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Universal ground state hexagonal phases and mechanical properties of stoichiometric transition metal tetraborides: TMB_4 (TM = W, Tc, and Re)

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ABSTRACT

Using particle swarm optimization technique on crystal structural prediction, a universal hexagonal MoB_4 -type structure was uncovered for WB_4 , TcB_4 , and ReB_4 . This MoB_4 -type structure is energetically much superior to the previously proposed WB_4 -type structure and stable against decomposition into the mixture of TM and B at ambient conditions. The Young's modulus and shear modulus as a function of crystal orientation for the TMB_4 (TM = W, Tc, and Re) have thus been systematically investigated. TMB_4 within this hexagonal structure are found to be ultra-incompressible and hard due to their high bulk modulus and large hardness. Especially, they exhibit an unusual incompressibility along the *c* axis, close to that of diamond. Their ultra-incompressibility is attributed to a staking of B–TM–B “sandwiches” layers linked by strong covalent TM–B bonding, which is manifested by the PDOS and ELF analysis.

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1. Introduction

Ultra-incompressible and superhard materials are of considerable interest and practical important due to their unique physical and chemical properties in fundamental science and technological applications. Besides the conventional strongly covalent superhard compounds (diamond, *c*-BN, BC_2N , etc.) formed by the light elements, namely, B, C, N, and O, the interaction of these light elements into the transition metal (TM) to form strong covalent bonds yet keeping a high valence-electron density (VED) and bulk moduli, is a well-known strategy for designing new potential superhard materials suggested by Kaner et al. [1,2]. Following the first synthesized ultra-incompressible material OsB_2 [3], extensive experimental and theoretical investigations have been carried out for other TM borides in view of their synthesis is more straightforward. Nowadays, some TM borides such as ReB_2 , WB_2 , $\text{RhB}_{1.1}$, and $\text{IrB}_{1.35}$ has been synthesized and were proposed to be superhard with claimed hardness of >40 GPa [4–6]. It is known that crystal structures are the key for the understanding of mechanical properties of materials. However, common issues on the ambiguity of crystal structures still remain in transition metal borides on account of two points. Firstly, the transition metal borides with metal-deficient or boron-deficient compositions can be easily obtained in actual experiments. Secondly, the positions of boron

atoms in crystal lattice are difficult to be determined by X-ray diffraction because of the large mass difference between TM and B atoms, particularly at extreme conditions (e.g., high pressure). Therefore, theoretical prediction of crystal structures with the only known information of chemical composition independent of previous experimental knowledge is greatly necessary.

A promising material, WB_4 , has been synthesized at ambient pressure and was proposed to be superhard with claimed hardness of 31.8–46.2 GPa [7], comparable to that (45–50 GPa) of *c*-BN, though continuing debate exists in crystal structure. Currently, it seems as if the experimental and theoretical studies have reached the consensus that WB_4 adopts the hexagonal WB_4 -type structure ($P6_3/mmc$, $Z = 4$, hereafter denoted as Hex-I) [7–9]. Furthermore, Wang et al. [9] further predicted that Hex-I- ReB_4 and Hex-I- TcB_4 are all potential superhard materials by density functional theory (DFT) calculations. However, Zhao et al. [10] have found that the Hex-I- WB_4 had large positive formation enthalpy (~ 0.37 eV/atom) with respect to W and B under ambient conditions, indicating that it is metastable. Recently, the MoB_4 -type structure ($P6_3/mmc$, $Z = 2$, hereafter denoted as Hex-II) proposed in our recent work [11] was identified as a potential ground state structure for WB_4 by Gou et al. [12]. More recently, Zhang et al. [13] and Liang et al. [14,15] have revealed that the long regarded WB_4 within Hex-I structure is actually WB_3 , which adopts the MoB_3 -type structure [16]. Strikingly, theoretical calculations for this newly identified stable WB_3 structure correctly reproduce its structural and mechanical properties, as well as the experimental X-ray diffrac-

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tion pattern. Accordingly, exploring the ground state structure with the ideal stoichiometry B/W = 4 and related mechanical of WB₄ is highly desirable and of great interest. In addition, the previous proposed Hex-I structure for ReB₄ and TcB₄ is based on the knowledge of known information. There is a possibility that hitherto unknown ground state structures are stable instead for these two compounds.

Here, we have extensively explored the ground state of TMB₄ (TM = W, Re, and Tc) based on a global minimization of free-energy surfaces merging *ab initio* total energy calculations via Particle Swarm Optimization technique [17], unbiased by any known information. This method has been successfully applied to many other systems [18–23], among which the blind prediction of high-pressure orthorhombic structure of FeTi₃O₇ [21], insulating Aba2-40 (or oC40) structure of dense Li [22–23], and two low-pressure monoclinic structures of Bi₂Te₃ have been confirmed by independent experiments [24]. Intriguingly, our structural prediction revealed a universally stable Hex-II structure for all TMB₄ (TM = W, Re, and Tc) compounds. The Hex-II structure uncovered for these TMB₄ is energetically much more preferable than the earlier proposed Hex-I structure at ambient conditions. First principles calculations were then performed to characterize the structural, thermodynamic, mechanical, and electronic properties of the Hex-II structure for all TMB₄ compounds.

2. Computational methods

The variable-cell structure predictions were performed at 0 GPa with 1–4 formula units (f.u.) per simulation cell as implemented in the Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code [25]. The details of this methodology have been described elsewhere [26]. The underlying *ab initio* structural relaxations and electronic calculations were carried out using density functional theory within the Perdew–Burke–Ernzerhof [27] exchange–correlation as implemented in the VASP code [28]. The electron and core interactions were included by using the frozen-core all-electron projector augmented wave (PAW) method [29], which called for *d*-electrons as valence states for all transition metals. The energy cutoff of 420 eV and appropriate Monkhorst–Pack *k* meshes [30] for all cases were chosen to ensure that energy calculations are well converged to better than 1 meV/atom. The phonon calculations were carried out by using a supercell approach as implemented in the PHONOPY code [31]. Single crystal elastic constants were determined from evaluation of stress tensor generated small strain and bulk modulus, shear modulus, Young's modulus, and Poisson's ratio were thus estimated by using the Voigt–Reuss–Hill approximation [32]. The theoretical Vickers hardness was estimated by using Šimůnek model [33].

3. Results and discussion

3.1. The ground state structures of the TMB₄ (TM = W, Re, and Tc)

For each TMB₄ (TM = W, Re, and Tc) compound at 0 GPa, considering simulation cell ranging from one to four f.u., our structural predictions revealed a universal and the most stable hexagonal phase, which is isostructural to MoB₄ (the Hex-II structure mentioned above, Fig. 1a). As has been observed in MoB₄, this Hex-II structure is characterized by intriguing “B–TM–B” sandwiches stacking order along the crystallographic *c* axis, resembled with the Hex-I structure (Fig. 1c). In every pair of congruent planes, there are edge-sharing TM₈ polyhedrons (Fig. 1b) which are connected by B atoms and form the sandwiches layer along the *c* axis. In more detail, the TM atoms are packed in a hexagonal close-packed (*hcp*) structure along the crystallographic *b* axis. And a

three-dimensional boron network composed of three strongly puckered networks of titled hexagon layers connected by the common B atoms along the *b* axis. At zero temperature a stable crystal-line structure requires all phonon frequencies to be positive. We have calculated the phonon dispersion curves of all TMB₄ compounds at 0 GPa, respectively. No imaginary phonon frequencies are found in the whole Brillouin zones, indicating the dynamical stability of this new ground state structure for all TMB₄ compounds. The equilibrium lattice constants, volumes, bulk moduli, and pressure derivatives of the Hex-II structures for all TMB₄ are presented in Table 1, along with available experimental data and previous theoretical values [7,9,14] of the Hex-I and Hex-II structures for comparison. The bulk moduli and their pressure derivatives are obtained by fitting pressures and cell volumes with the third-order Birch–Murnaghan equation of state (EOS) [34]. Furthermore, it is important to explore the thermodynamic stability of each of these TMB₄ compounds within Hex-II structure for further experimental synthesis. The thermodynamic stability at ambient pressure with respect to decomposition is quantified in terms of the formation enthalpy, using $\Delta H_f = H_{(TMB_4)} - H_{(TM)} - 4H_{(B)}$. The ΔH_f is the formation enthalpy, the cubic W (space group: *Im-3m*), hexagonal Re (space group: *P6₃/mmc*), Tc (space group: *P6₃/mmc*), and α -B (space group: *R-3m*) were chosen as the reference phases. As shown in Table 1, the calculated ΔH_f per atom of these compounds within Hex-II (Hex-I) structures are −1.186 (1.997) eV for WB₄, −0.175 (1.851) eV for TcB₄, and −0.093 (1.296) eV for ReB₄. Clearly, these results indicated that the TMB₄ compounds within Hex-I structures are all metastable at ambient conditions. On the contrary, results obtained for the Hex-II-TMB₄ in this reaction route have demonstrated their stability against the decomposition into the mixture of TM and α -B. Therefore, present calculations give direct evidence that the predicted Hex-II structure for each of the TMB₄ (TM = W, Re, and Tc) is indeed the ground state structure and can be synthesized at ambient pressure. Further experimental work is thus strongly recommended.

3.2. Mechanical properties of the Hex-II-TMB₄

The mechanical properties (elastic constants, elastic moduli, elastic anisotropy, etc.) of the Hex-II-TMB₄ are important for their potential technological and industrial applications. They define the behavior of the solid that undergoes stress, deforms, then recovers, and returns to its original shape after stress ceases. We calculated the zero-pressure elastic constants C_{ij} of these three Hex-II-TMB₄ compounds by the strain–stress method. A small finite strain was applied on the optimized structure and the atomic positions were fully optimized. Then, the elastic constants were obtained from the stress of the strained structure. The five independent zero pressure elastic constants for the Hex-II-TMB₄ were calculated in order to check their mechanical stability, as listed in Table 2. The key criterion for mechanical stability of a crystal is that strain energy must be positive. This means in a hexagonal crystal that the elastic constants should satisfy the following inequalities [35]: $C_{33} > 0$, $C_{44} > 0$, $C_{12} > 0$, $C_{11} > |C_{12}|$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$. According to these criteria, it is clear that all these Hex-II-TMB₄ are mechanically stable at ambient condition. It also can be seen that these compounds possess a remarkable value of C_{33} , especially for Hex-II-ReB₄ (978 GPa), which is only 9.4% smaller than that of diamond (1079 GPa) [36]. These results indicate that their *c*-axis directions are extremely stiff. Based on the calculated C_{ij} , the corresponding five independent elastic compliance constants s_{ij} of the hexagonal crystal are given by Sirdeshmukh et al. [37], and the calculated results are also shown in Table 2. The elastic anisotropy of crystals can exert great effects on the properties of physical mechanism, such as anisotropic plastic deformation, crack behavior, and elastic instability. Hence, it is important to calculate elastic anisotropy in

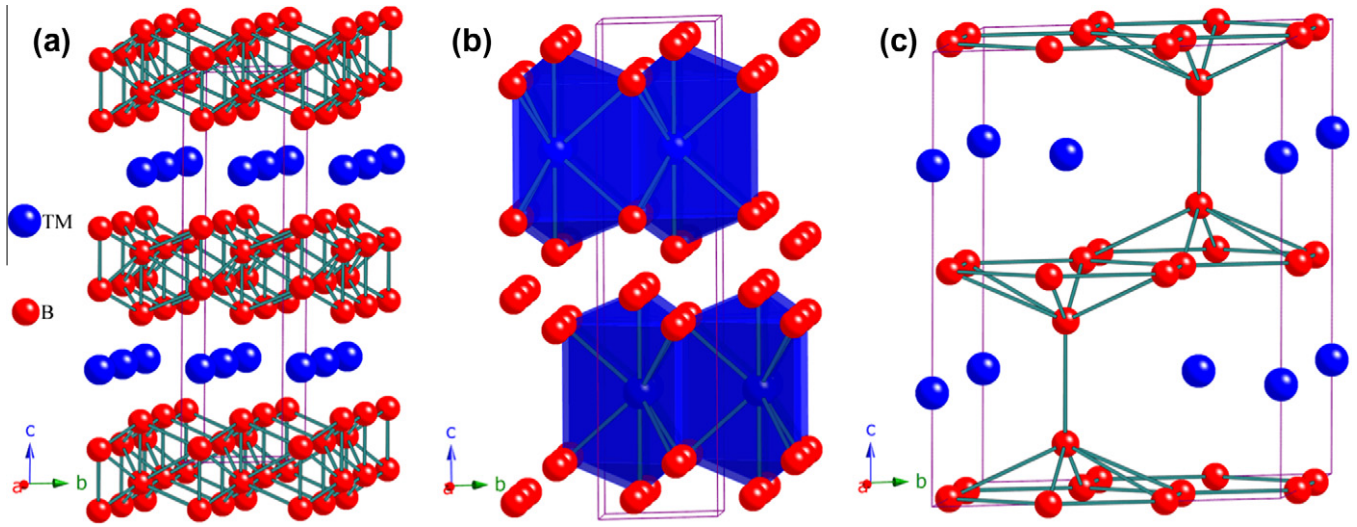


Fig. 1. Crystal structure of the Hex-II (a), polyhedral views of the Hex-II (b), and crystal structure of the Hex-I (c). The large and small spheres represent TM and B atoms, respectively.

Table 1

Calculated equilibrium lattice constants a_0 (Å), c_0 (Å), equilibrium volume V_0 (Å³/f.u.), EOS fitted bulk modulus B_0 (GPa), its pressure derivative B'_0 , and formation enthalpy ΔH_f (eV/f.u.) for the Hex-II-TMB₄, respectively.

Compound	Structure	Source	a_0	c_0	V_0	B_0	B'_0	ΔH_f
WB ₄	Hex-II	This work	2.961	11.004	83.569	285	3.981	−1.186
		Theo. ^a	2.951	10.980				
	Hex-I	This work	5.370	6.459				1.997
		Exp. ^b	5.195	6.332				
		Theo. ^c	5.370	6.457				
TcB ₄	Hex-II	This work	2.932	10.787	80.308	282	3.914	−0.175
	Hex-I	This work	5.354	6.365				1.851
		Theo. ^c	5.322	6.440				
ReB ₄	Hex-II	This work	2.938	10.851	81.110	300	3.969	−0.093
	Hex-I	This work	5.456	6.185				2.796
		Theo. ^c	5.453	6.177				

^a Ref. [12].

^b Ref. [7].

^c Ref. [9].

Table 2

Calculated elastic constants C_{ij} (in GPa), compliance constants s_{ij} (in 10^{-3} GPa^{−1}), and elastic anisotropy factors of the Hex-II-TMB₄.

Compound	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	s_{11}	s_{12}	s_{13}	s_{33}	s_{44}	A_{comp}	A_{shear}
MoB ₄ ^a	505	141	103	936	189	2.176	−0.571	−0.177	1.107	5.291	0.527	1.038
WB ₄	546	127	100	961	165	1.960	−0.427	−0.160	1.074	6.060	0.549	0.788
WB ₄ ^b	551	117	104	971	162							
TcB ₄	532	115	117	912	194	2.009	−0.389	−0.208	1.150	5.155	0.520	0.930
ReB ₄	567	111	129	987	187	1.873	−0.320	−0.203	1.066	5.348	0.489	0.897

^a Ref. [11].

^b Ref. [12].

order to improve their mechanical durability. In crystal of hexagonal symmetry, the elastic anisotropy is reflected in the anisotropy of linear compressibility in addition to the usual shear anisotropy. Conventionally, the compression elastic anisotropy of a crystal in hexagonal symmetry is given by

$$A_{comp} = \chi_c / \chi_a = (s_{33} + 2s_{13}) / (s_{11} + s_{12} + s_{13}) \quad (1)$$

where χ_c and χ_a are the linear compressibility along c -axis and that perpendicular to the c -axis. The shear anisotropy is simply the ratio of two shear moduli C_{44} and C_{66}

$$A_{shear} = C_{44} / C_{66} = 2C_{44} / (C_{11} - C_{12}) \quad (2)$$

Any departure from 1.0 is a measure of the degree of elastic anisotropy. The obtained values of A_{comp} and A_{shear} for these compounds are listed in Table 2. It can be seen that all these compounds exhibit a large degree of elastic anisotropy, especially for ReB₄ and WB₄. On the other hand, the elastic anisotropy of hexagonal crystals can be described in the following way [38]. The six stiffness constants are normalized to the corresponding quantities for isotropy, i.e. C_{11} and C_{33} to $\lambda + 2G$, C_{12} and C_{13} to λ , C_{44} and C_{66} to G , where λ and G are the Lamé constant and Shear modulus obtained by the Hill average, and the companion constants are

plotted along the same axis in the opposite direction. Relative elastic anisotropy can be described by comparing the polygon drawn from the six normalized constants and the hexagon. As shown in Fig. 2, these four borides have a similar elastic anisotropy behavior, with the large elastic anisotropy along c -axis (C_{33}) for all Hex-II-TMB₄.

For engineering applications that make use of single crystals, it is necessary to know the values of Young's modulus E and shear modulus G as a function of crystal orientation. A variation of the Young's modulus for a tensile stress applied along an arbitrary $[uvw]$ direction for hexagonal symmetry can be written as [39]

$$E^{-1} = s_{11}(\alpha^2 + \beta^2)^2 + s_{33}\gamma^4 + (2s_{12} + s_{44})(\beta^2\gamma^2 + \alpha^2\gamma^2) \quad (3)$$

where α , β , and γ are the direction cosines of $[uvw]$ direction. We have calculated the orientation dependence of Young's modulus when the tensile axis within specific planes as outlined by Chu et al. [40]. The obtained results for these Hex-II-TMB₄ compounds are plotted in Fig. 3. It can be seen that these compounds have similar variation trend of the Young's modulus. For Young's modulus in the (0001) plane, let θ be the angle between tensile stress and $[10\bar{1}0]$. From Eq. (3), one obtains $E^{-1} = (s_{11})^{-1}$. This indicates that Young's modulus on the basal plane is independent of tensile stress direction, which is a result of the isotropy of elasticity in the basal plane for hexagonal crystal. For the orientation dependence of Young's modulus from $[0001]$ ($\theta = 0^\circ$) to $[\bar{1}2\bar{1}0]$ ($\theta = 90^\circ$) on the

prismatic plane ($10\bar{1}0$), the Hex-II-TMB₄ possess a maximum of $E_{[1000]}$ and a minimum of $E_{[\bar{1}2\bar{1}0]}$. For the pyramidal plane ($\bar{1}012$) in the Fig. 3 display the variation of Young's modulus with $E_{\max}$ along $[\bar{1}2\bar{1}0]$ directions and $E_{\min}$ along $[10\bar{1}0]$ directions. For the pyramidal ($12\bar{1}2$) plane Young's moduli E behave again very similar for the directions between $[10\bar{1}0]$ and $[\bar{1}2\bar{1}1]$ with minima of $E_{[1010]}$ and maximum of $E_{[\bar{1}2\bar{1}1]}$. Therefore, the ordering of Young's modulus as a function of the principal crystal tensile $[uvw]$ for these Hex-II-TMB₄ compounds is: $E_{[0001]} > E_{[\bar{1}2\bar{1}1]} > E_{[10\bar{1}1]} > E_{[10\bar{1}0]}$, among which the largest $E_{[0001]}$ corresponds to the largest value of C_{33} in Table 2 for the Hex-II-TMB₄.

To understand plastic deformation in the Hex-II-TMB₄, the study of the dependence of the shear modulus on stress direction is also plotted in Fig. 4. We choose a shear plane (hkl) and vary the shear stress direction $[uvw]$ within that plane. The axis normal to the (hkl) plane is denoted as $[HKL]$. Thus, the shear modulus on the (hkl) shear plane with shear stress applied along $[uvw]$ direction can be expressed as [40]

$$G^{-1} = 4s_{11}(\alpha_1^2\alpha_2^2 + \beta_1^2\beta_2^2) + 4s_{33}\gamma_1^2\gamma_2^2 + 8s_{12}\alpha_1\alpha_2\beta_1\beta_2 + s_{66}(\alpha_1\beta_2 + \alpha_2\beta_1)^2 + 8s_{13}(\beta_1\beta_2\gamma_1\gamma_2 + \alpha_1\alpha_2\gamma_1\gamma_2) + s_{44}[(\beta_1\gamma_2 + \beta_2\gamma_1)^2 + (\alpha_1\gamma_2 + \alpha_2\gamma_1)^2] \quad (4)$$

where α_1 , β_1 , γ_1 , α_2 , β_2 , γ_2 are the direction cosines of the $[uvw]$ and $[HKL]$ directions in the coordinate systems. It can be seen from

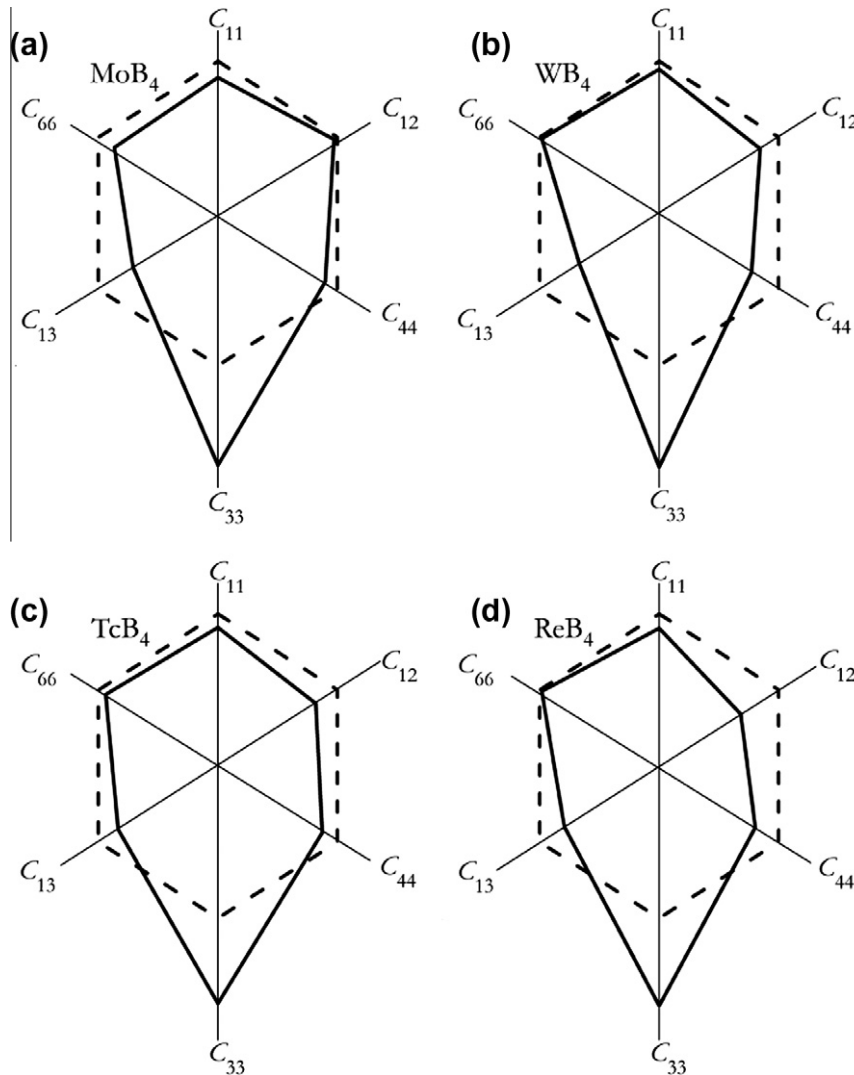


Fig. 2. Diagrams showing relative elastic anisotropy of (a) MoB₄, (b) WB₄, (c) TcB₄, and (d) ReB₄.

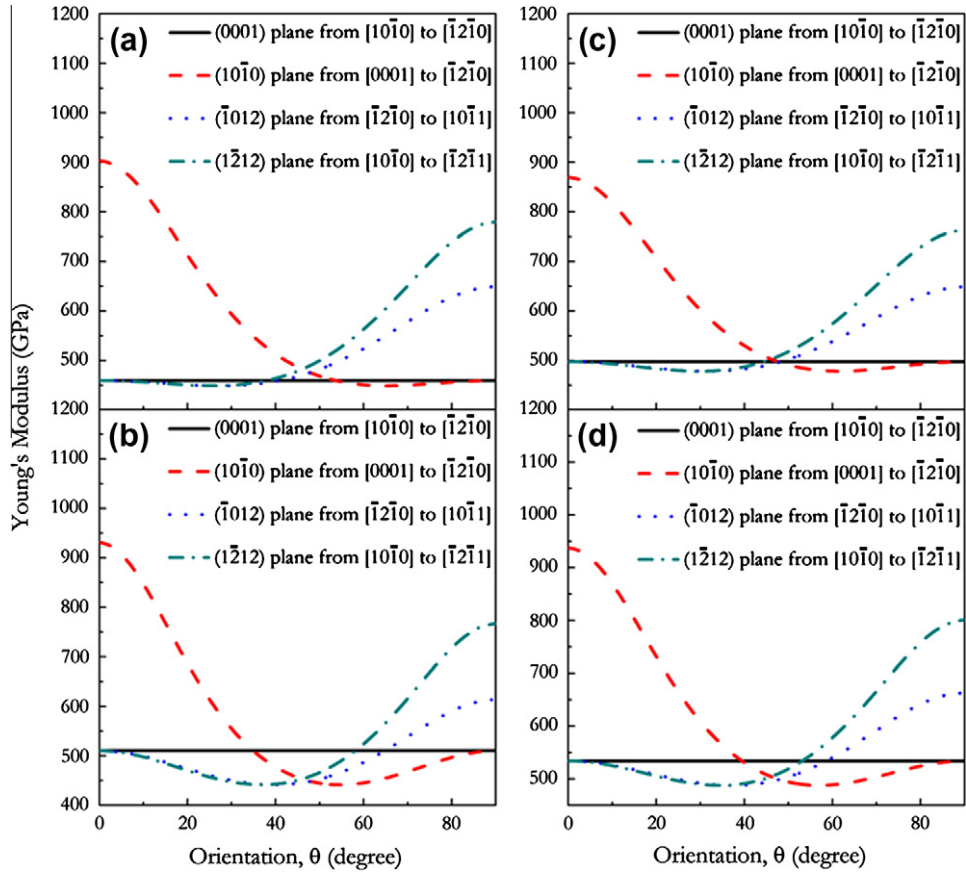


Fig. 3. Orientation dependence of the Young's modulus E of the Hex-II-TMB₄: (a) MoB₄, (b) WB₄, (c) TcB₄, and (d) ReB₄.

Fig. 4, the orientation dependence of the shear modulus is basically the same for these four Hex-II-type compounds. Firstly, the shear modulus of the Hex-II-TMB₄ is independent of the shear directions from $[10\bar{1}0]$ to $[\bar{1}2\bar{1}0]$ directions within (0001) basal plane. Secondly, except for Hex-II-MoB₄, the shear modulus is the smallest on the (0001) basal plane, where the corresponding shear deformation involves a shear displacement between pure TM atoms (as shown in Fig. 1a). In other words, these weak TM–TM layers, which are deformed easily by shear stresses in the a -direction and b -direction, reduce greatly the resistance of the Hex-II-TMB₄ against large shear deformations in these easy-slip directions. Therefore, the (0001) planes may be the cleavage planes of these Hex-II-TMB₄ compounds. Thirdly, the shear modulus of 5d Hex-II-WB₄ and Hex-II-ReB₄ within shear plane $(1\bar{2}12)$ increasing with the shear stress direction rotating from $[10\bar{1}0]$ to $[\bar{1}2\bar{1}1]$ directions, while on the contrary it decreases with the shear stress direction rotating from $[10\bar{1}0]$ to $[\bar{1}2\bar{1}1]$ directions for the 4d Hex-II-MoB₄ and Hex-II-TcB₄.

Based on the calculated elastic constants, the isotropic bulk modulus (B_H) and shear modulus (G_H) for the Hex-II-TMB₄ polycrystalline are calculated by the Voigt-Reuss-Hill approximation [32] in Table 3. The Young's modulus E_H and Poisson's ratio ν_H are obtained from the equations of $E_H = 9B_H G_H / (3B_H + G_H)$ and $\nu_H = (3B_H - 2G_H) / (6B_H + 2G_H)$. The calculated bulk moduli of the Hex-II-TMB₄ are around 300 GPa, indicating ultra-incompressible structural nature. It should be noted that the calculated bulk moduli agree well with those directly obtained from the fitting of the third-order Birch–Murnaghan equation of state (EOS) (see Table 1), which further demonstrates the reliability of our elastic calculations. For the partially covalent transition metal-based materials, the shear modulus of a material quantifies its resistance to the shear deformation and is a better indicator of potential hardness.

Remarkably, the Hex-II-ReB₄ possesses the largest shear modulus of 232 GPa, which is close to the experimental data of ReB₂ (223–276 GPa) [41,42]. Thus, the Hex-II-ReB₄ is expected to withstand shear strain to a large extent as many known hard materials. In addition, the relative directionality of the bonding in the material also has an important effect on its hardness and can be determined by the G_H/B_H ratio. The obtained values of G_H/B_H ratio for these compounds are in range from 0.732 to 0.771, which are larger than those of ultra-incompressible OsB₂ (0.5) [43], PtN₂ (0.71) [44], IrN₂ (0.66) [45], and OsN₂ (0.72) [46], suggesting the strong direct bonding between the TM and B atoms. All these excellent mechanical properties strongly suggest that the Hex-II-TMB₄ compounds are potential candidate to be ultra-incompressible and hard.

In view of the large bulk and shear moduli of the Hex-II-TMB₄ compounds, the hardness calculations are of great interest. According to the Šimůnek model [33], the hardness of the idea single crystal is proportional to the bond strength and to their number in the unit cell. More specifically, the hardness of crystals having different bond strengths is given by the following expressions:

$$H = (C/\Omega) \cdot n \cdot \left[\prod_{i,j=1}^n (N_{ij} S_{ij}) \right]^{1/n} e^{-\sigma f_e}, \quad (5)$$

$$f_e = 1 - \left[k \left(\prod_{i=1}^k e_i \right)^{1/k} / \sum_{i=1}^k e_i \right] 2, \quad (6)$$

$$\text{and } S_{ij} = \sqrt{e_i e_j} / (n_i n_j d_{ij}), \quad (7)$$

where N_{ij} is the number or multiplicity of the binary system, S_{ij} is the strength of the individual bond between atoms i and j ; the reference energy e_i is defined as $e_i = Z_i/r_i$, Z_i is the number of valence electrons and r_i is the radius of the sphere (centered at atom i) in

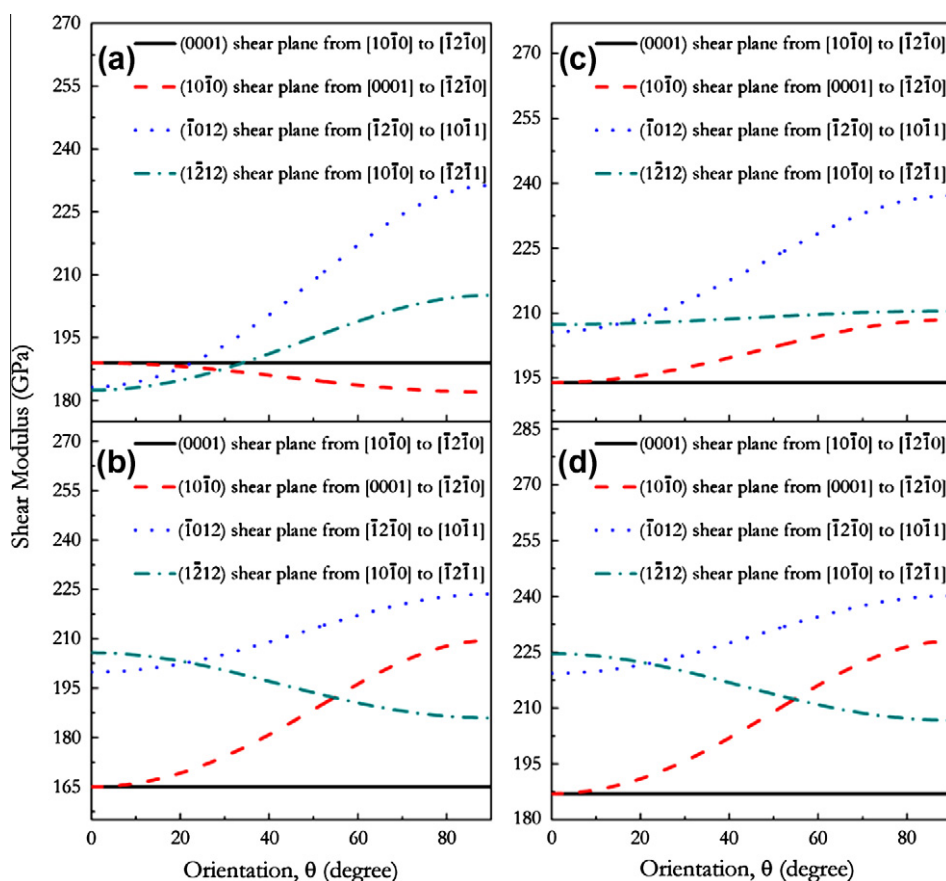


Fig. 4. Orientation dependence of the shear modulus E of the Hex-II-TMB₄: (a) MoB₄, (b) WB₄, (c) TcB₄, and (d) ReB₄.

Table 3

The isotropic bulk modulus B_H , shear modulus G_H , Young's modulus E_H , and the hardness H in unit of GPa for the Hex-II-TMB₄. Also shown are Poisson's ratio ν_H and G_H/B_H ratio.

Compound	B_H	G_H	E_H	ν_H	G_H/B_H	H
MoB ₄ ^a	285	210	506	0.204	0.737	24.8
WB ₄	292	213	514	0.207	0.730	21.3
WB ₄ ^b	294	215	519	0.206		
TcB ₄	288	222	530	0.193	0.771	22.3
ReB ₄	317	232	560	0.206	0.732	22.1

^a Ref. [11].

^b Ref. [12].

which Z_i electrons are contained; n_i and n_j are coordination numbers of atoms i and j , respectively; d_{ij} is the interatomic distance, k corresponds to the number of different atoms in the system. In the present work, the values $C = 1450$, $\sigma = 2.8$, and the atomic radii r_i of elements from Kittel's textbook are used. The estimated values of hardness by this method are tabulated in Table 3, and the results indicated all these TMB₄ within the Hex-II structures are hard materials. There are no available experimental data, however, taking account of the case of the molybdenum borides in our recent work [11], we believe our predicted values should be reliable.

3.3. Electronic properties of the Hex-II-TMB₄

To illustrate the mechanical properties of these Hex-II-TMB₄ compounds on a fundamental level, their total and site projected electronic densities of states (DOSs) were calculated at ambient pressure, as shown in Fig. 5. The obtained DOS curves show large

similarities in these compounds as follows. All these compounds exhibit clear metallic behavior by evidence of the finite electronic DOS at the Fermi level (E_F). From the partial DOS, it reveals that the states from -15 to 0 eV mainly originate from TM- d and B- $2p$ orbitals. Moreover, the partial DOS profiles for both TM- d and B- $2p$ are very similar in the range of -15 to 0 eV, reflecting the strong orbital hybridization between these two orbitals. This fact also shows that a strong covalent interaction between the TM and B atom, as demonstrated in many other TM borides. The typical feature of the total DOS is the presence of so-called pseudogap, which is considered as the borderline between the bonding and antibonding states [11,47,48]. For MoB₄ and WB₄, the E_F is perfectly lying on the pseudogap, suggesting the p - d bonding states started to be saturated. This full occupation of the bonding states and without filling on the antibonding states enhances the stability of the Hex-II-MoB₄ and Hex-II-WB₄. Compared to MoB₄ and WB₄, the TcB₄ and ReB₄ possess more valence electrons, and its bonding states are fully filled and the antibonding states are mainly occupied with the TM- d electrons. Therefore, it can be seen that the calculated Fermi energies of Hex-II-TcB₄ and Hex-II-ReB₄ are located above the pseudogap that indicating the whole bonding states and partial antibonding states have been filled. In addition, the contribution to E_F is mainly due to TM- d orbital which is the principal cause for metallicity in these Hex-II-TMB₄ compounds.

To gain a more detailed insight into the bonding character of the Hex-II-TMB₄, we have calculated the Electronic Localization Function (ELF) [49], which is based on a topological analysis related to the Pauli Exclusion Principle. The ELF is a contour plot in real space where different contours have values ranging from 0 to 1. A region with ELF = 1 is where there is no chance of finding two electrons

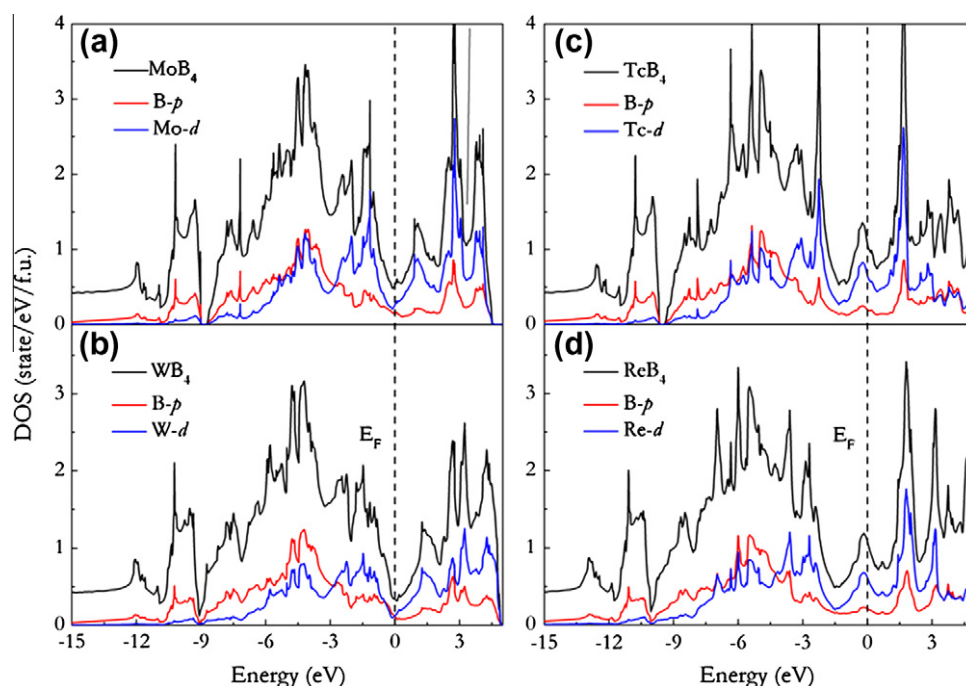


Fig. 5. Total and partial densities of states of the Hex-II-TMB₄: (a) MoB₄, (b) WB₄, (c) TcB₄, and (d) ReB₄ at ambient pressure. The vertical dashed line denotes the Fermi level at zero.

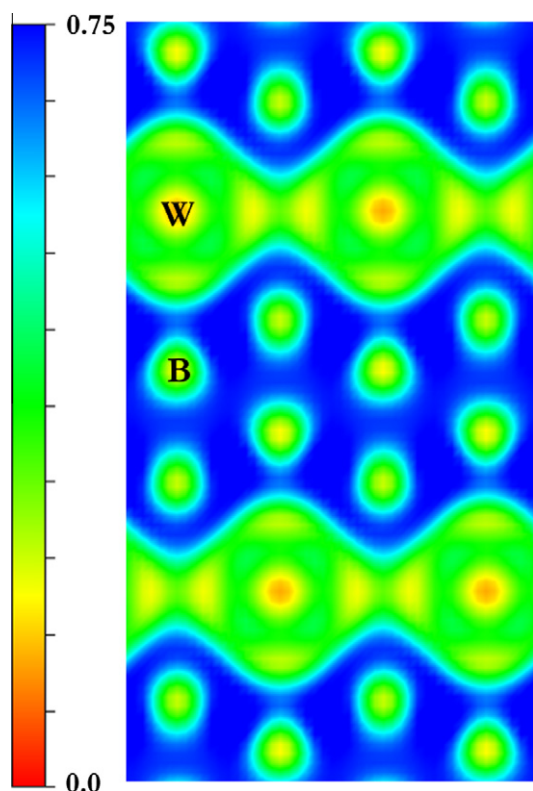


Fig. 6. Contours of electronic localization function (ELF) of Hex-II-WB₄ on (100) plane.

with the same spin. This usually occurs in places where covalent bonds or lone pairs (filled core levels) reside. An area where ELF = 0 is typical for vacuum (no electron density) or areas between atomic orbitals. This is where electrons of like spin approach

each other the closest. ELF = 0.5 for a homogeneous electron gas, values of this order indicating regions with bonding of a metallic character. It should be noted that ELF is not a measure of electron density, but is a measure of the Pauli principle, and is useful in distinguishing metallic, covalent, and ionic bonding. The contours of ELF domains for the Hex-II-WB₄ on its (100) plane are shown in Fig. 6. The high electron localization can be seen in the region between adjacent B and B atoms indicative of covalent bonding, with nearly identical B–B covalent “point attractors” at ELF = 0.75. There are also W–B covalent bonds manifested at about ELF = 0.55, although not as strong as B–B bonds. Moreover, the region around B has an overall higher ELF value than the region around the W atom, reflecting the ionicity in the bond with B withdrawing charge from W. Therefore, the strong covalent interaction between B–B bonds and W–B bonds is main driving force for their high bulk and shear moduli.

4. Conclusions

In summary, a universal hexagonal MoB₄-type structure (Hex-II) is unraveled to be the ground state structure for TMB₄ (TM = W, Tc, and Re) through the PSO algorithm, and it is energetically much superior to the earlier proposed WB₄-type (Hex-I) structure. The phonons and formation enthalpy calculations have confirmed that the Hex-II phase is dynamically stable and synthesizable at ambient conditions. The dependences of the Young's modulus E along the principal crystal tensile directions obey the following order: $E_{[10\bar{1}0]} > E_{[12\bar{1}1]} > E_{[1011]} > E_{[10\bar{1}0]}$. Except for Hex-II-MoB₄, the shear modulus of the Hex-II-TMB₄ is the smallest on the (0001) which may be viewed as the cleavage planes. The calculated bulk moduli and hardness suggested that these structures are ultra-incompressible and hard materials. The electronic densities of states and ELF analysis have demonstrated that the strong covalent TM–B bonding in TMB₈ polyhedrons play a key role in the ultra-incompressibility and hardness of the Hex-II-TMB₄. These

findings will inevitably stimulate extensive experimental works on synthesizing these technologically important materials.

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