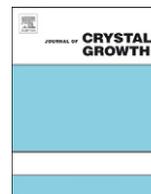




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journal homepage: www.elsevier.com/locate/jcrysgroGrowth of single crystals of B₂₈ at high pressures and high temperaturesE.Yu. Zarechnaya^{a,*}, N. Dubrovinskaia^{b,c}, L. Dubrovinsky^a, Y. Filinchuk^d, D. Chernyshov^d, V. Dmitriev^d^a Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany^b Mineralphysik, Institut für Geowissenschaften, Universität Heidelberg, 69120 Heidelberg, Germany^c Lehrstuhl für Kristallographie, Physikalisches Institut, Universität Bayreuth, 95440 Bayreuth, Germany^d Swiss Norwegian Beam lines at ESRF, 38043 Gernoble, France

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ABSTRACT

A method of the high-pressure high-temperature synthesis of single crystals of orthorhombic high-pressure boron B₂₈ from metal solutions is presented. The method is based on the high-pressure multi-anvil technique. The feasibility of single-crystal growth was demonstrated in a number of experiments conducted at various pressure–temperature conditions with various precursors including β-boron of 99.99% purity and various metals (Cu, Au, and Pt) used as fluxes and capsule materials. It was found that after dissolution in metals at high pressures and high temperatures, boron crystallizes in the form of single crystals at low temperature. The process is accompanied by chemical reactions resulting in the formation of borides. The maximum length of the B₂₈ crystals achieved is ~100 μm.

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1. Introduction

Scientific studies of elemental boron have long-time history of more than 200 years [1]. Earlier attempts of chemical extraction of boron from solid substances or acids resulted in formation of different borides or products containing not more than 90% of pure boron [1,2]. The first pure single crystals of α-boron were grown by McCarty et al. [3]. The pyrolytic decomposition of BI₃ on different substrates (Ta, W, and BN) at temperatures 1073–1273 K resulted in the formation of red crystals of 0.25 mm long [3]. The rhombohedral α-boron was found to be stable at temperatures lower than 1473 K. Under higher temperatures it irreversibly transforms into a more complex rhombohedral structure of β-boron (with 105–108 atoms in a unit cell) [4]. Single crystals of β-boron were obtained as a result of crystallization of the melt [5]. From the reduction of BBr₃ by H₂ at atmospheric pressure and temperatures as high as 1813 K, the so-called T-192 (or T-II) tetragonal-II boron phase was obtained [6]. The existence of the tetragonal-I (proposed as B₅₀=B₄₈B₂) form of pure boron is still under suspicion since reproducible synthesis yielded borides (B₅₀C₂ or B₅₀N₂) crystallized in the T-I structure [2].

For the first time, a high-pressure high-temperature (HPHT) modification of boron in a powder form was obtained at 10 GPa and 1773 K by Wentorf [7]. Recently, the existence of this phase

was confirmed both experimentally and theoretically [8–10] and its structure was solved in the Pnnm space group. The unit cell of the HPHT allotrope of boron consists of 28 atoms (B₂₈) combined into icosahedra covalently linked with additional B₂ dumbbells filling the channels along the *a*-axis (Fig. 1). The orthorhombic B₂₈ may become a promising material for electronics due to the combination of useful physical properties such as optical transparency, high hardness, and semiconductor behavior. We have already shown a feasibility of synthesis of single crystals of B₂₈ [8] at high pressures and high temperatures and report in this paper the results of more systematic investigations on single-crystal growth of B₂₈ using the HPHT technique.

2. Experimental details

High-pressure experiments were carried out using 6–8-type multi-anvil Sumitomo 1200 t and Zwick/Voggenreiter 5000 t presses. The cell assembly consisted of eight truncated WC cubes with an enclosed MgO+5 wt% Cr₂O₃ octahedron as a pressure medium. LaCrO₃ heaters were used. A cross-section of the HPHT cell is shown in Fig. 2. In experiments conducted in the 1200 t press, the volume of a cylindrical capsule was smaller (~5.5 mm³) than that in the 5000 t press assembly (~11 mm³).

It was shown [8,9] that the B₂₈ phase appears in the HPHT synthesis only if a highly purified boron precursor with a purity better than 99.99% are used. All powders of α-B and especially

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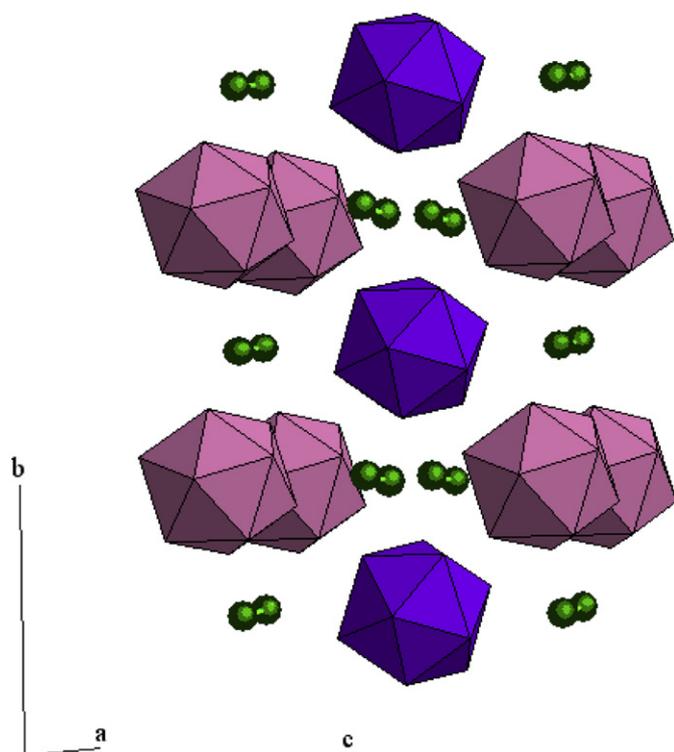


Fig. 1. The structure of the high-pressure high-temperature orthorhombic boron phase (B_{28}) shown in the bc projection.

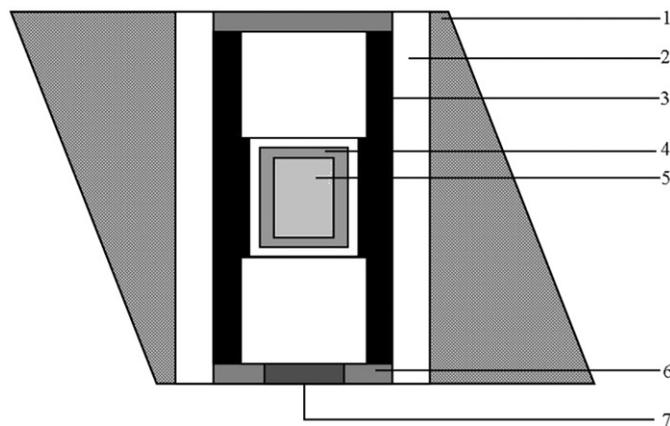


Fig. 2. Cross-section of the HPHT cell used for the single-crystal growth: (1) $MgO+5\% Cr_2O_3$ octahedron; (2) ZrO_2 ; (3) $LaCrO_3$ heater; (4) capsule; (5) sample; (6) molybdenum ring; (7) pyrophyllite inset.

amorphous boron available to us were contaminated and their use resulted in the formation of complex mixtures of different compounds [8]. In the present study, polycrystalline, commercially available β -boron in the form of granules with a typical size of ~ 50 – $100 \mu m$ (Chempur Inc., 99.995% purity) or mixtures of β -boron with 5, 10, 15, and 20 at% of Pt or Cu were used as starting materials for HPHT synthesis. In various runs, β -boron granules were loaded into Pt, Cu, or Au capsules (Table 1). Mixtures of boron with Pt (99.999% purity) or Cu (99.995% purity) powders were loaded into gold capsules (Table 1).

The gradual compression of samples to pressures of 12, 14, and 20 GPa was performed in 14/8 or 18/11 assemblies [11]. The temperature was increased stepwise with a speed of about 200 K/min. Based on the literature data [12,13] we calculated melting temperatures of metals we used as capsules to be 1678

and 1571 K at 12 GPa for Au and Cu, respectively, and 2426 K at 14 GPa for Pt. In fact, in our experiments we achieved melting of these metals at 2073 K at 12 GPa (Au), 1523 K at 12 GPa (Cu), and 2173 K at 14 GPa (Pt). In experiments with β -boron mixed with metal powders, the heating was performed up to 1773 K. Duration of heating varied between 2 and 7 min in various runs. The temperature quenching was done by switching off the power. In the experimental run S4390, after 2 min of heating at temperature above 1773 K we gradually decreased the temperature during 18 min down to 1073 K, and then quenched the sample. In all the experiments, the uncertainties in pressure and temperature determination were estimated to be 1 GPa and 50 K, respectively.

After experiments the capsules were extracted from the octahedra. Products of synthesis with capsules were treated in a mixture of concentrated HNO_3 and HCl (1:3) at ~ 373 K during several hours. Products of the treatment were extracted from a suspension and cleaned in distilled water.

The morphology and chemical composition of the synthesized samples of single crystals were studied by means of the scanning electron microscopy (SEM) (LEO-1530). Chemical purity of the samples was confirmed using WDX microprobe analysis (Jeol JXA-8200; focused beam; 20 keV, 20 nA). Counting time for each element was 20 s at the peak position and 10 s at each background position. For calibration, BN, Pt, Au, carbon, and MgO were used as standards. ZAF corrections method was applied. All samples and standards were carbon coated with thickness of the coating of 10 nm.

Phase compositions of products were checked using X-ray diffraction. The *in-house* powder X-ray diffraction studies were conducted using a high-brilliance Rigaku diffractometer (Mo $K\alpha$ radiation) equipped with Osmic focusing X-ray optics and Bruker Apex CCD detector.

The quality of the grown single crystals obtained in experiment Z612 (Table 1) with a size of about of $25 \mu m \times 6 \mu m \times 6 \mu m$ was checked at Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF, France). The diffraction data were collected at 293 K using a single-crystal diffractometer KUMA KM6-CH equipped with a CCD detector with a monochromatic beam (0.7146 Å).

The Raman system with a He–Ne laser (632.8 nm) at a power of 15 mW for excitation and a LabRam spectrometer (the spectral resolution of 2 cm^{-1}) was used to collect Raman spectra from the samples. In order to avoid heating of the samples by the laser, Raman spectra were collected for 2 s using the $\times 50$ objective and D2 filter.

3. Results and discussion

The transition from β -B to the B_{28} phase occurs at pressures higher than 8.5 GPa and temperatures above ~ 1773 K [8]. We conducted a series of experiments on synthesis of single crystals of B_{28} from HT solutions in metals at pressures above 12 GPa and temperatures in the range 1523–2173 K. Table 1 summarizes experimental data on synthesis of single crystals of B_{28} at HPHT conditions.

3.1. Characterization of the quality of B_{28} single crystals

The formation of red needle-shaped single crystals of B_{28} in HPHT experiments (20 GPa, 1873 K) performed in Pt capsules has been already reported [8]. The grown single crystals (experimental run Z612) were analyzed using synchrotron radiation at SNBL (ESRF). The rocking curves were measured with a 0.01° step in ω and the peaks were found to be almost symmetrical. As examples, the rocking curves of the distant reflections ($2\bar{1}4$)

Table 1
Summary of experiments on synthesis of single crystals of the orthorhombic B₂₈ phase. Intermetallic phases originated from chemical reactions between precursor powders and capsule materials are marked as asterisks (*). Abbreviation “SC” means “single crystal”. The size of B₂₈ single crystals is given as an average value for every experiment.

| Experiment | Starting material | Conditions | | | | Synthesis products | Average size of B ₂₈ crystals (μm) |
|------------|-------------------------|------------------|-----------------|----------------|----------------------|---|---|
| | | Capsule material | Temperature (K) | Pressure (GPa) | Heating time (min) | | |
| S4439 | 95 at% β-B+5 at% Cu | Au | 1723 | 12 | 7 | Orthorhombic B ₂₈ (*) | – |
| S4409 | 90 at% β-B+10 at% Cu | Au | 1723 | 12 | 6 | Orthorhombic B ₂₈ (*) | SC, 8 × 8 × 100 |
| S4442 | 85 at% β-B+15 at% Cu | Au | 1923 | 12 | 2 | Orthorhombic B ₂₈ , B ₂₄ Cu (*) | 25 × 50 |
| S4445 | 80 at% β-B+20 at% Cu | Au | 1723 | 12 | 3 | Orthorhombic B ₂₈ , B ₂₄ Cu (*) | SC, 6 × 10/6 × 60, irregular shape |
| S4457 | β-B | Cu | 1523 | 12 | 3 | Orthorhombic B ₂₈ , B ₂₄ Cu (*) | SC, 6 × 6 × 58 |
| S4390 | 98.5 at% β-B+1.5 at% Pt | Au | 1723 | 12 | 2 | Orthorhombic B ₂₈ , BPt (*) | – |
| S4490 | 95 at% β-B+5 at% Pt | Au | 1723 | 12 | 3 | Orthorhombic B ₂₈ , BPt (*) | SC, 4 × 4 × 92 |
| S4486 | 90 at% β-B+10 at% Pt | Au | 1723 | 12 | 3 | Orthorhombic B ₂₈ , BPt (*) | SC, 9 × 9 × 80, irregular shape |
| S4480 | 85 at% β-B+15 at% Pt | Au | 1723 | 12 | 3–4 | Orthorhombic B ₂₈ , BPt (*) | – |
| S4400 | 80 at% β-B+20 at% Pt | Au | 1723 | 12 | 6 | Orthorhombic B ₂₈ , BPt (*) | SC, 3 × 3 × 21 |
| Z612 | β-B | Pt | 2173 | 20 | 5 | Orthorhombic B ₂₈ , BPt (*) | SC, 6 × 6 × 25 |
| Z657 | β-B | Pt | 2173 | 14 | Quenched immediately | Unknown phases | SC, 6 × 6 × 58 |
| S4477 | β-B | Au | 1723 | 12 | 4 | Orthorhombic B ₂₈ (*) | SC, 8 × 8 × 70 |
| S4492 | β-B | Au | 2073 | 12 | Quenched immediately | Orthorhombic B ₂₈ +unknown phases | SC, 25 × 25 × 104 |

and (113)) of the B₂₈ phase are presented in Fig. 3. The full-width at half-maximum (FWHM) of the chosen reflections was fitted by the pseudo-Voigt function and determined to be 0.0379(5)^o (Fig. 3(a)) and 0.0346(4)^o (Fig. 3(b)) in ω, correspondingly. These values are comparable with the pure instrumental function of the KUMA diffractometer, thus proving an evidence of a high quality of the B₂₈ single crystals. The direction of elongation of B₂₈ crystals was established to coincide with the crystallographic a-axis, i.e. with the direction of channels in the structure filled by B₂ dumbbells. The crystal faces are formed by the (0 1 1) prism.

3.2. Influence of experimental conditions on the synthesis products

The results of synthesis, in particular, the shape and size of grown crystals, their quality, etc. depend on many factors including materials used as a flux. The binary phase diagrams of boron with some metals, in particular Pt, Cu, Au (used in the present work as solvents for boron), were studied mostly at atmospheric pressures [14]. Reaction of Pt and B under pressure was studied by Whitney and Giese [15] at pressures below 5 GPa and temperatures up to about 1023 K. They found that the reaction B+Pt→BPt occurs at non ambient conditions. The slope of the curve representing the boundary in the P–T phase diagram for this reaction was found to have a value of $dP/dT=133 \text{ bars}/^{\circ}$. Strong and Bundy [16] found a value of dP/dT for the melting point of Pt to be 140 bars/^o. Thus, the formation of BPt occurs at temperatures very close, but slightly lower than those necessary for melting of Pt at high pressure.

At atmospheric pressure [14] B and Pt react together and form the phases with the following stoichiometry: B₂Pt₃, BPt₂, and BPt₃. In fact, according to Ref. [14], in reality B₂Pt₃ may be BPt and thus high-pressure BPt [15] can also be produced at ambient pressure [14]. Interestingly, the BPt phase in high-pressure high-temperature experiments of Whitney and Giese [15] was traced to the reaction of boron and the platinum foil used to encapsulate the

boron-containing samples. In our experiments, on synthesis of B₂₈ single crystals Pt capsules were also used (Table 1). The eutectic point of the B–Pt system at ambient pressure occurs at 1213 K according to Ref. [14]. Following the P–T phase diagram of Whitney and Giese [15] we intended to reach temperature above the eutectic point of the B–BPt system at pressures above 8.5 GPa, i.e. in the pressure–temperature range of stability of B₂₈ [9]. Decrease in temperature below liquidus had to result in crystallization of B₂₈. Indeed, X-ray diffraction patterns collected from all “as-synthesized” samples (i.e. those before the acid treatment, obtained from HP synthesis with β-boron in Pt capsules or with precursors with up to 20 at% of Pt-additive (see Table 1)), show the presence of the BPt phase additionally to the B₂₈ phase. The diffraction peaks of the observed BPt phase (Table 2) match well with those of the ICDD PDF #13-0288 for BPt.

In order to explore other possible solvents for the single-crystal growth, Cu was used as both an additive to boron and a capsule material, while Au was used only as a capsule material. The Cu–B phase diagram is not complicated by Cu–B compounds. Melting temperature of Cu is considerably lower than that of Au and Pt at the same pressures. This and the relatively low eutectic point (1283 K) at ambient pressure suggest a possibility for the successful single-crystal synthesis of B₂₈. The same procedure as for a series of experiments with Pt was used in experiments with Cu. Various amounts of a Cu powder (5, 10, 15, 20 at%) were used as an additive to β-B. The mixtures were loaded into an Au-capsule. X-ray diffraction patterns of products showed the presence of the diffraction lines of intermetallic compounds (CuAu, Cu₃Au, CuAu₃, etc.) or alloys [14], which form when Cu reacts together with Au. Thus, the B₂₈ crystals likely grow in the Cu–Au flux. At higher Cu content (above 15 at%) in a mixture with β-B in an Au capsule or at synthesis from pure β-B in a Cu capsule a formation of the Cu-boride (CuB₂₄, ICDD PDF #26-1111) (Table 2) was observed. At low amount of Cu additive (up to 10 at%), Cu-boride did not appear. The analysis of the dependence of chemical compositions of intermetallic compounds or alloys as

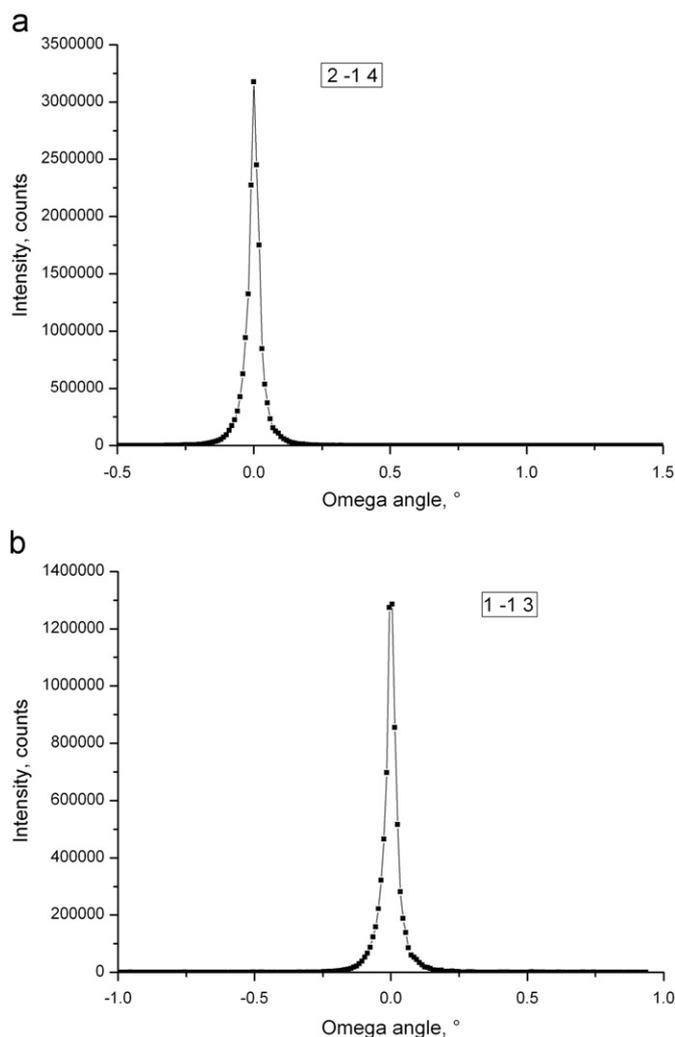


Fig. 3. Rocking curves of $(2\bar{1}4)$ (a) and $(1\bar{1}3)$ (b) reflections of B_{28} singly crystal (Z612, see Table 1) measured at room temperature.

a function of the synthesis conditions was out of the scope of the present work, but seems that in our experiments the only use of an Au capsule and a pure boron precursor resulted in the formation of pure B_{28} single crystals mixed with polycrystalline aggregates of B_{28} (Fig. 4) free from any borides.

As already mentioned, all used metals, as well as produced intermetallic compounds or alloys, are dissolvable in the mixture of acids: HCl and HNO_3 (3:1). Copper and platinum borides are also dissolvable in the mixture of these acids. After several hours of boiling of samples in the acids at ~ 373 K, we did not see any trace of these compounds in the residual material. Only crystals of a characteristic red color and their aggregates are left.

Raman spectra (Fig. 5a) of all “as-synthesized” samples are similar and resemble that of B_{28} well characterized by various methods in our previous works [8,9,17]. The spectra do not show any difference in the number of active vibration modes or shifts of modes that could indicate metal incorporation into the structure of the B_{28} phase (Fig. 5a).

The electrical resistivity of single crystals along the longer direction (Fig. 4) was measured by the four-probe method [9] (shorter directions of our crystals are too small for connection of electrodes). Changes in conductivity of orthorhombic B_{28} boron single crystals as a function of temperature are very similar to that observed for the bulk material (Fig. 5b).

Table 2

d-spacings of BPt (experiment S4486) and $B_{24}Cu$ (experiment S4445) phases determined from X-ray powder diffraction and those reported in the powder diffraction database (#13-0288 (BPt), #26-1111 ($B_{24}Cu$)).

| Phase | d(PDF) (Å) | d(OBS) (Å) | hkl | I/I ₀ |
|--------|------------|------------|--------|------------------|
| BPt | 2.9100 | 2.9300 | 100 | 75 |
| | 2.3620 | 2.3694 | 101 | 100 |
| | 2.0270 | 2.0314 | 002 | 50 |
| | 1.6780 | 1.6833 | 110 | 75 |
| | 1.6670 | 1.6672 | 102 | 75 |
| | 1.4570 | 1.4452 | 200 | 25 |
| | 1.3700 | 1.3638 | 201 | 75 |
| | 1.2950 | 1.2917 | 112 | 90 |
| | 1.2260 | 1.2292 | 103 | 60 |
| | $B_{24}Cu$ | 8.8500 | 8.7484 | 101 |
| 7.9800 | | 8.0211 | 003 | 90 |
| 5.4900 | | 5.0639 | 110 | 100 |
| 4.5200 | | 4.5499 | 113 | 12 |
| 4.4200 | | 4.4425 | 202 | 16 |
| 4.2800 | | 4.2839 | 015 | 10 |
| 3.9800 | | 4.0592 | 006 | 60 |
| 3.5500 | | 3.4883 | 211 | 100 |
| 3.4400 | | 3.4394 | 122 | 30 |
| 3.3700 | | 3.3357 | 205 | 4 |
| 3.2200 | | 3.1910 | 107 | 30 |
| 3.0800 | | 3.1016 | 214 | 12 |
| 2.8700 | | 2.8679 | 125 | 5 |
| 2.7800 | | 2.7787 | 027 | 20 |
| 2.5300 | | 2.5345 | 208 | 6 |
| 2.4800 | | 2.5144 | 306 | 50 |
| 2.4100 | | 2.4707 | 134 | 4 |
| 2.3330 | | 2.3200 | 042 | 55 |
| 2.3100 | | 2.2947 | 315 | 4 |
| 2.1230 | | 2.1478 | 0111 | 12 |
| 2.0870 | | 2.0936 | 137 | 25 |
| 2.0490 | | 2.0481 | 324 | 65 |
| 2.0360 | | 2.0329 | 309 | 35 |
| 1.9940 | | 1.9919 | 0012 | 10 |
| 1.9800 | | 1.9615 | 318 | 12 |
| 1.8310 | | 1.8398 | 330 | 16 |
| 1.7830 | | 1.7991 | 333 | 14 |
| 1.7650 | | 1.7668 | 505 | 60 |
| 1.7150 | 1.7311 | 0213 | 20 | |
| 1.6860 | 1.6830 | 4010 | 40 | |

It is worth noticing that X-ray diffraction of the samples synthesized at elevated temperatures (2073 and 2173 K) showed the presence of unknown phases (experiments Z657 and S4492). These phases are likely the products of chemical reactions of precursors and the capsule materials with other materials of the HP assembly surrounding the sample chamber that happened as a result of full melting of capsules.

3.3. Discussion of the mechanism of single-crystal growth of B_{28}

Growth of crystals from the liquid state plays a dominant role for many technical applications and in basic research. Adverse aspects of the crystal growth from HT solutions are the low growth rate and the low crystal yield, especially if the slope of the liquidus curve is large [18]. Growth processes are characterized by a slow lowering of the temperature in order to force crystallization. Technically, precise knowledge of the liquidus curve is required in order to avoid either a spontaneous crystallization or dissolving of the seed crystals in synthesis from HT solutions. The application of a suitable solvent or nonstoichiometric composition is capable of reducing a high growth temperature or pressure, so that growth close to thermal equilibrium may yield crystals with a high structural perfection [18]. Our choice of solvents was based on general principles: high solubility of the component of interest, low chemical reactivity between the material and solvent,

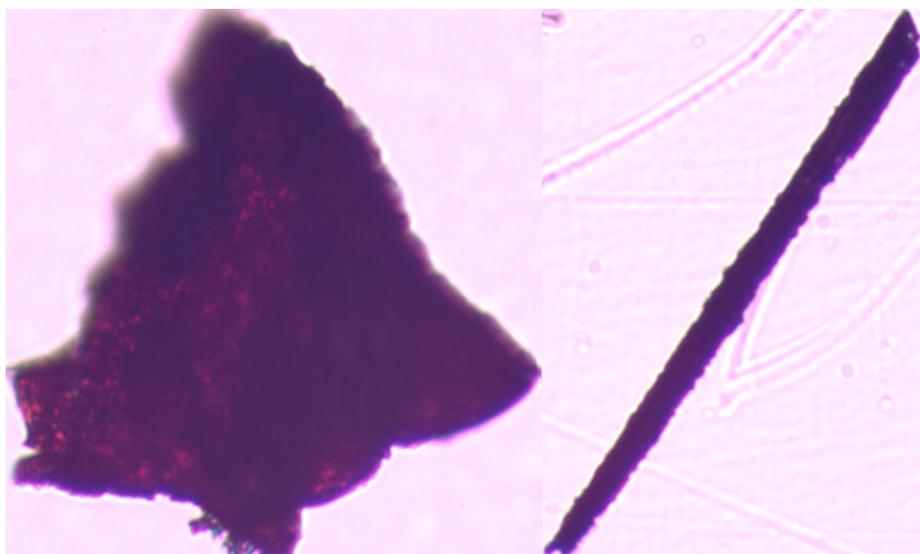


Fig. 4. Microphotograph of a polycrystalline aggregate (left) and a single crystal (right) of B_{28} phase synthesized in an Au capsule at $P=12$ GPa and $T=1723$ K (experiment S4477, see Table 1).

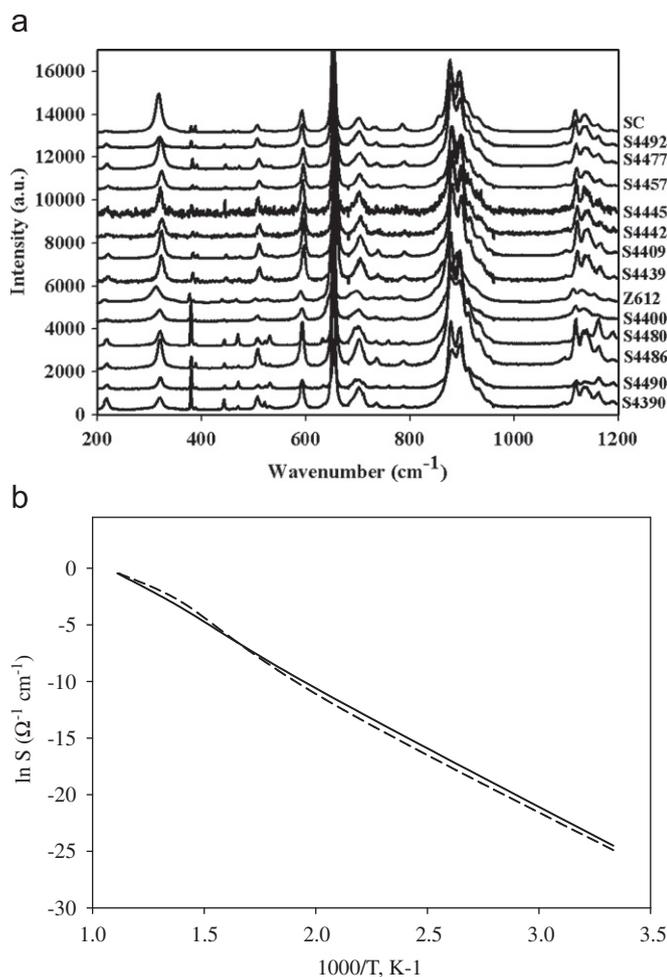


Fig. 5. (a) Raman spectra from products of B_{28} synthesis of various experiments compared with those from a well-characterized single crystal (SC-experiment Z612); (b) changes in conductivity of orthorhombic B_{28} boron single crystals (continuous line; measured along longer direction) and bulk material (dashed line) as a function of temperature.

a possibility to easily remove the solvent after the growth process, its high purity, and low toxicity. Dealing with crystal growth at high pressure, we did not have the HP phase diagrams of the systems we explored, as well as we did not introduce seeds and relied on a spontaneous crystallization. In choice of the temperature we oriented on HP melting curves known for the solvents of choice [12].

Single-crystal growth can be performed by several methods, for example by controlling the speed of crystallization, degree of oversaturation or overcooling, etc. In one of the experiments we checked if a gradual temperature decrease affects the size of grown single crystals. In the experiment S4390, a mixture of β -B and 1.5 at% of Pt was loaded into an Au capsule (see Table 1). At 12 GPa the sample was heated at ~ 1723 K for 2 min. Then, the temperature was decreased during 18 min to ~ 1023 K and after that the sample was quenched. After treatment of the synthesized sample in acids mixture, we observed aggregates of single crystals of B_{28} . Such a “gradual temperature decrease” did not have any visible effect on the size of single crystals in comparison with those grown only upon heating at the same temperature.

Growth of B_{28} single crystals could be controlled by the amount of the boron-containing melt in the pressure chamber. Complete melting of the whole pressure chamber potentially depends on the amount of flux material. Series of synthesis experiments were carried out using different amounts of various metallic powders as fluxes (Table 1). Experiments S4439 and S4400 were conducted at 12 GPa and 1723 K using Au capsules and mixtures of granulated β -B with 5 at% of Cu-additive and 20 at% of Pt-additive, respectively (Table 1). The back scattered electron (BSE) images of polished surfaces of the S4390 and S4400 samples (Figs. 6(a) and (b), respectively) show elongated crystals of various sizes up to tens of microns of B_{28} surrounded by Cu–Au or Pt–Au matrices. Such crystals could be found only in the inner parts of the capsules (at the boron-metal capsule interface). The rest of the samples (i.e. their inner parts that were not in direct contact with the capsules) was composed of granules of polycrystalline B_{28} . Their surface was covered by very thin, reddish, only a few microns long B_{28} crystals with an irregular or a plate-like shape (the quality of these tiny crystals was not investigated). We believe that this observation, typical for almost

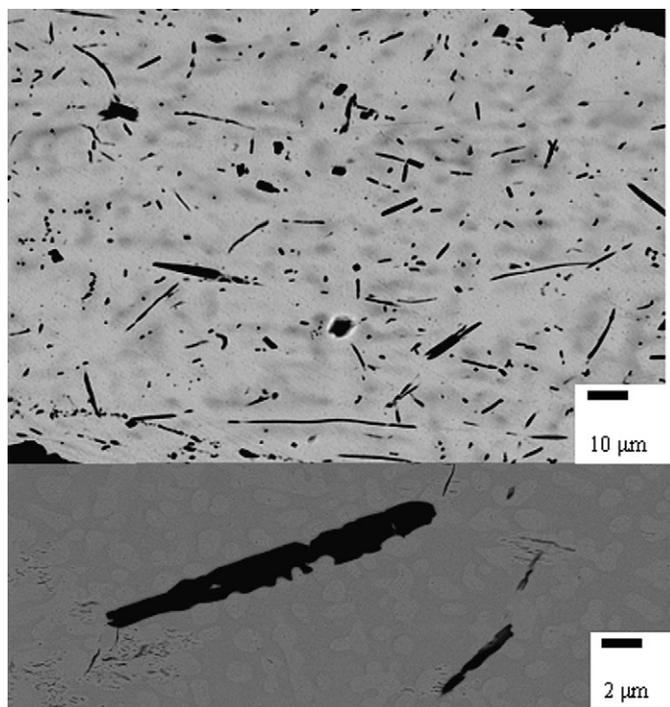


Fig. 6. BSE image of polished surfaces of samples synthesized in Au capsules at 12 GPa and 1723 K with use of (a) 5 at% of Cu-additive (experiment S4439, Table 1) and (b) 20 at% of Pt-additive (experiment S4400, Table 1).

all of our experiments, is imposed by a specific character of the B precursor we used. As we already mentioned, only granules (~ 50 – $100 \mu\text{m}$ in size) of pure β -B were available. We could not grind or mill them without a risk of contamination because of extreme hardness of the material, so that we used the granules as they were. It means that dissolution of boron in metals in sufficient amounts for spontaneous crystallization and formation of relatively big single crystals was reached only for the granules which were embedded into the capsules' walls at the capsule-sample boundary. The amount of metallic powders that surrounded the granules was likely insufficient to penetrate deep into the boron grains and cause their complete melting. Boron, only partially dissolved in metals in the inner parts of the samples, on cooling likely either precipitated on polycrystalline aggregates of B_{28} formed due to the solid–solid transition within non-molten granules, or formed numerous tiny crystallites described earlier. Although temperature was high enough to melt whole material in the capsule, only a part of it was actually molten. Potentially, not complete melting could be caused by the temperature gradient within the pressure chamber. However, usually the temperature gradient is estimated to be not more than 50 K across the sample [11], so that taking into account that melting in the inner parts of the sample was also observed, we could eliminate problems related to the temperature gradient. In principle, it is possible to reach complete melting by overheating a sample. Indeed, in experiments conducted at higher temperatures a complete melting of a capsule was achieved (for example, the gold capsule in the experiment S4492 at ~ 2073 K and 12 GPa) and we succeeded in synthesis of larger crystals of orthorhombic B_{28} with the length of over $100 \mu\text{m}$. However, in such cases of complete melting of capsules chemical reactions with the materials of the assembly surrounding the capsule and samples are unavoidable. Thus, we cannot be sure that the amount of melted Au, and not the presence of other chemical compounds, promotes B_{28} crystal growth. In the future experiments a

precaution should be undertaken to find a refractory, non-reactive material to separate the capsule from its surrounding.

Based on our observations, we can suggest that mechanism of growth of B_{28} single crystals may be similar to that of diamond grown from metallic solutions [19]. Assuming that phase relations of boron with Pt, Cu, and Au remain similar to those under atmospheric pressure, we could expect that some amount of boron dissolves in metals: according to [14], several at% of B could incorporate into Pt; solubility limit of B in Cu is less than 1 at%, and there are indications that small amount of B could be dissolved in Au-melt as well. On cooling boron dissolved in metals crystallizing as the B_{28} phase. It means that growth of B_{28} crystals is controlled by the amount of B-containing liquid in the pressure chamber.

4. Conclusions

We presented and discussed a procedure of growing single crystals of orthorhombic B_{28} from metal solutions at high-pressure high-temperature conditions. Various (Cu, Au, Pt) capsules and solvent materials were tested. In all experiments we observed that B_{28} crystals form from the boron-metal solution during cooling; thus, the mechanism of formation of HPHT boron may be similar to that of diamond growth [19]. A maximal size of the grown B_{28} crystals of a very high quality was about $100 \mu\text{m}$. It did not depend on the volume of the pressure chamber and the duration of heating. In our experiments the crystal size was likely imposed by the amount of the solution formed by the melted metallic flux and boron. Only use of Au did not lead to formation of borides. To increase the total yield of B_{28} single crystals the search for less reactive solvents could be suggested.

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