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ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · JUNE 2008

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Phase Diagram of the B–B<sub>2</sub>O<sub>3</sub> System at 5 GPa: Experimental and Theoretical StudiesVladimir L. Solozhenko,<sup>\*,†</sup> Oleksandr O. Kurakevych,<sup>†</sup> Vladimir Z. Turkevich,<sup>‡</sup> and Dmitry V. Turkevich<sup>‡</sup>

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Received: January 22, 2008

X-ray diffraction with synchrotron radiation has been used to study *in situ* the chemical interaction of  $\beta$ -rhombohedral boron with boron (III) oxide and phase relations in the B–B<sub>2</sub>O<sub>3</sub> system at pressures up to 6 GPa in the temperature range from 300 to 2800 K. The B–B<sub>2</sub>O<sub>3</sub> system has been thermodynamically analyzed, and its equilibrium phase diagram at 5 GPa has been constructed. Only one thermodynamically stable boron suboxide, B<sub>6</sub>O, exists in the system. It forms eutectic equilibria with boron and B<sub>2</sub>O<sub>3</sub>.

## Introduction

Much attention is paid to boron suboxides due to the fortunate combination of high hardness, low density, high tensile strength, semiconductivity, high chemical stability, and large values of bulk modulus; B<sub>6</sub>O is the most extensively studied.<sup>1–12</sup> B<sub>6</sub>O can be synthesized by the chemical interaction of boron with boron (III) oxide at high temperatures and pressures from ambient<sup>8</sup> to 8 GPa.<sup>5,10,12,13</sup> However, according to Hubert et al.,<sup>10</sup> the formation of stoichiometric B<sub>6</sub>O is possible only at pressures above 4 GPa and temperatures of about 2000 K. Synthesis and studies of B<sub>x</sub>O boron suboxides having other stoichiometry ( $x = 2, 4, 7, 8, 10, 12, 16, 18, 20, 22$ , and 26) were also reported.<sup>14–19</sup> Among boron suboxides, B<sub>2</sub>O holds a special place as an “unsymmetrical” analog of carbon.<sup>14,16,18–22</sup> The synthesis of B<sub>2</sub>O in graphite-like<sup>14,18</sup> and diamond-like<sup>18,19</sup> forms has been reported but never reproduced. The studies of Hubert et al.<sup>5,10</sup> and Nieto-Sanz et al.<sup>13</sup> have shown that B<sub>2</sub>O phase cannot be synthesized by chemical interaction in the B–O system at pressures up to 43 GPa and temperatures up to 2500 K. Very recently it has been shown that the so-called graphite-like B<sub>2</sub>O reported by Hall and Compton<sup>14</sup> is a product of hydrolysis.<sup>23</sup> All mentioned raise doubts about the existence of B<sub>2</sub>O<sup>5,10,13,23</sup> and calls for further investigation.

The hypothetical version of the B–B<sub>2</sub>O<sub>3</sub> phase diagram at pressures up to 10 GPa has been proposed by McMillan et al.<sup>12</sup> However, the lack of experimental data on phase equilibria and thermodynamic properties of B<sub>6</sub>O did not allow them to perform a correct thermodynamic calculation of the diagram. Later, Nieto-Sanz et al.<sup>13</sup> proposed another diagram constructed from the limited *in situ* data on the interaction between  $\beta$ -rhombohedral boron ( $\beta$ -rh B) and B<sub>2</sub>O<sub>3</sub>. However, this diagram completely contradicts not only the one calculated by McMillan et al.<sup>12</sup> but also the well-established equilibrium  $p$ – $T$  phase diagram of B<sub>2</sub>O<sub>3</sub>.<sup>24</sup> Thus, the phase diagram of the B–B<sub>2</sub>O<sub>3</sub> system is still open to question until reliable experimental data

TABLE 1: Compositions of the Initial Mixtures

run	$\beta$ -B content, wt %	B <sub>2</sub> O <sub>3</sub> content, wt %	B <sub>6</sub> O content, wt %	B content, <sup>a</sup> at %
1801	4.46	95.54	0	43.40
1802	55.56	44.44	0	77.01
1803	0	17.05	82.95	79.06
1805	0	17.00	83.00	79.08
1806	0	51.61	48.39	64.26
1807	0	51.61	48.39	64.26
1808	0	76.27	23.73	52.47
1809	55.75	44.25	0	77.12
1810	0	67.46	32.54	56.81
1812	6.67	0	93.33	86.73
1813	7.14	0	92.86	86.80
1815	54.17	45.83	0	76.21
1907	0	90.91	9.09	44.92
2401	38.32	61.68	0	66.67
2405	38.32	61.68	0	66.67
2602	54.94	45.06	0	76.65
2603	54.94	45.06	0	76.65
2703	66.33	0	33.67	95.40
2705	49.50	0	50.50	93.20

<sup>a</sup> Atomic percentage of boron according to the B–O scale.

on the liquidus lines for the B–B<sub>6</sub>O and B<sub>6</sub>O–B<sub>2</sub>O<sub>3</sub> subsystems are available.

In the present work, the chemical interaction and phase relations in the B–B<sub>2</sub>O<sub>3</sub> system at pressures up to 6 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 thermodynamic calculations, and the phase diagram of the system at 5 GPa was constructed.

## Experimental Section

As the initial materials we have used boron (III) oxide (99.999%, produced by Aldrich Chemical Co.);  $\beta$ -rh B ( $R$ -3 $m$ ,  $a = 10.932$  Å,  $c = 23.819$  Å) prepared by arc remelting of amorphous boron in an argon atmosphere; and B<sub>6</sub>O synthesized from the stoichiometric mixture of  $\beta$ -rh B and B<sub>2</sub>O<sub>3</sub> at 6 GPa and 2000 K ( $R$ -3 $m$ ,  $a = 5.385$  Å,  $c = 12.32$  Å). The compositions of the starting mixtures are given in Table 1. All the samples containing B<sub>2</sub>O<sub>3</sub> have been prepared inside a glovebox under a dry air atmosphere.

The high-pressure experiments up to 6 GPa were carried out using a multianvil X-ray system MAX80 at beamline F2.1,

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HASYLAB-DESY. The experimental setup has been described elsewhere.<sup>25–27</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 to  $60 \times 100 \mu\text{m}^2$  (vertical by horizontal) and the detector optics with a  $2\theta$  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 electromotive force (emf) was made using the data of Li et al.<sup>28</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>25</sup> [According to mass-spectrometry, spectral analysis, and X-ray microanalysis, the impurity content of a boron sample did not exceed 0.2 wt %.]

Samples 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.

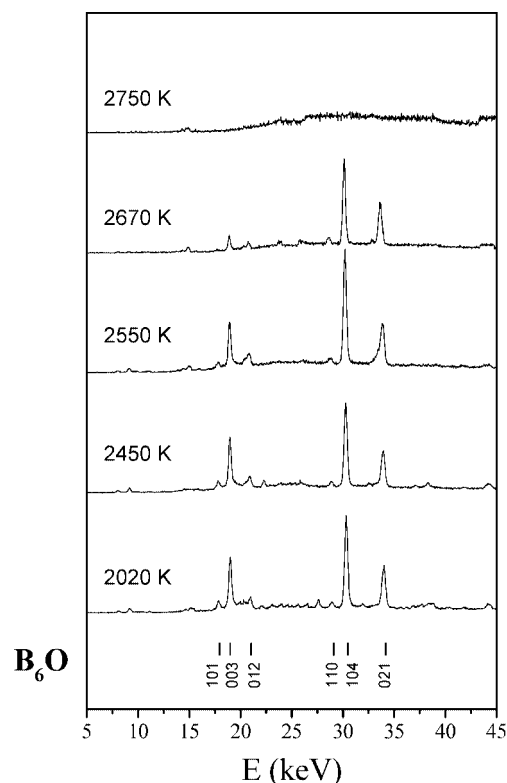
The quenched samples were studied by X-ray powder diffraction using D5000 (Siemens) and G3000 TEXT (Inel) diffractometers ( $\text{CuK}_\alpha$  radiation).

## Results and Discussion

**In Situ Studies of Phase Equilibria.** Up to now, only one measurement of the boron melting temperature under pressure has been reported.<sup>29</sup> The value of 2480(50) K at 7.7 GPa has been estimated;<sup>29</sup> however, the error may be significantly higher than the stated 50-K value because the conclusion about melting has been made from the quenching experiments. Our *in situ* studies of  $\beta$ -rh 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.

The melting temperature of  $\text{B}_2\text{O}_3$  boron oxide at pressures up to 8 GPa may be evaluated from the equilibrium phase diagram of  $\text{B}_2\text{O}_3$ .<sup>24</sup> Our *in situ* studies of  $\alpha$ - $\text{B}_2\text{O}_3$  at high pressures and temperatures have shown that the boron oxide lines completely disappeared at 1230 K (2.5 GPa) and 1310 K (5 GPa), which is in good agreement with the data reported in ref 24 and corresponds to the melting curve slope of  $\sim 70$  K/GPa in the pressure range under study.

At present time there is no data available on the  $\text{B}_6\text{O}$  boron suboxide melting. At ambient pressure,  $\text{B}_6\text{O}$  decomposes into boron and oxygen already at 2000 K, therefore, the congruent melting of this phase may be observed at high pressures only. Figure 1 shows a sequence of energy-dispersive diffraction patterns taken *in situ* at 5.8 GPa in the course of the stepwise heating of  $\text{B}_6\text{O}$ . The disappearance of  $\text{B}_6\text{O}$  lines has been observed between 2670 and 2750 K, which was accompanied by the appearance of a diffuse band typical for a liquid phase. This has allowed us to estimate the melting temperature of boron suboxide as 2710(40) K at 5.8 GPa, which is higher by  $\sim 250$  K than the melting temperature of  $\beta$ -rh B at this pressure. The cooling of the melt down to 2100 K at a rate of  $\sim 10$  K/s was accompanied by  $\text{B}_6\text{O}$  crystallization. At the same time, the rapid quenching by the power switch off (the cooling rate of  $\sim 1000$ – $2000$  K/s at the initial stage) resulted in formation of



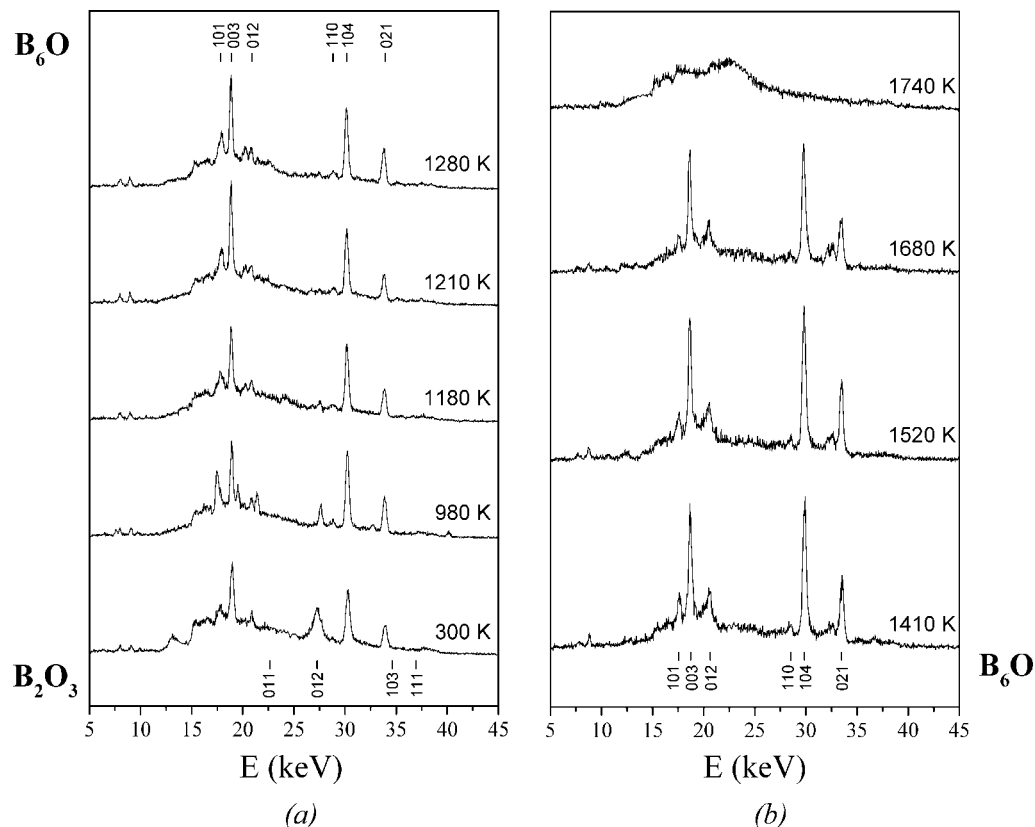
**Figure 1.** Energy-dispersive diffraction patterns taken at 5.8 GPa in the course of heating of  $\text{B}_6\text{O}$  to 2750 K.

$\beta$ -rh B and  $\alpha$ - $\text{B}_2\text{O}_3$ , while  $\text{B}_6\text{O}$  was absent in the quenched samples. This fact may be attributed to the high free energy of formation of  $\text{B}_6\text{O}$  critical nuclei.

As a result of the contact interaction between  $\text{B}_6\text{O}$  and  $\text{B}_2\text{O}_3$ , which is accompanied by the formation of a liquid phase, at 5 GPa the  $\text{B}_2\text{O}_3$  lines disappear already at 1200 K (run 1907, 44.9 at % B, see Figure 2a). At higher temperatures, solid  $\text{B}_6\text{O}$  coexists with the liquid. The heating up to 1740 K results in the complete disappearance of  $\text{B}_6\text{O}$  lines, and the system is a uniform liquid phase (see Figure 2b). This temperature of  $\text{B}_6\text{O}$  liquidus, 1740 K, is noticeably lower than the 2170 K value that was estimated in the quenching experiments<sup>30</sup> for the same limiting solubility (44.9 at % B) of  $\text{B}_6\text{O}$  in the melt of the  $\text{B}_6\text{O}$ – $\text{B}_2\text{O}_3$  subsystem. Our attempts to establish the  $\text{B}_6\text{O}$  liquidus temperatures at higher boron content (52–80 at % B; runs 1803 and 1805–1808) have failed because the strong overheat of the  $\text{B}_6\text{O}$ – $\text{B}_2\text{O}_3$  eutectic liquid has resulted in blowouts from high-pressure cells. In all these runs, the sequences of patterns qualitatively repeat run 1907, except that the lines of  $\text{B}_6\text{O}$  are distinctly observed up to the highest temperatures (2130–2170 K) attained in these experiments.

In the case of the B– $\text{B}_6\text{O}$  mixtures, at 5 GPa the appearance of the liquid phase was observed above 2460 K only (runs 2703 and 2705, 95.4 and 93.2 at % B, respectively), which corresponds to the B– $\text{B}_6\text{O}$  eutectic melting (Figure 3).

Our *in situ* experiments on the interaction between boron and relatively small amounts of boron oxide at 2.5 GPa (runs 1815, 2602, and 2603) has shown that, after the  $\text{B}_2\text{O}_3$  melting at about 1250 K, boron was in metastable equilibrium with the liquid phase over a wide temperature range, while the formation of  $\text{B}_6\text{O}$  was observed only above 1730 K. This fact indicates that the construction of an equilibrium phase diagram from the data on the chemical interaction of boron with  $\text{B}_2\text{O}_3$ , which had been done in ref 13, is hardly possible.



**Figure 2.** Energy-dispersive diffraction patterns taken at 5 GPa in the course of heating of the B<sub>6</sub>O–B<sub>2</sub>O<sub>3</sub> mixture to 1740 K (run 1907, 44.9 at % B). The B<sub>2</sub>O<sub>3</sub> lines disappear starting from 1180 K (a); while the B<sub>6</sub>O reflections disappear at ~1740 K (b).

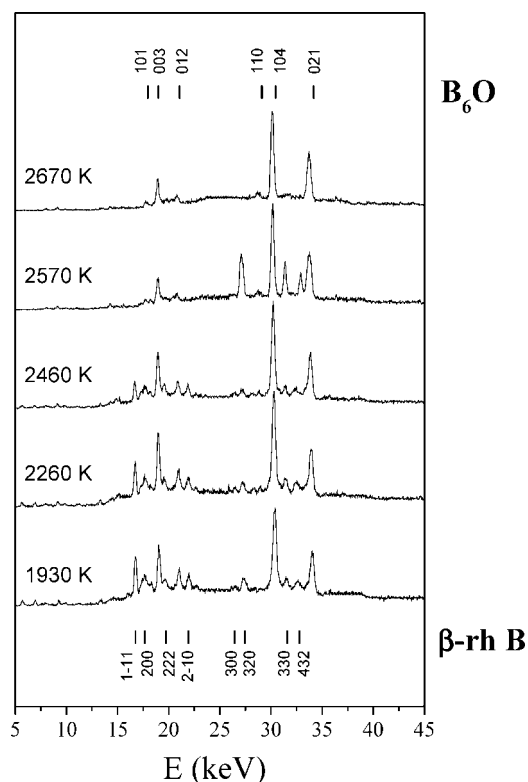
Besides the experimental data on the B<sub>6</sub>O liquidus lines, the stoichiometry of B<sub>6</sub>O in the equilibrium state at various  $p$ – $T$  conditions is also of importance for the calculations of phase equilibria in the system. The oxygen deficiency of the B<sub>6</sub>O lattice has been previously reported for samples synthesized at pressures below 4 GPa<sup>8,10</sup> and temperatures up to 1970 K. However, very recently we have shown that, at temperatures above 2100 K, the crystallization of stoichiometric B<sub>6</sub>O takes place already at 1 GPa.<sup>31</sup> Thus, for construction of the equilibrium phase diagram, B<sub>6</sub>O should be considered as a stoichiometric phase.

The lines that could be interpreted as those of B<sub>2</sub>O (or any boron suboxide other than B<sub>6</sub>O) have been never revealed in X-ray diffraction patterns for all employed compositions over the whole  $p$ – $T$  range under study, and, therefore, the equilibrium phase diagram should not contain all these suboxides.

**Thermodynamic Calculation of the Phase Diagram.** For calculations of the phase equilibria in the B–B<sub>2</sub>O<sub>3</sub> system at high pressure, we used both the thermodynamic data available in the literature and experimental results obtained in the present study.

Because of the low mutual solubility in the solid state,  $\beta$ -rh B, B<sub>2</sub>O<sub>3</sub>, and B<sub>6</sub>O were considered as the phases of constant composition. Temperature dependences of the Gibbs free energy of  $\beta$ -rh B and B<sub>2</sub>O<sub>3</sub> were taken from ref 32. The literature data on heat capacity<sup>33</sup> were used for the calculation of temperature dependences of the Gibbs free energy of B<sub>6</sub>O boron suboxide. The B<sub>6</sub>O formation enthalpy of  $\Delta H_f = -1244.5$  kJ/mol was taken from ref 12.

The pressure increase of the Gibbs free energy was described as  $\int_p^p V_m^p dp$ , where  $V_m^p$  is the molar volume of the  $\Phi$  phase. The pressure contributions to the free energies of crystalline ( $\alpha$ -phase) and liquid B<sub>2</sub>O<sub>3</sub> have been used in the forms



**Figure 3.** Energy-dispersive diffraction patterns taken at 5 GPa in the course of heating of the mixture of B<sub>6</sub>O and  $\beta$ -rh B to 2670 K (run 2705, 93.2 at % B). All lines of initial  $\beta$ -rh B have disappeared above 2460 K, while at 2570 K three intensive reflections have suddenly arisen in the pattern because of the formation of single-crystal boron by the temperature-fluctuation-induced recrystallization in the vicinity of the melting point.

$$\int_0^p V_m^{\alpha\text{-B}_2\text{O}_3} dp = (27.26 \times 10^{-6})(18.4 \times 10^9) \times \left[ 1 - \exp\left(-\frac{p - 1 \times 10^4}{18.4 \times 10^9}\right) \right], \quad \text{J/mol}$$

$$\int_0^p V_m^{\text{L-B}_2\text{O}_3} dp = (33.7 \times 10^{-6})(15 \times 10^9) \times \left[ 1 - \exp\left(-\frac{p - 1 \times 10^4}{15 \times 10^9}\right) \right], \quad \text{J/mol}$$

where the bulk modulus of the  $\alpha\text{-B}_2\text{O}_3$ , 18.4 GPa, has been obtained by fitting the pressure dependence of the  $\text{B}_2\text{O}_3$  melting temperature<sup>24</sup> under the assumption that the bulk modulus of the liquid phase is equal to 15 GPa (the same as for the amorphous phase).<sup>34</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  $\beta\text{-rh B}$  at 5 GPa,  $0.37 \text{ cm}^3 \text{ mole}^{-1}$ , has been established by fitting the experimental melting points of  $\beta\text{-rh B}$  at various pressures (data obtained in the present work and reported in ref 29).

To describe the pressure contribution to the Gibbs energy of  $\text{B}_6\text{O}$ , we used the data from ref 35:

$$\int_0^p V_m^{\text{B}_6\text{O}} dp = (30.9 \times 10^{-6}) \cdot \frac{\exp[(32 \times 10^{-7})T]}{(4.6 \times 10^{-12})6.2} \cdot [(1 + 7.2(4.6 \times 10^{-12})p)^{1-\frac{1}{7.2}} - 1], \quad \text{J/mol}$$

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

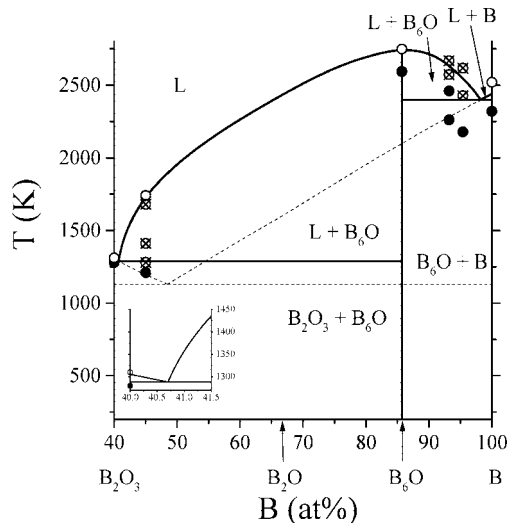
$$V_m^{\text{L}} = x_{\text{B}} V_{\text{B}}^{\text{L}} + x_{\text{B}_2\text{O}_3} V_{\text{B}_2\text{O}_3}^{\text{L}}.$$

Fitting the experimental value of the  $\text{B}_6\text{O}$  limiting solubility (44.9 at % B) in the  $\text{B}_6\text{O-B}_2\text{O}_3$  melt at 1740 K and 5 GPa to the model of regular solutions (when describing the concentration dependence of the Gibbs free energy of the liquid phase) gives an unjustified high temperature of the  $\text{B}_6\text{O}$  congruent melting, above 3000 K, while, in our experiments, the  $\text{B}_6\text{O}$  was completely molten at temperatures above 2750 K. This fact points to the asymmetrical concentration dependence of the Gibbs free energy of the  $\text{B-B}_2\text{O}_3$  melt. Thus, the Gibbs free energy of the liquid phase should be better described in the approximation of subregular solutions, i.e.,

$$G_m^{\text{L}} = x_{\text{B}}^{\circ} G_{\text{B}}^{\text{L}} + x_{\text{B}_2\text{O}_3}^{\circ} G_{\text{B}_2\text{O}_3}^{\text{L}} + RT(x_{\text{B}}^{\circ} \ln x_{\text{B}}^{\circ} + x_{\text{B}_2\text{O}_3}^{\circ} \ln x_{\text{B}_2\text{O}_3}^{\circ}) + W_1(1 + W_2 x_{\text{B}}^{\circ}) x_{\text{B}}^{\circ} x_{\text{B}_2\text{O}_3}^{\circ},$$

where  $G_{\text{B}}^{\text{L}}$  and  $G_{\text{B}_2\text{O}_3}^{\text{L}}$  are the molar Gibbs energies of boron and  $\alpha\text{-B}_2\text{O}_3$  in the liquid state;  $x_{\text{B}}^{\circ} = (5/3)(x_{\text{B}} - 0.4)$  and  $x_{\text{B}_2\text{O}_3}^{\circ} = 1 - x_{\text{B}}^{\circ}$ , while  $x_{\text{B}}$  is the atomic fraction of boron;  $W_1$  and  $W_2$  are the parameters describing the interatomic interactions in the subregular solution. The values of  $W_1 = -8.53 \text{ kJ mol}^{-1}$  and  $W_2 = 2.58$  have been found by the fitting of two experimental liquidus temperatures at 5 GPa (2750 K for  $\text{B}_6\text{O}$  and 1740 K for the  $\text{B}_6\text{O-B}_2\text{O}_3$  mixture containing 44.9 at % B).

The calculated equilibrium phase diagram of the  $\text{B-B}_2\text{O}_3$  system at 5 GPa (Figure 4) is well consistent with all our experimental data. The diagram is characterized by the congruent melting of  $\text{B}_6\text{O}$  boron suboxide and two eutectic equilibria, i.e.,  $\text{L} \rightleftharpoons \text{B}_6\text{O} + \text{B}$  (2400 K) and  $\text{L} \rightleftharpoons \text{B}_2\text{O}_3 + \text{B}$  (1290 K).



**Figure 4.** Phase diagram of the  $\text{B-B}_2\text{O}_3$  system at 5 GPa. The black circles correspond to the solid state of the system, the crossed circles correspond to the coexistence of a liquid phase with a solid, and the open circles correspond to the completely molten samples. Solid lines show the equilibrium phase diagram, while dashed lines represent the metastable diagram.

The above-mentioned unexpected fact that the rapid quenching of molten  $\text{B}_6\text{O}$  does not lead to crystallization of this phase may be comprehensively explained in the framework of the metastable  $\text{B-B}_2\text{O}_3$  diagram that is represented by the calculated liquidus lines of  $\beta\text{-rh B}$  and  $\alpha\text{-B}_2\text{O}_3$  and contains the corresponding metastable eutectic equilibrium (see Figure 4). When the temperature drops down to  $\sim 2000 \text{ K}$ , the metastable liquidus of boron intersects the  $\text{B}_6\text{O}$  isopleth, and boron crystallization occurs. Upon further cooling, the melt composition changes according to the metastable liquidus line, and at 1130 K (46.8 at % B) the metastable eutectic crystallizes. Thus, the rapid quenching of molten  $\text{B}_6\text{O}$  results in the formation of primary crystals of  $\beta\text{-rh B}$  and metastable  $\text{B-B}_2\text{O}_3$  eutectic, while the slow cooling results in the crystallization of  $\text{B}_6\text{O}$ .

## Conclusions

The chemical interaction and phase relations in the  $\text{B-B}_2\text{O}_3$  system have been *in situ* studied at pressures up to 6 GPa and temperatures up to 2800 K using powder X-ray diffraction with synchrotron radiation. On the basis of the experimental data obtained, thermodynamic calculations of the equilibrium and metastable  $\text{B-B}_2\text{O}_3$  phase diagrams at 5 GPa have been performed. It has been found that  $\text{B}_6\text{O}$  is the only thermodynamically stable boron suboxide. At 5 GPa  $\text{B}_6\text{O}$  is a congruently melting compound that enters into eutectic reactions with boron and  $\text{B}_2\text{O}_3$ .

**Acknowledgment.** The authors thank Dr. C. Lathe for assistance in the high-pressures studies. Experiments at HASYLAB-DESY were supported by the GFZ-Potsdam under the MAX80 program. This work was financially supported by the Agence Nationale de la Recherche (Grant No. NT05-3\_42601) and by the North Atlantic Treaty Organization (CLG # 981851).

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