

## The Crystal Structure of PrBN<sub>2</sub> and Isotypic Compounds REBN<sub>2</sub> (RE = Nd, Sm, Gd)

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New compounds REBN<sub>2</sub> have been synthesized by direct sintering of mixtures of hex-BN and the rare earth metal under nitrogen at 1800°C. The crystal structure of PrBN<sub>2</sub> has been determined from single crystal X-ray counter data. PrBN<sub>2</sub> crystallizes in a unique structure type with the noncentrosymmetric rhombohedral space group  $R\bar{3}c - C_{3v}^6$ , No. 161. The hexagonal lattice parameters are  $a = 1.21144(13)$  nm and  $c = 0.70126(15)$  nm;  $Z = 18$ . For 388 reflections ( $|F_0| > 3\sigma$ ) the residual values are  $R = \Sigma|\Delta F|/\Sigma|F_0| = 0.038$ ,  $R_w = 0.028$ . The structure type of PrBN<sub>2</sub> is a combination of the typical net-type structural units B<sub>3</sub>N(1)<sub>3</sub> of hex-BN and of irregular bipyramidal units [Pr<sub>3</sub>B] centered by the N(2) nitrogen atoms. In accordance with the typical arrangement of B and N atoms in hex-BN, there are no direct B–B or N–N contacts in PrBN<sub>2</sub>. With respect to the structural chemical building blocks, the crystal structure of PrBN<sub>2</sub> is intermediate between the hexagonal BN type and structure types such as Pr<sub>3</sub>B<sub>2</sub>N<sub>4</sub>. Isotypic compounds REBN<sub>2</sub> were synthesized with the early rare earth metals Nd, Sm, and Gd. GdBN<sub>2</sub> was only observed at temperatures above 1400°C. No REBN<sub>2</sub> phase was found with the smaller rare earth members Tb → Lu, Sc, and yttrium. © 1992 Academic Press, Inc.

### 1. Introduction

In an attempt to study the phase relations and crystal chemistry of ternary rare earth boron nitrides (1–3), we have investigated the crystal structure of the novel ternary compounds REBN<sub>2</sub>, where RE is one of the early rare earth elements Pr, Nd, Sm, and Gd. Gaudè (4) claimed the existence of two isotypic compounds, NdBN<sub>2</sub> and SmBN<sub>2</sub>, whose X-ray powder diffraction patterns he tentatively indexed on the basis of a monoclinic cell with  $a = 0.6950(3)$ ,  $b = 1.2077(4)$ , and  $c = 0.5856(2)$  nm and  $\beta = 99^\circ 32'$ .  $P2_1$ ,  $P2_1/m$ , or  $P2_1/c$  were assigned as the possible space group types and a structural resemblance with the structure type of KFeS<sub>2</sub>

(space group  $C2/c$ ) was suggested (4). The X-ray powder pattern presented by (4), however, did not show a convincing similarity with that expected for the KFeS<sub>2</sub> type, rather suggesting the existence of a novel structure type.

### 2. Experimental

Alloys with a nominal composition REBN, each weighting ca. 1 g, were prepared by reacting compacts of hex-BN powder (99%, Alfa Ventron, Karlsruhe, FRG, which prior to use was outgassed in vacuum at 1500°C) and filings of the rare earth metals (freshly prepared in an argon-filled glove box from 3 N pure metal ingots supplied by

Auer Remy, Hamburg, FRG). After a first reaction for several hours at 1800°C, the samples were heat treated for another 20 hr at 1400°C before cooling to RT when the power to the furnace was shut off. For all heat treatments in a 0.9-MHz high frequency (HF) furnace the specimens were contained in a molybdenum can within a Mo-HF susceptor-crucible inside of a quartz vessel filled with 6  $N_2$ . Due to the sensitivity of the samples to moisture, handling of the specimens was performed in an argon-filled glove box with an oxygen level of less than 2 ppm  $O_2$  and ca. 4 ppm  $H_2O$ .

From X-ray powder analyses, these sample preparation and heat treatments proved sufficient to obtain homogeneous products. Weight increases corresponded roughly to a nominal formula  $REBN_{\approx 2}$ . Precise lattice parameters and standard deviations were obtained by a least-squares refinement of room temperature 114.59-mm Debye-Scherrer ( $CrK\alpha$ ) or Guinier-Huber ( $CuK\alpha_1$ ) X-ray powder data employing an internal standard of 6  $N$  pure germanium ( $a_{GE} = 0.5657906$  nm). For protection during measurement the powders were contained in sealed glass capillaries.

A rather small but isodimensional single crystal fragment ( $35 \times 40 \times 60 \mu m^3$ ) was broken from an elongated part selected by mechanical fragmentation of the densely reacted sinter cake. X-ray intensity data were collected on an automatic STOE four-circle diffractometer for one hemisphere of the reciprocal space out to a limit of  $\sin \theta/\lambda = 8.1 \text{ nm}^{-1}$  using monochromatized  $MoK\alpha_1$  radiation. A set of 527 symmetry independent reflections was obtained by averaging symmetry equivalent reflections out of a total number of 3263 recorded intensities; all observed intensities (388 for  $|F_0| > 3\sigma(F_0)$ ) were used in the structure refinement. An empirical absorption correction was applied using  $\psi$ -scans of three independent reflections.

### 3. Structure Determination

Laue and Weissenberg photographs, taken along the  $|001|$  axis, revealed rhombohedral lattice geometry with high Laue symmetry and without any superstructure reflections. A few of the ( $h\bar{h}0l$ ) reflections with  $h + l = 3n$  and  $l = 2n + 1$  were observed with low intensity. However, there were inconsistencies in comparison with their symmetry equivalent counterparts which never exceeded values of about 5 to  $6\sigma$ , suggesting Renninger enhancement. Thus the only observed systematic extinctions were those of a rhombohedral Bravais lattice and ( $h\bar{h}0l$ ) with  $l = 2n + 1$ , altogether compatible with  $R\bar{3}c$  as the centrosymmetric and  $R3c$  as the noncentrosymmetric types of space groups.

As statistical tests for the existence of a center of symmetry were not conclusive, solutions were attempted using direct methods in both the space groups  $R\bar{3}c$  and  $R3c$ . A first structure model was obtained in the noncentrosymmetric space group type  $R3c$ . This structure model was satisfactorily refined employing the STRUCSY full-matrix least-squares program system (STOE & CIE, Darmstadt, FRG). The weights used were based upon counting statistics  $w_i = 1/(\sigma F_i)^2$ , and structure factors were furthermore corrected for isotropic secondary extinction. Different weighting schemes had no significant influence on the  $R$ -values obtained. The refinement of the atom occupancies did not result in a significant deviation from full occupation, and B- and N-site distribution was undoubtedly solved with respect to reasonable temperature factors. The final  $R$ -values calculated for anisotropic thermal parameters for Pr but isotropic thermal parameters for B and N were  $R = 0.038$ ,  $R_w = 0.028$ . At this stage a final electron density difference map was featureless, thereby confirming the composition  $PrBN_2$ . Positional and thermal parameters are listed in Table I; interatomic distances are shown in Table II. A listing of  $F_0$  and  $F_c$  data is

TABLE I  
CRYSTALLOGRAPHIC DATA FOR PrBN<sub>2</sub> (PrBN<sub>2</sub> TYPE)

Space group	<i>R</i> 3 <i>c</i> - <i>C</i> <sub>3v</sub> , No. 161, origin on 3; <i>Z</i> = 18										
Unit-cell dimensions (X ray, 295 K)	<i>a</i> = 1.21144(13) nm, <i>c</i> = 0.70126(15) nm, <i>c/a</i> = 0.579, <i>V</i> = 0.8913(2) nm <sup>3</sup> , ρ <sub>x</sub> = 6.03 Mg · m <sup>-3</sup>										
Residual values	<i>R</i> <sub>F</sub> = 0.038, <i>R</i> <sub>w</sub> = 0.028										
Atom parameters											
Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> <sub>11</sub> <sup>a</sup> (× 10 <sup>-4</sup> )	<i>U</i> <sub>22</sub> (× 10 <sup>-4</sup> )	<i>U</i> <sub>33</sub> (× 10 <sup>-4</sup> )	<i>U</i> <sub>12</sub> (× 10 <sup>-4</sup> )	<i>U</i> <sub>13</sub> (× 10 <sup>-4</sup> )	<i>U</i> <sub>23</sub> (× 10 <sup>-4</sup> )
Pr	18 <i>b</i>	0.4548(1)	0.4536(1)	1/4	1.0	0.74(6)	0.64(5)	0.38(3)	0.29(2)	0.07(6)	-0.18(6)
B	18 <i>b</i>	0.4547(20)	0.6688(36)	0.4219(87)	1.0	0.58(14)					
N1	18 <i>b</i>	0.3276(19)	0.5409(11)	0.4196(39)	1.0	0.74(12)					
N2	18 <i>b</i>	0.6656(27)	0.5745(15)	0.0842(59)	1.0	0.87(17)					

<sup>a</sup> The isotropic thermal factor is expressed as  $T = \exp[-2\pi^2 \cdot U_{33}(2 \sin \theta/\lambda)^2]$ ; the anisotropic thermal factors are defined as  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ ; the isotropic secondary extinction parameter (Zachariasen) was  $g = 2.0(2) \times 10^{-6}$ .

TABLE II  
INTERATOMIC DISTANCES (nm) IN PrBN<sub>2</sub>

	Pr		N(1)
2Pr	0.3678(1)	Pr	0.256(3)
2Pr	0.3449(1)	Pr	0.246(2)
2Pr	0.3732(1)	B	0.140(5)
2Pr	0.3726(1)	B	0.155(3)
B	0.2873(5)		
B	0.279 (3)		N(2)
N(1)	0.256 (3)	Pr	0.269(4)
N(1)	0.246 (2)	Pr	0.268(4)
N(2)	0.269 (4)	Pr	0.257(3)
N(2)	0.268 (4)	Pr	0.254(3)
N(2)	0.257 (3)	Pr	0.251(3)
N(2)	0.254 (3)	B	0.147(4)
N(2)	0.251 (3)		
	B		
Pr	0.287 (5)		
Pr	0.279 (3)		
N(1)	0.140 (5)		
N(1)	0.155 (3)		
N(2)	0.147 (4)		

available on request. For identification purposes a listing of the X-ray powder pattern of PrBN<sub>2</sub> is presented in Table III.

#### 4. Structural Chemistry

Figure 1 is a representation of the crystal structure of PrBN<sub>2</sub>, revealing fragments of the hex-BN type as the most characteristic structural unit. As in binary hex-BN, B and N(1) atoms alternate in the planar B<sub>3</sub>N(1)<sub>3</sub> hexagons which are stacked to form infinite columns along |001| much the way they are in hex-BN, especially as far as bond lengths and bond angles are concerned. Each boron atom is bonded to two N(1) atoms within the B<sub>3</sub>N(1)<sub>3</sub> hexagons and also, in the same plane, to one additional N(2) atom to form a boron-centered BN(1)<sub>2</sub>N(2)<sub>1</sub> triangle (see Fig. 2). The average B–N bond of about 0.1437 nm compares well to B–N bonds formed in Ce<sub>3</sub>B<sub>2</sub>N<sub>4</sub> (0.1464 nm, Ref. (3)) or in Ce<sub>15</sub>B<sub>8</sub>N<sub>24</sub> (0.1455 nm, Ref. (5)). N(2) atoms are found in the basal plane of a dis-

TABLE III  
POWDER INTENSITY DATA FOR PrBN<sub>2</sub> (CuKα<sub>1</sub>  
RADIATION, λ = 0.154056 nm)

<i>hkl</i>	<i>d</i> (nm)	Intensity	<i>hkl</i>	<i>d</i> (nm)	Intensity
110	0.6057	62	421	0.1908	25
300	0.3497	2	223	0.1851	3
211	0.3452	29	151	0.1820	37
012	0.3326	3	502	0.1801	2
220	0.3029	49	600	0.1749	2
202	0.2915	100	104	0.1729	1
311	0.2688	78	422	0.1726	4
122	0.2627	15	250	0.1680	5
410	0.2289	69	341	0.1675	6
231	0.2277	14	024	0.1663	18
312	0.2239	20	152	0.1660	8
113	0.2181	19	143	0.1636	26
042	0.2100	19	214	0.1603	3
330	0.2019	14	611	0.1560	8
232	0.1984	1	342	0.1548	0

Note. Intensity data were calculated with the point positions obtained from single crystal data.  $I = mF^2(1 + \cos^2 2\theta)/\sin^2 \theta \cos \theta$  is normalized to the strongest reflection having an intensity of 100.

torted quadratic metal pyramid |Pr<sub>5</sub>|N(2) whose counter apex is formed by a B-atom, thereby providing an irregular octahedral |Pr<sub>5</sub>B|N(2) coordination for the N(2) atoms, typically found in the structure types of Ce<sub>3</sub>B<sub>2</sub>N<sub>4</sub> (3) and of Nb<sub>2</sub>BN (2). Combining these structural units, the crystal structure

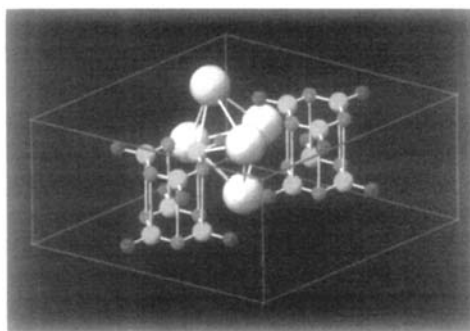


FIG. 1. The crystal structure of PrBN<sub>2</sub> in three-dimensional view. Large atoms, Pr; medium atoms, B; small atoms, N.

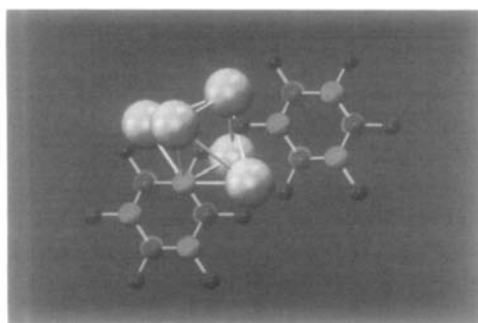


FIG. 2. The arrangement of B-N atoms as seen in projection along  $[001]$ . The bipyramidal surrounding  $|\text{Pr}_3\text{B}|$  around the N(2) atoms is outlined.

of PrBN<sub>2</sub> is intermediate between the structure types of hex-BN and Ce<sub>3</sub>B<sub>2</sub>N<sub>4</sub>, and shows close resemblance to the structure type of Ce<sub>15</sub>B<sub>8</sub>N<sub>24</sub> (5). From this point of view, the columns  $\frac{1}{2}(\text{B}_3\text{N}_3)$  are the central units in PrBN<sub>2</sub> (see also Fig. 1) with a shield of  $|\text{Pr}_3\text{B}|$ N(2) octahedra between them, thus forming an outer metal atom tube around each column or between columns, respectively.

### 5. Isotypic Compounds REBN<sub>2</sub>, (RE = Nd, Sm, Gd)

Room temperature X-ray powder patterns of samples REBN, which have been

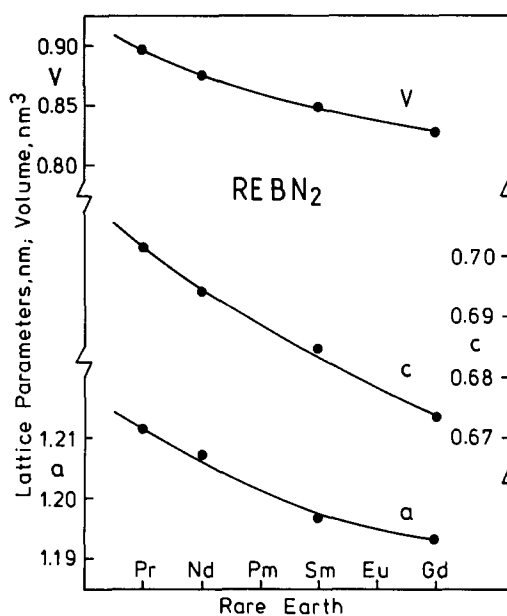


FIG. 3. Comparison of the unit-cell dimensions of REBN<sub>2</sub> compounds (RE = Pr, Nd, Sm, Gd).

annealed at 1800 and 1400°C under nitrogen, revealed a striking resemblance to the PrBN<sub>2</sub> type and were completely indexed on the basis of a rhombohedral unit cell (see Table IV). Employing the atom parameters derived for PrBN<sub>2</sub>, excellent agreement is obtained between the experimentally observed and calculated reflection intensities,

TABLE IV

CRYSTAL DATA OF THE RARE EARTH BORON NITRIDES REBN<sub>2</sub> (RE = Pr, Nd, Sm, AND Gd) (PrBN<sub>2</sub> TYPE)

Compound	Lattice Parameters (nm)		Volume (nm <sup>3</sup> )	Density, $\rho_x$ (Mg · m <sup>-3</sup> )
	a	c		
PrBN <sub>2</sub>	1.2114(1)	0.7013(2)	0.8913 (2)	6.03
NdBN <sub>2</sub>	1.2074(2)	0.6945(3)	0.8768 (4)	6.24
SmBN <sub>2</sub>	1.1972(3)	0.6850(2)	0.8502 (5)	6.65
SmBN <sub>2</sub> <sup>a</sup>	1.1952(7)	0.6824(6)	0.8442(11)	—
GdBN <sub>2</sub>	1.1932(5)	0.6736(4)	0.8305 (7)	7.06

<sup>a</sup> Parameters evaluated from reindexing X-ray powder data published by Gaudé (4).

confirming the isotopy with the crystal structure of  $\text{PrBN}_2$ .

Formation of a  $\text{PrBN}_2$ -type phase among the rare earth elements seems to be confined to the light rare earth members. Due to competing equilibria with further ternary compounds, formation of isotypic homologues with the largest rare earth elements La and Ce is suppressed. The stability appears reduced with decreasing radius of the rare earth element and  $\text{GdBN}_2$  is only observed as a high temperature compound in phase equilibria at or above  $1800^\circ\text{C}$ . A plot of the unit-cell dimensions of the isostructural  $\text{REBN}_2$  phases in Fig. 3 essentially reflects the lanthanoid contraction.

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