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Thermoelastic equation of state of boron subphosphide $B_{12}P_2$

Compressibility of boron subphosphide $B_{12}P_2$ has been studied under quasi-hydrostatic conditions up to 26 GPa and 2600 K using laser-heated diamond anvil cell and angle-dispersive synchrotron X-ray diffraction. 300-K data fit yields the values of bulk modulus B_0 = 192(11) GPa and its first pressure derivative B_0' = 5.5(12). It has been found that at ambient pressure the thermal expansion is quasi-linear up to 1300 K with average volume expansion coefficient $\alpha = 17.4(1)\cdot10^{-6}$ K^{-1}. The whole set of experimental p–V–T data is well described by the Anderson-Grüneisen model with δ_T = 6.

Keywords: *boron subphosphide, high pressure, equation of state, thermal expansion.*

Boron subphosphide $B_{12}P_2$ is a hard (Vickers hardness H_V = 35(3) GPa [1]) and refractory (melting temperature T_m = 2393(30) K [2] with positive pressure slope [3]) compound with a wide band gap (~ 2 eV [4]) and superior chemical resistance. It crystallizes in the *R*-3*m* space group [5], similar to α-rhombohedral boron allotrope (α-B_{12}) stable at high pressures [6], and other (super)hard boron-rich solids (B_6O, $B_{13}N_2$, B_4C, etc. [7–10]). Here we report the *p–V–T* equation of state (EOS) of boron subphosphide up to 26 GPa and 2600 K.

Polycrystalline powders of single-phase stoichiometric boron subphosphide were produced by self-propagating high-temperature synthesis [1] and mechanochemical synthesis [11]. The lattice parameters of synthesized $B_{12}P_2$ (*a* = 5.992(4), *c* = 11.861(8) Å) are in a good agreement with the literature data (*a* = 5.9879, *c* = 11.8479 Å [5]).

At pressures 3.9–5.5 GPa and temperatures to 2000 K $B_{12}P_2$ was studied by energy-dispersive synchrotron X-ray diffraction using MAX80 multianvil system at F2.1 beamline, DORIS III (DESY). Standard assemblies with hBN pressure medium were used. The experimental details are described elsewhere [12]. The sample pressure at different temperatures was determined from the thermal equation of state of hBN [13]; temperature was measured by a Pt-30%Rh/Pt-6%Rh thermocouple.

In-situ experiments in the 14–26 GPa pressure range have been performed in a membrane diamond anvil cell (DAC) using angle-dispersive synchrotron X-ray diffraction at P02.2 beamline, PETRA III (DESY). We used rhenium gasket and KCl pressure medium insuring quasi-hydrostatic conditions at high temperatures, with advantage of chemical inertness with regard to the sample. The monochromatic X-ray beam (42 keV, λ = 0.2898 Å) was focused down to 2×4 μm.

The diffraction patterns were recorded using XRD1621 (Perkin-Elmer) flat panel detector; sample-detector distance was calibrated using CeO_2 NIST standard. A typical acquisition time was 30 seconds. The sample pressure has been determined using equation of state of KCl [14].

The 300-K p–V data (Fig. 1, *a*) have been fitted to Murnaghan EOS [15], i.e.,

$$V(p,300) = V(0,300)\left[1 + B_0' p / B_0\right]^{-1/B_0'}, \quad (1)$$

that allowed us to determine the isothermal bulk modulus B_0 = 192(11) and its first pressure derivative B_0' = 5.5(12).

Laser heating in a DAC was performed using double-sided off-axis infrared laser system (continuous fiber YAG laser focused down to 20 μm, λ = 1070 nm). Temperature measurements were performed through standard grey body radiation measurement via an Acton spectrometer SP-2356 (Princeton Instruments). The temperature uncertainties in the 1500–2500 K range were ±40 K.

High-temperature (300–1300 K) thermal expansion of $B_{12}P_2$ in argon at ambient pressure was studied at MCX beamline of Elettra synchrotron (Trieste). Debye-Scherrer geometry with rotating quartz-glass capillary was used. X-ray diffraction patterns were collected in the 5–120 2θ-range (λ = 1.0352 Å) for 120 s using a translating image plate detector upon stepwise heating with 25-K steps. Thermal expansion data (Fig. 1, *b*) shows quasi-linear behavior following the equation $V(T)/V_0 = 1 + \alpha(T - 300)$, where $\alpha = 17.4(1)\cdot 10^{-6}$ K^{-1}, with a 10 % higher thermal expansivity in the *c*-axis direction.

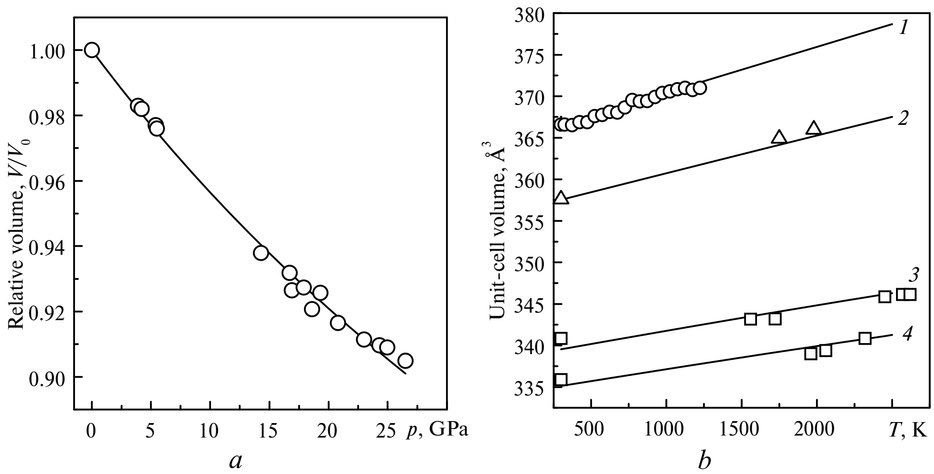

Fig. 1. (*a*) 300-K equation of state of $B_{12}P_2$: the curve shows the data fit to Murnaghan EOS (Eq. 1); (*b*) isobars $V(T)$ at 0.1 MPa (*1*), 5 (*2*), 18 (*3*) and 22 (*4*) GPa: the curves show the data fit to the simplified Anderson-Grüneisen model (Eq. 2) with $\delta_T = 6$.

Temperature dependences of the unit-cell volume ($V_0 = V(0, 300) = 366.59$ Å^3 corresponds to 300 K and ambient pressure) at different pressures are shown in Fig. 1, *b*. Below 2500 K these dependences are very close to linear ones. The slopes, however, noticeably depend on pressure. To describe this dependence, we have used the thermoelastic EOS based on simplified Anderson-Grüneisen model [16] in the form

$$V(p,T) = \left[V(0,T)^{-\delta_T} + V(p,300)^{-\delta_T} - V(0,300)^{-\delta_T}\right]^{-1/\delta_T}. \quad (2)$$

The fitted value of the Anderson-Grüneisen parameter $\delta_T = 6$ allows describing all present experimental *p–V–T* data for $B_{12}P_2$.

Figure 2 shows the comparison of bulk moduli of boron-rich compounds with structure related to α-rhombohedral boron. To get the correct scaling, the reported experimental data for B_6O [16, 17], $B_{13}N_2$ [18, 19], B_4C [20], and $B_{12}As_2$ [21] were fitted to Murnaghan EOS. In the case of $B_{12}As_2$ [21], we used the *p–V* data up to 10 GPa only, i.e., in the range where the pressure medium used (ethanol-metanol) remains liquid, and conditions are hydrostatic. The general tendency is the decrease of bulk modulus with increase of covalent radius of an interstitial atom in the intericosahedral voids. Only boron suboxide does not follow this tendency, most probably due to the absence of boron atoms connecting oxygen atoms, i.e., O– –O, contrary to the N–B–N and C–B–C chains in boron subnitride and carbide, respectively. *Ab initio* calculations [22, 23] confirm the maximal bulk modulus for boron subnitride $B_{13}N_2$, although give overestimated B_0 values.

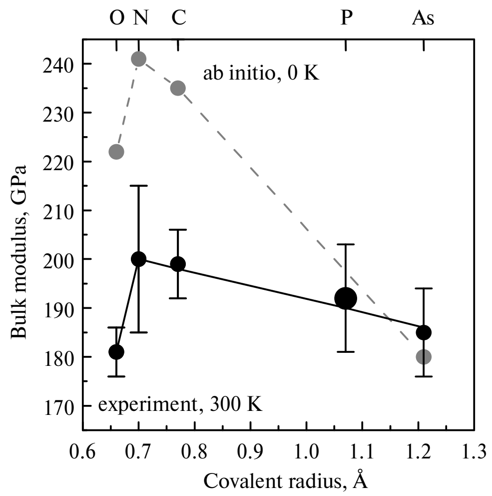

Fig. 2. Bulk moduli of boron-rich solids with structures related to α-rhombohedral boron as a function of the covalent radius of an interstitial atom; large circle shows the result of the present paper.

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Вивчено стисливість субфосфіда бору $B_{12}P_2$ в квазігідростатичних умовах до 26 ГПа і 2600 К в алмазних ковадлах з лазерним нагрівом методом дифракції синхротронного випромінювання. Оцінка даних, отриманих при 300 К, дає значення модуля об’ємного стиснення B_0 = 192(11) ГПа і його першої похідної по тиску B_0' = 5,5(12).

При атмосферному тиску термічне розширення є квазілінійним до 1300 К із середнім коефіцієнтом об'ємного розширення $\alpha = 17{,}4(1)\cdot 10^{-6}$ K^{-1}. Всі експериментальні p–V–T дані добре описуються моделлю Андерсена-Грюназена з $\delta_T = 6$.

***Ключові слова**: субфосфід бору, високий тиск, рівняння стану, термічне розширення.*

Изучена сжимаемость субфосфида бора $B_{12}P_2$ в квазигидростатических условиях до 26 ГПа и 2600 К в алмазных наковальнях с лазерным нагревом методом дифракции синхротронного излучения. Оценка данных, полученных при 300 К, дает значения модуля объемного сжатия $B_0 = 192(11)$ ГПа и его первой производной по давлению $B'_0 = 5.5(12)$. При атмосферном давлении термическое расширение является квазилинейным до 1300 К со средним коэффициентом объемного расширения $\alpha = 17{,}4(1)\cdot 10^{-6}$ K^{-1}. Все экспериментальные p–V–T данные хорошо описываются моделью Андерсена-Грюназена с $\delta_T = 6$.

***Ключевые слова**: субфосфид бора, высокое давление, уравнение состояния, термическое расширение.*

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