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Equations of state of new boron-rich selenides B_6Se and $B_{12}Se$

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Abstract

Two novel of boron-rich selenides, orthorhombic B_6Se and rhombohedral $B_{12}Se$, have been recently synthesized at high pressure – high temperature conditions. Room-temperature compressibilities of these phases were studied in a diamond anvil cell using synchrotron powder X-ray diffraction. A fit of experimental p - V data by third-order Birch-Murnaghan equation of state yielded the bulk moduli of 155(2) GPa for $B_{12}Se$ and 144(3) GPa for B_6Se . No pressure-induced phase transitions have been observed in the studied pressure range, i.e. up to 35 GPa.

Keywords : *boron-rich selenides; high pressure; equation of state*

Introduction

Boron-rich compounds containing B_{12} -icosahedra have been known since the 1960-s [1]. The majority of these compounds are the structural derivatives of elemental α -rhombohedral boron (α - B_{12}) with general stoichiometry: $B_{12}X_y$ (where X is an interstitial atom, $y \leq 2$). They received a considerable attention due to the high hardness, chemical inertness, thermal conductivity, radiation resistance and unusual electronic properties [2-5]. For instance, boron carbide $B_{12}C_3$ is a hard compound widely used as abrasive and armor material [6,7], boron suboxide $B_{12}O_2$ is the hardest known oxide [8,9], and $B_{12}As_2$ was found to be extremely stable under electron bombardment and able to self-healing [10].

Despite a great number of boron-rich compounds discovered during last decades [1,3], their physical properties still remain unknown. Very recently two new boron-rich selenides, rhombohedral $B_{12}Se$ [11] and orthorhombic B_6Se [12], have been synthesized at high pressures and high temperatures. The crystal structures of these compounds have been refined by synchrotron X-ray diffraction studies combined with *ab initio* calculations. The theoretically predicted bulk modulus of B_6Se is 144 GPa [12], however this value has not been experimentally supported so far. Here we report a study of the

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compressibilities of B₁₂Se and B₆Se in a diamond anvil cell up to 35 GPa in the neon quasi-hydrostatic pressure transmitting medium.

Experimental

B₁₂Se and B₆Se were synthesized at 6.1 GPa and 2600-2700 K by reaction of amorphous boron (Grade I ABCR) with elemental selenium (Alfa Aesar, 99.5%) in a toroid-type high-pressure apparatus. Synthesis details are described elsewhere [11,12].

The study of B₁₂Se and B₆Se compressibilities was performed at the Xpress beamline (Elettra) in membrane diamond anvil cells with 300- μ m culet anvils. In order to provide the same compression conditions, the polycrystalline samples of both compounds were mixed and loaded together with small ruby balls into a 150- μ m hole drilled in a rhenium gasket pre-indented down to 25 μ m. Neon was chosen as pressure transmitting medium providing quasi-hydrostatic compression [13]. Pressure was determined *in situ* from the calibrated shift of the ruby R1 fluorescent line [14]; the pressure drift at each pressure point did not exceed 0.6 GPa. The synchrotron radiation was set to a wavelength of 0.4957 Å using a channel-cut Si (111) monochromator and focused down to 20 μ m. The X-ray diffraction patterns were collected in the 2-23 degree 2 θ -range using MAR 345 image plate detector with an exposure time of 600 seconds. The diffraction patterns were further processed using FIT2D [15] and Powder Cell [16] software; the lattice parameters of B₁₂Se and B₆Se at different pressures are presented in Table I.

Results and discussion

The unit cells of both boron-rich selenides are presented in Fig. 1. Rhombohedral B₁₂Se is a typical α -B₁₂-related boron-rich compound with B₁₂-icosahedra placed in the corners and on one of the main diagonals of the hexagonal unit cell. As was previously found [11], the occupation of 6*c* site by Se atom is ~50%, which can be explained by the short Se-Se distance (2.02 Å) compared with the covalent radius of selenium (1.20 Å). B₆Se has an orthorhombic crystal structure containing B₁₂-icosahedra with side-centered packing in the unit cell similar to that in B₃Si [17]. Unlike B₁₂Se, the occupancy of Se atoms (in 4*h* Wykoff positions) in B₆Se was found to be close to 100% [12]. The latter resulted in a higher B₆Se density (3.58 g/cm³) compared to that of B₁₂Se (2.90 g/cm³).

During compression the reflections of B₁₂Se and B₆Se monotonously shifted towards larger 2 θ -values, and no evidence of any phase transition has been observed for both phases over the whole studied pressure range (Fig. 2).

We employed a one-dimensional analogue of the first-order Murnaghan equation of state [18] in order to approximate of the nonlinear relation between relative lattice parameters of B₁₂Se and B₆Se unit cells and pressure (Fig. 3):

$$r = r_0 \left[1 + P \left(\frac{\beta'_{0,r}}{\beta_{0,r}} \right) \right]^{-\frac{1}{\beta'_{0,r}}} \quad (1),$$

where r is the lattice parameter (index 0 refers to ambient pressure), $\beta_{0,r}$ is the axial modulus and $\beta'_{0,r}$ is its pressure derivative. The axis moduli and the corresponding pressure derivatives that best fit the experimental data are collected in Table II. According to these data, the compression of $B_{12}Se$ unit cell is quasi isotropic (similar to that of $B_{12}As_2$ [19]), whereas compression of B_6Se is noticeably anisotropic with the highest compressibility along b -axis.

The changes of $B_{12}Se$ and B_6Se unit cell volumes under pressure are shown in Fig. 4. The third-order Birch-Murnaghan [20] equation of state was used to fit the experimental data:

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (2)$$

The bulk moduli (B_0) and corresponding first pressure derivatives (B'_0) are 154.6 ± 2.2 GPa and 5.9 ± 0.2 for $B_{12}Se$ and 143.9 ± 2.6 GPa and 4.0 ± 0.2 for B_6Se .

The experimentally determined bulk modulus of $B_{12}Se$ was found to be in agreement with the 147 GPa value theoretically predicted in the framework of the thermodynamic model of hardness [21]. According to our findings, $B_{12}Se$ has the lowest bulk modulus value among all boron-rich compounds with structure related to α -rhombohedral boron (Fig. 5). Our results support the general trend – increase of covalent radius of interstitial atom in the row of boron-rich chalcogenides (α - B_{12} [22] – $B_{12}O_2$ [23] – $B_{12}Se$) leads to a decrease of bulk modulus – which has been already observed in the row of boron-rich pnictides (α - B_{12} [22] – $B_{13}N_2$ [24] – $B_{12}P_2$ [25] – $B_{12}As_2$ [19]). However, as it follows from Fig. 5, the ways of such decrease for boron-rich chalcogenides and boron-rich pnictides are different (red and black dashed lines, respectively). It is not surprising that the bulk moduli of $B_{12}As_2$ (150.1 GPa) and $B_{12}Se$ (154.6 GPa) containing interstitial atoms with very close covalent radii ($r_{As} = 1.19$ Å, $r_{Se} = 1.20$ Å) are very close to each other.

The experimental bulk modulus (144(3) GPa) and X-ray density (3.58 g/cm³) of B_6Se are in good agreement with the theoretically predicted values, i.e. 144 GPa and 3.66 g/cm³ [12]. Despite rather high density, orthorhombic B_6Se remains yet the most compressible boron-rich solid.

Conclusions

The compressibilities of two new boron-rich selenides, $B_{12}Se$ and B_6Se , synthesized at high pressures and high temperatures were studied up to 35 GPa using synchrotron X-ray powder diffraction in a diamond anvil cell. At room temperature, both selenides were found to be stable in the whole studied pressure range, and no pressure-induced phase transitions were observed.

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Table I. Experimental values of lattice parameters and unit cell volumes of B₁₂Se (in hexagonal setting) and B₆Se as a function of pressure at room temperature.

P (GPa)	B ₁₂ Se			B ₆ Se			
	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
0.0	5.9617(5)	11.8961(9)	366.2(1)	5.9463(5)	5.3579(4)	8.3824(7)	267.1(1)
0.6	5.9530(4)	11.8780(5)	364.5(1)	5.9420(5)	5.3500(3)	8.3800(7)	266.4(1)
1.0	5.9465(3)	11.8663(6)	363.4(1)	5.9300(4)	5.3230(3)	8.3688(7)	264.2(1)
2.2	5.9330(7)	11.8353(4)	360.8(1)	5.9205(5)	5.3230(3)	8.3550(6)	263.3(1)
3.6	5.9195(6)	11.8100(4)	358.4(1)	5.9188(4)	5.3137(3)	8.3200(5)	261.7(1)
4.7	5.9039(3)	11.7802(6)	355.6(1)	5.9000(7)	5.2980(3)	8.2900(5)	259.1(1)
6.6	5.8850(5)	11.7423(6)	352.2(1)	5.8780(4)	5.2700(4)	8.2645(5)	256.0(1)
9.2	5.8600(7)	11.6875(7)	347.6(1)	5.8423(6)	5.2330(5)	8.2525(4)	252.3(2)
11.4	5.8440(7)	11.6528(5)	344.6(1)	5.8200(5)	5.2120(4)	8.2355(5)	249.8(1)
16.6	5.8005(6)	11.5643(6)	336.9(1)	5.7540(6)	5.1425(6)	8.2023(7)	242.7(1)
20.3	5.7725(7)	11.4983(8)	331.8(1)	5.7210(7)	5.1095(6)	8.1550(7)	238.4(1)
23.6	5.7511(8)	11.4535(6)	328.1(1)	5.6900(8)	5.0851(5)	8.1295(8)	235.2(2)
25.4	5.7415(9)	11.4260(7)	326.2(1)	5.6720(9)	5.0752(8)	8.1100(7)	233.5(2)
27.6	5.7268(8)	11.3978(8)	323.7(1)	5.6530(8)	5.0568(7)	8.0875(9)	231.2(2)
30.8	5.7060(9)	11.3403(9)	319.8(1)	5.6300(8)	5.0273(8)	8.0640(9)	228.2(2)
33.6	5.6938(8)	11.3070(9)	317.5(2)	5.6107(9)	5.0165(7)	8.0410(8)	226.3(2)
34.8	5.6868(9)	11.2900(9)	316.2(1)	5.6090(8)	5.0087(9)	8.0150(9)	225.2(2)

Table II. Bulk moduli (B_0) with first derivatives (B'_0) and axial moduli ($\beta_{0,r}$) with first derivatives ($\beta'_{0,r}$) of $B_{12}Se$ and B_6Se obtained from fits to the experimental data using Birch-Murnaghan and one-dimensional analogue of Murnaghan EOSs.

	$B_{12}Se$	B_6Se
B_0 (GPa)	155(2)	144(3)
B'_0	5.9(2)	4.0(2)
$\beta_{0,a}$ (GPa)	456(6)	483(20)
$\beta'_{0,a}$	19(1)	6(2)
$\beta_{0,b}$ (GPa)	–	340(12)
$\beta'_{0,b}$	–	11(1)
$\beta_{0,c}$ (GPa)	480(9)	528(43)
$\beta'_{0,c}$	12(1)	19(4)

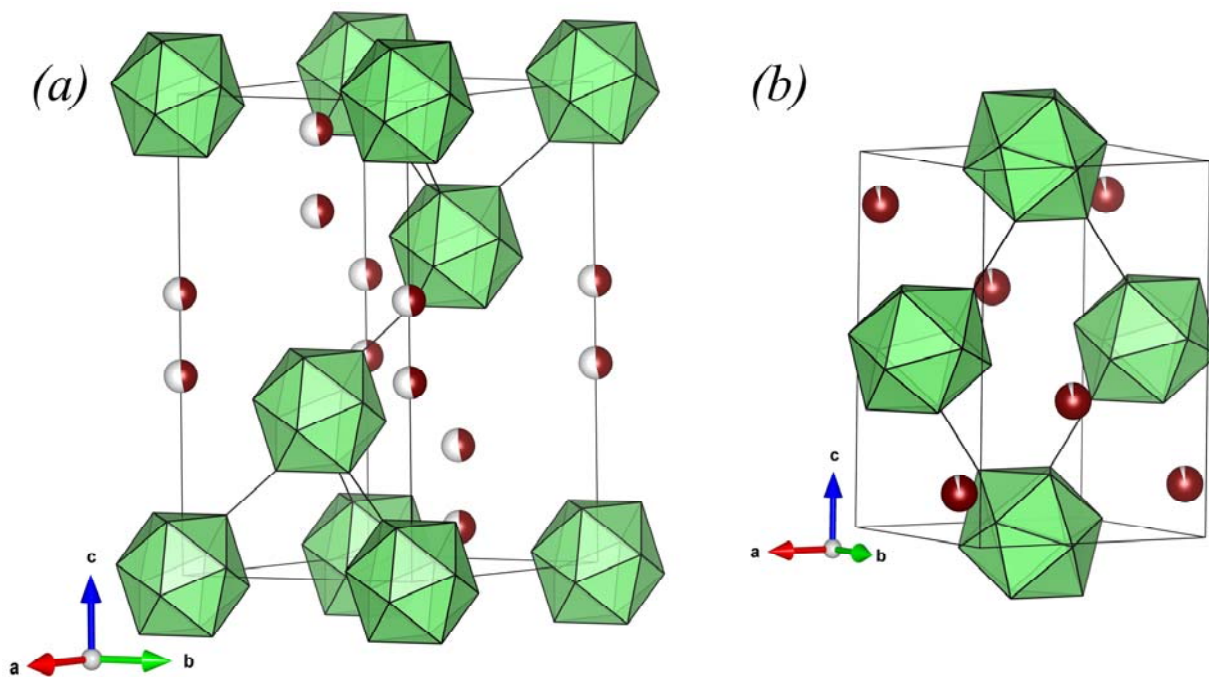


Fig. 1. The unit cells of $B_{12}Se$ (in hexagonal setting) (a) and B_6Se (b); B_{12} -units are presented by green icosahedra, Se atoms are shown as balls.

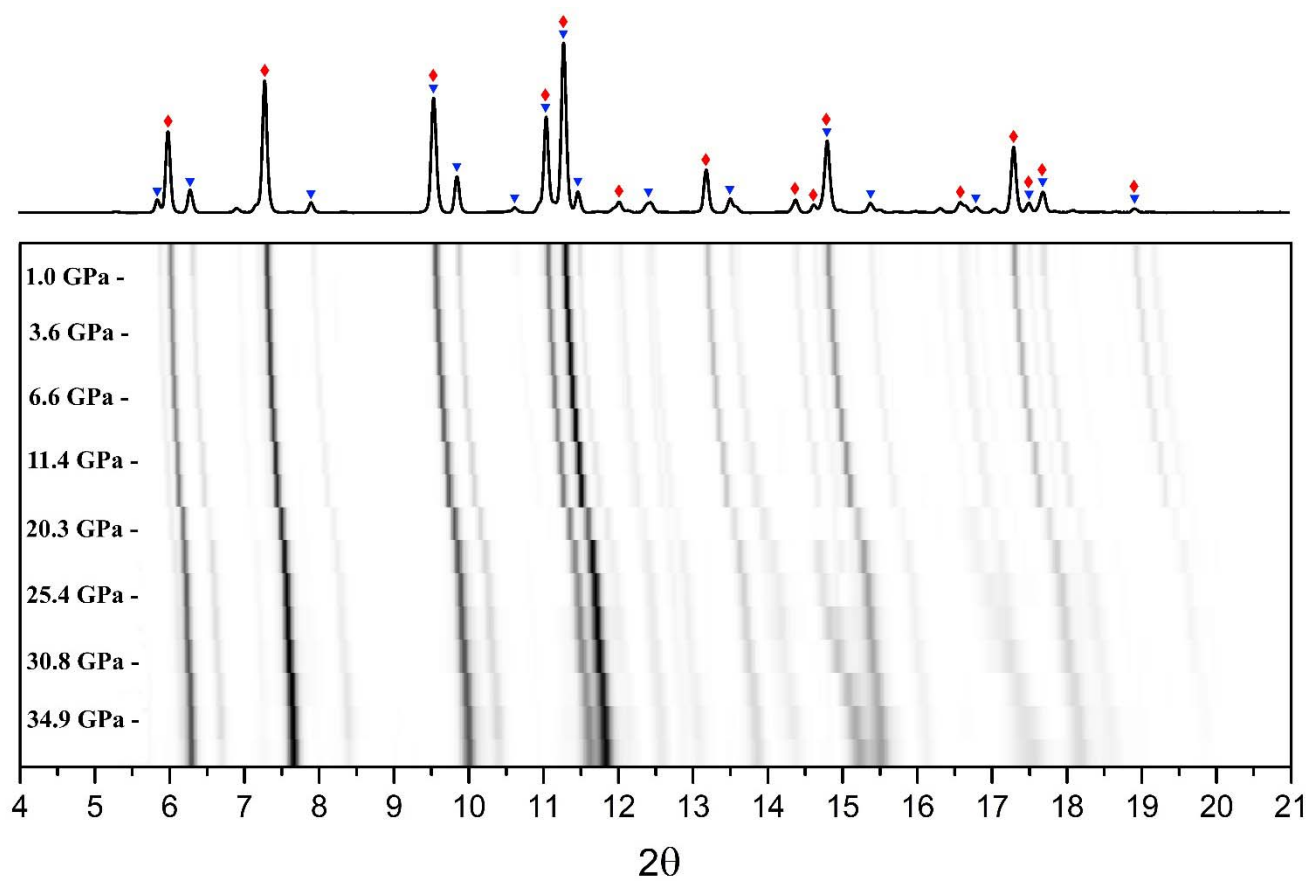


Fig. 2. 2D representation of X-ray diffraction patterns ($\lambda = 0.4957 \text{ \AA}$) of B₁₂Se/B₆Se mixture *versus* pressure. The diffraction lines of B₁₂Se and B₆Se phases are presented by red diamonds and blue triangles, respectively.

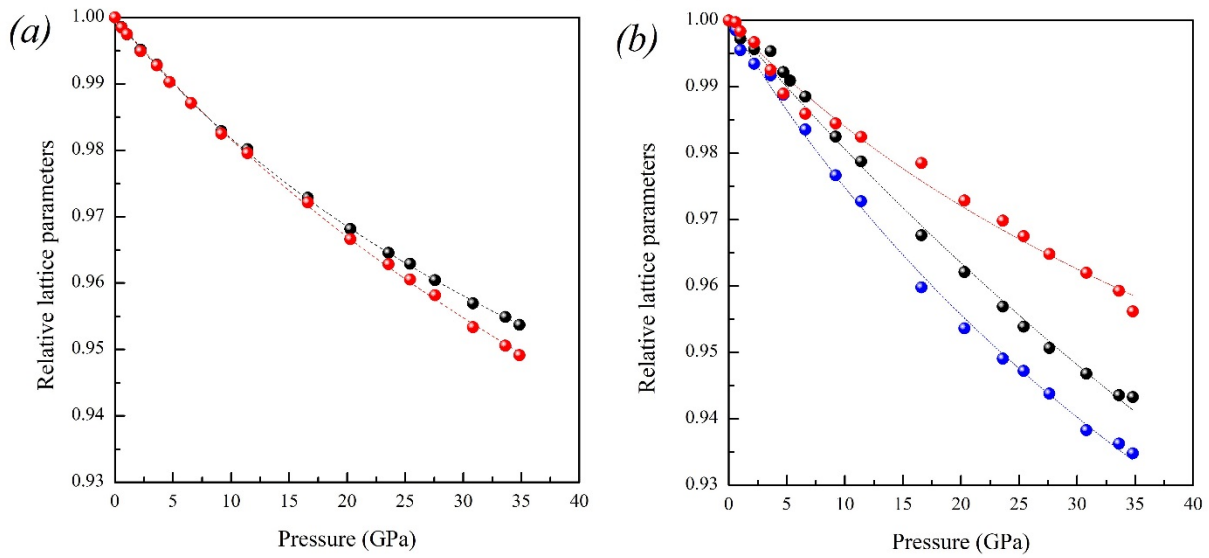


Fig. 3. The relative lattice parameters of B₁₂Se and B₆Se *versus* pressure: a/a_0 (black), b/b_0 (blue) and c/c_0 (red). The dashed lines represent the fits to a one-dimensional analogue of the Murnaghan equation of state.

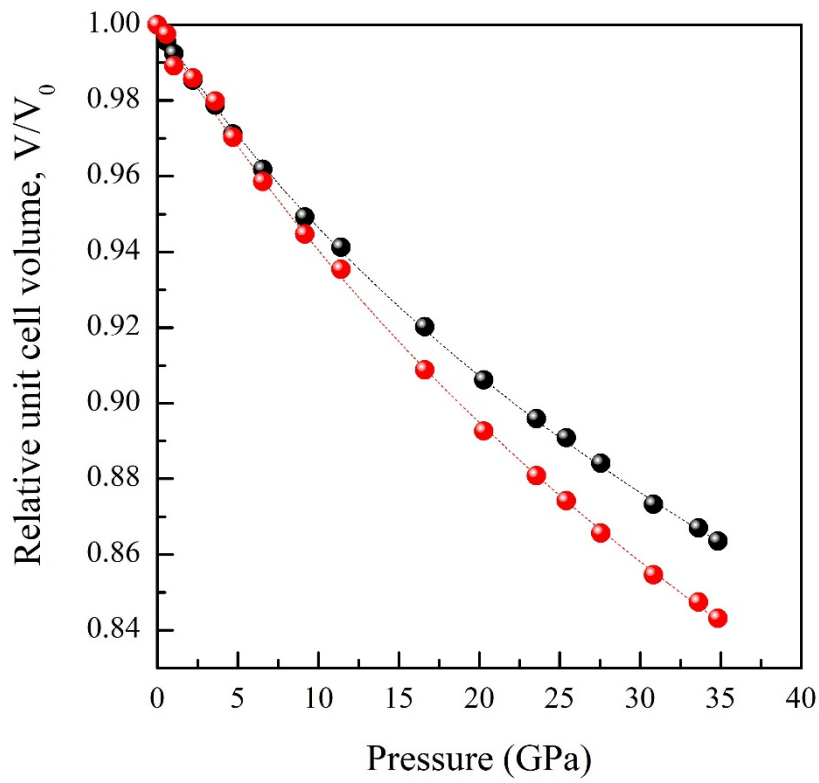


Fig. 4. Equation of state of $B_{12}Se$ (black) and B_6Se (red). The dashed lines represent Birch-Murnaghan equation of state fit to the experimental data.

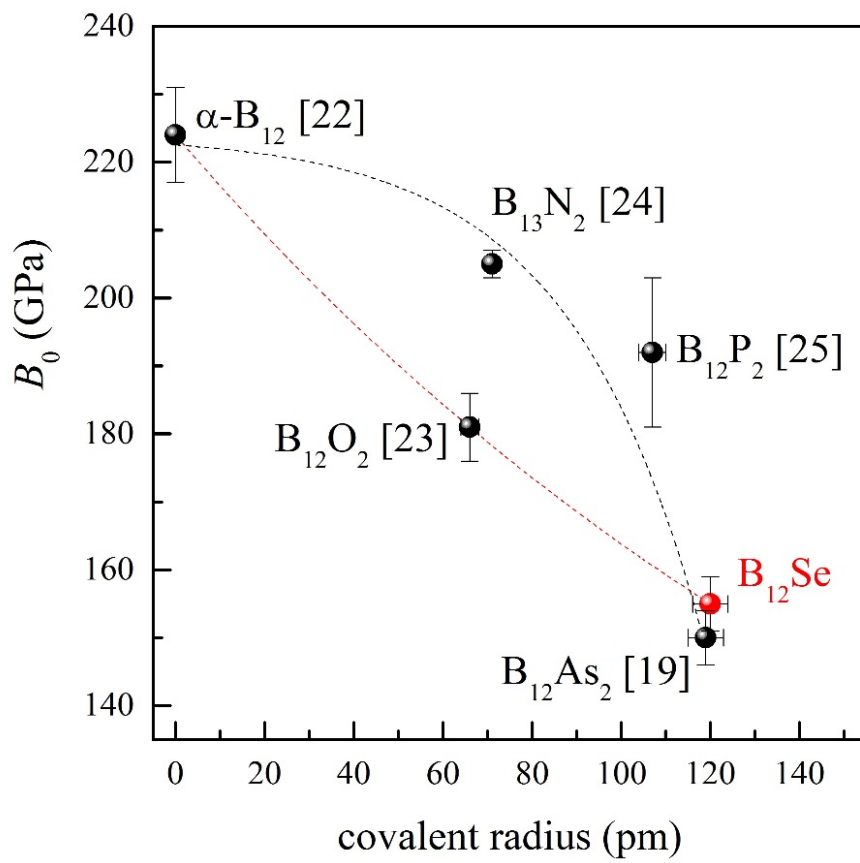


Fig. 5. Bulk moduli of α -rhombohedral boron and related boron-rich compounds.