

## Phase Diagram of the B–BN System at 5 GPa

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The chemical interaction and phase relations in the B–BN system have been in situ studied at 5 GPa and temperatures up to 2800 K using X-ray diffraction with synchrotron radiation. The thermodynamic analysis of the B–BN system based on experimental data allowed us to construct equilibrium and metastable phase diagrams of the system at 5 GPa. The only thermodynamically stable boron subnitride, B<sub>13</sub>N<sub>2</sub>, melts incongruently at 2600 K and forms eutectic equilibrium with boron at 2300 K and 4 at. % of nitrogen.

### Introduction

Boron-rich solids give rise to a large group of hard refractory compounds with unique crystal structures and interesting physical and chemical properties related to the strongly covalent and electron-deficiency character of their chemical bonds.<sup>1,2</sup> For a long time only two phases with structures related to  $\alpha$ -rhombohedral boron ( $\alpha$ -B) have been thoroughly studied in the B–C–N–O system,<sup>1–4</sup> i.e., boron carbide B<sub>4</sub>C and boron suboxide B<sub>6</sub>O that combine lightness, strength, high hardness and wear resistance, chemical inertness, high melting point, semiconducting properties, and a high cross-section for neutron absorption.<sup>2,5</sup> As for the B–N system, the existence of boron subnitride B<sub>6</sub>N with an  $\alpha$ -B structure was first suggested as early as in 1976.<sup>6</sup> Later, a number of boron subnitrides of different stoichiometries have been reported (i.e., B<sub>4</sub>N,<sup>7</sup> B<sub>13</sub>N<sub>2</sub>,<sup>8</sup> and B<sub>6</sub>N<sub>0.92</sub><sup>3</sup>); however, neither their structure nor thermodynamic stability have been established.<sup>3,9</sup> Very recently, Solozhenko and Kurakevych<sup>10</sup> have synthesized rhombohedral boron subnitride B<sub>13</sub>N<sub>2</sub> with  $\alpha$ -B structural type by crystallization from the melt of the B–BN system at 5 GPa and studied its structure<sup>11</sup> and properties.<sup>10–14</sup>

To date, the phase diagram of the B–BN system has not been experimentally studied even at ambient pressure. It is known that  $\beta$ -B, hexagonal graphite-like boron nitride (hBN), and cubic boron nitride (cBN) have  $p$ – $T$  domains of thermodynamic stability<sup>15–18</sup> and, hence, should participate in phase equilibria. As for  $\alpha$ -B, according to the most recent phase diagram of boron,<sup>19</sup> it is stable only at relatively low temperatures (i.e., below 660 K at 5 GPa). Thermodynamic stability regions of two known boron subnitrides B<sub>13</sub>N<sub>2</sub><sup>10,11</sup> and B<sub>50</sub>N<sub>2</sub>,<sup>20</sup> have not been studied so far. Moreover, the calculation of the phase diagram with the participation of these two phases is impossible because of the lack of thermodynamic data.

In the present work, the chemical interaction and phase relations in the B–BN system at 5 GPa and high (up to 2800 K) temperatures have been studied in situ by X-ray diffraction with synchrotron radiation. The data obtained have been used

in the thermodynamic calculations, and the phase diagram of the system at 5 GPa was constructed.

### Experimental Section

As the initial materials we used hexagonal graphite-like boron nitride (99.999%, Sigma-Aldrich Co.) and  $\beta$ -rhombohedral boron ( $R\bar{3}m$ ,  $a = 10.932$  Å,  $c = 23.819$  Å) prepared by arc remelting of amorphous boron in an argon atmosphere. (According to mass spectrometry, spectral analysis, and X-ray microanalysis, the impurity content of a boron sample did not exceed 0.2 wt %.) The B–BN mixtures of various stoichiometries (compositions are given in Table 1) were thoroughly ground in a mortar of sintered diamond, compressed into disks, and placed into capsules of high-purity pyrolytic boron nitride.

The high-pressure experiments were carried out using a multianvil X-ray system MAX80 at beamline F2.1, HASYLAB-DESY. The experimental setup and sample assembly have been described elsewhere.<sup>21</sup> Energy-dispersive X-ray diffraction data were collected on a Canberra solid state Ge-detector with fixed Bragg angle  $2\theta = 9.188(3)^\circ$  using a white beam collimated down to  $100 \times 100 \mu\text{m}^2$  and the detector optics with  $2\theta$  acceptance angle of  $0.005^\circ$ , which ensures a high resolution of the observed diffraction patterns. The detector was calibrated using the K $\alpha$  and K $\beta$  fluorescence lines of Cu, Rb, Mo, Ag, Ba, and Tb.

The sample temperature up to 2200 K was measured by a W3%Re–W25%Re thermocouple. The correction for the pressure effect on the thermocouple emf was made using the data of Li et al.<sup>22</sup> Above 2200 K the power–temperature calibration curve was linearly extrapolated to the high-temperature region (up to 2800 K). Pressures at different temperatures were found from the  $p$ – $V$ – $T$  equation of state of highly ordered ( $P_3 = 0.98 \pm 0.02$ ) graphite-like hexagonal boron nitride.<sup>23</sup>

B–BN mixtures were gradually compressed to the required pressure at ambient temperature, and then diffraction patterns were collected at the stepwise ( $\sim 50$  K) temperature increase. With the storage ring operating at 4.44 GeV and  $150 \pm 50$  mA, diffraction patterns were collected for 1–2 min in real time. After heating, the samples were quenched by switching off the power, and then the pressure was slowly released down to ambient.

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**TABLE 1: Summary of Experimental Conditions and Phase Composition of Recovered Samples**

set no.	N content, at. % <sup>a</sup>	maximal $p$ - $T$ conditions		phase composition of the quenched samples <sup>b</sup>			
		$p$ , GPa	$T$ , K	$\beta$ -B	"I-t B"	B <sub>13</sub> N <sub>2</sub>	hBN
1	3.8	5.0	2450	++	+	—	—
2	12.5	5.0	2700	++	+	+	+
3	14.3	5.0	2670	++	+	+	++
		5.0	2590	++	+	+	++
		4.7	2690	++	+	+	++
		4.9	2700	++	++	++	++
4	22.0	5.0	2340	+	+	+	++
		4.9	2590	++	++	++	++

<sup>a</sup> Atomic percentage of nitrogen according to the B–N scale. <sup>b</sup> "++" corresponds to the well-crystallized phase, "+" represents the poorly crystallized phases. "—" shows the absence of the corresponding phase in the resulting sample.

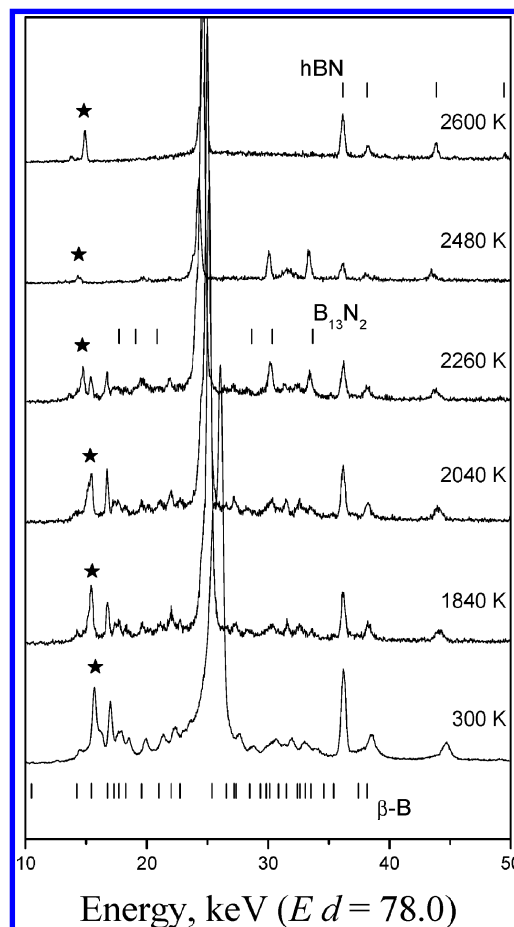
The quenched samples have been studied by X-ray powder diffraction (D5000, Siemens and G3000 TEXT, Inel diffractometers; Cu K $\alpha$  radiation) and X-ray electron probe microanalysis (S440 Leica/Spirit, Princeton Gamma-Tech).

## Results and Discussion

**In Situ Studies of the Phase Equilibria.** Our previous in situ studies of  $\beta$ -B at 5 GPa have shown that all boron lines disappear between 2420 and 2460 K, which has allowed us to estimate the boron melting temperature at this pressure as 2440(20) K.<sup>24</sup> The melting temperature of hBN (3490 K) and temperature of the hBN  $\rightleftharpoons$  cBN equilibrium (3220 K) at 5 GPa have been evaluated from the refined equilibrium phase diagram of boron nitride.<sup>18</sup>

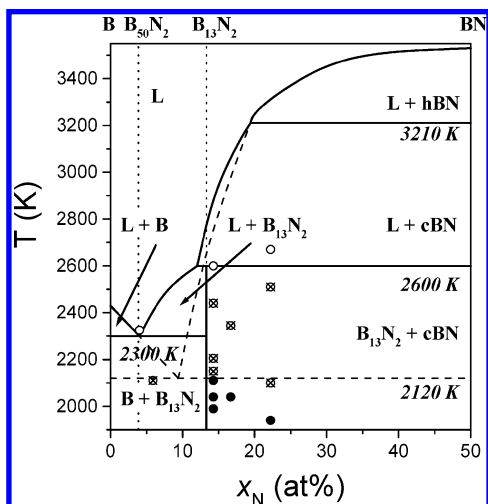
Figure 1 shows a typical sequence of X-ray diffraction patterns taken in situ on heating a mixture of hBN and  $\beta$ -B at 5 GPa. The disappearance of boron lines was observed at temperatures  $\sim$ 2100 K, which is lower than the melting temperature of boron at this pressure (2400 K)<sup>24</sup> by  $\sim$ 300 K. This fact points to the contact interaction of boron and boron nitride that gives rise to a metastable liquid in the system according to the B + hBN  $\rightleftharpoons$  L eutectic reaction, whose temperature at 5 GPa is 2120(20) K. On subsequent heating to 2200–2250 K, the lines of B<sub>13</sub>N<sub>2</sub> boron subnitride appear in the diffraction patterns. This phase forms rather quickly (a considerable quantity of the subnitride was observed already at 30–45 s), which reveals the existence of a liquid phase, from which the crystallization of B<sub>13</sub>N<sub>2</sub> occurs. When the reaction mixtures containing more than 13.3 at. % N are heated, B<sub>13</sub>N<sub>2</sub> crystallizes from the melt of the B–BN metastable eutectic and, as a result, the metastable liquid phase disappears. The fact that no crystallization of thermodynamically stable cBN is observed may be attributed to a high energy of the cubic phase nucleation similar to that observed for the BN–MgB<sub>2</sub> system.<sup>25</sup>

The temperature of complete melting of B<sub>13</sub>N<sub>2</sub> in B–BN mixtures heavily depends on the initial composition. Thus, when the mixture containing 4 at. % N (composition of the B<sub>50</sub>N<sub>2</sub> phase) was heated, the B<sub>13</sub>N<sub>2</sub> lines completely disappeared already at 2310 K, which evidently corresponds to the equilibrium eutectic melting according to the B + B<sub>13</sub>N<sub>2</sub>  $\rightleftharpoons$  L reaction. In the sample containing 22 at. % nitrogen a drastic change in mutual intensities of B<sub>13</sub>N<sub>2</sub> lines caused by the inferred motion of crystallites, typical for an onset of formation of the B–BN equilibrium melt, was observed only at temperatures of about 2600 K (similar behavior has been previously observed at the initial stage of melting in the B–B<sub>2</sub>O<sub>3</sub> system<sup>24</sup>). All our attempts to overheat the liquid always resulted in blowouts from the high-pressure cell, which indicates that at 2600 K either the liquidus line of B<sub>13</sub>N<sub>2</sub> at the concentration of 22 at. % N or the line of the L + BN  $\rightleftharpoons$  B<sub>13</sub>N<sub>2</sub> peritectic equilibrium is attained.



**Figure 1.** Typical sequence of the energy-dispersive X-ray diffraction patterns taken at 5 GPa in the course of heating of the B–BN mixture (14.3 at. % N) to 2600 K. The stars represent the hBN escape line, while vertical bars show the positions of the phase reflections. The  $\beta$ -B lines disappear between 2040 and 2260 K. The reflections of B<sub>13</sub>N<sub>2</sub> appear at 2260 K and are observed at temperatures below 2600 K.

According to electron microprobe data, the recovered samples contain only boron and nitrogen, while other elements (e.g., carbon and oxygen), if present in the samples, are at an undetectable level. The phase compositions of quenched products of the boron interaction with hBN are given in Table 1. The diffraction patterns of all quenched samples irrespective of the composition are characterized by the presence of the lines of four phases, namely,  $\beta$ -B, "I-tetragonal boron", B<sub>13</sub>N<sub>2</sub> boron subnitride, and hBN. This is indicative of the incompleteness of reactions proceeding in a sample on cooling and is characteristic for systems whose phase diagrams are of peritectic type.  $\beta$ -B crystallizes from the eutectic melt by the L  $\rightleftharpoons$   $\beta$ -B + B<sub>13</sub>N<sub>2</sub> reaction, while metastable "I-tetragonal boron" evidently forms



**Figure 2.** Phase diagram of the B–BN system at 5 GPa. The black circles correspond to the solid state of the system; the crossed circles, to the coexistence of a liquid with solid phase(s); and the open circles, to the completely molten samples. Solid lines show the equilibrium phase diagram, while dashed lines show the metastable diagram.

because of the stabilization of the boron tetragonal structure by nitrogen impurities from starting boron nitride. However, unlike the synthesis by vapor phase deposition, which results in the formation of stoichiometric  $B_{50}N_2$  boron subnitride,<sup>20</sup> at pressures of about 5 GPa a solid solution of  $B_{50}N_{2-x}B_x$  (“I-t B”) composition forms.<sup>10,11</sup> The stoichiometric  $B_{50}N_2$  boron subnitride has not been revealed in any of the quenched samples, which allows us to make a conclusion that this phase is metastable at 5 GPa.

The above-described set of experimental data may be explained by the existence of the following nonvariant equilibria in the phase diagram of the B–BN system at 5 GPa:  $L + BN \rightleftharpoons B_{13}N_2$  of peritectic type, according to which the melting of  $B_{13}N_2$  boron subnitride occurs at  $\sim 2600$  K;  $L \rightleftharpoons \beta\text{-B} + B_{13}N_2$  of eutectic type at  $\sim 2300$  K; and  $L \rightleftharpoons \beta\text{-B} + BN$  metastable eutectic, whose temperature is 2120 K and which assures the appearance of the liquid phase, from which  $B_{13}N_2$  crystallizes.

**Thermodynamic Calculation of the Phase Diagram.** For the thermodynamic analysis of the B–BN system and calculation of the phase diagram, all obtained experimental data have been used to define the three unknown parameters of the employed phenomenological model: two parameters of the interaction in the model of subregular solutions describing the thermodynamic potential of the B–BN liquid phase, and the free energy of the  $B_{13}N_2$  formation.

Because of low mutual solubility of  $\beta\text{-B}$ , cBN, hBN, and  $B_{13}N_2$  in the solid state, the formation of solid solutions does not complicate the phase diagram. Temperature dependencies of the Gibbs free energy of  $\beta\text{-B}$  and BN polymorphs were taken from ref 15 and refs 18 and 26, respectively, while the data on melting temperatures of boron and hBN at various pressures were taken from refs 15, 24, and 27 and ref 18, respectively. The Gibbs free energy of boron subnitride was calculated using equation

$$G_{B_{13}N_2} = (11G_B + 2G_{BN}) + \Delta G_{fB_{13}N_2}^0$$

The thermodynamic potential of the liquid phase was described in the approximation of subregular solutions,

$$G_m^L = x'_B G_B^L + \frac{1}{2} x'_{BN} G_{BN}^L + RT(x'_B \ln x'_B + x'_{BN} \ln x'_{BN}) + W_1(1 + W_0 x'_B) x'_B x'_{BN}$$

where  $G_B^L$  and  $G_{BN}^L$  are the molar Gibbs energies of boron and BN in the liquid state;  $x'_B = 2(0.5 - x_N)$  and  $x'_{BN} = 1 - x'_B$ , while  $x_N$  is the atomic fraction of nitrogen;  $W_0$  and  $W_1$  are the parameters describing the interatomic interactions in the subregular solution.

The pressure increase of the Gibbs free energy was described as,  $\int \beta V_m^{\Phi} dp$ , where  $V_m^{\Phi}$  is the molar volume of the  $\Phi$  phase. The experimental  $p$ – $V$ – $T$  data are available for hBN,<sup>23</sup> cBN,<sup>28</sup> and  $\beta\text{-B}$ .<sup>29,30</sup> As no data on the values of the thermal expansion coefficient and bulk modulus of liquid boron can be found in the literature, we assumed that these values are equal for the solid and liquid phases. A volume change during melting of  $\beta\text{-B}$  at 5 GPa,  $0.37 \text{ cm}^3 \text{ mol}^{-1}$ , has been established by fitting the experimental melting points of  $\beta\text{-B}$  at various pressures in our previous work.<sup>24</sup>

In the zero mixing volume approximation, the liquid phase volume was calculated by the formula

$$V_m^L = x'_B V_B^L + \frac{1}{2} x'_{BN} V_{BN}^L$$

The free energy of the  $B_{13}N_2$  formation ( $\Delta G_{fB_{13}N_2}^0 = -138.8 \text{ kJ/mol}$ ) and the interaction parameters  $W_0 = 60$  and  $W_1 = -40 \text{ kJ mol}^{-1}$  have been found by fitting the experimental temperature values for three nonvariant equilibria: peritectic  $L + BN \rightleftharpoons B_{13}N_2$  (2600 K), eutectic  $L \rightleftharpoons \beta\text{-B} + B_{13}N_2$  (2300 K), and metastable eutectic  $L \rightleftharpoons \beta\text{-B} + BN$  (2120 K).

The equilibrium phase diagram of the B–BN system at 5 GPa is shown in Figure 2. The diagram contains peritectic  $L + BN \rightleftharpoons B_{13}N_2$  (2600 K, 12 at. % N) and eutectic  $L \rightleftharpoons \beta\text{-B} + B_{13}N_2$  (2300 K, 4 at. % N) equilibria. The dashed lines in the Figure 2 indicate the metastable extensions of the liquidus lines of hBN and  $\beta\text{-B}$ , as well as the metastable eutectic  $L \rightleftharpoons \beta\text{-B} + BN$  (2120 K, 9 at. % N).

The calculated metastable and equilibrium phase diagrams of the B–BN system at 5 GPa are well consistent with all our experimental data. The contact interaction between hBN and boron leads to the formation of a liquid by metastable eutectic reaction  $\beta\text{-B} + hBN \rightleftharpoons L$  already at temperatures of about 2120 K. From the metastable liquid  $B_{13}N_2$  boron subnitride crystallizes. On subsequent heating,  $B_{13}N_2$  melts either by peritectic reaction  $B_{13}N_2 \rightleftharpoons L + BN$  (nitrogen content of a mixture above 12 at%) at 2600 K or by attaining the  $B_{13}N_2$  liquidus temperature (mixtures containing 4–12 at% N), or as a result of the eutectic melting (mixtures containing below 4 at% N). (In this region of the diagram, the experimental determination of the liquidus line position is hardly possible as the required overheating of the eutectic liquid results inevitably in blow-out from a high-pressure cell.) The general tendency of peritectic reactions to incompleteness makes impossible the synthesis of single phase  $B_{13}N_2$  by quenching from high pressures and high temperatures. Even after the completion of the  $L + BN \rightleftharpoons B_{13}N_2$  peritectic reaction, some amount of the liquid phase remains in the sample. In cooling the liquid phase composition varies along the liquidus line to the eutectic point  $L \rightleftharpoons \beta\text{-B} + B_{13}N_2$ , with the result that the quenching products always contain  $\beta\text{-B}$ .

## Conclusions

Powder X-ray diffraction with synchrotron radiation has been used to study in situ the chemical interaction of  $\beta\text{-boron}$  with

hexagonal graphite-like boron nitride and phase relations in the B–BN system at 5 GPa and temperatures up to 2800 K. It has been found that B<sub>13</sub>N<sub>2</sub> is the only thermodynamically stable boron subnitride that melts incongruently at 2600 K, while B<sub>50</sub>N<sub>2</sub> is metastable. The equilibrium phase diagram is characterized by the L + cBN  $\rightleftharpoons$  B<sub>13</sub>N<sub>2</sub> (2600 K, 12 at. % N in the liquid phase) peritectic and L  $\rightleftharpoons$   $\beta$  B + B<sub>13</sub>N<sub>2</sub> (2300 K, 4 at. % N) eutectic equilibria.

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