High-pressure high-temperature synthesis and structure of α-tetragonal boron

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Erratum

High-pressure high-temperature synthesis and structure of α-tetragonal boron

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The publisher regrets that there is a typographical error on page 2 of this article. The fourth sentence of section 3 should read as follows:
The lines characteristic of B–H–B (1700–2000 cm\(^{-1}\)) and B–H (2550–2650 cm\(^{-1}\)) bonds of decaborane were not found in the Raman spectra of the crystals (figure 3) that confirms the complete decomposition of decaborane [19, 20].
High-pressure high-temperature synthesis and structure of $\alpha$-tetragonal boron

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Abstract

Microcrystals of $\alpha$-tetragonal ($\alpha$-t) boron with unit cell parameters $a = 9.05077(6)$ and $c = 5.13409(6)$ Å and measured density 2.16–2.22 g cm$^{-3}$ were obtained by pyrolysis of decaborane B$_{10}$H$_{14}$ at pressures of 8–9 GPa and temperatures of 1100–1600 °C. The crystal structure is in good agreement with the model proposed by Hoard $et$ $al$ (1958 J. Am. Chem. Soc. 80 4507). However, compared to the original model, we found small deformations of icosahedra and changes in the interatomic distances within the unit cell of the synthesized $\alpha$-t boron.

Keywords: high-pressure, synthesis, $\alpha$-tetragonal boron

1. Introduction

The first reports [1, 2] of the structure of $\alpha$-t boron have given rise to much controversy. In the original work, the crystals of $\alpha$-t boron in the form of needles and plates were grown by reduction of boron tribromide with hydrogen on a hot tantalum filament at temperatures of 1300 °C or above [1]. The crystal structure determined by Hoard $et$ $al$ [2] belongs to the $P4_2/mnm$ space group ($a = 8.75$ Å and $c = 5.06$ Å, $Z = 50$). The unit cell (figure 1) contains four B$_{12}$ icosahedra bonded to each other by direct B–B bonds and through two isolated atoms at the 2$b$ sites (0, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0). In addition, a partial occupation of natural holes in the framework at the 2$a$ (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and 4$c$ (0, $\frac{1}{2}$, 0; $\frac{1}{2}$, 0, 0; 0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0) sites was found in variable concentrations with extra boron atoms. It was later shown that the structure of $\alpha$-t boron proposed by Hoard $et$ $al$ [2] is not of pure boron but of B$_{50}$C$_2$ ($a = 8.753$, $c = 5.093$ Å) and B$_{50}$N$_2$ ($a = 8.634$, $c = 5.128$ Å) [3, 4]. In these compounds, carbon and nitrogen impurities occupy the 2$b$ sites in the unit cell of $\alpha$-t boron and stabilize the structure. The lowest limit of carbon or nitrogen content in the borides is about 1.7–1.8 at.% [5, 6]. The discussion on the existence of $\alpha$-t boron has reinvigorated after the synthesis of $\alpha$-t boron in a nanocrystalline form [7, 8]. It was theoretically shown that the low surface energy of an $\alpha$-t boron nucleus can induce its formation and a further metastable crystal growth [9].

Also, first-principles calculations revealed that the structure of $\alpha$-t boron B$_{50}$ is stabilized if two extra boron atoms enter the 4$c$ sites of the unit cell (B$_{50}$ + B$_2$) [10]. At high pressures and high temperatures (HPHT), the formation of phases having an ‘$\alpha$-t boron’ structure was detected during the crystallization of amorphous boron [11] and in the B–N [12] and B–C [13] systems. The crystallization of amorphous boron in the presence of a boric acid impurity resulted in the synthesis of an $\alpha$-t boron phase with lattice constants close to those of B$_{52}$N$_1$N [11], and the B$_{50}$C$_2$ [13] and B$_{50}$(N$_{1–x}$B$_x$)$_2$ ($a = 8.8044$, $c = 5.0395$ Å) [12] borides were found in the B–C [13] and B–N [12] systems, respectively.

The formation of pure $\alpha$-t boron from thermodynamically stable boron phases is unlikely (see phase diagrams of boron [14, 15]). In this connection, it is of interest to produce boron by pyrolysis of boron hydrides (boranes) at high pressures when energy barriers for chemical transformations are low. For instance, thermal conversions of hydrocarbons at $P = 8$ GPa and temperatures up to 1300 °C (thermodynamically stable $P$–$T$ region of diamond) result in the synthesis of diamond crystals along with microcrystalline graphite and various nanosized metastable forms of carbon [16]. Meanwhile, it is impossible to convert diamond into graphite under the same $P$–$T$ conditions. Decaborane, one of the most available boranes, is a stable white crystalline solid with a melting point of about 100 °C.
It can be purified to 99.9 $\sim$ 99.9999\% by sublimation and used for the preparation of pure boron.

Here we report the synthesis of metastable forms of boron, including $\alpha$-t boron, by the pyrolysis of decaborane at high pressures.

2. Synthesis and characterization

Decaborane synthesized via pyrolysis of diborane $\text{B}_2\text{H}_6$, was twice purified by sublimation at 90 °C in pure nitrogen atmosphere. The thus produced crystals of decaborane melted at a temperature of not lower than 99.8 °C, indicating their high purity. The overall amount of impurities (including C, N and O) in the crystals of decaborane was at a level of tens of ppm (‘AVIABOR’, Russia). HPHT experiments were conducted at 3 and 8–9 GPa in a toroid-type device. In an atmosphere of pure argon (99.998\%), a weighed amount of decaborane was pressed into a pellet (5 mm in diameter, 3 mm in thickness) and placed in a capsule made of Ti or Ta with a wall thickness of 0.2–0.3 mm. The capsule with decaborane was installed in a container made of sintered BN or $\text{ZrO}_2$. After the pressure was applied, the reaction system was heated to a specified temperature up to 1600–1700 °C, held at constant $P$ and $T$ for a minute, and then cooled. The heating was carried out by passing an electric current through the capsule walls and two graphite leads mounted in the cell at the capsule ends. A 0.3–0.5 mm thick Mo plate was inserted between the capsule and a graphite lead to prevent their reaction. The temperature in the HPHT cell was measured using Ni–Cr/Ni–Al or Pt–Rd30/Pt–Rd6 thermocouples located at the capsule wall. The temperature reached 1400–1500 °C in the experiments using the Ti-capsule and 1600–1700 °C with the Ta-capsule. The samples obtained were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray analysis (EDX, JEOL JSM-6390LV SEM and FEI Quanta 600 SEM), x-ray diffractometry (XRD, DRON-2.0 and BRUKER AXS) atomic emission spectroscopy (AES), electron energy loss spectroscopy (EELS, LEO912 AB OMEGA TEM) and Raman spectroscopy. Raman scattering was excited with a He–Ne laser and detected with a LabRam HR–800 spectrometer. The laser beam was focused to a 5 µm spot by a 50× objective. A quantitative AES analysis (with copper electrodes) was performed using standard samples. The density of microcrystalline boron samples was determined by the flotation method using CHBr$_3$ and CCl$_4$ solutions.

3. Pyrolysis of decaborane

The XRD phase analysis and optical microscopic observations of the synthesized samples revealed that the thermal decomposition of decaborane at 8–9 GPa begins at 1100 °C. In the samples synthesized at this temperature, separate dark crystals of several micrometers in size were detected by optical microscopy among white crystals of the host material. Above 1200–1300 °C, decaborane completely decomposes with the formation of microcrystals of $\alpha$-t boron. The morphology of the crystals reflects a tetragonal structure of the boron phase (figure 2). The lines characteristic of B–N–B (1700–2000 cm$^{-1}$) and B–N (2550–2650 cm$^{-1}$) bonds of

Figure 1. Crystal structure of $\alpha$-t boron proposed by Hoard et al [2]. Extra boron atoms are shown in the 4c sites.

Figure 2. SEM image of $\alpha$-t boron crystals synthesized at 8–9 GPa and 1200–1300 °C.

Figure 3. Characteristic Raman spectrum of an $\alpha$-t boron crystal.
decaborane were not found in the Raman spectra of the crystals (figure 3) that confirms the complete decomposition of decaborane [19, 20].

The SEM and EDX analyses have been used to establish that the penetration of the material of the capsule (Ti, Ta) into the reaction volume did not exceed 20 µm in depth from the capsule wall at temperatures 1400 and 1600 ºC, for capsules made of Ti and Ta, respectively, whereas the material of the container did not enter the samples at all. The chemical composition of the α-t boron microcrystals was analyzed by EELS and EDX. No impurities (including C, N and O) were detected in the α-t boron microcrystals; besides, no carbon and metal impurities were found by AES. Using standards consisting of boron and carbon at various ratios, the concentration of carbon in the samples of α-t boron was estimated at below 0.2 at.% by AES.

The density of the α-t boron crystals measured by the flotation method was 2.16–2.22 g cm\(^{-3}\). To assess the reliability of the density measurements we have additionally determined the density of β-rhombohedral (β-rh) boron particles (∼100 µm in size, purity 99.9%, Alfa Aesar) isotopically enriched with either \(^{10}\text{B} (96\% \;^{10}\text{B}) or \(^{11}\text{B} (96\% \;^{11}\text{B}) isotope. The measured densities, 2.16 for \(^{10}\text{B} and 2.37 ± 0.01 g cm\(^{-3}\) for \(^{11}\text{B}, agree well with the isotopic composition of the β-rh boron samples.

The results were independent of the material of the capsule (Ti, Ta) and HPHT cell (BN, ZrO\(_2\)). No boron polymorphs of boron other than the α-t were detected by XRD for the synthesis temperatures up to 1600 ºC at 8–9 GPa.

Pyrolysis of decaborane at lower pressure of about 3 GPa at 1200–1300 ºC resulted in the synthesis of samples containing β-rh boron (figure 4). Note that pyrolysis of decaborane at a pressure of about 10\(^{-2}\) Pa results in α-rhombohedral boron [18, 21]. Thus, pressure is a key factor in the pyrolysis of decaborane.

4. Structure refinement of α-t boron

The crystal structure of the α-t boron phase synthesized at high pressures and temperatures was investigated through the full-profile Rietveld analysis of the x-ray powder diffraction data. The structure model suggested by Hoard et al (figure 1) was used as the starting basis for the structure refinement.
Table 2. Atomic coordinates, cite occupancy (Occ.) and isotropic displacement parameters ($U_{iso}$, Å²) for α-t boron.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occ.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>16(m)</td>
<td>1.0</td>
<td>0.3179(3)</td>
<td>0.1011(3)</td>
<td>0.3906(7)</td>
<td>0.0258(9)</td>
</tr>
<tr>
<td>B2</td>
<td>16(m)</td>
<td>1.0</td>
<td>0.2257(3)</td>
<td>0.0798(2)</td>
<td>0.0796(5)</td>
<td>0.0181(7)</td>
</tr>
<tr>
<td>B3</td>
<td>8(m)</td>
<td>1.0</td>
<td>0.1244(2)</td>
<td>0.1244(2)</td>
<td>0.3765(11)</td>
<td>0.0291(13)</td>
</tr>
<tr>
<td>B4</td>
<td>8(m)</td>
<td>1.0</td>
<td>0.2454(2)</td>
<td>0.2454(2)</td>
<td>0.5865(5)</td>
<td>0.0209(10)</td>
</tr>
<tr>
<td>B5</td>
<td>2(b)</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0357(28)</td>
</tr>
<tr>
<td>B6</td>
<td>4(c)</td>
<td></td>
<td>0.310(9)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.025</td>
</tr>
<tr>
<td>B7</td>
<td>4(g)</td>
<td></td>
<td>0.062(8)</td>
<td>0.0</td>
<td>0.183</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table 3. Selected interatomic distances (Å) in α-t boron.

<table>
<thead>
<tr>
<th></th>
<th>Intricosahedral</th>
<th>Intericosahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1–B1</td>
<td>1.778(6)</td>
<td>B1–B1 2.148(5)</td>
</tr>
<tr>
<td>B1–B3</td>
<td>1.827(4)</td>
<td>B4–B4 1.683(5)</td>
</tr>
<tr>
<td>B1–B4</td>
<td>1.765(3)</td>
<td>B3–B5 1.714(3)</td>
</tr>
<tr>
<td>B2–B2</td>
<td>1.868(5)</td>
<td></td>
</tr>
<tr>
<td>B2–B3</td>
<td>1.824(5)</td>
<td></td>
</tr>
<tr>
<td>B2–B4</td>
<td>1.816(3)</td>
<td></td>
</tr>
<tr>
<td>B3–B4</td>
<td>1.887(5)</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.811</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 shows measured and calculated XRD patterns and their difference. The crystal data, position parameters and selected interatomic distances for α-t boron are presented in tables 1–3. A rather large difference between the reliability factors $R_{B}$ and $R_{p}$ or $R_{wp}$ (table 1) is probably due to a small signal-to-background ratio in the 2θ range 10–40° (figure 5) where the strongest peaks are located. The calculated density of α-t boron (2.198 g cm⁻³) agrees well with the value 2.16–2.22 g cm⁻³ measured by the flotation method.

The unit cell parameters of the synthesized α-t boron phase are larger than those reported by Hoard et al [2]. As a result, the average interatomic distance within the icosahedra (1.811 Å) is a little longer than in the original model (1.805–1.806 Å) [2]. According to our calculations, the shortest intricosahedral bonds B2–B2 and B4–B4 (along the c-axis, figures 1 and 6) are 1.659 and 1.683 Å long (table 3) that agrees with the published data [2]: 1.658–1.710 Å and 1.664–1.709 Å, respectively. By contrast, the B1–B1 distance (2.148 Å, 3, 6) is shorter than the value 2.18 Å measured by the flotation method.

The intricosahedral bond length B2–B2 is 2.0135 Å. The distance between the icosahedra and boron atom B5 in the position 2$b$ of the unit cell becomes to 1.714 Å in our case (table 3, figure 6). In our samples, partial occupancies of natural holes in the unit cell of α-t boron with extra boron atoms were found in the 4c and 4g positions (table 2). Such a long B–B bond was found in the interstitial positions 4g sites in our model, but found no electron density in these positions. The B1–B6 distance between the boron atom B6 in the partially occupied position 4c and boron atoms B1 of the nearest icosahedra (figures 1 and 6) is 1.967(2) Å. Note that according to the first-principles calculations of the electronic band structure and density of states [10] the presence of two boron atoms at the 4c sites makes α-t boron the most stable boron phase. Hayami and Otani [10] analyzed three values of the 4c site occupation: Occ. = 0.25, 0.5 and 0.75. In the structure refinement, the ratio of the 4c site occupation Occ. = 0.310(9) (table 2) agrees well with those calculations.
5. Discussion

The unit cell volume of the α-t boron B\textsubscript{51.5} (420 Å\textsuperscript{3}) synthesized at high pressure is larger than those of the isostructural compounds B\textsubscript{50}C\textsubscript{2} (390 Å\textsuperscript{3}) and B\textsubscript{50}N\textsubscript{2} (382 Å\textsuperscript{3}) obtained at ambient pressure [3, 4]. Correspondingly, the density of the α-t boron B\textsubscript{51.5} (2.16–2.22 g cm\textsuperscript{-3}) is smaller than those of B\textsubscript{50}C\textsubscript{2} (2.43 g cm\textsuperscript{-3}) and B\textsubscript{50}N\textsubscript{2} (2.46 g cm\textsuperscript{-3}) [3, 4]. Each of the atoms at the 2\textsubscript{b} sites in the unit cells is bonded to four icosahedra and has a distorted tetrahedral surrounding. An increase in the tetrahedral covalent radius of atoms (N, C, B) at the 2\textsubscript{b} sites leads to the stretching of the unit cell diagonals (l, l\textsuperscript{2} = 2a\textsuperscript{2} + c\textsuperscript{2}) and to the expansion of the unit cell (figure 7).

The B\textsubscript{3}–B\textsubscript{5} bond length (between an atom in the 2\textsubscript{b} position and the boron atom B3 of an icosahedron) naturally increases with the tetrahedral covalent radius in the order N (0.719 Å), C (0.774 Å) and B (0.853 Å) [26]; B\textsubscript{3}–B\textsubscript{5}\textsubscript{B–N} = 1.59 Å [3], B\textsubscript{3}–B\textsubscript{5}\textsubscript{B–C} = 1.63 Å [3] and B\textsubscript{3}–B\textsubscript{5}\textsubscript{B–B} = 1.714 Å (our result, table 3). The B\textsubscript{3}–B\textsubscript{5} bond in the model by Hoard \textit{et al} is shorter (1.601–1.648 Å [2]) than expected for a B–B bond, strongly indicating the presence of nitrogen or carbon atoms at the 2\textsubscript{b} sites of the crystal structure. It is possible that the crystals studied in [1, 2] had inhomogeneous distributions of impurities. The B\textsubscript{3}–B\textsubscript{5} bond length increases in the order B\textsubscript{50}N\textsubscript{2}, B\textsubscript{50}C\textsubscript{2}, B\textsubscript{51.5} sequence, while the bond lengths B\textsubscript{2}–B\textsubscript{2} and B\textsubscript{4}–B\textsubscript{4} (between the icosahedra) remain relatively unchanged; this leads to a deformation of the icosahedra and redistribution of the electron density. An average B–B bond length within an icosahedron in B\textsubscript{50}N\textsubscript{2}, B\textsubscript{50}C\textsubscript{2} and α-t boron B\textsubscript{51.5} is 1.808 Å [3], 1.809 Å [3] and 1.811 Å (our result, table 3), respectively.

6. Conclusions

We have shown the possibility of synthesizing crystalline boron by the pyrolysis of decaborane at high pressures and temperatures. At T > 1100 °C, the crystals of α-t boron and the aggregates of β-rh boron were obtained at 8–9 and 3 GPa, respectively. The crystal structure of the α-t boron phase was determined by the Rietveld refinement using x-ray powder diffraction data, and the results agreed well with the model proposed by Hoard \textit{et al} [2].

Acknowledgments

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