Synthesis of an orthorhombic high pressure boron phase

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Abstract

The densest boron phase ($2.52\,\mathrm{g\,cm^{-3}}$) was produced as a result of the synthesis under pressures above 9 GPa and temperatures up to $\sim$1800 °C. The x-ray powder diffraction pattern and the Raman spectra of the new material do not correspond to those of any known boron phases. A new high-pressure high-temperature boron phase was defined to have an orthorhombic symmetry (*Pnnm* (No. 58)) and 28 atoms per unit cell.

Keywords: boron, high-pressure high-temperature, crystal structure

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Boron is one of the nonmetal elements which has been widely studied due to its complex polymorphism. Boron's three valence electrons are too localized to make it metallic and insufficient in number to form a simple covalent structure. As a result, boron atoms form B_{12} icosahedra linked together in a variety of ways. Only α- (rhombohedral, within a 12-atom unit cell) and β- (high-temperature form, rhombohedral, structure is not fully understood and consists of 105 or 108 atoms in the unit cell) crystalline modifications of elemental boron are currently established as pure boron forms [1–3]. Elemental boron can be prepared as an amorphous material of different purity by various techniques [4, 5]. It was proposed that β-boron is stable up 30 GPa and 3500 K, and at higher temperatures and pressures, a phase transition to the tetragonal 'T-192' structure occurs [3, 6]. The existence of 'tetragonal boron T-50' as a true modification of pure elemental boron or as boron-rich nitride or carbide has been a subject of controversy [7, 8]. On compression up to 100 GPa of a single crystal at room temperature the amorphization of β-boron was observed [9]. Resistivity measurements demonstrate

metallization of boron and occurrence of superconducting state at about 160 GPa [10]. However, the structural model of metallic boron is unknown. Thus, the behavior of boron at high pressure remains poorly understood. Here, we report a new pure boron modification synthesized at pressures up to 20 GPa and temperatures up to $\sim$1800 °C using a multianvil apparatus.
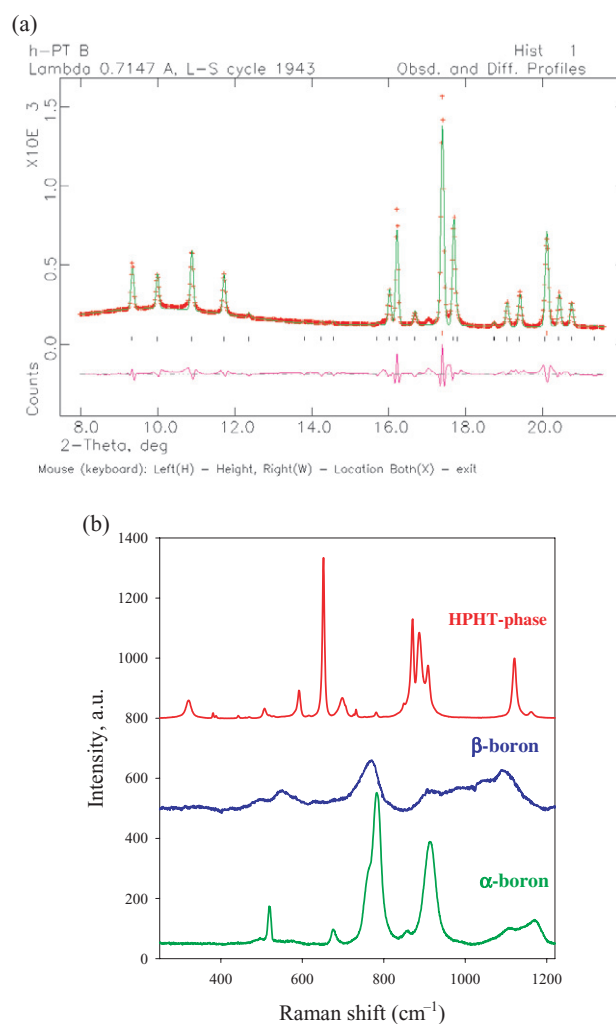
2. Experiments

As starting materials for synthesis we used β-boron (Sigma-Aldrich Inc, 99.95 and 99.7% purity; Goodfellow Inc, 99.6% purity; Chempur Inc, 99.995% purity), α-boron (Inorganic Chemistry Institute, Kiev, Ukraine, 98% purity), and amorphous boron (Chempur Inc, 95–97% purity).

High-pressure high-temperature (HPHT) experiments were carried out using 6–8-type multianvil Sumitomo 1200-ton and Zwick 5000-ton presses. Starting materials were loaded into BN, Au, Pt or In capsules of $\sim$2.6 mm ($\sim$2 mm) in diameter and of $\sim$2.7 mm ($\sim$3.5 mm) in height. The temperature reached 1500 °C in experiments with Au capsules and 1800 °C for BN capsules. The cell

(a)

(b)
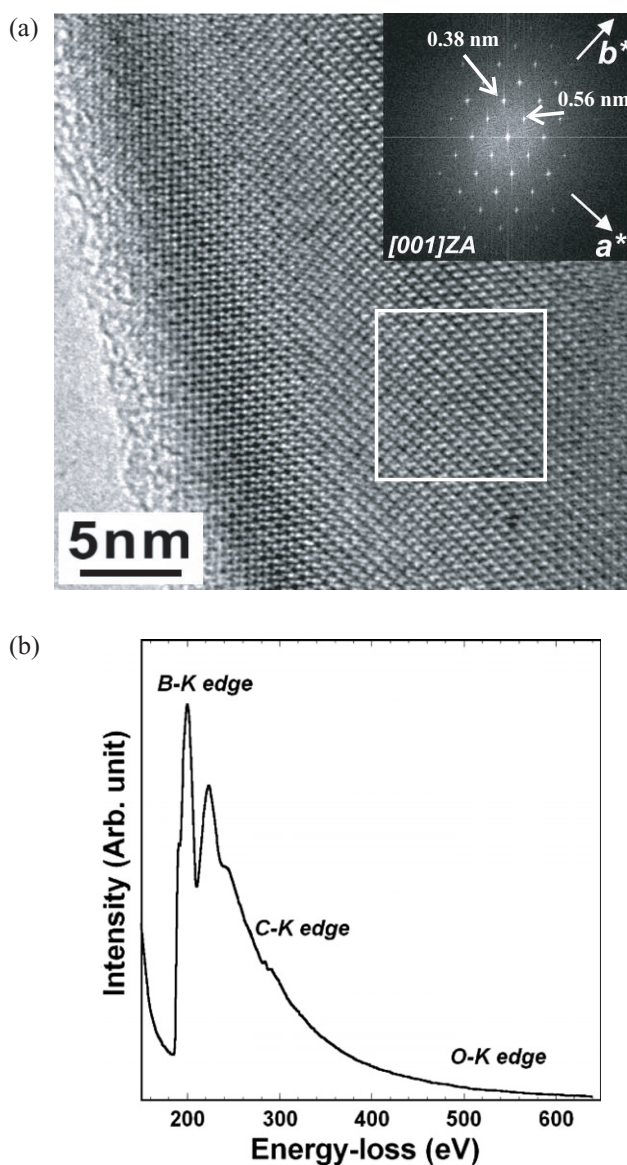
Figure 1. (a) High-resolution TEM image of the orthorhombic high-pressure high-temperature boron phase (sample S4120, see table 1.). Inset is a fast Fourier transform (FFT) pattern from the area marked by the white rectangle. ZA refers to zone axis. (b) A core-loss EELS spectrum, confirming the purity of the boron phase. The spectrum has been gain-normalized and deconvoluted using the low-loss spectrum.

(a)

(b)

Figure 2. (a) Diffraction pattern of the boron phase synthesized at 14 GPa and 1650 °C (S4120 as denoted in table 1). It was refined using the GSAS package (18) ($\lambda = 0.7147$ Å, wRp = 6.5%, Rp = 5.5%; space group *Pnnm*, $a = 5.0563(4)$ Å, $b = 5.6126(5)$ Å, $c = 6.9710(7)$ Å, B1 (0.152(2), 0.599(2), 0.794(9)), B2 (0.645(2), 0.725(2), 0.5), B3 (0.335(2), 0.505(2), 0.0), B4 (0.837(2), 0.719(1), 0.870(1)), B5 (0.669(2), 0.986(2), 0.0). Upper red ticks indicate the gold peaks (residuals of capsule material) and the lower black ticks mark the HPHT boron phase. Broad feature at ~10° is due to a glass capillary. (b) Raman spectra of the boron phase (sample S4120 of table 1) synthesized at 14 GPa and 1650 °C in comparison with the spectra of the known α and β phases.

assembly included truncated WC cubes, $MgO + 5wt.\% Cr_2O_3$ octahedra and $LaCrO_3$ heaters. The pressure and temperature uncertainties were estimated as 1 GPa and 50 °C, respectively. After gradual compression of the samples to desired pressures the temperature was increased stepwise with a speed of about 200 °C/min^{-1} to the desired value. Duration of heating was up to 10 min in different runs. The temperature quenching was done by switching off the power. The chemical composition, structure and texture of the quenched samples were studied with the scanning electron microscopy (SEM, LEO-1530) and electron energy loss spectroscopy (EELS, Gatan 666 PEELS in a Philips CM20 FEG analytical transmission electron microscope, operated at 200 kV).

Raman scattering was excited with a He–Ne laser (632.8 nm, power 100 mW) and detected with a LabRam spectrometer at resolution of 2 cm^{-1}.

The in-house x-ray powder diffraction studies were conducted using a high-brilliance diffractometer (MoK_α radiation) equipped with the Osmic focusing x-ray optics and the Bruker Apex CCD detector. At SNBL (ESRF, France) powder x-ray data were collected using a monochromatic beam (0.7 Å) and a MAR345 detector.

3. Results and discussion

Experiments in large-volume presses at pressures above 10 GPa and temperatures above 1500 °C starting from

Table 1. Summary of experiments on synthesis of the orthorhombic HPHT boron phase.

| Experiment | Starting material | Conditions | | | | Characterization |
		Capsule material	Temperature (°C)	Pressure (Gpa)	Heating time (min)	
S4096	β-boron	BN	1800	14	3	Orthorhombic HPHT phase, pure
S4120	β-boron	Au	1650	14	3	Orthorhombic HPHT phase, pure
Z612	β-boron	Pt	1600	20	5	Orthorhombic HPHT phase + PtB
Z628	β-boron	In	1600	20	5	Orthorhombic HPHT phase, pure
S4285	β-boron, isotope ^{10}B	Au	1500	14	7	Orthorhombic HPHT phase, pure
S4141	Amorphous boron	Au	1500	14	5	Orthorhombic HPHT phase + boron oxides + unknown phases
S4202	α-boron	Au	1650	14	6	Orthorhombic HPHT phase + unknown phase
S4228	β-boron, isotope ^{11}B	Au	1650	14	4	Orthorhombic HPHT phase, pure

boron precursors with purity higher than 99.7% result in formation of an optically homogeneous reddish material. Energy dispersive x-ray spectroscopy (not shown) and EELS reveal that the samples synthesized from crystalline β-boron powders are not contaminated by any impurity other than the capsule material (figure 1). SEM images of the sample surfaces in backscattered electrons indicate homogeneity of the synthesized HPHT samples. High resolution transmission electron microscopy (HRTEM) images can be interpreted in terms of a combination of boron spheres (figure 1). The diameter of the spheres (3.29–3.68 Å) is comparable with that of the circumscribed circle around the B_{12} icosahedron (3.34 Å, see figure 3). The x-ray powder diffraction pattern (figure 2(a)) and the Raman spectrum (figure 2(b)) of the new material are drastically different from those of any established boron phase. Nevertheless, the powder diffraction pattern of the phase we synthesized closely resembles that reported by Wentorf [11]. The structure of the material reported in [11] was unknown, and we did not find any further confirmation of its existence in the literature. For some time, the data from Wentorf's paper [11] were included into the Powder Diffraction Files (#00-017-0788), but later the file was deleted and no reason was provided. Positions of some lines reported by Wentorf [11] could be explained as those from boron suboxides or/and carbides and it was probably a motivation for discarding this material as pure boron. However, we establish here that the HPHT phase is pure boron and it can be synthesized from various precursors, in different environment, and at different conditions (table 1). Thus, we confirm the existence of the pure boron phase first reported by Wentorf [11].

By indexing the powder x-ray diffraction data and using Endeavour© software, the structure of quenched samples was solved in the framework of an orthorhombic unit cell ($a = 5.0563$, $b = 5.6126(5)$ and $c = 6.9710(7)$ Å, and $V = 197.83(3)$ Å^3). The suggested structure of the HPHT boron with a space group Pnnm (No. 58) contains 28 atoms in a
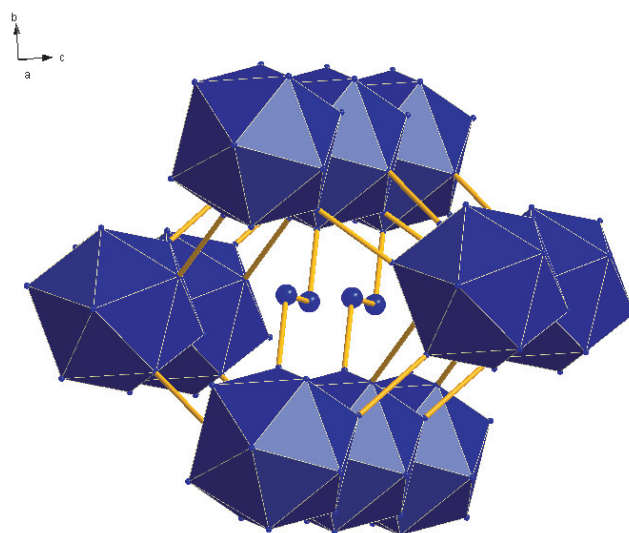
Figure 3. The structure of the high-pressure high-temperature orthorhombic boron phase shown in the *bc* projection. Boron atoms forming dumbbells are shown by larger blue spheres.

unit cell. The *bc* projection (figure 3) shows that the structure is built of B_{12} icosahedra linked into a three-dimensional network. Nearly rectangular channels running along the *a*-axis are filled with boron chains, composed of B_2 dumbbells and aligned almost parallel to the a-axis. Replacing the geometrical centres of icosahedra by one sort of atoms and the middle of dumbbells by another sort of atoms leads to an *Immm* structure, which is a distorted derivative of the NaCl structure type. In the *Pnnm* structure, the centre of the B_2 dumbbell is at $\frac{1}{2}$ 0 0, and of B_{12}—at $\frac{1}{2}$ 0 $\frac{1}{2}$. The distances B–B within the B_{12} icosahedron (1.75–1.95 Å) are slightly longer than those within the dumbbell (1.73 Å). The shortest distances in the structure are those between atoms linking (1) the two icosahedra—1.64 Å, (2) the icosahedron and the dumbbell—1.63 Å, and (3) the two boron atoms within a

dumbbell—1.73 Å. Chemical bonds in the B_2 dumbbell and between an icosahedron and a dumbbell are strongly covalent, as evident from the presence of residual electron density peaks (0.53 and 0.40 e Å^{-3} respectively) in the difference Fourier maps.

4. Conclusions

We demonstrate that the boron phase first reported by Wentorf [11] is pure boron and can be synthesized directly form different precursors at pressures above 9 GPa. Our study shows that this phase has a new orthorhombic structure consisting of B_{12} icosahedra and boron chains. The orthorhombic high-pressure high-temperature boron phase has the density of 2.52 g cm^{-3} which is the highest among any other known boron modifications.

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