Experimental pressure-temperature phase diagram of boron: resolving the long-standing enigma

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Boron, discovered as an element in 1808 and produced in pure form in 1909, has still remained the last elemental material, having stable natural isotopes, with the ground state crystal phase to be unknown. It has been a subject of long-standing controversy, if α-B or β-B is the thermodynamically stable phase at ambient pressure and temperature. In the present work this enigma has been resolved based on the α-B-to- β-B phase boundary line which we experimentally established in the pressure interval of ~4 GPa to 8 GPa and linearly extrapolated down to ambient pressure. In a series of high pressure high temperature experiments we synthesised single crystals of the three boron phases (α-B, β-B, and γ-B) and provided evidence of higher thermodynamic stability of α-B. Our work opens a way for reproducible synthesis of α-boron, an optically transparent direct band gap semiconductor with very high hardness, thermal and chemical stability.
properties (including the effect of atomic disorder and phonons) of \(\alpha\)- and \(\beta\)-B and found that at zero temperature \(\alpha\)-B is more stable than \(\beta\)-B. That agrees with the conclusion of Shang et al., who considered defect free \(\alpha\)- and \(\beta\)-B using first-principle quasi-harmonic phonon calculations. By considering the phonon contribution as the major source of the temperature dependence of the free energy, Masaga et al. obtained 970 K as the transition temperature of \(\alpha\)-to-\(\beta\)-B.

This is at odds with conclusions of van Setten et al., who introduced the quantum mechanical zero-point vibrational energy as a mechanism to stabilize \(\beta\)-B at absolute zero temperature and made \(\beta\)-B in their DFT calculations the ground state of elemental boron. Moreover, investigations indicate that it is possible to find an arrangement of partially occupied states in \(\beta\)-boron that also increase its stability with respect to the \(\alpha\)-phase. Ogitsu et al., using lattice model Monte Carlo techniques combined with ab initio calculations, found that boron could be a frustrated system and a series of \(\beta\)-boron structures, nearly degenerate in energy, may be stabilized by a macroscopic amount of intrinsic defects. According to Ogitsu et al., defects are responsible not only for entropic effects but also for a reduction in internal energy making \(\beta\)-B more stable than \(\alpha\)-B at zero temperature. Thus, if the \(\beta\)-B phase happens to be the ground state, the presence of geometrical frustration will lead to an exotic thermodynamic property in the vicinity of zero temperature that would be very unusual for a pure elemental material.

In the present work we report the results of systematic experimental exploration of the pressure-temperature (PT) phase diagram of boron at pressures of 3 GPa to 14 GPa and temperatures of 1073 to 2423 K aimed at establishing phase boundaries and resolving the long-standing problem regarding relative stability of the \(\alpha\)- and \(\beta\)-B phases.

**Results**

**Boron phases.** In order to experimentally constrain relations between \(\alpha\)-, \(\beta\)-, and \(\gamma\)-boron phases we performed more than 30 experiments in a multi-anvil apparatus (Fig. 1, Table 1, see also Methods below). In all experiments a boron source (commercially available polycrystalline high purity (99.9995%) \(\beta\)-B, see Methods Summary) was enclosed into a metallic (Au or Pt) capsule with or without addition of a Pt powder and treated at various high-pressure high-temperature (HPHT) conditions. Every trial aimed at determining of spots (Fig. 3) (space group \(R\overline{3}\))m, \(a=10.965(2)\) Å, \(c=23.859(4)\) Å). Its Raman spectrum is distinctly different from that of the precursor and characterised by much sharper peaks compared to the latter (Fig. 4).

Dependent on the pressure-temperature conditions, the experiments resulted in formation of the following pure boron phases:

(1) **Re-crystallised \(\beta\)-B**, which is different from the precursor polycrystalline \(\beta\)-B. It forms black or slightly reddish in thin sections single crystals of an irregular or sometimes hexagonal shape (Fig. 1), gives a typical for single crystals diffraction pattern consisting of spots (Fig. 3) (space group \(R\overline{3}\)-m, \(a=10.965(2)\) Å, \(c=23.859(4)\) Å). Its Raman spectrum is distinctly different from that of the precursor and characterised by much sharper peaks compared to the latter (Fig. 4).

(2) **\(\gamma\)-B**, which appears as purple elongated prismatic crystals, gives the characteristic strong Raman spectra (Figs. 1, 4) and the X-ray diffraction pattern (space group \(Pnm\), \(a=5.0576(4)\) Å, \(b=5.6245(8)\) Å, \(c=6.9884(10)\) Å). This material is identical to that described in our previous works.

(3) \(\alpha\)-B. It forms single crystals of semi-transparent orange-red colour and relatively isometric shape (Fig. 1, 2). Like other boron phases, \(\alpha\)-B is easily identified by the Raman spectrum (Fig. 4) and X-ray diffraction (space group \(R\overline{3}\)-m, 4.9065(4) Å, 12.5658(5) Å).

The SEM (EDX), microprobe (WDX), and EELS data have shown that boron phases obtained from crystalline \(\beta\)-boron powders are not contaminated independently on the type of the capsule material or pressure-temperature conditions (Fig. 5). SEM images of the sample surfaces in backscattered electrons demonstrate homogeneity of the synthesized at HPHT boron phases. High resolution transmission electron microscopy (HRTEM) images of \(\alpha\)-B, for example, reveal almost dislocation free regular packing of spheres (Fig. 5) with a diameter of 3.3-3.4 Å, comparable with that of a circumscribed circle around the B\(_{12}\) icosahedron (3.3 Å).

**Boron phase diagram.** Proven chemical and phase purity of boron crystals obtained at different pressure-temperature condition creates a basis for construction of the experimental phase diagram. Different runs resulted in crystallization of one, two or even all three boron phases simultaneously (Fig. 1, Table 1) that allows defining stability.
fields of the $\alpha-$, $\beta-$, and $\gamma-$ B phases. The phase boundary separating the $\beta-$ and $\gamma-$B phase stability fields agrees well with the phase relations experimentally found in our previous work\(^6\).

The other two phase boundaries ($\alpha-$/$\beta-$, and $\alpha-$/$\gamma-$ B) have not been reported so far based on experimental data. We argue that the $\alpha-$B has the thermodynamic stability field, because its crystallization is controlled only by pressure and temperature conditions of the experiments independently on the type of metallic solvent (Au or Pt, Table 1). In the experiment at 5.5 GPa and 1600 K (S5155 MA, see Table 1) the sample was kept at high temperature for one hour to check if the prolonged heating can affect the result. Like in short-duration experiments at similar P-T conditions we observed two phases, recrystallized beta-boron and $\alpha-$B crystals. The $\alpha-$B crystals reached up to 0.2 mm in width and up to 0.5 mm in length that is much bigger compared with those (only tens of microns in length) obtained in other experiments with a short annealing time. Growth of the $\alpha-$B crystals confirms that it is a stable phase at conditions of the experiment. Observation of simultaneous crystallization of chemically pure $\alpha-$ and $\beta-$B (at 5 GPa and 1520 K, for example) or $\alpha-$ and $\gamma-$B (at 8 GPa and 1570 GPa, for example) demonstrates the existence of monovariant points in the pressure-temperature phase diagram. The invariant (triple) point in the phase diagram could be determined by intersections of $\alpha-$/$\beta-$, $\alpha-$/$\gamma-$B, and $\beta-$/$\gamma-$B boundaries. The all three lines cross at 7.6(5) GPa and 1880(50) K (Fig. 1). Indeed, at 7.5 GPa and 1920 K we observed simultaneous crystallisation of all $\alpha-$, $\beta-$, and $\gamma-$Boron phases (Table 1, Fig. 1).

The transition of $\alpha$-to-$\beta$ boron upon heating at ambient pressure was already reported in literature\(^{10,11}\). In a diamond anvil cell (DAC) experiment (see Methods Summary) we loaded two pre-synthesized...
a-B crystals into the sample chamber along with sodium chloride, NaCl, acting as a pressure transmitting medium and thermal insulator. One of the crystals was laser-heated at 4.7(3) GPa and 1600(100) K and another one at 11.5(5) GPa and 1550(100) K. In the first case we observed formation of $\beta$-B, while at higher pressure $\alpha$-B transformed directly into the $\gamma$-phase (Fig. 6). One more MA experiment was conducted at 7 GPa and 1623 K in the Au capsule which does not dissolve boron. As in other experiments $\beta$-B was used as starting material, but in the recovered sample we found polycrystalline $\alpha$-B. Direct solid-solid phase transformation of $\beta$-to-$\alpha$ phase proves that $\alpha$-boron is a thermodynamically stable phase at certain PT conditions (Fig. 1).

**Discussion**

Extrapolation of the $\alpha$-$/\beta$-B boundary to ambient pressure (Fig. 1) suggests that $\alpha$-boron is the thermodynamically stable low-temperature boron phase below ~933(50) K. Indeed, in 1960s and 1970s arguments were raised that crystallization of small crystals of $\alpha$-B from different metallic solvents (Pt, Au, Ag, Cu, Cu-Ni, etc.) at...
boron-rich metallic flux solidified at relatively low temperature 20.

Moreover, we observed direct transformation of boron from an amorphous boron precursor supported arguments that α-B may be just a metastable, or even monotropic, form of boron. In our experiments at appropriate pressure-temperature conditions (Fig. 1) α-B crystals grow at the expense of β-B and in some runs (Table 1) all starting β-boron transforms into the α-phase. All mentioned observations prove that α-boron is a thermodynamically stable phase. Previously reported difficulties and even failure to synthesize α-B at ambient pressure could be explained based on the phase diagram we have experimentally constructed (Fig. 1): α-B is stable below about 1000 K, in good agreement with our experimental results. However, these authors22,23 calculated total energy of β-B using an ideal, defect free structural model which contradicts available experimental crystallographic data. Such a simplification of the structure of β-B in calculations could result in “underestimating” β-boron stability compared to other calculations; i.e. the agreement with the experimental results could be reached just by chance, because indeed, according to Refs. 7, 15, 22, and 25 structural defects in β-B play key role in stabilization of the phase. Thus, our results call for further detailed theoretical investigations related to stability of boron polymorphs.

Boron has been for a long time known as prospective material14,15 for numerous applications. α-boron demonstrates a truly spectacular combination of properties – it is a direct band gap semiconductor (with the reported band gap of 2.0 eV (Ref. 36), 2.4 eV (Ref. 37), or 2.15(2) eV as derived by us from EELS data), has a very high hardness (we measured the Vickers hardness of 38(2) GPa on polycrystalline aggregates), thermally and chemically highly resistive, and quite light (the density of α-B is 2.46 g/cm³ vs 4.89 g/cm³ of CdS or 6.11 g/cm³ of GaN having comparable band gaps). Such properties may make α-B material of choice in many industrial semiconductors applications, and, especially, as a working element of solar cells with high efficiency of sun light conversion into electrical power. So far research and development on potential applications of α-boron were hindered by concerns of its thermodynamic instability and the absence of a reliable way of synthesis of single crystals. A phase diagram, as a projection of the fundamental property diagram, allows materials scientists indirect use of thermodynamics16. It can be utilized to understand materials behaviour and propose optimal ways of their synthesis. The phase diagram of boron (Fig. 1) shows that α-B is not only thermodynamically stable phase in a large pressure-temperature range, but it also can be reproducibly synthesized21 at conditions readily accessible by modern industry for large-scale production (like synthetic diamonds, for example).

Summarising, our serial exploration of the pressure-temperature field using the large volume press synthesis technique resulted in establishing the phase diagram of boron in the pressure interval of 3 GPa to 14 GPa at temperatures between 1073 K and 2423 K. Based on our experimental data and linear extrapolation of the α/β phase boundary down to ambient pressure we could resolve a long-standing controversy on the ground state of boron in favour of the α-B phase.

Methods

Policrystalline β-boron (purity of 99.9995 at. %, grain size of <1000 microns), purchased from Chempur Inc., was used as a boron source material.

High-pressure techniques. Experiments in multianvil apparatuses were conducted in installed at BGI 1000-ton (Hymag) and 1200-ton (Sumitomo) hydraulic presses. The Kawai-type multi-anvil system employs six tool-steel outer-anvils and eight tungsten carbide cubic inner-anvils to focus an applied load on an octahedral high-pressure chamber formed as a result of corner truncations on the inner-anvils. By varying the corner truncation size of the inner-anvils, various sample-pressure ranges can be attained. An octahedron made of magnesium oxide that matches the pressure chamber was used as a pressure medium. In our experiments 18/11 (the edge-length of an octahedron/ inner-anvil truncation edge-length, in millimeters) assemblies for pressures of 7–11 GPa and 25/15 assemblies for pressures of 5–8 GPa were used. Although an indubitable advantage of using large assemblies is the increase of the amount of synthesized material, reaching highest temperatures in big assemblies is more difficult. Temperature in our experiments was increased stepwise with a speed ~10 K/min, or quenched. “Pressure in chamber” vs “hydraulic oil pressure” in experiments was calibrated by observations of phase transitions in standard materials, and temperature determined using W5Re/W5Re thermocouple. Uncertainties estimated in pressure 0.5 GPa and in temperature 50 K.
Experiments at pressures below 4 GPa were conducted using an end-loaded piston-cylinder type apparatus. The sample material was loaded into 6 mm diameter, 13 mm long Pt capsules (sample area 3 mm diameter, 6 mm long) which were placed into 1/8 inch t alc- pyrex sample assemblies. These sample assemblies contained an internal, tapered, graphite resistance furnace to ensure minimal temperature gradients along the length of the capsule. Temperature gradients are estimated to be less than ±2 °C for the experimental conditions used. Pressure was calibrated against the quartz-coeite and kyanite-sillimanite transitions, as well as the melting point of diopside, and pressures are considered accurate to within less than ± 5% of the stated value. Temperatures were measured with a Pt-Pt10%Rh thermocouple. Run pressures and temperatures were continually monitored and maintained for the duration of the experiment. The experiments were quenched isobarically by turning off power to the heating circuit.

Diamond anvil cell experiments we conducted using diamond anvils with the cuvet diameter of 300 μm. Pre-synthesized α-B and NaCl (used as a pressure medium and thermal insulating material) were loaded into the pressure chamber in the Re gasket preintended to about 45 μm thickness with the hole of 125 μm in diameter. Several ruby chips were placed into the sample chamber for pressure measurements. For double-side laser heating we employed two UniHead systems installed at BGI. The size of the laser beam was of about 30 μm in diameter with a temperature variation of ± 50 K within the beam. The heating duration was about 5 minutes. Temperature was measured by means of multilayer wavelength spectroradiometry.

Analytical techniques. For the phase identification, selection of single crystals, and preliminary structural analysis a high-brightness Rigaku diffractometer (Mo Kα radiation) equipped with Osmic focusing X-ray optics and Bruker Apex CCD detector was used. The diffraction patterns were processed using Fit2D software. A LabRam spectrometer (with a resolution of 2 cm−1), a He–Ne laser (632.8 nm) with a power of 15 mW for excitation, and a 50 μm diameter with a temperature variation of ± 50 K within the beam. The heating duration was about 5 minutes. Temperature was measured by means of multilayer wavelength spectroradiometry.

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L.D. and N.D. designed research; G.P., N.D., L.D., E.B., and R.W. performed research and analyzed data; G.P., L.D. and N.D. wrote the paper.

Additional information
Competing financial interests: The authors declare no competing financial interests.

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