrounded by a B_{24} cubo-octahedron. The tetragonal structure of ScB_{12} is described by Matkovich *et al*. [16].

Reported attempts to prepare diborides and dodecaborides of the larger lanthanide elements have not been successful [2, 17, 18], apparently because of the increased sizes of the metal atoms, Since the compressibilities of the lanthanides are greater than that of boron, an increase in pressure would tend to make the larger lanthanides behave more like the smaller ones. If the effect of metal atom size is important in the formation of diborides and dodecaborides, then the application of high pressure and temperature to appropriate reaction mixtures should make it possible to extend these boride series to some of the larger lanthanides.

Experimental

The tetrahedral-anvil high pressure device designed by Hall [21, 22] was used for the high pressure synthesis experiments. Stoichiometric mixtures of the elements were exposed to high pressure, high temperature conditions in a BN crucible surrounded by a graphite heater. Details of pressure cell construction and pressure/temperature calibration procedures may be found in earlier publications [23, 24].

Boron was obtained as a -325 mesh powder of reported 99.5% purity from Research Organic/Inorganic Chemical Corporation. The lanthanides used in this work were obtained as ingots of reported 99.9% purity (metals only) from Research Organic/Inorganic Chemical Corporation and from Research Chemicals Inc. These ingots were filed in the open atmosphere and those filings that passed through a 100 mesh sieve were used. There may have been some oxide formation during filing of these ingots, but no oxide was visible and lines characteristic of lanthanide oxides were not observed in any of the X-ray diffraction patterns.

The product of each high pressure experiment was crushed, loaded into a 0.5 mm capillary and exposed to Ni-filtered Cu X-radiation ($\lambda(K_\alpha) = 1.54178$ Å and $\lambda(K_{\alpha1}) = 1.54051$ Å) on a G.E. XRD-5 powder diffraction unit. A Debye-Scherrer camera 143.2 mm in diameter was used and the sample was rotated during exposure. The Nelson-Riley [25] extrapolation procedure was used to correct for absorption. A cubic internal standard (SmN) was used with the SmB_2 samples. Lattice parameters of the hexagonal materials were determined by a least squares refinement [26] after the absorption correction had been applied. The computer program POWDER [27] was used to calculate X-ray line intensities expected for the structure types encountered in this study. Observed X-ray line intensities were estimated visually without reference to a calibration strip.

Results

Lattice parameters for new compounds and for compounds prepared for comparison with the literature are found in Table 1. X-ray data for the new compounds are found in Tables 2 and 3. Results for each of the systems examined are as follows.

Nd + 12B

Experiments made at 65 kbar and 2100°C resulted only in the preparation of NdB_6.

TABLE 1

Crystallographic data

Compound	Crystal system	*a* (Å)	*c* (Å)	Reference
GdB_{12}	Cubic	7.524(1)[a]		This work
TbB_{12}	Cubic	7.509(1)		This work
		7.505		4
		7.504(1)		15
SmB_2	Hexagonal	3.310(1)	4.019(1)	This work
GdB_2	Hexagonal	3.315(3)	3.936(3)	This work
		3.318	3.933	2, 10, 19
		3.31	3.94	4
HoB_2	Hexagonal	3.279(2)	3.811(2)	This work
		3.17[b]	3.81	4
		3.281	3.811	8
		3.273	3.814	10
TmB_2	Hexagonal	3.258(3)	3.745(3)	This work
		3.250	3.739	8
		3.261	3.755	10

[a] Numbers in parentheses are standard deviations in the last significant figure.

[b] This is almost certainly a misprint. The intended value is probably 3.27 Å

Sm + 12B

The only identifiable phase obtained in experiments at 65 and 70 kbar was SmB_6. At 70 kbar and temperatures of 2100°C and 2700°C a minor phase that could not be identified was also obtained.

Gd + 12B

At 2100°C and pressures above 60 kbar, pure[*] GdB_{12} was obtained. Between 33 and 60 kbar, mixtures of GdB_{12} and GdB_6 were obtained. Below 33 kbar, GdB_{12} was not found. A comparison of line intensities observed in the X-ray diffraction pattern of GdB_{12} with those calculated assuming a UB_{12}-type structure (see Table 2) shows that the UB_{12}-type structure is consistent with the observed intensities. The calculated intensities were corrected for temperature (B = 1.0 and 1.5 for Gd and boron, respectively) and absorption ($\mu R = 54$). The variable boron position parameter was assumed to be 0.166.

Tb + 12B

The dodecaboride was prepared at 65 kbar and 1650°C.

TABLE 2
X-ray data for GdB_{12}

hkl	------------d (Å)------------		-----------Intensity----------	
	calc.	obs.	obs.	calc.[a]
1 1 1	4.344	4.313	40	31
2 0 0	3.762	3.740	30	33
2 2 0	2.660	2.642	30	33
3 1 1	2.269	2.260	100	100
2 2 2	2.172	2.161	25	31
4 0 0	1.881	1.871	10	14
3 3 1	1.726	1.721	50	48
4 2 0	1.683	1.679	30	34
4 2 2	1.536	1,533	50	46
3 3 3	1.448	1.444	25	3
5 1 1	1.448			25
4 4 0	1.330	1.329	5	10
5 3 1	1.272	1.269	6.0	57
6 0 0	1.254	1.252	40	12
4 4 2	1.254			28
6 2 0	1.1897	1.1877	15	20
5 3 3	1.1475	1.1461	20	18
6 2 2	1.1343	1.1331	10	14
4 4 4	1.0861	1.0871	5	7
5 5 1	1.0536	1.0537	20	12
7 1 1	1.0536			12
6 4 0	1.0434	1.0419	10	15
6 4 2	1.0055	1.0046	25	22
7 3 1	0.9796	0.9789	80	35
5 5 3	0.9796			17
8 0 0	0.9405	N.O.	N.O.	4
7 3 3	0.9193	0.9190	10	14
8 2 0	0.9125	0.9126	20	11
6 4 4	0.9125			11
8 2 2	0.8868	0.8865	70	18
6 6 0	0.8868			15
7 5 1	0.8688	0.8685	30	24
5 5 5	0.8688			4
6 6 2	0.8631	0.8630	8	15
8 4 0	0.8413	0.8415	5	13
7 5 3	0.8259	0.8259	90	45
9 1 1	0.8259			23
8 4 2	0.8210	0.8210	80	46
6 6 4	0.8021	0.8023	10	23
9 3 1	0.7888	0.7888	70	60

[a] Corrected for temperature (*B* = 1.0 for Gd and 1.5 for boron) and for absorption ($\mu R = 54$).

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[*] Pure in this context means that all lines in the X-ray diffraction pattern were attributable to GdB_{12}.

TABLE 3
X-ray data for SmB_2

hkl	-----------d (Å)-----------		------------------Intensity---------------------		
	calc.	obs.	obs	calc.[a]	calc.[b]
0 0 1	4.020	3.991	50	19	20
1 0 0	2.867	2.872	50	52	47
1 0 1	2.334	2.332	100	100	100
0 0 2	2.010	2.007	40	14	18
1 1 0	1.655	1.652	20[c]	28	26
1 0 2	1.646	1.645	50[c]	43	55
1 1 1	1.531	1.530	20	32	31
2 0 0	1.434	1.435	5	15	13
2 0 1	1.350	1.350	15	30	30
0 0 3	1.340	1.339	5	4	8
1 1 2	1.278	1.277	40	28	36
1 0 3	1.214	1.213	80	22	44
2 0 2	1.1671	1.1667	10	16	21
2 1 0	1.0837	1.0836	8	13	11
2 1 1	1.0463	1.0458	25	29	29
1 1 3	1.0415	1.0421	25	11	22
0 0 4	1.0050	1.0042	6	2	9
2 0 3	0.9789	0.9777	25	13	26
3 0 0	0.9557	N.O.	N.O.	7	7
9 1 2	0.9539	0.9538	25	20	26
1 0 4	0.9484	0.9481	30	10	41
3 0 1	0.9298	0.9294	5	9	8
3 0 2	0.8631	0.8628	10	13	19
1 1 4	0.8591	0.8589	40	13	53
2 1 3	0.8426	0.8428	40	25	56
2 2 0	0.8277	0.8278	5	7	8
2 0 4	0.8229	0.8228	35	11	48
2 2 1	0.8107	0.8112	5	11	10
0 0 5	0.8040	0.8043	5	2	21
3 1 0	0.7952	0.7946	5	15	13
3 1 1	0.7801	0.7803	50	54	65
3 0 3	0.7781	0.7783	50	23	48
1 0 5	0.7742	0.7741	60	42	412

[a] Corrected for absorption ($\mu R = 130$) and for temperature using isotropic temperature factors with B = 1.5.

[b] Corrected for absorption ($\mu R = 130$) and for temperature using anisotropic temperature factors for Sm with $\beta_{11} = 0.10$ and $\beta_{33} = 0.005$ and an isotropic temperature factor for boron with B = 1.5.

[c] Uncertain estimates because of mutual interference.

Ln + 2B for Ln = Gd, Ho and Tm

The diborides of these lanthanides were prepared at 60 - 70 kbar and 1240 - 1780°C. The lattice parameters obtained in this work compare favorably with those reported in the literature (see Table 1). Absorption corrections were not made on the X-ray data of these compounds.

Sm + 2B

It was found that SmB_2 could be prepared at 65 kbar and 1140 - 1240°. The best material prepared gave only a fair X-ray diffraction pattern; high angle lines were fuzzy and had poorly resolved $K_{\alpha1}$ - $K_{\alpha2}$ doublets. Extraneous lines were identified with SmN, which was apparently obtained by reaction with the BN crucible. The data shown in Table 3 were taken from the X-ray diffraction pattern of material prepared at 65 kbar and 1240°C for 75 min.

Initially there was some doubt as to whether SmB_2 had been obtained. Positions of the lines in the X-ray diffraction pattern were consistent with an AlB_2-type material and the hexagonal lattice parameters were about what one would expect for SmB_2, but the observed line intensities did not all agree with those calculated on the assumption that SmB_2 has an AlB_2-type structure. In drawing this conclusion, only adjacent lines were compared with one another. This was made necessary by the crude means used to determine observed line intensities. However, even with this limited method of comparison it was apparent that the observed intensities of the 103, 113, 104, 114 and 204 lines were greater than calculations indicated they should be.

Comparisons with our data for other diborides showed the same intensity deviations for GdB_2 but not for HoB_2 nor TmB_2. Among sets of published X-ray data we found similar deviations for ErB_2 and TmB_2 [7] and for GdB_2 [19] but none for LuB_2 [5]. The literature data for ErB_2 and TmB_2 were taken from Gandolfi-type X-ray diffraction patterns of single crystal platelets, so the intensity deviations in this case may have been due to lack of completely random crystal orientation. Literature data on GdB_2 were obtained from a diffractometer and precautions were taken to ensure that crystallite orientations were random [20]. To ensure that our intensity deviations were not caused by preferred orientation, crushed samples of SmB_2 and GdB_2 were dispersed in corn starch and the X-ray diffraction patterns were redetermined. No significant changes in the relative intensities were observed.

Attempts at reconciliation were made by calculating new intensity sets for structures which differed slightly from the AlB_2-type, but which retained the same hexagonal cell size. This was done by shifting the positions of the boron atoms. However, the boron atoms provide so little X-ray scattering power compared with the metal atom that relative line intensities were changed very little by this approach.

Finally, new intensity calculations were made in which the Sm atom was distorted from a sphere to a prolate spheroid, with the long axis of the spheroid parallel to the crystallographic *c* axis. This followed a recent suggestion in the literature [10] that the larger lanthanide atoms have such a distortion in LnB_2 compounds because of the rigidity of the boron hexagonal net. Such an hypothesis appeared, reasonable in view of the fact that the c/a ratio for these compounds increases as the size of the lanthanide atom increases. The symmetry of the Sm atom was altered via the anisotropic temperature factors. It resulted in changes that were exactly opposite to those desired. Consequently new calculations were made in which the Sm atom was flattened at the poles like an oblate spheroid. These calculations gave intensities that were in good agreement with those observed (see Table 3).

It is difficult to understand why the hexagonal cell *c* axis increases when the metal atom is extended along the *a* and *b* axes and shortened in the direction of the *c* axis. This would seem to indicate considerable weakening of the metal-boron bond and perhaps a strengthening of the metal-metal bonds. This may account for the unexpectedly short a axis of the SmB_2 unit cell (the a axis for SmB_2 is actually shorter than for GdB_2).

A few attempts were made to grow single crystals of SmB_2 by slow-cooling the reaction mixture at high pressure. Unfortunately the hoped-for single crystals did not materialize. If single crystal X-ray intensity data could be collected, a much more detailed determination of the departure of the metal atom from spherical symmetry could be made. It would be interesting to see what such data on SmB_2, GdB_2 and TbB_2 would reveal.

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