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# Hardness of new boron-rich chalcogenides $B_{12}S$ and $B_{12}Se$

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Hardness of bulk polycrystalline boron-rich chalcogenides, rhombohedral $B_{12}S$ and $B_{12}Se$, has been predicted using contemporary theoretical models and experimentally studied by microindentation. Both chalcogenides exhibit Vickers hardness of about 33 GPa exceeding that of boron carbide and hence belong to a family of (super)hard phases.

*Keywords*: boron-rich chalcogenides, hardness, bulk modulus.

Two new boron-rich chalcogenides, rhombohedral $B_{12}S$ and $B_{12}Se$, have been recently synthesized by direct reactions of the elements at high pressures and high temperatures, and their crystal structures have been refined by synchrotron X-ray diffraction study combined with *ab initio* calculations [1]. In the present Letter we report the hardness of these compounds from theoretical and experimental studies.

Vickers hardness ($H_V$) of boron-rich chalcogenides were predicted using two contemporary theoretical models of hardness i.e. thermodynamic model developed for the particular case of boron-rich solids [2] and Lyakhov-Oganov model [3]. The thermodynamic model is based on the crystal structure and thermodynamic properties, while Lyakhov-Oganov approach considers the strength of covalent bonding, degree of ionicity and directionality, as well as topology of the crystal structure. The results are summarized in Table 1. Note that bulk modulus of $B_{12}Se$ estimated from thermodynamic model is in reasonable agreement with the experimental value [4].

Stoichiometric boron-rich chalcogenides $B_{12}X$ (X = S, Se) have been synthesized according to the method described elsewhere [1]. Polycrystalline bulks for hardness measurements have been produced in a toroid-type apparatus by crystallization from a melt at 2.6 GPa. According to X-ray diffraction study (TEXT 3000 Inel, CuKα1 radiation) the recovered bulks contain well-crystallized single-phase boron-rich chalcogenides with lattice parameters identical to the literature data [1].

The recovered samples (cylinders 4-mm diameter and 3-mm height) were hot mounted in carbon-fiber reinforced resin, and were planar ground with diamond 500 grit and subsequently polished with 9-μm and 1-μm diamond suspensions. Mechanical polishing was followed by vibropolishing with 0.04-μm $SiO_2$ colloidal solution that ensured the minimal sample surface damage.

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Microstructure of the polished samples was studied using TESCAN MIRA3 Field Emission scanning electron microscope (SEM) in secondary electron and backscatter modes. It was found that all samples are homogeneous and their average grain size varies from 0.2 to 2 μm; the residual porosity was not observed.

Microhardness measurements have been performed using a Mitutoyo HM-220B Microhardness Testing Machine under loads from 1 to 20 N and 15 seconds dwell time; five indentations have been made at each load. The values of Vickers and Knoop ($H_K$) hardness were determined from the residual imprints upon indentation and were calculated following the standard definitions (for details see [5]).

The measured Vickers hardness of boron-rich sulfide $B_{12}S$ decreases with the load and at 10 N reaches the asymptotic value $H_V$ = 32(3) GPa (Fig. 1a) that is in perfect agreement with the value predicted in the framework of thermodynamic model of hardness (see Table 1). The load dependence of the measured Knoop hardness is presented in Fig. 1b; the asymptotic value of $H_K$ = 26(2) GPa is achieved already at 5 N load.

The measured Vickers hardness of boron-rich selenide $B_{12}Se$ as a function of load is presented in Fig. 2a; the asymptotic value of 33(2) GPa is attained at 8 N. This $H_V$ value is also in good agreement with $B_{12}Se$ hardness calculated in the framework of thermodynamic model (see Table 1). Load dependence of Knoop hardness (Fig. 2b) is characterized by the asymptotic value $H_K$ = 22(2) GPa that is somewhat low and demonstrates abnormal lag to the Vickers hardness value. This can be attributed to a low fracture toughness and related cleavage of the material under Knoop indenter (see Inset in Fig. 2b).

Thus, boron-rich chalcogenides $B_{12}S$ and $B_{12}Se$ exhibit experimental Vickers hardness of about 33 GPa that is higher than that of boron carbide $B_4C$, a conventional superabrasive. Both theoretical models used work properly, however, the thermodynamic model appears to be more reliable since the hardness values calculated using Lyakhov-Oganov model are slightly underestimated.

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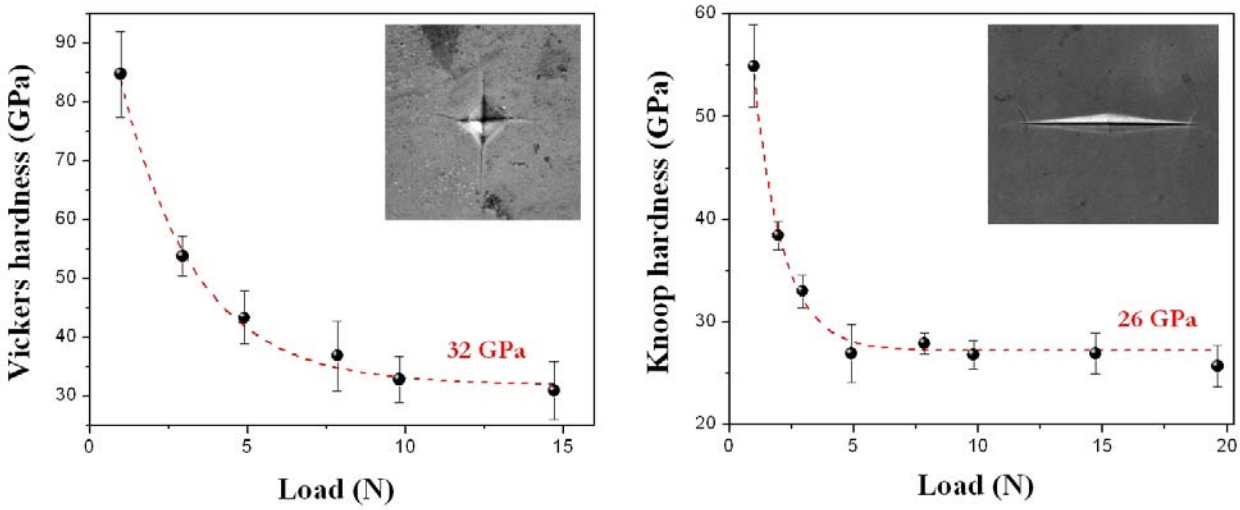
Table 1 X-ray densities (ρ), bulk moduli ($B_0$) and Vickers hardness ($H_V$) of boron-rich chalcogenides

| | Lattice parameters (Å) [1] | ρ (g/cm$^3$) | $B_0$ (GPa) | | $H_V$ (GPa) | | |
|---|---|---|---|---|---|---|---|
| | | | T* | *exp*. | T* | LO† | *exp*. |
| $B_{12}S$ | $a$ = 5.8196<br>$c$ = 11.9653 | 2.34 | 154 | — | 31 | 27 | 32(3) |
| $B_{12}Se$ | $a$ = 5.9385<br>$c$ = 11.9144 | 2.90 | 147 | 155(2) [4] | 30 | 29 | 33(2) |

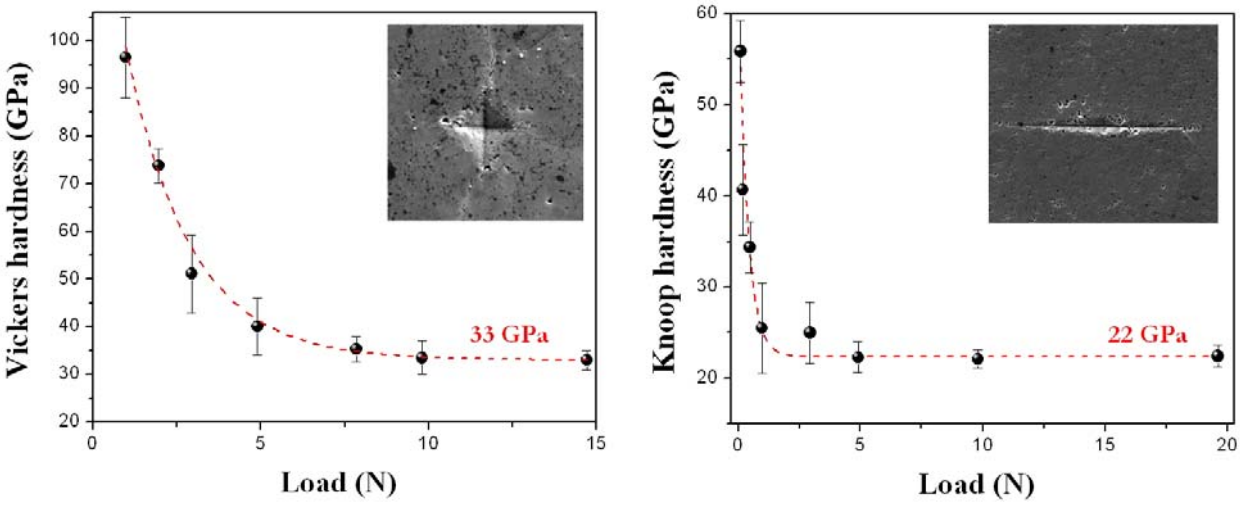
* Thermodynamic model [2]

† Lyakhov-Oganov model [3]




(*a*) (*b*)

Fig. 1 Vickers (*a*) and Knoop (*b*) microhardness of bulk boron-rich sulfide $B_{12}S$ *vs* load. Insets: SEM images of the imprints formed by Vickers and Knoop indenters under 8 N loads.




(*a*) (*b*)

Fig. 2 Vickers (*a*) and Knoop (*b*) microhardness of bulk boron-rich selenide $B_{12}Se$ *vs* load. Insets: SEM images of the imprints formed by Vickers and Knoop indenters under 5 N loads.