New boron subnitride B$_{13}$N$_2$: HP-HT synthesis, structure and equation of state

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Abstract. Here we report the synthesis of new B-rich phase, boron subnitride B$_{13}$N$_2$ by crystallization from the B–BN melt at 5 GPa. The structure of B$_{13}$N$_2$ has been resolved by the Rietveld analysis and represents a new structural type formed by the distorted boron icosahedra linked together by N–B–N chains and inter-icosahedral B–B bonds. From the 300-K equation-of-state data, the bulk modulus of B$_{13}$N$_2$ has been found to be $B_0 = 200(15)$ GPa.

1. Introduction
Boron-rich solids give a rise to a large group of hard refractory compounds, i.e. B$_6$O, B$_4$C, etc., with unique crystal structures and interesting physical and chemical properties related to the strongly covalent and electron-deficiency character of the chemical bonds [1-2]. The fortunate combination of lightness, hardness, strength, chemical inertness, high melting point as well as high cross-section for neutron absorption has suited boron and boron-rich compounds to many technological applications [3-6]. The synthesis of new phases with boron-like structures in the B–C–N–O system may lead to novel materials with advanced properties exceeding those of B$_4$C and B$_3$O.

The existence of boron subnitride "B$_6$N" was suggested by Condon et al. [7]. Later, the synthesis of the B–N films containing "B$_6$N" with the structure related to α- rhombohedral boron was described by Saitoh et al. [8]; however, neither structure nor composition of the synthesized B–N compounds were established. Hubert et al. [9] reported the high-pressure solid-state synthesis of boron subnitride "B$_6$N" by reacting amorphous boron and hBN at 7.5 GPa and ~2000 K. Based on the EELS data, the authors have claimed the B$_6$N composition; however, according to our previous results [10], the diffraction pattern reported in [9] cannot belong to any B$_6$O-like structure. Moreover, our in situ experiments under the same p–T conditions have shown that β-rhombohedral boron does not react with hBN [10].

In the present work, we have in situ studied the crystallization of new boron subnitride B$_{13}$N$_2$ from the B–BN melt at 5 GPa. Quenched samples have been characterized by X-ray diffraction, Raman spectroscopy and ATEM-EELS; and the crystal structure and equation of state of B$_{13}$N$_2$ have been established.

2. Experimental
A powder of β-rhombohedral boron (β-rh B) has been mixed with hexagonal graphite-like BN (claimed purity 99.99%, Alfa) in the 5:1 molar ratio that corresponds to the B$_6$N composition. The HP-HT synthesis has been carried out using a multianvil X-ray system MAX80 at beamline F2.1,
HASYLAB-DESY. The experimental set up has been described elsewhere [11]. Energy-dispersive X-ray diffraction data has been collected on a Canberra solid state Ge-detector with fixed Bragg angle $2\theta = 9.28(4)\degree$ using a white beam collimated down to $60\times100\ \text{µm}^2$ (vertical by horizontal). The detector has been calibrated using the $K_{\alpha}$ and $K_{\beta}$ fluorescence lines of Cu, Rb, Mo, Ag, Ba, and Tb. The sample pressure has been determined from the equation of state of highly ordered hBN [12]. Up to 2400 K, the sample temperature has been measured with the W3%Re–W25%Re thermocouple without correction for the pressure effect on the thermocouple emf. Temperatures above 2400 K have been estimated by the extrapolation of the power–temperature calibration curve.

The recovered samples were analyzed by powder X-ray diffraction using Seifert MZIII and G3000 TEXT (Inel) X-ray diffractometers in Bragg-Brentano geometry employing Cu Kα radiation. Highly ordered hBN has been used as an internal standard. Unit cell parameters were derived from the LeBail profile refinement procedure, while structure refinement has been performed by Rietveld analysis using the GSAS software [13].

Microstructure and phase composition of the samples have been studied using a JEM 2010HR (JEOL) transmission electron microscope equipped with a GIF2000 (GATAN) parallel electron energy-loss spectrometer. The Raman scattering measurements have been performed at 300 K using a Dilor XY system with the 514.5 nm Ar$^+$ ion laser as the excitation source. The scattered light was collected in the backscattering geometry using a CCD detector. The spectrometer was calibrated using the $I_{25}$ phonon of d-Si ($Fd-3m$).

For the equation-of-state measurements, X-ray diffraction experiments in a diamond anvil cell have been performed at ID27 beamline, European Synchrotron Radiation Facility (ESRF). Pressure has been determined in situ from both the calibrated shift of the ruby $R_1$ fluorescent line [14] and equation

![Figure 1](image-url)
of state of neon [15] that has been employed as a pressure medium. High-brilliance synchrotron radiation from a two-phased undulator has been set to a wavelength of 0.3738(1) Å. Angle-dispersive X-ray diffraction patterns have been collected with on-line MAR 345 image plate detector and processed with FIT2D software [16].

3. Results and discussion
At 7 GPa, the solid-phase interaction between β-rh B and hBN does not occur up to 2000 K [10]. In the present study, at 5 GPa formation of new "B₆N" phase was observed only in the samples heated to the temperatures above 2450 K, i.e. upon the boron melting (Fig. 1). From the EELS data, the stoichiometry of the phase with B₆O-like electron diffraction pattern has been determined to be B₆±₁N. In the whole p–T range under study, the "B₆N" phase has been always obtained in mixture with β-rh B, I-tetragonal-boron-like phase ("I-t B" [17]), and hBN (Figs. 1&2). This fact points to the "B₆N" formation from the B–BN melt by a peritectic reaction.

X-ray powder diffraction patterns of quenched samples show the lines of a B₆O-like lattice, namely 101, 003, 012, 110, 104, 021, 024, 303, 018, 125, 220, 131, 223, 217, 119 and 134 (Fig. 2). The lattice parameters have been found to be \(a = 5.4585(8)\) Å and \(c = 12.253(2)\) Å (trigonal syngony, hexagonal axis, space group R-3m), which are intermediate between those of boron suboxide B₆O (\(a = 5.367(2)\) Å, \(c = 12.325(3)\) Å [JCPDS No. 87-1143]) and boron carbide B₄C (\(a = 5.633(8)\) Å, \(c = 12.164(2)\) Å [18]). Since lattice parameters of the resulting B₆O-like phase have been well reproducible in various experiments, one can conclude that the phase of a constant stoichiometry has been synthesized. The relative line intensities, however, do not exactly correspond to the B₆O structure. Thus, most probably, the unit cell of "B₆N" compound is similar to that of B₆O with some linking atoms between nitrogen. In the case of B₄C, the C–C–C and C–B–C chains occur; at the same

**Figure 2.** Rietveld full profile refinement of the X-ray powder diffraction pattern of B₁₃N₂ boron subnitride. Red stars represent the main lines of B₁₃N₂.
Table. Results of the Rietveld refinement of atomic coordinates and fractions. The refined parameters are given in bold.

| No. | Atom | Wickers index | x     | y     | z     | Fraction |
|-----|------|---------------|-------|-------|-------|----------|
| 1   | B    | 18h           | 0.1721| -0.1721| 0.0363| 1        |
| 2   | B    | 18h           | 0.1198| -0.1198| 0.8832| 1        |
| 3   | N    | 6c            | 0     | 0     | 0.3749| 1        |
| 4   | B    | 3b            | 0     | 0     | 0.5000| 1        |

$R - 3m$

$Z = 6$

$D = 2.607 \text{ g cm}^{-3}$

No. of reflections: 11

$wr_p = 0.1445$

$R_p = 0.1036$

time neither O–O–O nor O–B–O linking exist in boron suboxide. In the case of "B$_6$N", the N–N–N bonding is hardly expected, but N–B–N links may occur.

The structure of the "B$_6$N" phase has been established from the Rietveld analysis of the diffraction patterns obtained by X-ray powder diffraction (conventional and with synchrotron radiation) (Fig. 2 & Table). The satisfactory quality of fitting may be seen from the R-factor value, $R_p = 0.1036$. The structure is formed by the B$_{12}$ icosahedra linked by the N–B–N chains (Fig. 3). The ideal composition of the "B$_6$N" phase obtained by the refinement of the starting B$_8$C-like unit cell is B$_{13}$N$_2$. The site occupancies of atoms of each crystallographic type are close to unit, so the synthesized phase is stoichiometric.

Figure 3. Unit cell of the boron subnitride B$_{13}$N$_2$. The grey and black balls represent boron and nitrogen atoms, respectively.
The Raman spectra of the B$_{13}$N$_2$ crystals are similar to those of α-rh B and B$_4$C [19] (Fig. 4). We observe the intericosahedral modes above 950 cm$^{-1}$, the intraicosahedral modes between 400 and 950 cm$^{-1}$ and the modes with wavenumber less than 400 cm$^{-1}$ that are, most probably, librational (involving rotation of icosahedra, etc.). All the lines above 600 cm$^{-1}$ are usually attributed to vibrations of the atoms of boron-rich icosahedra [19]. The fine feature just below 500 cm$^{-1}$ corresponds to the symmetric stretching of the N–B–N groups and the narrow line just above 500 cm$^{-1}$, to the motion of icosahedron about nitrogen atom [19].

The equation of state of B$_{13}$N$_2$ has been studied at pressures up to 30 GPa at ambient temperature (Fig. 5). In the whole pressure range under study, the linewidth of reflections has not remarkably changed; that is indicative of the quasi-hydrostatic conditions. At least three well-resolved lines have been used for the estimation of the lattice parameters at each pressure point; usually we have employed the 003, 012, 104 and 021 reflections. The value of bulk modulus, $B_0 = 200(15)$ GPa, has been estimated by plotting the normalized pressure versus the Eulerian strain under assumption of $B_0' = 4$.

4. Conclusions
Thus, new rhombohedral boron subnitride B$_{13}$N$_2$ has been synthesized by crystallization from the B–BN melt at 5 GPa. The structure of B$_{13}$N$_2$ has been established by Rietveld analysis and represents a new structural type produced by the distorted B$_{12}$ icosahedra linked together by N–B–N chains and inter-icosahedral B–B bonds. The Raman data is consistent with a fact that the subnitride belongs to a group of boron-rich compounds with structures related to α-rhombohedral boron. The 300-K equation of state of B$_{13}$N$_2$ has been measured up to 30 GPa. The bulk modulus was found to be $B_0 = 200(15)$ GPa with the pressure derivative $B_0' = 4$ (fixed).
Figure 5. 300-K equation-of-state data of boron subnitride $B_{13}N_2$. The open circles represent the experimental points, while the dashed line corresponds to the $p-V$ data fit to the Birch-Murnaghan equation of state.

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