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Enhancing the Vickers hardness, melting point and thermodynamic properties of hafnium dodecaboride†

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Although HfB₁₂ is a promising superhard material because of the boron cuboctahedron cage, the Vickers hardness of HfB₁₂ remains controversial. We apply first-principles calculations to investigate the influence of a transition metal on the structural stability, Vickers hardness and thermodynamic properties of HfB₁₂. The Vickers hardness of HfB₁₂ is 39.3 GPa. In particular, the Vickers hardness of TM-doped HfB₁₂, which are novel superhard materials, is larger than 40 GPa. The Vickers hardness of Re-doped HfB₁₂ is up to 47.6 GPa. The improvement of Vickers hardness is that the introduction of an alloying element improves the localized hybridization between B and Hf, and then enhances the bond strength of the B–B covalent bond and the Hf–B bond. In addition, these alloying elements enhance the melting-point and Debye temperature of the HfB₁₂. Therefore, we believe that alloying is an effective method to improve the Vickers hardness and thermodynamic properties of HfB₁₂ superhard material.

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1. Introduction

Compared to diamond and boron nitride superhard materials, transition metal borides (TMBs) are attractive superhard materials because of their fascinating mechanical, electronic and thermodynamic properties *etc.*^{1–9} However, hardness is a complex phenomenon, which is related to the structural configuration, chemical bonding, electronic structure, deformation, defects, *etc.*^{10–14} For TMBs superhard materials, previous work has shown that the Vickers hardness is determined by the network and shorter B–B covalent bonds.^{15,16} Namely, the boron concentration plays a crucial role in hardness. Therefore, research has focused on the boron-rich borides such as TMB₃, TMB₄ and TMB₁₂ in recent years.^{17–21} However, the investigation of boron-rich boride faces two key problems: one is that the boron-rich boride has difficulty meeting stable conditions. For example, the published TMB₁₂ mainly focuses on the ZrB₁₂ and HfB₁₂.²² The investigation of other TMB₁₂ is scarce. Another important factor is that the Vickers hardness of TMBs is also influenced by the TM–B bond, in addition to the B–B covalent bond.

Thus, alloying is an effective approach to improve the bond strength of TM–B bond and then enhance the Vickers hardness of TMBs superhard material.^{23–26} For example, Kaner *et al.* work has shown that the measured Vickers hardness of WB₄ with alloyed 20 at% Ti, 10 at% Zr and 6 at% Hf is up to 50.9 ± 2.2 GPa, 55.9 ± 2.7 GPa and 51.6 ± 2.8 GPa, respectively.²⁷ The WB is not a superhard material. However, Ta addition markedly improves the Vickers hardness of WB, while the measured Vickers hardness of W_{0.5}Ta_{0.5}B is up to 42.8 GPa.²⁸ Similarly, the Y and Sc additions enhance Vickers hardness of ZrB₁₂, while the measured Vickers hardness of Zr_{0.5}Y_{0.5}B₁₂ and Zr_{0.5}Sc_{0.5}B₁₂ is up to 45.8 GPa and 48.0 GPa,²⁹ respectively. Based on the design principle, we believe that the alloying is to improve the bonding state (TM–B bond) and Vickers hardness of TMBs superhard materials.

Among these TMBs, HfB₁₂ with cubic structure (*Fm* $\bar{3}$ *m*) is an attractive superhard material because this dodecaboride is composed of the boron cuboctahedron cage (24 B atoms).^{30,31} The boron cage can enhance the Vickers hardness and elastic modulus of HfB₁₂. However, the superhard characteristic of HfB₁₂ remains controversy. For example, the recent work has shown that the calculated Vickers hardness of HfB₁₂ is 39.1 GPa,³² which is not a superhard material (≥ 40 GPa). Therefore, the great challenge of TMBs superhard material is how to enhance the Vickers hardness of HfB₁₂. On the other hand, the thermodynamic properties must be considered as the important factor because the thermal stability plays a crucial role in industrial applications. For instance, diamond does not cut the ferrous material because of the formation of iron when the temperature is above than 600 °C.³³ As a result, an important

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work is how to improve the melting point and Debye temperature of superhard materials.

In the present work, we apply the first-principles approach to investigate the influence of alloying elements on the Vickers hardness, elastic modulus and thermodynamic properties of HfB₁₂. We consider five possible transition metals: Nb(4d-), Mo(4d-), W(5d-), Re(5d-) and Os(5d-), respectively. Our work shows that these alloying elements not only enhance the Vickers hardness, but also improve the melting point and Debye temperature of HfB₁₂. Therefore, we predict that TM-doped HfB₁₂ is a novel superhard material.

2. Theoretical methods

To explore the TMBs superhard materials, we mainly focus on the boron-rich TMBs. Therefore, HfB₁₂ with the cubic structure is likely to a potential superhard material. The experimental lattice parameter of HfB₁₂ is $a = 7.377$ Å. HfB₁₂ with a unit-cell has 52 atoms, which are composed of B cuboctahedron cage. The structural configuration of HfB₁₂ is shown in ESI.† It is obvious that the network B-B covalent bond is the origin of high hardness of HfB₁₂. However, the Vickers hardness of HfB₁₂ is also affected by the bond strength of Hf-B bond, in addition to the network B-B covalent bonds. To improve the bond strength of Hf-B bond and enhance the Vickers hardness, one Hf atom in a unit-cell is replaced by the 4d- and 5d-transition metal.

In this paper, the Vickers hardness of HfB₁₂ with alloying elements is calculated by the semiempirical model.³⁴ On the other hand, the Vickers hardness of a solid is indirectly estimated by the elastic modulus and brittle behavior. Here, the elastic constants of TM-doped HfB₁₂ are calculated by the stress vs. strain method.^{35,36} The elastic modulus of TM-doped HfB₁₂ is obtained by the elastic constants. Here, we consider three elastic parameters: bulk modulus, shear modulus and Young's modulus,^{37–41} respectively. The bulk modulus and shear modulus of TM-doped HfB₁₂ are calculated by the Voigt–Reuss–Hill (VRH) approximation.^{42,43} In addition, the Vickers hardness of TMBs is indirectly demonstrated by the B/G ratio.^{44,45} The general trend is, the lower the B/G ratio, the high Vickers hardness for the TMBs.^{46,47}

In addition, we should be considered the thermodynamic stability of alloying elements in HfB₁₂. Here, the thermodynamic stability of TM-doped HfB₁₂ is estimated by the impurity formation energy (E_f),⁴⁸ which is given by:

$$\Delta E_f = E_{\text{HfB}_{12}}^{\text{Hf} \rightarrow \text{TM}} - E_{\text{HfB}_{12}} + \mu_{\text{Hf}} - \mu_{\text{TM}} \quad (1)$$

where $E_{\text{HfB}_{12}}^{\text{Hf} \rightarrow \text{TM}}$ and $E_{\text{HfB}_{12}}$ are the total energy of TM-doped HfB₁₂ and the HfB₁₂, respectively. μ_{Hf} and μ_{TM} are the chemical potential of Hf and TM (TM = Nb, Mo, W, Re and Os) elements. The chemical potential of a solid is estimated by the electronic energy difference. When considering the elemental phases, the chemical potential is simply proportional to the Gibbs energy of the system.^{49,50}

About thermodynamic properties, we consider two important parameters: the melting point and Debye temperature, respectively. The melting point of TM-doped HfB₁₂ is calculated by:^{51,52}

$$T_m = 354 + 4.5(2C_{11} + C_{33})/3 \quad (2)$$

The Debye temperature of TM-doped HfB₁₂ is calculated by the average sound velocity, which is obtained by:^{53,54}

$$\theta_D = \frac{h}{k_B} \left(\frac{3n}{4\pi\Omega} \right)^{1/3} \times v_m \quad (3)$$

where h and n are the Planck constant and the number of atoms in a unit-cell, respectively. The average sound velocity (v_m) in a system is given by:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (4)$$

where v_t and v_l are the transverse elastic wave velocity and longitudinal elastic wave velocity, which are given by:

$$v_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (5)$$

$$v_l = \left(\frac{3B + 4G}{3\rho} \right)^{1/2} \quad (6)$$

All calculations in this paper were calculated by the first-principles calculations, as implemented in the CASTEP code.^{55,56} The exchange-correlation-function was treated by the generalized gradient correction(GGA) within Perdew–Burke–Ernzerhof functional (PBE) functional.^{57,58} The cutoff energy of HfB₁₂ with alloying element was 400 eV for the plane-wave expansion. The integration in the Brillouin zone was carried out by the k -point grid of $5 \times 5 \times 5$. The interaction between the ionic and valence electron was treated by the ultrasoft pseudo-potential.^{59,60} The SCF tolerance was smaller than 1.0×10^{-6} eV/atom and the maximal displacement was lower than 0.001 Å. During the process of structural optimization, all systems were relaxed.^{61–63}

3. Results and discussions

To investigate the influence of alloying elements on the Vickers hardness of HfB₁₂, Fig. 1 shows the calculated Vickers hardness of TM-doped HfB₁₂, and the HfB₁₂ for comparison. It can be seen that the calculated Vickers hardness of HfB₁₂ is 39.3 GPa, which is in good agreement with the Korozlu *et al.* work (39.1 GPa).⁶⁴ When TM atom is introduced, it is found that these alloying elements markedly enhance the Vickers hardness of HfB₁₂. In particular, the calculated Vickers hardness of Re-doped HfB₁₂ is up to 47.6 GPa, which is 21.1% larger than that of the HfB₁₂. It must be mentioned that the calculated Vickers hardness of TM-doped HfB₁₂ is above 40 GPa, indicating that TM-doped HfB₁₂ are novel superhard materials. Therefore, we believe that alloying is an effective method to enhance the Vickers hardness of TMBs.

To demonstrate the influence of transition metal on the hardness of HfB₁₂, Fig. 2 shows the calculated bulk modulus, shear modulus and Young's modulus of TM-doped HfB₁₂ and the HfB₁₂. Here, the calculated bulk modulus, shear modulus



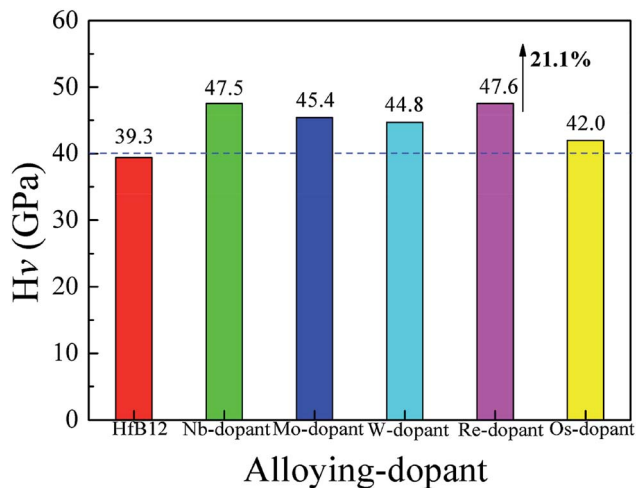


Fig. 1 Calculated Vickers hardness of TM-doped HfB₁₂ and the parent HfB₁₂.

and Young's modulus of HfB₁₂ are 238.2 GPa, 188.6 GPa and 447.6 GPa, respectively, which are in good agreement with the other theoretical results.⁶⁴ When Hf atom is substituted by the TM atom, although the calculated bulk modulus of TM-doped HfB₁₂ is smaller than that of the HfB₁₂, the calculated shear modulus and Young's modulus of TM-doped HfB₁₂ are larger than that of the HfB₁₂. As mentioned above, it is concluded that these alloying elements enhance the shear deformation resistance and elastic stiffness of the HfB₁₂. Here, the calculated shear modulus and Young's modulus of Nb-doped HfB₁₂ are 210.0 GPa and 487.3 GPa, respectively, which are larger than that of the other TM-doped HfB₁₂. Namely, the 4d-Nb enhances the shear deformation resistance and elastic stiffness of HfB₁₂ in comparison to 5d-TM. The increasing of shear deformation is that these alloying elements improve the localized hybridization between B and Hf along the shear direction. This result is demonstrated by the variation of chemical bonding (see charge density distribution).

As mentioned above, we know that the Vickers hardness of TMBs is indirectly demonstrated by the *B/G* ratio. To demonstrate the variation of hardness, Fig. 3 displays the calculated *B/G* ratio of TM-doped HfB₁₂ and the HfB₁₂. The calculated *B/G* ratio of the HfB₁₂ is 1.26, indicating that HfB₁₂ is a brittle

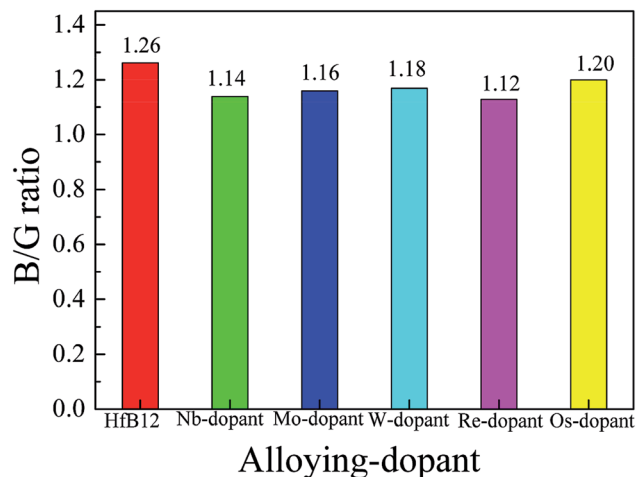


Fig. 3 Calculated *B/G* ratio of TM-doped HfB₁₂ and the parent HfB₁₂.

material. Note that the calculated *B/G* ratio of TM-doped HfB₁₂ is smaller than that of the HfB₁₂. This result indicates that these alloying additions enhance the Vickers hardness of the HfB₁₂. The trend of *B/G* ratio is consistent with the variation of Vickers hardness of TM-doped HfB₁₂.

Based on the analysis of mechanical properties, we believe that these alloying elements enhance the Vickers hardness of the HfB₁₂. Following, it is necessary to study the stability of alloying elements in HfB₁₂. Table 1 lists the calculated lattice parameter, density, volume and impurity formation energy of

Table 1 Calculated lattice parameters (Å), density, ρ (g cm⁻³), volume, *V* (Å³) and impurity formation energy *E_f* (kJ mol⁻¹) of HfB₁₂ with alloying elements, and the HfB₁₂

Element	Method	<i>a</i>	ρ	<i>V</i>	<i>E_f</i>
HfB ₁₂	Cal	7.389	5.07	403.4	
	Exp ⁶⁴	7.377			
	Theo ⁶⁵	7.312			
Nb-dopant		7.376	4.75	401.3	-16.63
Mo-dopant		7.373	4.76	400.8	-13.85
W-dopant		7.369	5.14	400.2	-13.28
Re-dopant		7.373	5.14	400.7	-11.08
Os-dopant		7.382	5.14	402.3	-7.46

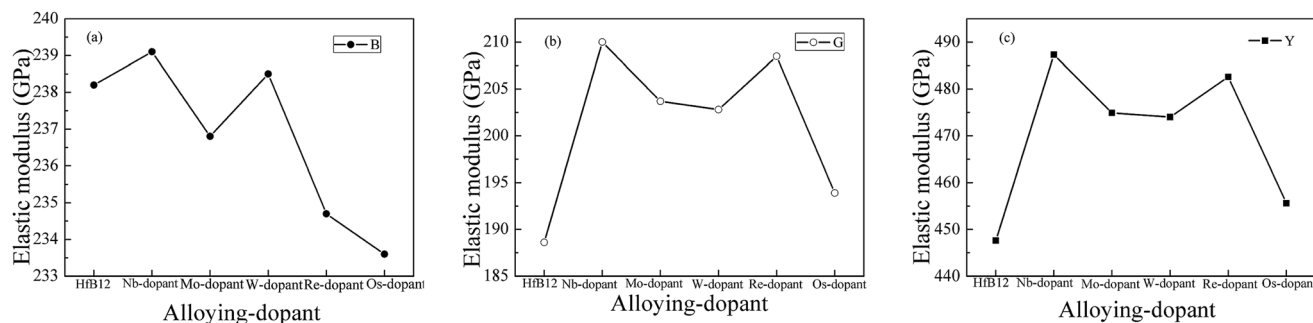


Fig. 2 Calculated elastic modulus of TM-doped HfB₁₂ and the HfB₁₂, (a) bulk modulus, (b) shear modulus and (c) Young's modulus, respectively.



TM-doped HfB_{12} . It is found that these alloying elements are thermodynamic stability in HfB_{12} because the calculated impurity formation energy of TM-doped HfB_{12} is smaller than zero. It is worth noticing that the calculated impurity formation energy of TM-doped HfB_{12} increases gradually with increasing the atomic number. This trend may be related to the valence electronic configuration of TM atom. Here, the thermodynamic stability of TM-doped HfB_{12} follows the order of Nb-dopant > Mo-dopant > W-dopant > Re-dopant > Os-dopant.

Naturally, the trend of thermodynamic stability is related to the electronic interaction between atoms, which are demonstrated by the variation of lattice parameter. As listed in Table 1, firstly, we find that the calculated lattice parameter of the HfB_{12} is $a = 7.389 \text{ \AA}$, which is in good agreement with the other theoretical result and experimental data.^{64,65} However, the alloying additions lead to lattice shrinkage of HfB_{12} because the calculated lattice parameter of TM-doped HfB_{12} is smaller than that of the parent HfB_{12} . This result also demonstrates that these alloying elements enhance the localized hybridization between B and Hf. As a result, alloying addition effectively enhances the bond strength of B–B covalent bond and Hf–B bond. This is why the Vickers hardness of TM-doped HfB_{12} is larger than that of the HfB_{12} .

It is well known that the structural stability is related not only to the thermodynamic stability but also to the dynamic stability.^{66,67} Generally, the dynamic stability of a solid is measured by the phonon frequency. The imaginary phonon frequency means the dynamic instability, and *vice versa*. To examine the dynamic stability, Fig. 4 shows the calculated phonon dispersion curves of TM-doped HfB_{12} and the HfB_{12} along the high symmetry direction. It can be seen that HfB_{12} is

a dynamic stability because no imaginary phonon frequencies are found in HfB_{12} . However, we observed the imaginary phonon frequency in TM-doped HfB_{12} , indicating that TM-dopant is a dynamic instability in HfB_{12} . That is to say, these alloying additions will form the solid solution in HfB_{12} . These results are similar to the Kaner *et al.* report.^{27,68}

To explore the influence of alloying elements on the thermodynamic properties of HfB_{12} superhard material, here, we consider two thermodynamic parameters: melting point and Debye temperature, respectively. Fig. 5 shows the calculated melting point of TM-doped HfB_{12} and the HfB_{12} . It can be seen that the calculated melting point of the HfB_{12} is 2093 K. In

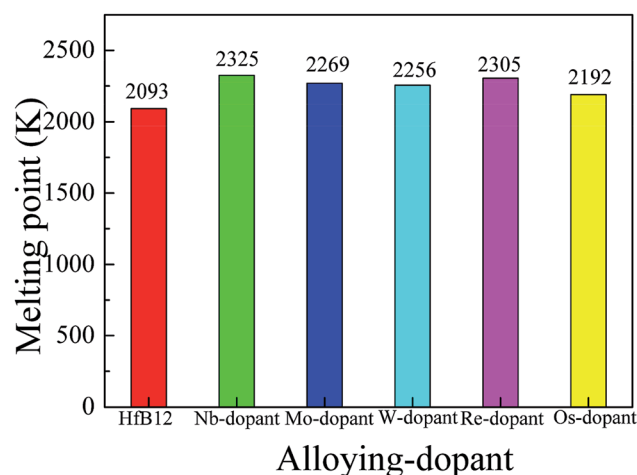


Fig. 5 Calculated melting point of TM-doped HfB_{12} and the HfB_{12} .

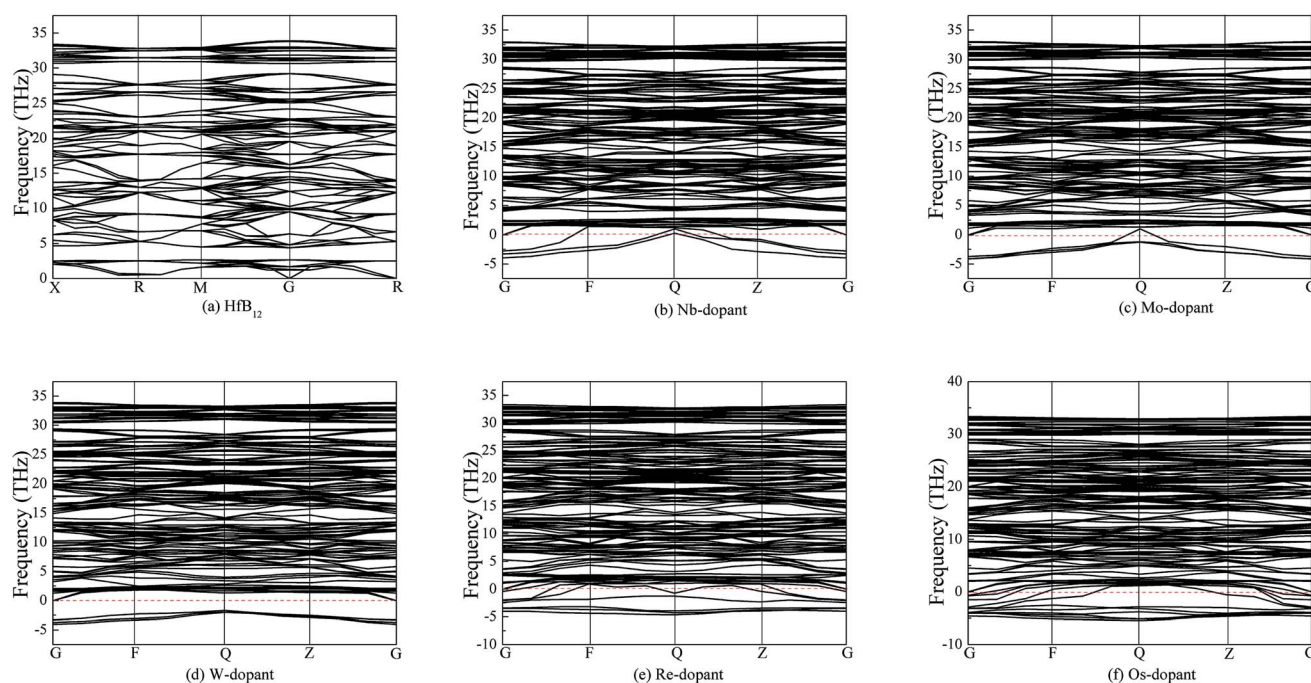


Fig. 4 . Calculated phonon dispersion curves of TM-doped HfB_{12} and the HfB_{12} , (a) the HfB_{12} , (b) Nb-dopant, (c) Mo-dopant, (d) W-dopant, (e) Re-dopant and (f) Os-dopant, respectively.



particular, we note that the calculated melting point of TM-doped HfB_{12} is much larger than that of the parent HfB_{12} . Here, the calculated melting point follows the order of Nb-dopant > Re-dopant > Mo-dopant > W-dopant > Os-dopant > HfB_{12} .

Fig. 6 shows the calculated Debye temperature of TM-doped HfB_{12} and the HfB_{12} for comparison. Here, the calculated Debye temperature of the HfB_{12} is 1010 K. Similarly, the calculated Debye temperature of TM-doped HfB_{12} is larger than that of the HfB_{12} . In our work, the trend of Debye temperature is similar to the variation of melting point. In particular, the calculated

Debye temperature of Nb-doped HfB_{12} is 1102 K, which is larger than that of the other TM-doped HfB_{12} and the HfB_{12} . Therefore, we believed that these alloying elements improve the thermodynamic properties of HfB_{12} . As mentioned above, it is concluded that Nb is the best element to enhance the thermodynamic properties of HfB_{12} in comparison to the other alloying elements.

Fig. 7 shows the calculated total and partial density of state (DOS) of TM-doped HfB_{12} and the HfB_{12} . It is found that the DOS profile of the HfB_{12} is composed of the B-2s state, B-2p state and Hf-5d state. In particular, the formation of B-B covalent bond is attributed to the localized hybridization between B and B. Based on the structural configuration, we suggest that the high hardness of HfB_{12} is attributed to the network B-B covalent bonds. The bond characteristic of B-B covalent bond is demonstrated by the charge density distribution.

When Hf atom is replaced by TM atom, it is found that the introduction of alloying element gives rise to B-2p state migration from the high energy region to the low energy region. This phenomenon will enhance the localized hybridization between B and B, and then improve the bond strength of B-B covalent bond. In addition, the band migration of B-2p state also changes the localized hybridization between Hf and B. As a result, the formation of B-B covalent bond and Hf-B bond enhances the Vickers hardness of the HfB_{12} . This result is well affirmed by the charge density distribution.

To reveal the nature of Vickers hardness, Fig. 8 displays the calculated charge density distribution in (001) plane for TM-doped HfB_{12} and the HfB_{12} . For charge density distribution, the red color means the maximum localization of electrons and

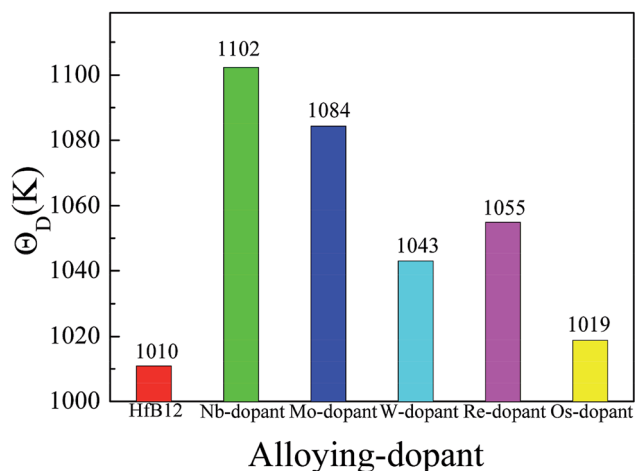


Fig. 6 Calculated Debye temperature of TM-doped HfB_{12} and the HfB_{12} .

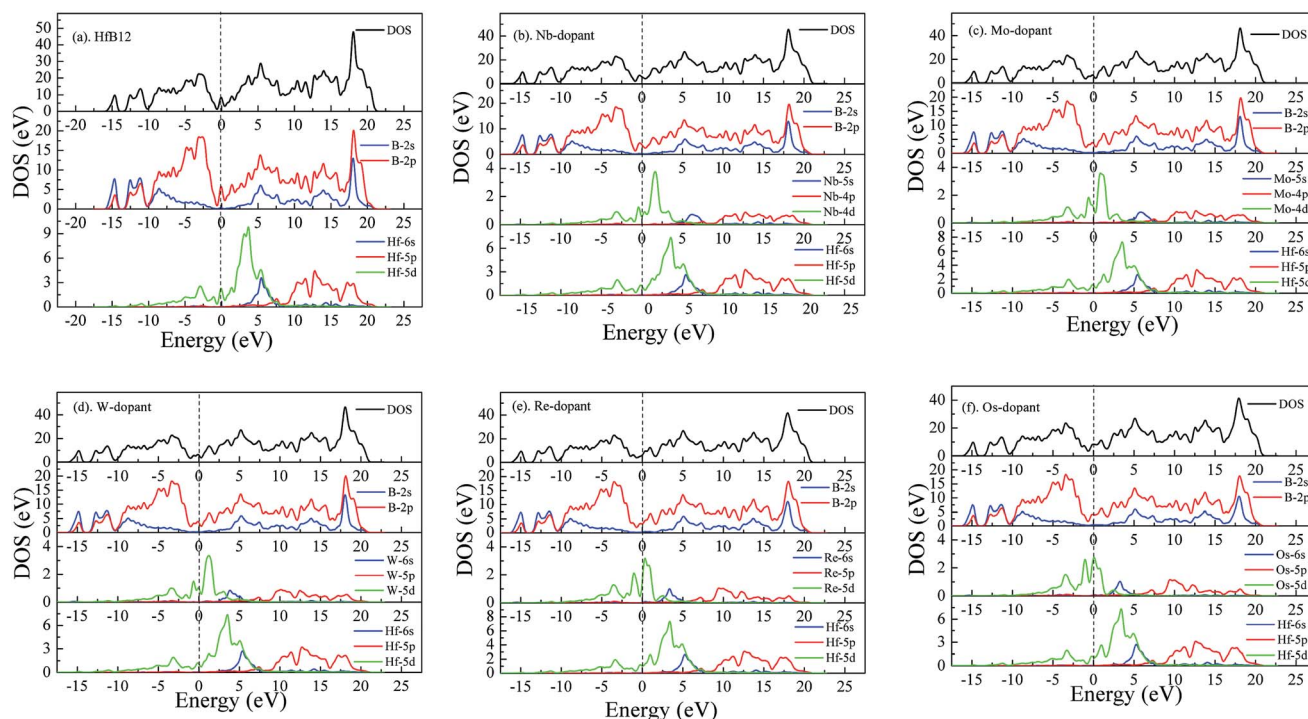


Fig. 7 Calculated density of state of TM-doped HfB_{12} and the HfB_{12} , (a) the HfB_{12} , (b) Nb-dopant, (c) Mo-dopant, (d) W-dopant, (e) Re-dopant and (f) Os-dopant, respectively.



the blue color implies the maximum delocalization of electrons.⁶⁹ Compared to the other alloying elements, it can be seen that the alloying element of Re markedly improves the Vickers hardness of the HfB₁₂. Hence, we will focus on the charge density distribution between HfB₁₂ and Re-doped HfB₁₂.

From Fig. 8, firstly, we observe the formation of directional B–B covalent bonds because of the strong localized hybridization between B and Hf. The B icosahedrons cage will form two different B–B covalent bonds, which are the origin of high hardness. For the parent HfB₁₂ (see Fig. 8(a)), in our work, the calculated bond length of B–B covalent bond is 1.679 Å and 1.773 Å, respectively, which are in good agreement with the

other theoretical result (1.682 Å).⁶⁵ In addition we find that the calculated bond length of Hf–B bond is 2.744 Å. In particular, the B–B covalent bonds will form the 3D-network bond, which can improve the mechanical properties of HfB₁₂. Therefore, it is concluded that the Vickers hardness of HfB₁₂ is also affected by the bond strength of Hf–B bond in addition to the B–B covalent bonds.

However, we find that the introduction of alloying element can improve the localized hybridization between B and the near B, which is demonstrated by the bond length of B–B covalent bond. From Fig. 8, it can be seen that the bond length of B–B covalent bond of TM-doped HfB₁₂ (near TM atom) is shorter

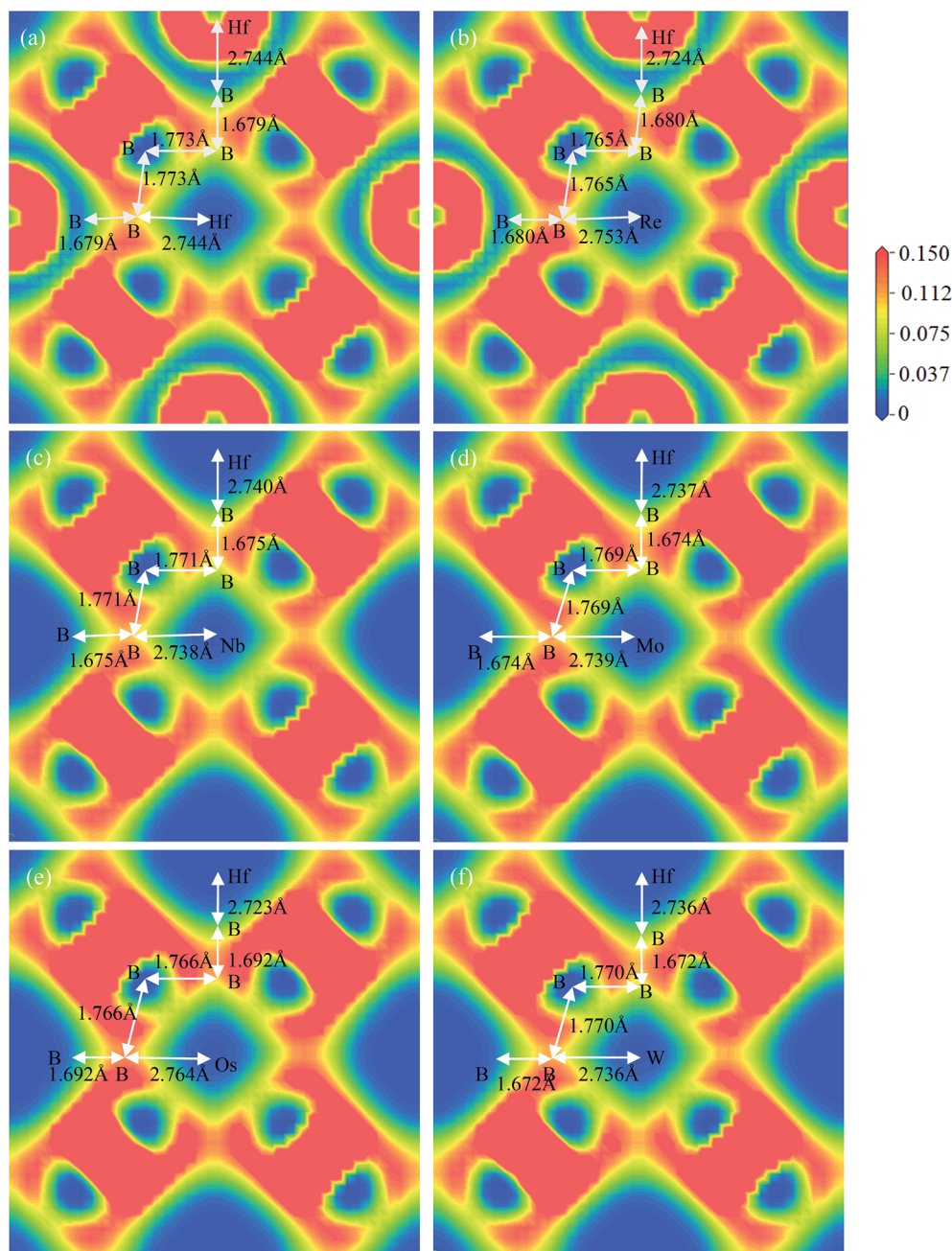


Fig. 8 Calculated charge density distribution along the (001) plane, (a) the HfB₁₂, (b) Re-dopant, (c) Nb-dopant, (d) Mo-dopant, (e) Os-dopant and (f) W-dopant, respectively.



than that of the corresponding B–B covalent bond of HfB₁₂ (1.773 Å). On the other hand, it is found that the calculated bond length of Hf–B bond for TM-doped HfB₁₂ is also shorter than that of the corresponding Hf–B bond for HfB₁₂. Namely, the alloying addition can improve the electronic interaction between Hf and B atoms. This is why the Vickers hardness of TM-doped HfB₁₂ is larger than that of the HfB₁₂.

For example, we find that the introduction of alloying element (Re) improves the localized hybridization between B and Hf. From Fig. 7 and 8, the introduction of alloying element (Re) changes the charge interaction between B and Hf, and then improves the bonding state. Here, the calculated bond length of the corresponding B–B covalent bond is 1.680 Å along the *a*–*c* plane and 1.765 Å along the shear direction, respectively. There is well explained why the shear deformation resistance of TM-doped HfB₁₂ is stronger than that of the parent HfB₁₂. On the other hand, the calculated bond length of Hf–B bond is 2.724 Å, which is shorter than the corresponding Hf–B bond for the HfB₁₂. As mentioned above, it is concluded that alloying is an effective method to improve the Vickers hardness of TMBs superhard material.

4. Conclusions

In summary, we apply the first-principles calculations to investigate the improvement of Vickers hardness, melting point and Debye temperature of HfB₁₂ with alloying element, together with the HfB₁₂ for comparison. We consider five transition metals: Nb(4d-), Mo(4d-), W(5d-), Re(5d-) and Os(5d-) respectively. The results show that the calculated Vickers hardness of HfB₁₂ is 39.3 GPa, which is in good agreement with the other theoretical result. In particular, the calculated Vickers hardness of TM-doped HfB₁₂ is bigger than 40 GPa, indicating that TM-doped HfB₁₂ is a novel superhard material. The calculated Vickers hardness of Re-doped HfB₁₂ is up to 47.6 GPa, which is 21.1% larger than that of the HfB₁₂.

The variation of Vickers hardness is demonstrated by the elastic modulus and brittleness. The calculated shear modulus and Young's modulus of TM-doped HfB₁₂ are larger than that of the HfB₁₂. Interestingly, the calculated shear modulus and Young's modulus of Nb(4d)-doped HfB₁₂ are bigger than that of the Re(5d)-doped HfB₁₂. The calculated *B/G* ratio of TM-doped HfB₁₂ is smaller than that of the HfB₁₂, indirectly demonstrates that the Vickers hardness of TM-doped HfB₁₂ is bigger than that of the HfB₁₂. In addition, the calculated melting point and Debye temperature of TM-doped HfB₁₂ are larger than that of the HfB₁₂. In particular, the calculated melting point and Debye temperature of Nb-doped HfB₁₂ are 2325 K and 1102 K, which are higher than that of the other TM-doped HfB₁₂. The improvement of Vickers hardness is that the introduction of alloying element improves the localized hybridization between B and Hf, and then enhances the bond strength of B–B bond and Hf–B bond.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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