Theoretical investigation on the transition metal borides with Ta$_3$B$_4$-type structure: a class of hard and refractory materials

Naihua Miao, Baisheng Sa, Jian Zhou, Zhimei Sun,*

Department of Materials Science and Engineering, College of Materials, Xiamen University, 361005 Xiamen, People’s Republic of China

*Author to whom correspondence should be addressed. Tel and Fax: +86-592-2186664. Email addresses: zmsun@xmu.edu.cn and zhmsun2@yahoo.com.

Abstract

Based on density functional theory, we have systematically studied the structural stability, mechanical properties and chemical bonding of the transition metal borides M$_3$B$_4$ (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W) for the first time. All the present studied M$_3$B$_4$ have been demonstrated to be thermodynamically and mechanically stable. The bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio, microhardness, Debye temperature and anisotropy have been derived for ideal polycrystalline M$_3$B$_4$ aggregates. In addition, the relationship between Debye temperature and microhardness has been discussed for these isostructural M$_3$B$_4$. Furthermore, the results of the Cauchy pressure, the ratio of bulk modulus to shear modulus, and Poisson’s ratio suggest that the valence electrons of transition metals play an important role in the ductility of M$_3$B$_4$. The calculated total density of states for M$_3$B$_4$ indicates that all these borides display a metallic conductivity. By analyzing the electron localization function, we show that the improvement of the ductility in these M$_3$B$_4$ might attribute to the decrease of their angular bonding character.

Keywords: Transition metal borides; Mechanical properties; Density functional theory; Electronic structure; Chemical bonding; Electron localization functions.
1. Introduction

Transition metal borides (TMBs) have been the focus of attention during the recent years due to their useful mechanical and electrical properties and their potential industrial applications (e.g. cutting tools and coatings). Among these TMBs, ReB₂ and OsB₂ are ultra-incompressible and superhard [1-3]; MgB₂ has been observed to be a superconductor at 39 K [4]; HfB₂, ZrB₂, MoB, CrB₂, CrB, TiB₂, Ti₃B₄ and TiB have been used as coatings or reinforcements in various composites because of their great hardness and good thermal stability [5-13]. As far as we know, most of the experimental works and theoretical studies are concentrated on the transition metal monoborides and diborides. While, another class of TMBs (M₃B₄) with Ta₃B₄-type structure (Space Group IMMM, No.71) also exhibit great hardness [14-16], possess high melting point[16-18], show good electrical conductivity [14, 17, 18], and display considerable oxidation-resistant in air [16-18], which can be regarded as potentially useful materials for high temperature engineering applications, but insufficient attention was paid to them. Theoretical works on the electronic and bonding properties of Ta₃B₄-type compounds have been carried out, but they were mainly performed for Ta₃B₄ [17]. A computational thermodynamic study on the stability of V₃B₄ suggested that it was stable enough as a refractory material for high temperature composite applications [19]. Experimentally, it has been shown that the platelet morphology of the Ti₃B₄ phase could improve the strength and toughness of the platelet composite [20], and the Ti₃B₄ and TiB₂ peritectic composite particulates have been in-situ synthesized to reinforce metal matrix composite [11]. Large crystals of Cr₃B₄, Ta₃B₄ and related solid solutions have been prepared and measured to have a Vickers microhardness (Hᵥ) around 22 GPa by Shigeru Okada et al. [14, 16]. A relatively larger Hᵥ value of 33±2 GPa has also been reported for Ta₃B₄, indicating its
potential applications for nanostructured superhard materials [15]. However, up to now, due to the limited published works on M₃B₄, the knowledge of these materials is rather scarce, e.g., their structural stability, mechanical properties and chemical bonding are still unknown. Therefore, a systematic investigation on this class of hard and refractory materials is of great practical interest and importance.

Computational technique based on density functional theory is a powerful tool to explore the phase stability and physical and mechanical properties of materials. In the present work, by means of density functional theory calculations, we focused on transition metal borides M₃B₄ (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W). Among these borides, Hf₃B₄ and W₃B₄ have not yet been reported experimentally and their structural stabilities are still unknown. Hence, we began with our study on the thermodynamic stabilities of M₃B₄ (Section 3.1), and then systematically explored their mechanical properties (Section 3.2), Debye temperature (Section 3.3), anisotropy (Section 3.4), electronic structure and chemical bonding (Section 3.5), and dynamical stability (Section 3.6). Our results will provide a fundamental understanding on these hard and refractory materials and offer reference data for experimentalists. The remainder of the paper is organized as follows. In Section 2, we describe the computational methods and details. In Section 3, the results and discussions are presented. Finally, the conclusions are given in Section 4.

2. Calculation methods

The present calculations are based on the density functional theory (DFT). And there are 14 atoms for each cell, i.e., 8 boron atoms and 6 transition metal atoms.

Firstly, the Cambridge Serial Total Energy Package (CASTEP) [21] was used for geometry optimizations and elastic constants calculations. The interactions between
the ions and the electrons were described by using the Ultrasoft Vanderbilt pseudopotentials (USPP) [22]. The valence electrons were treated as: 2s2p for B; 3s3p3d4s for Ti, V and Cr; 4s4p4d5s for Zr, Nb and Mo; 5d6s for Hf, Ta; and 5s5p5d6s for W. The generalized gradient approximation (GGA) [23] and Perdew Burke Ernzerhof functional (PBE) [24] were employed for exchange correlation functional. The structures were optimized through the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [25]. A cutoff energy of 600 eV was chosen for plane wave basis set and the 12×4×12 k-points were automatically generated by Monkhorst-Pack (MP) scheme [26]. The convergence criteria were set to maximum force tolerance within 0.03 eV/Å for geometry optimization, and 0.006 eV/Å for elastic constants calculations.

To obtain the force constants for phonon calculations and to check the reliability of results gained by CASTEP, the Vienna ab initio simulation package (VASP) code as implemented to solve the Kohn-Sham equations employing the projector augmented wave (PAW) method [27-30] was also used. The semi-core p states and possibly the semi-core s states were treated as valence states. PAW-GGA-PBE [23, 24, 29, 30] pseudopotentials with electronic configurations of B 2s2p1, Ti 3p63d24s2, V 3p63d24s2, Cr 3p63d24s2, Zr 4s24p65s24d2, Nb 4p65s24d2, Mo 4p65s24d2, Hf 5p66s25d2, Ta 5p66s25d2, and W 5p66s25d2 were employed. The cutoff energy for plane wave basis set was 700 eV. 12×4×12 k-points and MP scheme [26] were adopted for Brillouin Zone sampling. The relaxation convergence for ions and electrons were 1×10⁻⁵ eV and 1×10⁻⁶ eV, respectively. The force constants, lattice parameters, density of states, and electron localization function (ELF) [31, 32] analyzed by VESTA [33] were calculated for the equilibrium structures.
Our phonon calculations were performed through the supercell approach [34]. Force constants of supercells were prepared by using the VASP, and the PHONOPY code [35, 36] was used to calculate the phonon frequencies and phonon density of states.

3. Results and discussions

3.1. Lattice parameters and thermodynamic stability

The calculated lattice parameters of M₃B₄ are given in Table 1. Note that the lattice constants predicted by CASTEP and VASP are in good agreement with each other and the available experimental data, indicating the reliability of the results obtained from the present density functional theory approaches. As seen from Table 1, the predicted lattice constants of Ti₃B₄, V₃B₄ and Nb₃B₄ are in good agreement with the experiments [37-39]. For Ta₃B₄, the calculated lattice parameters are a bit larger than the experimental data (e.g., about 1.6% larger for b) [16], while for Cr₃B₄, the calculated lattice constants are slightly smaller than the experiments (e.g., about 2.7% smaller for a) [40], which is within the GGA error. However, for the other compounds M₃B₄ such as Zr₃B₄, Mo₃B₄, Hf₃B₄ and W₃B₄, there are no theoretical or experimental data available for comparison. Therefore, the present results could provide useful information for further experimental or theoretical investigations. From Table 1, it is obvious that the lattice constants (a, b and c) follow the orders of Ti₃B₄<V₃B₄<Cr₃B₄ for 3d M₃B₄, Zr₃B₄<Nb₃B₄<Mo₃B₄ for 4d M₃B₄, and Hf₃B₄<Ta₃B₄<W₃B₄ for 5d M₃B₄, which is reasonable as the radii of elements in the same row of the periodic table decrease with increasing atomic numbers. Moreover, we also observed that the predicted lattice parameters for Zr₃B₄ and Hf₃B₄ were a bit larger than the other M₃B₄.
This can be understood as Zr and Hf possesses larger atomic radii than the other transition metals studied herein.

To investigate the possibility to obtain M₃B₄, we have calculated the formation energy $E_{\text{form}}$ by Eq. (1) according to the reaction (2).

$$E_{\text{form}} = E_{\text{total}}^{(\text{M₃B₄})} - 3E_{\text{total}}^{(\text{M})} - 4E_{\text{total}}^{(\text{B})} \quad (1)$$

$$3\text{M} + 4\text{B} \rightarrow \text{M₃B₄} \quad (2)$$

The total energy $E_{\text{total}}$ of M and B were calculated for stable crystalline transition metals and $\alpha$-boron, respectively. The results are also given in Table. 1. For all the M₃B₄ borides, the formation energies are negative, suggesting that all of them are thermodynamically stable. Hence, we expect that all of them, including two new compounds Hf₃B₄ and W₃B₄, could be realized experimentally.

### 3.2. Mechanical properties

The mechanical properties of solids are of great importance because they relate to many properties of materials, e.g. interatomic potentials, equation of states, melting points and phonon spectra. Here, we start with the calculations of elastic constants.

#### 3.2.1. Elastic constants

For orthorhombic M₃B₄ crystals, there are nine independent elastic constants which are usually referred to as $c_{11}$, $c_{22}$, $c_{33}$, $c_{44}$, $c_{55}$, $c_{66}$, $c_{12}$, $c_{13}$ and $c_{23}$. In the present work, we obtained the elastic constants by applying a given homogeneous deformation (strain) and calculating the resulting stress [41] as implemented in CASTEP. The calculated elastic constants are presented in Table. 2. Among these borides, V₃B₄ exhibits the largest elastic constants of $c_{22}$, $c_{33}$, $c_{44}$, $c_{55}$, and $c_{66}$, while W₃B₄ possesses the largest elastic constants of $c_{11}$, $c_{12}$, $c_{13}$ and $c_{23}$. As seen from Table. 2, $c_{11}$, $c_{12}$, $c_{13}$ and $c_{23}$ elastic constants increase with increasing valence electrons concentration (VEC), which indicates the valence electrons of transition metals in
M₃B₄ may play an important role in these elastic constants. For orthorhombic crystals, the Born mechanical stability criteria are given by: 
\[ c_{11} > 0, \quad c_{22} > 0, \quad c_{33} > 0, \quad c_{44} > 0, \quad c_{55} > 0, \quad c_{66} > 0, \quad (c_{11} + c_{22} - 2c_{12}) > 0, \quad (c_{11} + c_{33} - 2c_{13}) > 0, \quad (c_{22} + c_{33} - 2c_{23}) > 0, \quad (c_{11} + c_{22} + c_{33} + 2c_{12} + 2c_{13} + 2c_{23}) > 0. \]
It is obvious that all of the studied M₃B₄ crystals with Ta₃B₄-type structure satisfy the Born criteria, hence they are all mechanically stable.

### 3.2.2. Mechanical parameters for polycrystalline aggregates

From the calculated elastic constants, other mechanical parameters for polycrystalline aggregate such as bulk modulus \( K \), shear modulus \( G \), Young’s modulus \( E \), and Poisson’s ratio \( \sigma \) can be derived using Voigt–Reuss–Hill (VRH) approximation [42-44]. Voigt’s and Reuss’s schemes represent the upper and lower bounds to the elastic modulus, respectively. For orthorhombic crystals, the shear modulus \( G \) and the bulk modulus \( K \) according to Voigt and Reuss approximations are defined as:

\[
G_{V} = \frac{1}{15} (c_{11} + c_{22} + c_{33} - c_{12} - c_{13} - c_{23}) + \frac{1}{5} (c_{44} + c_{55} + c_{66}) \tag{3}
\]

\[
K_{V} = \frac{1}{9} (c_{11} + c_{22} + c_{33}) + \frac{2}{9} (c_{12} + c_{13} + c_{23}) \tag{4}
\]

\[
G_{R} = \frac{15}{4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{13} + s_{23}) + 3(s_{44} + s_{55} + s_{66})} \tag{5}
\]

\[
K_{R} = \frac{1}{(s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{13} + s_{23})} \tag{6}
\]

The Hill’s averages are taken from the averages of the two [44]:

\[
G = (G_{V} + G_{R})/2 \tag{7}
\]

\[
K = (K_{V} + K_{R})/2 \tag{8}
\]
Then the Young’s modulus \((E)\), and Poisson’s ratio \((\sigma)\) are calculated by the following formulas:

\[
E = \frac{9K G}{(3K + G)} \quad (9)
\]

\[
\sigma = \frac{(3K - 2G)}{2(3K + G)} \quad (10)
\]

Based on equations (3)-(10), we derived the corresponding values which are presented in Table. 3. As far as we know, there are no experimental results available related to the elastic modulus for \(M_3B_4\) studied here, but we can compare these modulus with other known ceramic crystals. As seen from Table. 3, the bulk modulus \(K\) follow the orders of \(Ti_3B_4 < V_3B_4 < Cr_3B_4\) for \(3d\) \(M_3B_4\), \(Zr_3B_4 < Nb_3B_4 < Mo_3B_4\) for \(4d\) \(M_3B_4\), and \(Hf_3B_4 < Ta_3B_4 < W_3B_4\) for \(5d\) \(M_3B_4\), indicating that the increased extra valence electrons of transition metals contribute to the chemical bonding of \(M_3B_4\). And for all studied borides, their shear modulus ranging from 165 GPa to 238 GPa may reveal that there are strong directional bonding in these borides. Among them, \(V_3B_4\) shows the largest shear modulus (238 GPa) and Young’s modulus (555 GPa). The shear modulus of \(V_3B_4\) is much larger than that of \(\alpha-Al_2O_3\) (143 GPa) [45] and is comparable to that of stishovite (218 GPa) [45] and \(\gamma-Si_3N_4\) (248 GPa) [45]. A largest bulk modulus value of 335 GPa for \(W_3B_4\) is also observed in Table. 3, suggesting that \(W_3B_4\) is very uncompressible, which is about 11% lower compared with c-BN (376 GPa) [45] but much higher than \(Ti_{0.25}Al_{0.75}N\) (178 GPa, the benchmark cutting tool material today) [46]. It is also noted in Table. 3 that, for all the borides studied here, their Poisson’s ratio \((\sigma)\) are very small, indicating all of them are relatively stable against shear. As is known, the range of Poisson’s ratio for central-force solids are 0.25–0.5 [47, 48], thus, the interatomic forces are central in \(Mo_3B_4\) and \(W_3B_4\), while they are non-central in the other \(M_3B_4\) as their Poisson’s ratio are all smaller than 0.25.

3.2.3. Microhardness
To estimate the microhardness ($H_V$) of M$_3$B$_4$, we used the following relation for isotropic solids:

$$H_V = \frac{(1-2\sigma)E}{6(1+\sigma)} \quad (11)$$

The estimated microhardness $H_V$ is also listed in Table 3. Our estimated $H_V$ values are ranging from 18.3 (W$_3$B$_4$) to 26.4 (V$_3$B$_4$) GPa indicating that all these M$_3$B$_4$ are hard materials. The calculated microhardness 23.9 GPa for Cr$_3$B$_4$ is in good agreement with the experimental value 21.9±1.0 GPa [18]. For Ta$_3$B$_4$, Shigeru Okada et al suggested that it had a same level of microhardness as Cr$_3$B$_4$ [16], which is consistent with our prediction. Nevertheless, when compared with the reported $H_V$ 33±2 GPa for Ta$_3$B$_4$ [15], our calculated $H_V$ is a bit smaller. However, it should be noted that our estimated $H_V$ 22.5 GPa for Ta$_3$B$_4$ is in the range of the values from 21.9 to 33±2 GPa. From Table 3, we can also observe that V$_3$B$_4$ shows the greatest microhardness value among these M$_3$B$_4$ borides. According to Teter [49], the polycrystalline shear modulus is a better predictor of hardness than bulk modulus, the microhardness can be calculated by: $H_T = 0.1769G^{-2.899}$. The result is also given in Table 3, which is a bit larger than the data obtained from equation (11). Note that the later estimated microhardness $H_T$ for Ta$_3$B$_4$ is in good agreement with the reported value 33±2 GPa [15]. For both estimated microhardness $H_V$ and $H_T$ of M$_3$B$_4$, the trends are quite similar, i.e., the higher shear modulus, the higher microhardness.

### 3.2.4. Ductility and brittleness

To explore the ductility and brittleness of M$_3$B$_4$, we refer to the Cauchy pressure and the ratio of bulk modulus to shear modulus ($K/G$). Pettifor [50] has suggested that the angular character of atomic bonding in metals and compounds, which also relates to their brittleness or ductility, could be described by the Cauchy pressure. For directional bonding with angular character, the Cauchy pressure is negative, with
larger negative pressure representing a more directional character, which will be further explored in Section 3.5. Generally speaking, a positive Cauchy pressure reveals damage tolerance and ductility of a crystal, while a negative one demonstrates brittleness. In Fig. 1, the Cauchy pressures \((c_{23} - c_{44})\) for orthorhombic crystals as a function of valence electrons concentration (VEC) are illustrated for \(M_3B_4\). Clearly, for all \(M_3B_4\), where transition metal elements \(M\) are in the same rows (3\(d\), 4\(d\), and 5\(d\)), the Cauchy pressures increase with increasing VEC, i.e., \(c_{23} - c_{44}\) follow the orders of \(\text{Ti}_3\text{B}_4<\text{V}_3\text{B}_4<\text{Cr}_3\text{B}_4\) for 3\(d\) \(M_3\text{B}_4\), \(\text{Zr}_3\text{B}_4<\text{Nb}_3\text{B}_4<\text{Mo}_3\text{B}_4\) for 4\(d\) \(M_3\text{B}_4\), and \(\text{Hf}_3\text{B}_4<\text{Ta}_3\text{B}_4<\text{W}_3\text{B}_4\) for 5\(d\) \(M_3\text{B}_4\), indicating that the increased valence electrons of transition metals contribute to the ductility of \(M_3\text{B}_4\). As seen from Fig. 1, it is obvious that the Cauchy pressure for \(\text{W}_3\text{B}_4\) is positive, suggesting the ductility of \(\text{W}_3\text{B}_4\), while for the other studied borides, their Cauchy pressures are all negative, showing that all of them have a brittle nature.

To qualify whether a material would fail in a ductile or brittle manner, Pugh proposed the ratio of bulk modulus to shear modulus \((K/G)\) \cite{51}. The transition from ductile to brittle behavior occurs around a \(K/G\) value of 1.75. Based on this assumption, materials with \(K/G\) values larger than 1.75 are associated with ductility, whereas materials with values smaller than 1.75 correspond to a brittle nature. The plot of \(K/G\) ratios as a function of valence electrons concentration (VEC) for \(M_3\text{B}_4\) is given in Fig. 2. Compared with Fig. 1, a similar trend can be observed for \(K/G\) ratios and VEC, i.e., \(K/G\) ratios increase with VEC and also follow the orders of \(\text{Ti}_3\text{B}_4<\text{V}_3\text{B}_4<\text{Cr}_3\text{B}_4\) for 3\(d\) \(M_3\text{B}_4\), \(\text{Zr}_3\text{B}_4<\text{Nb}_3\text{B}_4<\text{Mo}_3\text{B}_4\) for 4\(d\) \(M_3\text{B}_4\), and \(\text{Hf}_3\text{B}_4<\text{Ta}_3\text{B}_4<\text{W}_3\text{B}_4\) for 5\(d\) \(M_3\text{B}_4\). The calculated \(K/G\) value for \(\text{W}_3\text{B}_4\) is 1.97, obviously larger than 1.75, indicating the ductile nature of \(\text{W}_3\text{B}_4\). This is in good agreement with the above discussion on the ductility of \(\text{W}_3\text{B}_4\). For the other \(M_3\text{B}_4\),
their $K/G$ values are all more or less smaller than 1.75, hence they can be classified as brittle materials.

As is known, Poisson’s ratio has great correlation with ductility of crystalline alloys and amorphous metals, and it has been used as a screening parameter to identify intrinsic ductility of metals and alloys [52], i.e., the higher Poisson’s ratio, the better ductility at low temperature, and vice versa. The Poisson’s ratio as a function of valence electrons concentration (VEC) for $M_3B_4$ has also been given in Fig. 3. The trend for the relationship between Poisson’s ratio and VEC is quite similar to that in Fig. 1 and Fig. 2, i.e., Poisson’s ratio of $M_3B_4$ goes up with the increase of their VEC. As seen from Fig. 3, Ti$_3$B$_4$ possesses the smallest Poisson’s ratio, and hence it shows the greatest brittleness among these $M_3B_4$ compounds. While W$_3$B$_4$ exhibits the largest Poisson’s ratio indicating its greatest ductility. Furthermore, the brittleness of M$_3$B$_4$ follow the orders of Ti$_3$B$_4$>V$_3$B$_4$>Cr$_3$B$_4$ for 3d $M_3B_4$, Zr$_3$B$_4$>Nb$_3$B$_4$>Mo$_3$B$_4$ for 4d $M_3B_4$, and Hf$_3$B$_4$>Ta$_3$B$_4$>W$_3$B$_4$ for 5d $M_3B_4$. These results coincide well with the above analysis of Cauchy pressures and $K/G$ values.

### 3.3. Debye temperature

#### 3.3.1. The calculation of Debye temperature

Mechanical properties can be related to thermodynamical parameters such as Debye temperature, specific heat, thermal expansion and melting point [48]. We have calculated the Debye temperature ($\theta_0$) for $M_3B_4$ by the relation between the mean sound velocity $v_m$ and $\theta_0$ [53]:

$$\theta_0 = \frac{h}{k} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} v_m$$  \hspace{1cm} (12)

where $h$ is Planck’s constant, $k$ is Boltzmann’s constant, $N_A$ is Avogadro’s number, $\rho$ is the density, $M$ is the molecular weight and $n$ is the number of atoms in the molecule.
The mean sound velocity of polycrystalline materials can be obtained according to the following approximations [53]:

\[
v_m = \left[\frac{1}{3}\left(\frac{2}{v_l^3} + \frac{1}{v_t^3}\right)\right]^{-1/3}
\] (13)

where \(v_l\) and \(v_t\) are the longitudinal and transverse elastic wave velocity of the polycrystalline material which can be obtained by using the polycrystalline shear modulus \(G\) and the bulk modulus \(K\) from Navier’s equation [54]:

\[
v_l = \left(\frac{K + \frac{4G}{3}}{\rho}\right)^{1/2}
\] (14)

\[
v_t = \left(\frac{G}{\rho}\right)^{1/2}
\] (15)

The calculated results are listed in Table 4. Among these materials, V3B4 displays the highest Debye temperature of 1058 K, and about half of this value is obtained for W3B4. For Nb3B4, a theoretical \(\theta_D\) of 592 K has been reported by Blinder and Bolgar [55], which is 209 K smaller than our predicted value 801K. Nevertheless, it should be noted that, by using the same approach [55], they also obtained other \(\theta_D\) values of 339 K for HfB2 (580 K [56]), 440 K for NbB2 (720 K [56]) and 332 K for TaB2 (570 K [56]), which are much smaller than the experimental data (where the experimental values are in the parenthesis). As their theoretical approach generally underestimated the Debye temperature, it is understandable that our calculated \(\theta_D\) are higher than their predicted values. Therefore, although there is no other theoretical or experimental data available for comparison, we believe that our predicted \(\theta_D\) for M3B4 are reasonable and can be used as reference for the experimentalists or theorists. For materials, usually, the higher Debye temperature, the larger microhardness.
Interestingly, in the present work, Hf$_3$B$_4$, Ta$_3$B$_4$ and W$_3$B$_4$ show lower Debye temperature compared with Zr$_3$B$_4$, but all of them are harder than Zr$_3$B$_4$, which is quite different from the normal cases. Thus, it is worthy to discuss the relationship between $\theta_D$ and $H_V$ which will be given in the following subsection.

3.3.2. The relationship between Debye temperature and microhardness

The strength of interatomic cohesive forces in solids is exhibited by such properties as compressibility, microhardness, and melting point [48, 57]. The stronger these forces are, the higher the Debye temperature is; and vice versa [58]. For isostructural groups of crystals, the relationship between Debye temperature ($\theta_D$) and microhardness ($H_V$) can be defined as [59]:

$$\theta_D = p \times H_V^{1/2}V^{1/6}M^{-1/2} + q$$  (16)

where $M$ is molar mass, $V$ is molecular volume, and $p$ and $q$ are linear fitted parameters for specified crystal system. This relationship for M$_3$B$_4$ borides is illustrated in Fig. 4, where the data are taken from the preceding subsections. As seen from Fig. 4, the above relationship has been perfectly represented by using our predicted Debye temperature $\theta_D$ and microhardness $H_V$. The fitted parameters are 1826.13 for $p$, and 7.40 for $q$. And then these parameters were used to recalculate the $H_V$ values for M$_3$B$_4$ by using the equation (16). Little deviation has been observed in Fig. 4 when these newly obtained microhardness values were compared with the $H_V$ values in Table. 3. So according to the above relation (16), one can roughly estimate $H_V'$ ($\theta_D'$) for a class of isostructural crystals by some given data, i.e., we can firstly obtain the parameters ($p$, $q$) by fitting several pairs of $\theta_D$ and $H_V$, and then calculate corresponding $H_V'$ ($\theta_D'$) with a known $\theta_D'$ ($H_V'$) value.

3.4. Anisotropy
The anisotropy of crystals affects the physical properties in different directions of solids, e.g. microcracks are induced in ceramics due to their anisotropy of the coefficient of thermal expansion and elastic anisotropy. Therefore, it is necessary to investigate the elastic anisotropy of $M_3B_4$ borides. The shear anisotropic factors, which provide a measure of the degree of anisotropy in the bonding between atoms in different planes, are given by:

$$A_1 = \frac{4c_{44}}{c_{11} + c_{33} - 2c_{13}} \quad \text{for the \{100\} plane} \quad (17)$$

$$A_2 = \frac{4c_{55}}{c_{22} + c_{33} - 2c_{23}} \quad \text{for the \{010\} plane} \quad (18)$$

$$A_3 = \frac{4c_{66}}{c_{11} + c_{22} - 2c_{12}} \quad \text{for the \{001\} plane} \quad (19)$$

The calculated values of $A_1$, $A_2$ and $A_3$ for $M_3B_4$ are listed in Table. 5. For an isotropic crystal, the values of $A_1$, $A_2$ and $A_3$ equal to 1, while any value smaller or greater than 1 is a measure of the degree of shear anisotropy possessed by the crystal. As seen from Table. 5, none of the shear anisotropic factors comes up to 1, indicating the low anisotropy of $M_3B_4$ borides. Among them, $W_3B_4$ exhibits the largest anisotropic for all three planes, i.e., $W_3B_4$ possesses the highest degree of shear anisotropy for its \{100\}, \{010\} and \{001\} planes. Similar to $W_3B_4$, $Mo_3B_4$ also exhibits large anisotropic factors for all three planes. On the contrary, $Ti_3B_4$, $V_3B_4$ and $Cr_3B_4$ display low anisotropy for all their three planes. $Zr_3B_4$, $Nb_3B_4$, $Mo_3B_4$, $Hf_3B_4$, $Ta_3B_4$ and $W_3B_4$ show larger anisotropy in the \{001\} plane than their \{100\} and \{010\} planes.

In addition, we have also adopted another way to measure the elastic anisotropy by using the percentage of anisotropy in the compression and shear introduced by Chung and Buessum [60], which are defined as:
\[ A_k = \frac{K_V - K_R}{K_V + K_R} \]  

(20)

\[ A_G = \frac{G_V - G_R}{G_V + G_R} \]  

(21)

For crystals, a value of zero denotes elastic isotropy and a value of 100% represents largest anisotropy. The percentage of bulk and shear anisotropies are also given in Table. 5. We observed that all the M₃B₄ possessed low bulk anisotropy as the values ranging from 0 to 0.5%. It is obvious that W₃B₄ and Mo₃B₄ exhibit relatively high shear anisotropies among these borides, while the values of their bulk anisotropies are small.

3.5. Electronic structure and chemical bonding

In order to gain better understanding of the electronic structure and chemical bonding of M₃B₄, we have calculated the total density of states (TDOS), which are presented in Fig. 5. The calculated TDOS of Ta₃B₄ agrees well with the previous work [17]. Note that the TDOS of M₃B₄ in the same column show similar characters, and there are finite values at the Fermi Levels, indicating the metallic conductivity of M₃B₄ as observed by experiments [14, 18]. For all studied borides, their Fermi Levels locate at the shoulders of the peaks of TDOS, suggesting that all of them are stable [61], which is consistent with the previous discussion on their stability. Moreover, the Fermi Levels of M₃B₄ move from a lower energy level to a higher one, following the orders of Ti₃B₄<V₃B₄<Cr₃B₄, Zr₃B₄<Nb₃B₄<Mo₃B₄, and Hf₃B₄<Ta₃B₄<W₃B₄, which indicates that the increased valence electrons of transitions metals contribute to the bonding states in M₃B₄ and hence enhance their bulk modulus.

To further explore the chemical bonding of M₃B₄, the topological analysis of the electron localization function (ELF) [31, 32] has been carried out, since it gives a rather quantitative picture on the chemical bonding of compounds and provides a
convenient mathematical framework enabling an unambiguous characterization of bonds. Contour plots of ELF on the (100) plane of M₃B₄ are illustrated in Fig. 6. Clearly, the B₁-Hf₁, B₁-B₂ and B₂-B₃ covalent bonding of Hf₃B₄ with angular character can be observed in Fig. 6 (a), where the maximum ELF values between the bonded atoms are greater than 0.75. Moreover, as seen in Fig. 6 (a), two labeled regions P₁ and P₂ with relatively high ELF values are visible, and the ELF values of Hf₂-Hf₃ and Hf₂-Hf₁ bonding are obviously smaller than that of Hf₁-Hf₃ bond, which also indicates angular bonding character around Hf atoms in Hf₃B₄. A quite different chemical bonding character for Ta₃B₄ and W₃B₄ can be seen in Fig. 6 (b) and (c). The angular B₁-Ta₁, B₁-B₂ and B₂-B₃ covalent bonding in Ta₃B₄ are weakened compared with that in Hf₃B₄, and they are further weakened in W₃B₄, as characterized by the maximum ELF values or regions between the bonded atoms decreasing from Hf₃B₄ to Ta₃B₄ and to W₃B₄. Furthermore, when comparing Fig. 6 (b) with Fig. 6 (a), it is observed that the P₁ region of Ta₃B₄ almost disappears and its P₂ region becomes weaker. While in Fig. 6 (c), both regions P₁ and P₂ vanish and the bonding among the nearest W atoms become homogeneous, suggesting a non-angular character of W-W bonding in W₃B₄. Therefore, the angular character of B-B, M-B, M-M bonding is weakened from Hf₃B₄ to Ta₃B₄ and to W₃B₄ with the increasing of the extra valence electrons. The similar trend can be observed from the ELF plots for the other M₃B₄, where the angular bonding character of M₃B₄ follow the orders of Ti₃B₄>V₃B₄>Cr₃B₄, Zr₃B₄>Nb₃B₄>Mo₃B₄, and Hf₃B₄>Ta₃B₄>W₃B₄. Hence, the decrease of angular bonding character in M₃B₄ might be the reason for the increase of Cauchy pressure and the improvement of their ductility as seen in Section 3.2.

3.6. Dynamical stability
In the preceding subsections, we have demonstrated that all of the studied \( M_3B_4 \) are thermodynamically and mechanically stable. To further investigate the dynamical stability of two new predicted compounds \( \text{Hf}_3\text{B}_4 \) and \( \text{W}_3\text{B}_4 \), we calculated phonon dispersions for them, which are illustrated in Fig. 7 (a) and (b). The phonon dispersion curves of \( \text{Hf}_3\text{B}_4 \) and \( \text{W}_3\text{B}_4 \) are a little complex and show different characters. It is known that negative or imaginary frequencies indicate the dynamical instability of crystals. As seen from the phonon dispersion curves, no negative frequency have been found for \( \text{Hf}_3\text{B}_4 \) or \( \text{W}_3\text{B}_4 \), suggesting both compounds are dynamically stable.

4. Concluding remarks

In summary, by means of density functional theory calculations, we have systematically study the structural stability, mechanical properties, electronic structure and chemical bonding of \( M_3B_4 \) (\( M \) are IVB, VB and VIB transition metals, i.e., \( M = \text{Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W} \)). All the studied transition-metal borides with \( \text{Ta}_3\text{B}_4 \)-type structure are thermodynamically and mechanically stable. The predicted lattice parameters and microhardness for them are in good agreement with the available experimental results.

The bulk modulus, Young’s modulus, shear modulus, Poisson’s ratio, microhardness and Debye temperature have been derived from the calculated elastic constants for ideal polycrystalline \( M_3B_4 \) aggregates. Among them, \( \text{V}_3\text{B}_4 \) exhibits the highest shear modulus (238 GPa), Young’s modulus (555 GPa), microhardness (26.4 GPa) and Debye temperature (1059 K), while \( \text{W}_3\text{B}_4 \) possesses the largest bulk modulus (335 GPa) but the lowest Debye temperature (532 K). In addition, the relationship between Debye temperature and microhardness has been discussed for these isostructural \( M_3B_4 \). Furthermore, by analyzing the Cauchy pressure, the ratio of
bulk modulus to shear modulus, and Poisson’s ratio, we found that the ductility of M3B4 follows the orders of Ti3B4<V3B4<Cr3B4, Zr3B4<Nb3B4<Mo3B4, and Hf3B4<Ta3B4<W3B4, suggesting that the valence electrons of transition metals play an important role in the ductility of M3B4, i.e., the more valence electrons, the better ductility.

Moreover, the calculated total density of states of M3B4 indicates that all these borides display a metallic conductivity, and the increased valence electrons of transitions metals contribute to the bonding states in M3B4 and hence enhance their bulk modulus. By analyzing the electron localization function, in the view of chemical bonding, we show that the decrease of angular bonding character in M3B4 might be the reason for the increase of Cauchy pressure and the improvement of their ductility.

Finally, the calculated phonon dispersions of the new predicted compounds Hf3B4 and W3B4 suggest that both of them are dynamically stable. We expect our results provide a fundamental understanding on these hard and refractory materials and offer reference data for further investigation or applications of this class of transition metals borides.

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FIGURE CAPTIONS:

Fig. 1. (Color online) Plot for Cauchy pressure as a function of valence electron concentration (VEC).

Fig. 2. (Color online) Plot for $K/G$ as a function of valence electron concentration (VEC).

Fig. 3. (Color online) Plot for Poisson’s ratio as a function of valence electron concentration (VEC).

Fig. 4. The relationship between Debye temperature and microhardness $H_V$. The data points in squares are calculated using the data from the preceding sections.

Fig. 5. The calculated total density of states for M$_3$B$_4$. The Fermi Levels have been set to 0 eV and marked by short dash lines.

Fig. 6. (Color online) Contour plots of ELF on the (100) plane of M$_3$B$_4$ for (a) Hf$_3$B$_4$, (b) Ta$_3$B$_4$, (c) W$_3$B$_4$. The color scale for the ELF value is given at the left of the figure, where all the mappings are under the same saturation levels and the interval between two nearest contour lines is 0.13.

Fig. 7. The calculated phonon dispersion curve for (a) Hf$_3$B$_4$ and (b) W$_3$B$_4$. 
Table 1. The calculated lattice parameters ($a$, $b$ and $c$) and formation energy ($E_{\text{form}}$) for $M_3B_4$. US and PAW denote the results obtained from CASTEP and VASP; Exp. represents the experimental data.

| $M_3B_4$ | $a$(Å) | $b$(Å) | $c$(Å) | $E_{\text{form}}$ (eV/cell) |
|----------|--------|--------|--------|-----------------------------|
| Ti$_3$B$_4$ | US | 3.260 | 13.733 | 3.036 | -13.470 |
| | PAW | 3.263 | 13.755 | 3.042 | - |
| | Exp.[37] | 3.259 | 13.730 | 3.032 | - |
| V$_3$B$_4$ | US | 3.041 | 13.200 | 2.976 | -11.826 |
| | PAW | 3.043 | 13.221 | 2.981 | - |
| | Exp.[38] | 3.03 | 13.18 | 2.986 | - |
| Cr$_3$B$_4$ | US | 2.918 | 13.004 | 2.936 | -6.870 |
| | PAW | 2.923 | 13.030 | 2.942 | - |
| | Exp.[40] | 2.99 | 13.010 | 2.949 | - |
| Zr$_3$B$_4$ | US | 3.539 | 14.903 | 3.206 | -12.071 |
| | PAW | 3.553 | 14.943 | 3.217 | - |
| | Exp. | - | - | - | - |
| Nb$_3$B$_4$ | US | 3.307 | 14.103 | 3.144 | -11.494 |
| | PAW | 3.325 | 14.179 | 3.159 | - |
| | Exp.[39] | 3.296 | 14.094 | 3.151 | - |
| Mo$_3$B$_4$ | US | 3.161 | 13.900 | 3.074 | -6.561 |
| | PAW | 3.175 | 13.974 | 3.086 | - |
| | Exp. | - | - | - | - |
| Hf$_3$B$_4$ | US | 3.522 | 14.731 | 3.205 | -11.382 |
| | PAW | 3.502 | 14.679 | 3.188 | - |
| | Exp. | - | - | - | - |
| Ta$_3$B$_4$ | US | 3.332 | 14.227 | 3.176 | -10.183 |
| | PAW | 3.309 | 14.091 | 3.145 | - |
| | Exp.[16] | 3.291 | 13.994 | 3.133 | - |
| W$_3$B$_4$ | US | 3.185 | 13.923 | 3.073 | -4.054 |
| | PAW | 3.196 | 13.993 | 3.083 | - |
| | Exp. | - | - | - | - |
Table 2. The calculated elastic stiffness constants $c_{ij}$ (in GPa) for M$_3$B$_4$.

| M$_3$B$_4$ | $c_{11}$ | $c_{22}$ | $c_{33}$ | $c_{44}$ | $c_{55}$ | $c_{66}$ | $c_{12}$ | $c_{13}$ | $c_{23}$ |
|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Ti$_3$B$_4$ | 424      | 520      | 581      | 229      | 242      | 214      | 108      | 94       | 49       |
| V$_3$B$_4$  | 484      | 640      | 631      | 239      | 264      | 236      | 137      | 140      | 96       |
| Cr$_3$B$_4$ | 492      | 609      | 612      | 231      | 238      | 205      | 169      | 166      | 159      |
| Zr$_3$B$_4$ | 372      | 357      | 458      | 184      | 162      | 183      | 114      | 79       | 78       |
| Nb$_3$B$_4$ | 473      | 546      | 544      | 201      | 242      | 236      | 157      | 168      | 126      |
| Mo$_3$B$_4$ | 484      | 476      | 559      | 208      | 219      | 196      | 227      | 202      | 193      |
| Hf$_3$B$_4$ | 419      | 432      | 523      | 208      | 225      | 212      | 128      | 117      | 90       |
| Ta$_3$B$_4$ | 479      | 559      | 552      | 196      | 232      | 233      | 170      | 182      | 150      |
| W$_3$B$_4$  | 507      | 459      | 556      | 205      | 223      | 200      | 271      | 225      | 253      |
Table 3. The calculated Young’s modulus \( (K_V, K_R, \text{ and } K \text{ in GPa}) \), shear modulus \( (G_V, G_R, \text{ and } G \text{ in GPa}) \), elastic modulus \( (E \text{ in GPa}) \), Poisson’s ratio \( (\sigma) \) and microhardness \( (H_V \text{ and } H_T \text{ in GPa}) \) for polycrystalline \( M_3B_4 \) aggregates.

| \( M_3B_4 \) | \( K_V \) | \( K_R \) | \( K \) | \( G_V \) | \( G_R \) | \( G \) | \( E \) | \( \sigma \) | \( H_V \) | \( H_T \) |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ti\(_3\)B\(_4\) | 225 | 224 | 224 | 222 | 217 | 220 | 497 | 0.131 | 24.4 | 36.0 |
| V\(_3\)B\(_4\) | 278 | 275 | 277 | 240 | 236 | 238 | 555 | 0.166 | 26.4 | 39.2 |
| Cr\(_3\)B\(_4\) | 300 | 298 | 299 | 216 | 213 | 215 | 520 | 0.210 | 23.9 | 35.1 |
| Zr\(_3\)B\(_4\) | 192 | 191 | 192 | 167 | 163 | 165 | 385 | 0.166 | 18.3 | 26.3 |
| Nb\(_3\)B\(_4\) | 274 | 273 | 274 | 210 | 205 | 208 | 497 | 0.197 | 23.1 | 33.8 |
| Mo\(_3\)B\(_4\) | 307 | 306 | 307 | 184 | 177 | 181 | 453 | 0.254 | 20.1 | 29.1 |
| Hf\(_3\)B\(_4\) | 227 | 226 | 227 | 198 | 194 | 196 | 457 | 0.165 | 21.8 | 31.8 |
| Ta\(_3\)B\(_4\) | 288 | 288 | 288 | 205 | 201 | 203 | 493 | 0.215 | 22.5 | 33.0 |
| W\(_3\)B\(_4\) | 336 | 335 | 335 | 177 | 163 | 170 | 437 | 0.283 | 18.9 | 27.2 |
Table. 4. The calculated density ($\rho$ in g/cm$^3$), the longitudinal, transverse and mean elastic wave velocity ($v_l$, $v_t$ and $v_m$ in m/s), and the Debye temperature ($\theta_D$ in K) for M$_3$B$_4$.

| M$_3$B$_4$ | $\rho$ | $v_l$ | $v_t$ | $v_m$ | $\theta_D$ |
|------------|--------|-------|-------|-------|-----------|
| Ti$_3$B$_4$ | 4.57   | 10642 | 6935  | 7603  | 1055      |
| V$_3$B$_4$  | 5.45   | 10437 | 6607  | 7268  | 1059      |
| Cr$_3$B$_4$ | 5.94   | 9928  | 6012  | 6645  | 991       |
| Zr$_3$B$_4$ | 6.22   | 8133  | 5148  | 5663  | 735       |
| Nb$_3$B$_4$ | 7.29   | 8687  | 5334  | 5887  | 801       |
| Mo$_3$B$_4$ | 8.14   | 8203  | 4713  | 5234  | 732       |
| Hf$_3$B$_4$ | 11.56  | 6499  | 4118  | 4530  | 591       |
| Ta$_3$B$_4$ | 12.93  | 6572  | 3959  | 4378  | 590       |
| W$_3$B$_4$  | 14.50  | 6227  | 3426  | 3819  | 532       |
Table. 5. The calculated shear anisotropic factors ($A_1$, $A_2$, and $A_3$) for different planes and the percentage of anisotropy in the compression and shear ($A_K$ and $A_G$).

| M3B4  | $A_1$  | $A_2$  | $A_3$  | $A_K$ (%) | $A_G$ (%) |
|-------|--------|--------|--------|-----------|-----------|
| Ti3B4 | 1.122  | 0.964  | 1.175  | 0.306     | 0.989     |
| V3B4  | 1.143  | 0.978  | 1.110  | 0.415     | 0.856     |
| Cr3B4 | 1.195  | 1.053  | 1.073  | 0.415     | 0.598     |
| Zr3B4 | 1.095  | 0.982  | 1.462  | 0.191     | 1.107     |
| Nb3B4 | 1.182  | 1.153  | 1.336  | 0.055     | 1.070     |
| Mo3B4 | 1.300  | 1.347  | 1.554  | 0.095     | 1.948     |
| Hf3B4 | 1.175  | 1.164  | 1.425  | 0.222     | 1.169     |
| Ta3B4 | 1.177  | 1.145  | 1.334  | 0.107     | 0.990     |
| W3B4  | 1.335  | 1.753  | 1.876  | 0.083     | 4.045     |