Stability and Strength of Transition-Metal Tetraborides and Triborides

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Using density functional theory, we show that the long-believed transition-metal tetraborides (TB4) of tungsten and molybdenum are in fact triborides (TB3). This finding is supported by thermodynamic, mechanical, and phonon instabilities of TB3, and it challenges the previously proposed origin of superhardness of these compounds and the predictability of the generally used hardness model. Theoretical calculations for the newly identified stable TB3 structure correctly reproduce their structural and mechanical properties, as well as the experimental x-ray diffraction pattern. However, the relatively low shear moduli and strengths suggest that TB3 cannot be intrinsically stronger than c-BN. The origin of the lattice instability of TB3 under large shear strain that occurs at the atomic level during plastic deformation can be attributed to valence charge depletion between boron and metal atoms, which enables easy sliding of boron layers between the metal ones.

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Recent attempts to design new intrinsically superhard materials (H ≥ 40 GPa) have focused on the introduction of light elements forming strong bonds (B, C, N, and O) into transition metals (T) with high elastic moduli [1–5]. The suggested compounds include 5d transition-metal diborides (e.g., OsB2 [4] and ReB2 [5]) and nitrides such as PtN [6], IrN2 [7], and η-Ta3N5 [8,9]. Although some of these materials have high elastic moduli [4,5], the experimentally determined load-invariant hardnesses are typically below 30 GPa. Osmium diboride possesses high zero-pressure elastic moduli but a low hardness due to the presence of Os-Os layers with weak metallic bonds [10]. Rhenium diboride was believed to be intrinsically superhard [5], but its load-invariant hardness is also less than 30 GPa because of electronic and structural instabilities of 5d electrons under finite shear strain [11]. Rhenium nitrides, recently synthesized by Friedrich et al. [12] under high pressure and temperature, have attracted much interest because of their large bulk modulus of about 400 GPa, which is higher than that of ReB2 of 334–371 GPa [5,13]. However, our recent first-principles study showed that a combination of thermodynamic instability, relatively low shear moduli and strengths, and relatively soft polar Re-N bonds inherently limits their hardness [14]. These findings strongly challenge the general idea to design intrinsically superhard transition-metal diborides based only on their high elastic moduli [3–5].

Great effort has been recently devoted to the synthesis of tetraborides of transition metals by introducing more boron atoms to form a three-dimensional boron network with strong covalent bonds [15–17] because of their economically inexpensive constituents and relatively high hardness as well as the practically feasible synthetic conditions that do not require high pressure. Using the hardness models, Wang et al. [15] suggested that the transition-metal tetraborides, such as WB4 and MoB4, should be intrinsically superhard. Unfortunately, tungsten tetraboride has load-invariant hardness less than 30 GPa [16], as recently confirmed by Mohammadi et al. [17]. These results raise doubts regarding the predictability of that hardness model (see also [18], and the general stability issue will be unveiled below).

The stability of tetraborides was questioned by Zhang et al. [19]. Using the structural evolution method, they reported that MoB4 in WB4 structure cannot exist because of its high positive formation energy and the presence of imaginary phonon frequencies. More recently, similar thermodynamic instability was addressed for tungsten tetraborides by Liang, Yuan, and Zhang [20]. These researchers have shown that, while MoB4 and WB4 are unstable, MoB3 and WB3 with two-dimensional boron layers sandwiched between the transition metals are stable. These results raise several questions: (i) Are triborides with the two-dimensional network mechanically and dynamically stable? (ii) Does the simulated x-ray diffraction (XRD) pattern of the TB3 reproduce the experimental data? (iii) Could the calculated ideal shear resistance of the triborides support their possible superhardness? In this Letter, we show that the WB3 structure, albeit a three-dimensional covalent boron network, cannot exist due to its general thermodynamic, mechanical, and dynamic instabilities. Instead, the triborides should be experimentally...
accessible because of their thermodynamic, mechanical, and dynamic stability and because of the agreement of the simulated XRD pattern with the experimental one. We further demonstrate for the first time that, in spite of its two-dimensional covalent boron network, $TB_3$ possesses a high strength comparable to those of ReB$_2$ and B$_6$O. However, because the ideal shear strengths for $TB_3$ are much lower than those of $c$-BN, their intrinsic hardness should be also lower; i.e., they cannot be superhard.

First-principles calculations were performed by using the VASP code [21] with the generalized-gradient approximation proposed by Perdew and Wang for the exchange-correlation functional. Details of stress-strain calculations can be found in Refs. [22,23]. Dynamical properties of both $TB_4$ and $TB_3$ were calculated within the harmonic approximation by using the direct method based on the forces calculated via the Hellmann-Feynman theorem. To confirm our results, we also used a linear response method based on perturbation theory as implemented in the recent version of the VASP code. The resulting phonon dispersion and density of states (DOS) were the same as that using the $2 \times 2 \times 2$ supercell method. The equilibrium structural parameters for $TB_4$ and $TB_3$ ($T = W$ and Mo) (space groups: $P6_3/mmc$) were obtained by full relaxation of both lattice constants and internal atomic coordination. The relaxed atomic positions for $TB_3$ yielded four inequivalent crystallographic sites [T$2c$ (1/3, 2/3, 1/4), $T2b$ (0, 0, 1/4), $B_{12i}$ (1/3, 0, 0), and $B_{4f}$ (1/3, 2/3, 0.615)]. The relaxed structure for $TB_3$ can be regarded as the absence of four boron atoms at $B_{4f}$ (1/3, 2/3, 0.615) from the $TB_3$ structures, which are cross-linking the boron hexagonal layer [Figs. 1(a) and 1(b)]. The optimized lattice constants of the four borides ($a = 5.36$ Å, $c = 6.47$ Å for WB$_4$, $a = 5.21$ Å, $c = 6.86$ Å for MoB$_4$, $a = 5.20$ Å, $c = 6.34$ Å for WB$_3$, and $a = 5.21$ Å, $c = 6.31$ Å for MoB$_3$) are in good agreement with the previous values [17,20], thus confirming the reliability of the present calculations. In addition, the calculated lattice constants of WB$_3$ show a better agreement with the experimentally reported tungsten borides ($a = 5.16$ Å, $c = 6.33$ Å) than those of WB$_4$ [17].

The bond structures of WB$_4$ and WB$_3$ at equilibrium are shown in Figs. 1(a) and 1(b). $TB_4$ can be regarded as a three-dimensional boron network (intercalated between the transition metals), consisting of planar hexagonal boron rings and out-of-plane vertical B-B dimers, which connect the neighbor hexagonal boron layers. In comparison, $TB_3$ consists of the hexagonal boron layer intercalated between adjacent metal layers. The major difference between WB$_4$ and WB$_3$ is the absence of the cross-linking B-B dimers in the latter. The maps of the electron localization function (ELF) on the (1010) planes for WB$_4$ and WB$_3$ are also shown in Figs. 1(c) and 1(d), respectively. A higher value of ELF corresponds to higher electron localization. As one can see from Fig. 1(c), the strong B-B covalent bonds between the B-B dimers in WB$_4$ indicate significant electron localization there. One might believe that such a three-dimensional cross-linking of the boron layers should stabilize and strengthen the structure. However, as shown below, the tetraborides are thermodynamically and dynamically unstable.

To clarify the thermodynamic stability of $TB_4$ and $TB_3$, we calculated the formation energy with respect to the transition metal and boron (rhombohedral $\alpha$-phase) based on the reactions $T + 4B = TB_4$ and $T + 3B = TB_3$, respectively. The resulting positive formation energies of WB$_4$ and MoB$_4$ are 0.41 and 0.28 eV/atom, respectively, suggesting that both tetraborides are thermodynamically unstable. On the contrary, the calculated formation energies of WB$_3$ and MoB$_3$ of $-0.29$ and $-0.31$ eV/atom, respectively, are negative, indicating that both triborides are thermodynamically stable. The distinct thermodynamic stability of tetraborides and triborides is in good agreement with previous work [19,20]. However, thermodynamic stability of the triborides does not guarantee their stability.
TABLE I. Single-crystal elastic constants $c_{ij}$, the Voigt bulk modulus $B_V$, shear modulus $G_V$, and ideal strength (minimum tensile strength $\sigma_{\text{min}}$ and shear strength $\tau_{\text{min}}$) of WB$_3$ (all in GPa) and MoB$_3$ calculated by first-principles methods. Previous theoretical results for ReB$_2$ [22], B$_6$O [24], c-BN [23], and diamond [24] are included for comparison.

<table>
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<th>Compound</th>
<th>Reference</th>
<th>$c_{11}$</th>
<th>$c_{33}$</th>
<th>$c_{12}$</th>
<th>$c_{13}$</th>
<th>$c_{44}$</th>
<th>$B_V$</th>
<th>$G_V$</th>
<th>$\sigma_{\text{min}}$</th>
<th>$\tau_{\text{min}}$</th>
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<td>277</td>
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<td></td>
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<tr>
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<td>427</td>
<td>106</td>
<td>160</td>
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<td>276</td>
<td>226</td>
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against transformation into another phase. Therefore, an analysis of elastic and dynamic stabilities is necessary.

To evaluate the mechanical stability of both triborides and tetraborides, we calculated their single-crystal elastic constants by using both the linear response method and the efficient strain-energy method [22]. The obtained “unrelaxed” elastic constants of WB$_4$ ($C_{11} = 379$ GPa, $C_{12} = 279$ GPa, $C_{13} = 226$ GPa, $C_{33} = 436$ GPa, and $C_{44} = 149$ GPa) are in good agreement with the previous calculations ($C_{11} = 389$ GPa, $C_{12} = 280$ GPa, $C_{13} = 224$ GPa, $C_{33} = 437$ GPa, and $C_{44} = 151$ GPa [15]). Interestingly, we found that the tetraboride structure may spontanteously transform to a lower energy state if an ionic relaxation is allowed along some shear distortion paths, such as $\varepsilon = (0, 0, 0, 0, 0, \delta)$ with $\Delta E/V_0 = \frac{1}{4}(C_{11} - C_{12})\delta^2$ and $\varepsilon = (0, 0, 0, 0, \delta, 0)$ with $\Delta E/V_0 = \frac{1}{2}C_{44}\delta^2$. To confirm this instability, we have introduced a small fluctuation of atomic position of boron atoms within basal planes; the structure cannot recover to the original symmetry. Such mechanical instability may be correlated to its large positive formation energy as discussed above and the dynamic instability as will be shown below. In contrast, both triborides are mechanically stable, and the elastic constants (ionic relaxation included) are listed in Table I for WB$_3$ and MoB$_3$.

Lattice dynamics was investigated for both TB$_4$ and TB$_3$. The dispersion relations of WB$_4$ and WB$_3$ are shown in Figs. 1(e) and 1(f) as examples. The phonon dispersion relation of WB$_4$ exhibits imaginary (negative) frequencies in several important directions showing its dynamic instability at $T = 0$ K. Indeed, the slope of the negative acoustic branch along the $\Gamma$-$A$ high-symmetry direction in the vicinity of the $\Gamma$ point corresponds to elastic constants of $C_{44}$. Similarly, for $\Gamma$-$M$ and $\Gamma$-$K$ the lower two branches are also negative close to the $\Gamma$ point corresponding to negative $C_{44}$ and $C_{66} = (C_{11} - C_{12})/2$. In contrast, the WB$_3$ phase is stable as there are no imaginary modes. The partial phonon DOSs of WB$_3$ and WB$_4$ [shown in Figs. 1(g) and 1(h)] indicate that the lower frequencies of the total DOS are dominated by lattice dynamics of heavy W atoms and higher frequencies by light B atoms. Moreover, there is a gap in phonon frequencies between ca. 6.5 and 10.5 THz in WB$_3$ that almost entirely separates higher frequencies dominated by vibrations of B and lower frequencies dominated by W atoms. On the other hand, in WB$_4$, there is an admixture of phonon states due to dynamics of B and W atoms and no gap in the phonon DOS at the lower frequencies, and some of the optical modes of B atoms are separated by a gap above 25 THz. The imaginary frequencies originate from both the lattice dynamics of W and B atoms.

The electronic DOSs were analyzed in order to obtain insights into the electronic origin of the different stabilities of the tetra- and triborides. The calculated electronic DOSs of WB$_4$, WB$_3$, MoB$_4$, and MoB$_3$ are shown in Fig. 2. Both tetraborides show metallic bonding because of the finite value of the DOS at the Fermi level ($E_F$), which originates mostly from $d$ electrons of W or Mo and the $p$ electrons of B. In the triborides, however, the DOS around $E_F$ is lower than in tetraborides, and it shows a “splitting” into a pseudogap, thus underlying their stability. In the tetraborides, the pseudogap appears far below $E_F$, pointing to the electronic origin of their instability. Obviously, the B-B cross-linking dimers in the tetraborides weaken the bonds...
within the hexagonal boron layers and cause their less dense packing, because the nearest-neighbor B-B layer distances along the c axis of 3.168 Å for WB$_3$ and 3.154 Å for MoB$_3$ are shorter than those in tetraborides (3.235 Å for WB$_4$ and 3.429 Å for MoB$_4$). The Bader charge density analysis [25] shown in Fig. 1 further confirms the inhomogeneous charge transfer of the boron atoms at different crystallographic sites. Comparing the ELF of the tetraboride [Fig. 1(c)] with that of the triboride [Fig. 1(d)], one can understand that the weakening of the hexagonal boron layers in the former is due to a significant valence charge transfer to the cross-linking boron dimers.

In order to confirm the structure of the experimentally reported borides, we compared the simulated XRD patterns of triborides and tetraborides with the experimental one. Based on the similarity between tri- and tetraborides (the same space group $P6_3/mmc$), the triboride can be regarded as a boron-deficient tetraboride with an absence of B-B dimers. Therefore, a similar XRD pattern is expected for both. We calculated the XRD patterns for WB$_4$ and WB$_3$ and compared with the experimental one reported in Ref. [17]. The results are shown in Fig. 3. Obviously, all the simulated diffraction peaks for WB$_3$ are in excellent agreement with the experimental ones. In the simulated XRD pattern of WB$_4$, however, the intensity the (100), (200), (202), and (210) peaks is clearly higher than those shown in the experiment (almost invisible). These results demonstrate that the tungsten borides prepared by Gu, Krauss, and Steurer [16] and Mohammadi et al. [17] are WB$_3$ rather than the long-believed WB$_4$. None of the lower energy structures of possible WB$_4$ has a better agreement with the experimental XRD pattern than WB$_3$.

The anisotropic ideal strength of the triborides was obtained from the calculated stress-strain relationships, which are shown in Figs. 4(a) and 4(b) and also summarized in Table I, and compared with those of hard ReB$_2$ [22] and superhard B$_x$O [24], c-BN [23], and diamond [24]. The minimum tensile strengths of WB$_3$ of 43.3 GPa and MoB$_3$ of 37.7 GPa are slightly lower than those of ReB$_2$ and B$_x$O, but the minimum shear strengths along the weakest (0001)(1010) slip system are comparable to those of ReB$_2$ and B$_x$O. However, the ideal shear strengths of both triborides are lower than those of c-BN (58.3 GPa [23]), showing their lower shear resistance.

The structures of both WB$_3$ and MoB$_3$ before and after the shear instability were analyzed to understand their deformation mechanism. Both compounds show a similar instability mode. WB$_3$ is presented as an example in
Fig. 4, which shows the structure before and after lattice instability under the (0001)/(1010) shear deformation of about 20.4%. It can be seen that, after the lattice instability, the originally “flat” boron layers become wavy, and the valence charge density difference shows charge depletion between the boron and metal atoms, indicating breaking of the B–T bonds [see the arrows in Fig. 4(d)], which result in a sliding of the boron layers between the tungsten ones. This resembles the first shear instability in ReB$_2$ described in Ref. [11]. A more detailed comparison of the shear instabilities upon a larger shear, as described for ReB$_2$ in Ref. [11], is beyond the scope of the present study.

In summary, we carried out first-principles calculations to evaluate the thermodynamic, mechanical, and phonon stabilities of TB$_4$, which have been so far believed to be stable, in comparison with the TB$_3$. Electronic structure calculations reveal that the instability of tetraborides is associated with the weakening of the hexagonal boron layers due to strong localization of the p electron on the B–B dimers which are connecting adjacent boron layers. The stability issue of transition-metal tetraborides challenges the widely used “hardness model” (e.g., [15,26,27]), which incorrectly predicts them to be potentially superhard. The triborides are stable because such dimers are absent. The relatively low shear moduli and strength of transition-metal triborides indicate that they cannot be intrinsically superhard. An analysis of the deformed atomic and electronic structures reveals that the electronic instability is due to valence charge depletion between boron and metal atoms resulting in sliding of the boron layers between the tungsten ones, which limits their achievable strength.

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