Equations of state of new boron-rich selenides B6Se and B12Se

Kirill A Cherednichenko, Yann Le Godec, Vladimir Solozhenko

To cite this version:

Kirill A Cherednichenko, Yann Le Godec, Vladimir Solozhenko. Equations of state of new boron-rich selenides B6Se and B12Se. High Pressure Research, Taylor & Francis, 2021, 41 (3), pp.267-274. 10.1080/08957959.2021.1961765 . hal-03343722

HAL Id: hal-03343722
https://hal.archives-ouvertes.fr/hal-03343722

Submitted on 14 Sep 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Equations of state of new boron-rich selenides $B_6Se$ and $B_{12}Se$

Kirill A. Cherednichenko,1,2  Yann Le Godec,3  and  Vladimir L. Solozhenko1, *

1 LSPM–CNRS, Université Sorbonne Paris Nord, 93430 Villetaneuse, France
2 Department of Physical and Colloid Chemistry, Gubkin University, Moscow, 119991, Russia
3 IMPMC–CNRS, UPMC Sorbonne Universités, 75005 Paris, France

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 ($\alpha$-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
compressibilities of \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) in a diamond anvil cell up to 35 GPa in the neon quasi-hydrostatic pressure transmitting medium.

**Experimental**

\( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) 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 \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) compressibilities was performed at the Xpress beamline (Elettra) in membrane diamond anvil cells with 300-\( \mu \)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-\( \mu \)m hole drilled in a rhenium gasket pre-indented down to 25 \( \mu \)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 \( \mu \)m. The X-ray diffraction patterns were collected in the 2-23 degree 2\( \theta \)-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 \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) 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 \( \text{B}_{12}\text{Se} \) is a typical \( \alpha\text{-B}_{12} \)-related boron-rich compound with \( \text{B}_{12} \)-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 \( 6c \) 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). \( \text{B}_6\text{Se} \) has an orthorhombic crystal structure containing \( \text{B}_{12} \)-icosahedra with side-centered packing in the unit cell similar to that in \( \text{B}_3\text{Si} \) [17]. Unlike \( \text{B}_{12}\text{Se} \), the occupancy of Se atoms (in \( 4h \) Wykoff positions) in \( \text{B}_6\text{Se} \) was found to be close to 100% [12]. The latter resulted in a higher \( \text{B}_6\text{Se} \) density (3.58 g/cm\(^3\)) compared to that of \( \text{B}_{12}\text{Se} \) (2.90 g/cm\(^3\)).

During compression the reflections of \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) monotonously shifted towards larger 2\( \theta \)-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 \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) unit cells and pressure (Fig. 3):
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 \( \text{B}_{12}\text{Se} \) unit cell is quasi isotropic (similar to that of \( \text{B}_{12}\text{As}_2 \) [19]), whereas compression of \( \text{B}_6\text{Se} \) is noticeably anisotropic with the highest compressibility along \( b \)-axis.

The changes of \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \) 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:

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

(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 \( \text{B}_{12}\text{Se} \) and 143.9±2.6 GPa and 4.0±0.2 for \( \text{B}_6\text{Se} \).

The experimentally determined bulk modulus of \( \text{B}_{12}\text{Se} \) 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, \( \text{B}_{12}\text{Se} \) has the lowest bulk modulus value among all boron-rich compounds with structure related to \( \alpha \)-rhombohedral boron (Fig. 5). Our results support the general trend – increase of covalent radius of interstitial atom in the row of boron-rich chalcogenides (\( \alpha \)-\( \text{B}_{12} \) [22] – \( \text{B}_{13}\text{O}_2 \) [23] – \( \text{B}_{12}\text{Se} \)) leads to a decrease of bulk modulus – which has been already observed in the row of boron-rich pnictides (\( \alpha \)-\( \text{B}_{12} \) [22] – \( \text{B}_{13}\text{N}_2 \) [24] – \( \text{B}_{12}\text{P}_2 \) [25] – \( \text{B}_{12}\text{As}_2 \) [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 \( \text{B}_{12}\text{As}_2 \) (150.1 GPa) and \( \text{B}_{12}\text{Se} \) (154.6 GPa) containing interstitial atoms with very close covalent radii \((r_{\text{As}} = 1.19 \text{ Å}, r_{\text{Se}} = 1.20 \text{ Å})\) are very close to each other.

The experimental bulk modulus (144(3) GPa) and X-ray density (3.58 g/cm\(^3\)) of \( \text{B}_6\text{Se} \) are in good agreement with the theoretically predicted values, i.e. 144 GPa and 3.66 g/cm\(^3\) [12]. Despite rather high density, orthorhombic \( \text{B}_6\text{Se} \) remains yet the most compressible boron-rich solid.

**Conclusions**

The compressibilities of two new boron-rich selenides, \( \text{B}_{12}\text{Se} \) and \( \text{B}_6\text{Se} \), 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.
Acknowledgements

The authors thank Dr. V.A. Mukhanov (LSPM-CNRS) for the samples synthesis and Dr. B. Joseph (Elettra) for assistance at Xpress beamline. Synchrotron X-ray diffraction experiments were carried out during beamtime allocated to Proposal 20180186 at Elettra Synchrotron. This work was financially supported by the European Union's Horizon 2020 Research and Innovation Program under Flintstone2020 project (grant agreement No 689279).

ORCID IDs

Vladimir L. Solozhenko  https://orcid.org/0000-0002-0881-9761
Kirill A. Cherednichenko  https://orcid.org/0000-0002-1868-8232
References

1. Matkovich V Interstitial compounds of boron. J. Am. Chem. Soc. 1961; 83:1804-1806.
2. Emin D Unusual properties of icosahedral boron-rich solids. J. Solid State Chem. 2006; 179:2791-2798.
3. Albert B, Hillebrecht H Boron: elementary challenge for experimenters and theoreticians. Angew. Chem. Int. Ed. 2009; 48:8640-8668.
4. Slack GA, Morgan KE Some crystallography, chemistry, physics, and thermodynamics of B_{12}O_2, B_{12}P_2, B_{12}As_2, and related alpha-boron type crystals. J. Phys. Chem. Solids 2014; 75:1054-1074.
5. Slack GA, Morgan KE Crystallography, semiconductivity, thermoelectricity, and other properties of boron and its compounds, especially B_6O. Solid State Sci. 2015; 47:43-50.
6. Thevenot F Boron carbide - A comprehensive review. J. Eur. Ceram. Soc. 1990; 6:205-225.
7. Orlovskaya N, Lugovy M Proc. NATO Advanced Research Workshop on Boron-Rich Solids, Springer. 2009.
8. Leger JM, Haines J The search for superhard materials. Endeavour, 1997, 21:121-124.
9. McMillan PF New materials from high-pressure experiments. Nature Mater., 2002; 1:19-25.
10. Carrard M, Emin D, Zuppiroli L Defect clustering and self-healing of electron-irradiated boron-rich solids. Phys. Rev. B. 1995; 51:11270-11274.
11. Cherednichenko KA, Mukhanov VA, Kalinko A, Solozhenko VL High-pressure synthesis of boron-rich chalcogenides B_{12}S and B_{12}Se. arXiv:2105.04450
12. Cherednichenko KA, Mukhanov VA, Wang Z, Oganov AR, Kalinko A, Dovgaliuk I, Solozhenko VL Discovery of new boron-rich chalcogenides: orthorhombic B_6X (X = S, Se), Sci. Rep. 2020; 10:9277.
13. Klotz S, Chervin JC, Munsch P, Le Marchand G Hydrostatic limits of 11 pressure transmitting media. J. Phys. D: Appl. Phys. 2009; 42:075413.
14. Mao HK, Xu J, Bell PM Calibration of the ruby pressure gauge to 800 kbar under quasi hydrostatic conditions. J. Geophys. Res. 1986; 91:4673–4677.
15. Hammersley AP, Svensson SO, Hanfland M, Fitch AN, Häusermann D Two-dimensional detector software: From real detector to idealised image or two-theta scan. High Press. Res. 1996; 14:235-248.
16. Kraus W, Nolze G Powder Cell – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. J. Appl. Cryst. 1996; 29:301-303.
17. Salvador JR, Bilec D, Mahanti SD, Kanatzidis MG Stabilization of β-SiB3 from liquid Ga: A boron-rich binary semiconductor resistant to high-temperature air oxidation. *Angew. Chem. Int. Ed.* 2003; 42:1929-1932.

18. Murnaghan FD The compressibility of media under extreme pressures. *Proc. Natl. Acad. Sci.* 1944; 30:244-247.

19. Cherednichenko KA, Le Godec Y, Solozhenko VL Equation of state of boron subarsenide B12As2 to 47 GPa. *High. Press. Res.* 2018; 38:224-231.

20. Birch F Finite elastic strain of cubic crystals. *Phys. Rev. B.* 1947; 71:809-824.

21. Mukhanov VA, Kurakevych OO, Solozhenko VL Thermodynamic model of hardness: Particular case of boron-rich solids. *J. Superhard Mater.* 2010; 32:167-176.

22. Chuvashova I, Bykova E, Bykov M, Svitlyk V, Dubrovinsky L, Dubrovinskaia N Structural stability and mechanism of compression of stoichiometric B13C2 up to 68 GPa. *Sci. Rep.* 2017; 7:8969.

23. Nieto-Sanz D, Loubeyre P, Crichton W, Mezouar M X-ray study of the synthesis of boron oxides at high pressure: Phase diagram and equation of state. *Phys. Rev. B* 2004; 70:214108.

24. Cherednichenko KA, Solozhenko VL, Structure and equation of state of tetragonal boron subnitride B50N2. *J. Appl. Phys.* 2017; 122:155907.

25. Solozhenko VL, Cherednichenko KA, Kurakevych OO Thermoelastic equation of state of boron subphosphide B12P2. *J. Superhard Mater.* 2017; 39:71-74.
# 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) | B₁₂Se | | B₆Se | |
|---|---|---|---|---|
| | a (Å) | c (Å) | V (Å³) | a (Å) | b (Å) | c (Å) | V (Å³) |
| 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 $\text{Bi}_{12}\text{Se}$ and $\text{Bi}_6\text{Se}$ obtained from fits to the experimental data using Birch-Murnaghan and one-dimensional analogue of Murnaghan EOSs.

|                   | $\text{Bi}_{12}\text{Se}$ | $\text{Bi}_6\text{Se}$ |
|-------------------|---------------------------|-------------------------|
| $B_0$ (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$_6$Se (b); B$_{12}$-units are presented by green icosahedra, Se atoms are shown as balls.
Fig. 2. 2D representation of X-ray diffraction patterns ($\lambda = 0.4957$ Å) of $\text{B}_{12}\text{Se}/\text{B}_6\text{Se}$ mixture versus pressure. The diffraction lines of $\text{B}_{12}\text{Se}$ and $\text{B}_6\text{Se}$ phases are presented by red diamonds and blue triangles, respectively.
Fig. 3. The relative lattice parameters of $\text{B}_{12}\text{Se}$ and $\text{B}_6\text{Se}$ 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_{6}Se (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.