

HIGH-PRESSURE SYNTHESIS OF LANTHANIDE/ BORON AND ACTINIDE/BORON COMPOUNDS

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INTRODUCTION

Considerable work has been done on metal borides because of their interesting properties and crystal structures. Among the lanthanides and actinides, borides of general formulas MB_2 , M_2B_5 , MB_4 , MB_6 , MB_{12} and MB_{66} are formed (M = lanthanide and/or actinide) (1). The MB_2 , MB_6 , MB_{12} and MB_{66} phases are investigated in this study because their existence seems to depend on the metal atom size. The di-, dodeca- and heptaborides are known only for the smaller lanthanides and actinides and the hexaborides are known only for the larger members of each series.

There are quite a number of other compound types that appear to be size dependent and which are known to form with only part of the lanthanide elements. Our past experience has shown that more of the lanthanide elements can be made to form these compound types through high pressure synthesis if one of two conditions is met. If the compound type is known only for the smaller lanthanides, then the series may be extended by high pressure synthesis if the lanthanide element is more compressible than the non-lanthanide element. If the compound type is known only for the larger lanthanides, then high pressure synthesis may be used to extend the series if the lanthanide element is less compressible than the non-lanthanide element. The former condition is satisfied, for the MB_2 , MB_{12} and MB_{66} compound types but neither condition is satisfied for the MB_6 compound type.

EXPERIMENTAL

The tetrahedral-anvil high-pressure device designed by Hall (2) 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 the literature (3).

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 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. Thorium of 99.9% purity (metals only) in powder form was purchased from Alfa Division of Ventron Corporation.

The product of each high-pressure experiment was crushed, loaded into a 0.5 mm capillary and exposed to Ni-filtered Cu X-radiation on a G.E. XRD-5 powder diffraction unit. A Debye-Scherrer camera with 143.2 mm diameter was used, and the sample was rotated during exposure. The Nelson-Riley (4) 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 (5) after the absorption correction had been applied. The computer program POWDER (6) 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.

Table 1: X-ray Data for SmB₂

hkl	d (Å)		Intensity		cal.#
	cal.	obs.	obs.	cal.*	
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†	28	26
1 0 2	1.646	1.645	50†	43	55
1 1 1	1.531	1.530	20	32	31
2 0 0	1.434	1.435	5	15	13
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	.9789	.9777	25	16	26
3 0 0	.9557	N.O.	N.O.	7	7
2 1 2	.9839	.9538	25	20	26
1 0 4	.9484	.9481	30	10	41
3 0 1	.9298	.9294	5	9	8
3 0 2	.8631	.8628	10	13	19
1 1 4	.8591	.8589	40	13	53
2 1 3	.8426	.8428	40	25	56
2 2 0	.8277	.8278	5	7	8
2 0 4	.8229	.8228	35	11	48
2 2 1	.8107	.8112	5	11	10
0 0 5	.8040	.8043	5	2	21
3 1 0	.7952	.7946	5	15	13
3 1 1	.7801	.7803	50	23	48
3 0 3	.7781	.7783	50	23	48
1 0 5	.7742	.7741	60	42	412

* Corrected for absorption ($\mu_R=130$) and for temperature using isotropic temperature factors with $B= 1.5$,

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 isotropic temperature factor for boron with $B= 1.5$.

† Uncertain estimates because of mutual interference.

RESULTS AND DISCUSSION

The HB_2 compounds crystallize in the hexagonal AlB_2 -type structure. The metal atoms form close-packed layers and the boron atoms form hexagonal layers. The layers of metal atoms are stacked AA... and the boron atoms occupy the vacancies created by the AA... stacking sequence.

Attempts were made to synthesize SmB_2 , NdB_2 and ThB_2 . The former compound was successfully prepared at 65 kbar and 1140- 1240°C. whereas the latter two compounds could not be made. All SmB_2 preparations were accompanied by SmN , apparently obtained by reaction with the BN crucible. Table I contains X-ray diffraction data obtained from an experiment conducted for 75 minutes at 65 kbar and 1240°C; lattice parameters obtained from these X-ray data are $a = 3.310(1)$ and $c = 4.019(1)$ (numbers in parentheses represent the standard deviation in the last significant figure).

Initially there was some question whether SmB_2 had been obtained because the observed X-ray line intensities did not agree with those calculated assuming an AlB_2 -type structure. This problem was finally resolved by recalculating the line intensities using anisotropic temperature factors for the Sm atom. If the Sm atom is flattened along the crystallographic c -axis, then the calculated X-ray line intensities compare well with those observed. Intensity data requiring a non-spherical metal atom was also obtained for GdB_2 but not for HoB_2 , TmB_2 or LuB_2 (see also references 7 and 8). Lattice parameters determined for these latter four compounds compare favorably with those found in the literature.

The hexaborides crystallize in the cubic CaB_6 - type structure. The smallest hexaboride that could be synthesized at high pressure was GdB_6 . It is virtually impossible to prove that TbB_6 and, other hexaborides of smaller lanthanides cannot be prepared at high pressures. It will have to suffice to say that GdB_6 and other hexaborides of the larger lanthanides formed rapidly and often (a common contaminate of MB_{12} syntheses was MB_6) at high pressures, but that repeated efforts to prepare TbB_6 at high pressure under the most favorable conditions, consistently failed. In all, seven attempts were made to prepare TbB_6 at high pressure; the most common result was a mixture of TbB_4 and TbB_{12} . This indicates that the application of high pressure retards the formation of lanthanide hexaborides. This is consistent with the reverse application of the necessary condition for successful high pressure synthesis mentioned in the introduction.

The MB_{12} compounds generally crystallize in the cubic UB_{12} -type structure. Attempts to prepare SmB_{12} , GdB_{12} and ThB_{12} resulted in the preparation of the latter two only. Gadolinium dodecaboride was prepared at pressures above 33 kbar. Between 33 and 60 kbar, GdB_6 was also present, but above 60 kbar GdB_{12} was the only observable product. All experiments involving ThB_{12} were conducted at 65 kbar. The hexaboride was present in every case, but interestingly the hexaboride concentrated at the ends of the reaction chamber, leaving uncontaminated ThB_{12} in the center. X-ray powder diffraction data (see Table 2) for both GdB_{12} and ThB_{12} are consistent with the UB_{12} -type structure. Lattice parameters are $7.524(1)$ Å and $7.611(1)$ Å, respectively.

The heptaborides have the relatively complicated Cubic crystal structure described by Richards and Kasper (9). Our high pressure experiments yielded only poorly crystallized material. X-ray powder patterns had relatively broad, ill-defined lines that faded out in the high-angle region. At 65 kbar and about 2100°C SmB_{66} with lattice parameter $23.52(3)$ Å was obtained. This lattice parameter compares fairly well with literature values (10,11). Attempts to prepare PrB_{66} and NdB_{66} under the same conditions that were successful with Sm_{66} resulted only in mixtures of the hexaboride and unknown substances. The heptaboride series was therefore not extended by application of high pressure.

Table 2: X-ray Data for GdB₁₂ and ThB₁₂

hkl	GdB ₁₂				ThB ₁₂			
	d (Å)		Intensity		d (Å)		Intensity	
	cal.	obs.	obs.	cal.	cal.	obs.	obs.	cal.
1 1 1	4.344	4.313	40	31	4.394	4.394	50	35
2 0 0	3.762	3.740	30	33	3.805	3.808	45	33
2 2 0	2.660	2.642	30	33	2.691	2.690	35	39
3 1 1	2.269	2.260	100	100	2.29S	2.294	100	100
2 2 2	2.172	2.161	25	31	2.197	2.197	30	31
4 0 0	1.881	1.871	10	14	1.902	1.901	20	15
3 3 1	1.726	1.721	50	48	1.746	1.746	40	53
4 2 0	1.683	1.679	30	34	1.702	1.702	35	42
4 2 2	1.536	1.533	50	46	1.554	1.553	40	49
3 3 3, 5 1 1	1.448	1.444	25	28	1.465	1.466	35	36
4 4 0	1.330	1.329	5	10	1.345	1.345	15	12
5 3 1	1.272	1.269	60	57	1.286	1.286	50	60
6 0 0, 4 4 2	1.254	1.252	40	40	1.269	1.269	40	40
6 2 0	1.1897	1.1877	15	20	1.2034	1.2038	25	22
5 3 3	1.1475	1.1461	20	18	1.1606	1.1530	25	20
6 2 2	1.1343	1.1331	10	14	1.1474	1.1472	20	16
4 4 4	1.0861	1.0871	5	7	1.0985	1.0985	10	7
5 5 1, 7 1 1	1.0536	1.0537	20	24	1.06S7	1.065S	35	28
6 4 0	1.0434	1.0419	10	15	1.0554	1.0551	20	16
6 4 2	1.0055	1.0046	25	22	1.0170	1.0171	30	26
7 3 1, 5 5 3	.9796	.9789	80	52	.9908	.9910	60	51
8 0 0	.9405	N.O.	N.O.	4	.9513	.9514	2	4
7 3 3	.9193	.9190	10	14	.9298	.9298	20	14
8 2 0, 6 4 4	.9125	.9126	20	22	.9229	.9230	30	24
8 2 2, 6 6 0	.8868	.8865	70	33	.8969	.8971	35	28
7 5 1, 5 5 5	.8688	.8685	30	28	.8788	.8789	35	29
6 6 2	.8631	.8630	8	15	.8730	.8731	25	15
8 4 0	.8413	.841S	5	13	.8509	.8511	20	13
7 5 3, 9 1 1	.8259	.8259	90	68	.8354	.8355	90	57
8 4 2	.8210	.8210	80	46	..8304	.8305	70	39
6 6 4	.8021	.8023	10	23	.8115	.8114	30	19
9 3 1	.7888	.7888	70	60	.7978	.7979	75	46
8 4 4					.7768	.7768	60	51

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