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# Mechanical strength and origin of the strengthening effect of tantalum in superhard $W_{0.5}Ta_{0.5}B$ monoboride

Meiguang Zhang[a,*], Haiyan Yan[b], Yun Zhang[a], Qun Wei[c,*]

[a] College of Physics and Optoelectronic Technology, Nonlinear Research Institute, Baoji University of Arts and Sciences, Baoji 721016, China
[b] College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, China
[c] School of Physics and Optoelectronic Engineering, Xidian University, Xi'an 710071, China

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ABSTRACT

Tungsten borides with excellent mechanical properties have been recognized as a class of ultrahard compounds in various industrial applications. Here, motivated by the recent experimental work, a quantitative comparison analysis on the structure, mechanical strength, and electronic structure of the tantalum-strengthened superhard $W_{0.5}Ta_{0.5}B$ monoboride and its parent material WB has been studied by first-principles calculations. Excellent agreements of the calculated lattice parameters and simulated X-ray diffraction between present results and experimental data have confirmed the crystal structure of the synthesized $W_{0.5}Ta_{0.5}B$. Compared to the WB, the calculated stress-strain curves show an enhanced shear strength and improved ductility of $W_{0.5}Ta_{0.5}B$ on (100) and (010) crystal planes, originating from the reduction of antibonding states between the W-$e_g$ states which enables strenuous sliding of metal bilayer in $W_{0.5}Ta_{0.5}B$. Furthermore, the lattice instability of $W_{0.5}Ta_{0.5}B$ under large shear strain with an intriguing sequential bond-breaking mode that is derived from the first breaking of zigzag B chains and the subsequent collapsing of $WB_7$ and $TaB_7$ polyhedrons by simultaneously breaking of B–W and B–Ta bonds. These findings shed strong light on the strengthening mechanism of $W_{0.5}Ta_{0.5}B$ and the design for novel ultra-incompressible and superhard solids in transition metal monoborides.

## 1. Introduction

Currently, considerable interest has been renewed in a series of transition metal (TM) borides based on the design strategy [1,2] of intrinsically ultra-incompressible and superhard materials by intercalation the light elements (like B, C, N) into heavy TM with expected that TM atoms will contribute high valence-electron density to enhance incompressibility and light elements atoms will form a strong covalent network to strengthen the crystal structure. Compared to the TM nitrides and carbides, TM borides have been the focus of intense recent research because of their excellent mechanical properties (such as ultrahardness, high melting points, good chemical inertness, etc.) and favorable synthesis conditions (ambient-condition synthesis) that have led to the discovery of a series of novel materials, such as $OsB_2$ [3], $ReB_2$ [4–7], $WB_2$ [8], $WB_4$ [8–11], $CrB_4$ [12,13], $FeB_4$ [14,15], etc. Among these borides, TM tetraborides have attracted special attention for their high boron content which are expected to form three-dimensional (3D) covalent bond networks that enhances their ability to resist shear deformation. A prime example of which is $WB_4$ with a Vickers microindentation hardness of 43.3 ± 2.9 GPa under a load of 0.49 N [9], has recently drawn increasing research interest in its structural peculiarities and made the W-B system a hot topic [16–18].

More recently, another tungsten boride in W-B system, WB was induced to be superhard through solid solution strengthening approach by Yeung et al. [19] that partially substituting tungsten atoms of WB with tantalum, resulting a highly crystalline $W_{0.5}Ta_{0.5}B$ determined by transmission electron microscopy technique. The measured hardness of $W_{0.5}Ta_{0.5}B$ [19] reaches up to 42.8 GPa under the load of 0.49 N which is larger than that of parent material WB (36 GPa at 0.49 N) [20]. Compared to the aforementioned TM borides which are either highly covalent compounds or they are the highest boride, as one of few exceptions, it is rather surprising that the $W_{0.5}Ta_{0.5}B$ with boron-poor content and typical metallic behavior possesses an anomalous ultrahardness. These discoveries challenge the conventional wisdom of the design strategy generally used for heavy TM borides. The report has further demonstrated that the hardening effects of substituting tantalum into WB can be contributed to the reduction of slipping of the metallic planes through dislocation pinning, leading to a stronger resistance to shear deformation associated with the macroscopic hardness of $W_{0.5}Ta_{0.5}B$. Therefore, this pioneering work [19] provide an

* Corresponding authors.
*E-mail addresses:* zhmgbj@126.com (M. Zhang), weiaqun@163.com (Q. Wei).

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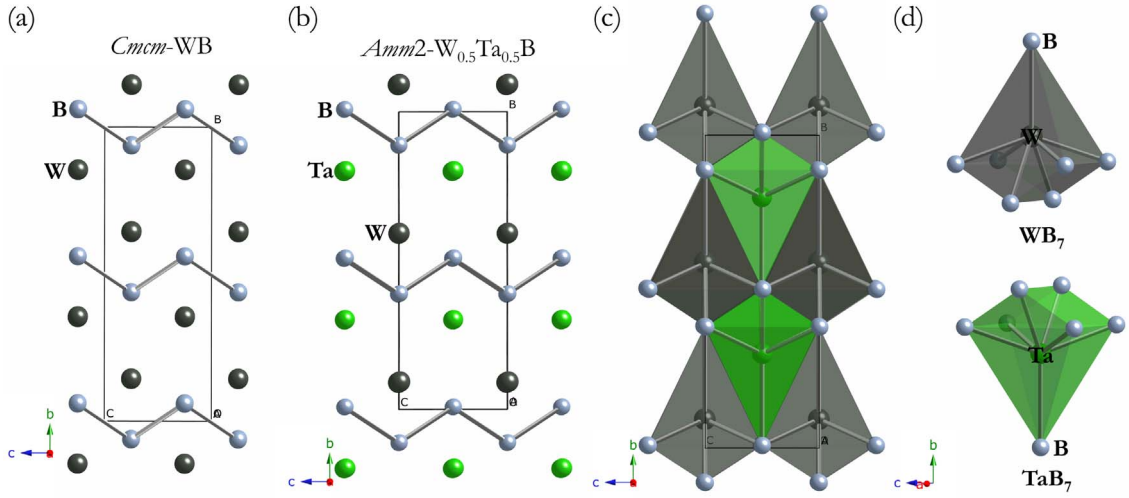


**Fig. 1.** Crystal structures of WB (a) and $W_{0.5}Ta_{0.5}B$ (b), polyhedral view of $W_{0.5}Ta_{0.5}B$ (c), and the $WB_7$ and $TaB_7$ polyhedrons in $W_{0.5}Ta_{0.5}B$ (d). The large, middle, and small spheres represent B, Ta, and W atoms, respectively.

alternate approach to making new superhard materials in more metallic materials by strengthening of the weakest crystal planes. In a subsequent theoretical work performed by Liang et al. [21], a deeper understanding of the hardening effects at the atomic level has been investigated on the valence-electron concentration and formation energy of TM monoborides by using first-principles calculations. This extraordinary stiffening from WB to $W_{0.5}Ta_{0.5}B$ mainly arises from the optimal valence-electron concentration of eight electrons per formula units (*e*/f.u.), and any deviations outside this value would lead to unexpected softening of the systems. This unique variation stems from the presence of two kinds of bands near the Fermi level that respond differently to the motion of dislocations between the metal bilayer. The claimed superhardness in these preliminary works thus places the synthesized $W_{0.5}Ta_{0.5}B$ atop the family of TM monoborides for their potential technical applications. Therefore, an explicit determination of the structure-strength relations of $W_{0.5}Ta_{0.5}B$ compared with that of WB and the detailed alterations of electronic bonding states in $W_{0.5}Ta_{0.5}B$ are not only of particular interest in understanding the intrinsic strengthening mechanism of the intercalation of tantalum, but also are essential for the design of novel ultrahard materials in the family of TM monoboride. Here, a quantitative study on the structure, mechanical strength, and electronic structure of the $W_{0.5}Ta_{0.5}B$ and WB are executed by using the first-principles calculations to address these issues. The obtained results can provide further details are highly desirable.

## 2. Computational methods

We have performed first-principles calculations based on the density functional theory with the Perdew-Burke-Ernzerhof generalized gradient approximation [22] and a plane-wave basis set as implemented in the VASP code [23]. The frozen-core all-electron projector augmented wave (PAW) method [24] was adopted to describe the electron-ion interactions and the valence states of $5p^6 5d^3 6s^2$, $5p^6 5d^4 6s^2$, and $2s^2 2p^1$ have been considered for Ta, W, and B, respectively. To confirm our manual constructed structure for $W_{0.5}Ta_{0.5}B$, meanwhile, a fixed-composition crystal structure search was conducted here by using the recently developed Crystal structure AnaLYsis by Particle Swarm Optimization package (CALYPSO) [25,26] with containing 1–4 formula units (f.u.) in the simulation cell at ambient conditions. During the structure search processes, the 60% structures of each generation with lower enthalpies were selected to generate the structures for the next generation by Particle Swarm Optimization (PSO) operation, and the other structures in new generation were randomly generated to increase the structural diversity. Usually, the structure searching simulation was stopped after ~ 900 structures generated (~ 30 generations). For both $W_{0.5}Ta_{0.5}B$ and WB, the total energy of the structure was minimized by relaxing the structural parameters using a conjugate gradient optimization method [27]. The total energy and stress calculations used an cutoff energy of 600 eV for the plane-wave expansions and Monkhorst-Pack *k*-point grid [28] with grid density of $0.03 \times 2\pi$ Å$^{-1}$ in the Brillouin zone. The energy convergence is about 1 meV per atom, with residual stresses and forces in the fully relaxed structures less than 0.1 GPa and 0.001 eV/Å, respectively. The phonon calculation was carried out by using a finite displacement approach implemented in the PHONOPY program [29]. The independent single crystal elastic constants were determined from evaluation of stress tensor generated small strain [30], and the polycrystalline elastic moduli including bulk modulus, shear modulus and Young's modulus as well as Poisson's ratio were thus estimated by the Voigt-Reuss-Hill approximation [31]. Details of stress-strain calculations for ideal strengths and relaxed loading path can be found in Refs. [32–35].

## 3. Results and discussion

Recent experiment has demonstrated [19] that the synthesized $W_{0.5}Ta_{0.5}B$ is well crystalline and adopts in an orthorhombic crystal lattice as the high temperature phase of its parent material WB. It is known that the accurate crystal structures are the key for the understanding of mechanical properties of materials. By substituting half of tungsten atoms of WB crystal lattice [as shown in Fig. 1(a)], the deduced unit cell of $W_{0.5}Ta_{0.5}B$ was then constructed as in Fig. 1(b) by the full relaxations of the lattice constants and internal atomic coordinations. The relaxed crystal lattice of the $W_{0.5}Ta_{0.5}B$ was identified as an orthorhombic form with space group of *Amm*2. As listed in Table 1, the optimized equilibrium lattice parameters of $W_{0.5}Ta_{0.5}B$ are

**Table 1**
Calculated the crystal lattices (Å), volume $V_0$ (Å$^3$/formula), EOS fitted Bulk modulus $B_0$ (GPa) and its pressure derivative $B_0'$ for $W_{0.5}Ta_{0.5}B$ and WB along with the available experimental data and theoretical results.

| Compound | Source | $a_0$ | $b_0$ | $c_0$ | $V_0$ | $B_0$ | $B_0'$ |
|---|---|---|---|---|---|---|---|
| $W_{0.5}Ta_{0.5}B$ | Exp. [19] | 3.240 | 8.545 | 3.126 | 86.55 | 337 | 4.0 |
| | This work | 3.242 | 8.591 | 3.133 | 86.529 | 314 | 4.08 |
| | Ref [21] | 3.250 | 8.593 | 3.129 | 87.40 | 310 | 4.30 |
| WB | Exp. [19] | 3.140 | 8.460 | 3.070 | | | |
| | This work | 3.181 | 8.509 | 3.104 | 84.016 | 343 | 4.16 |
| | Ref [21] | 3.180 | 8.514 | 3.103 | 84.04 | 341 | 4.22 |
| | Ref [36] | 3.179 | 8.480 | 3.102 | 83.623 | | |