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Correlation between hardness and bond orientation of vanadium borides

Y. Pan[†,*], Y.H. Lin[‡], J.M. Guo[†] and M. Wen[†]

[†] State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming 650106, PR China,

[‡] School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, PR China

E-mail address: yongp@ipm.com.cn (Y. Pan)

Tel: 86-0871-68328950, Fax: 86-0871-68328945.

Abstract:

The relationship between hardness and bond characteristic of vanadium borides is investigated by first-principles approach. The calculated lattice parameters of V-B system are in good agreement with previous experimental data. The convex hull indicates that the VB are most stable structure at ground state. The vanadium borides have higher bulk modulus, shear modulus and Young′s modulus, and lower B/G ratio. These vanadium borides exhibit brittle behavior. We predict that the V_5B_6 and VB_2 are potential superhard materials. The nature of hardness is related not only to the covalent bonding but also to the bond orientation. The B-B and V-B covalent bonds parallel to the load plane are the origin of high hardness.

1. Introduction

Transition metal borides (TMBs) as potential superhard materials have attracted much attention in recent years[1, 2]. Several TMBs such as OsB_2, RuB_2, $RuB_{1.1}$, $IrB_{1.1}$ and CrB_4 have been synthesized under ambient pressure[3-5]. The theoretical calculations show that these borides all have high elastic modulus, high hardness, ultra-incompressibility and exhibit a degree of metallic behavior[6]. However, numerous TMBs are not superhard materials[7-9]. On the other hand, Richard et al.[10] pointed out that the new design principle of TMBs superhard material is mainly determined by two design parameters: high valence electron density and bond covalency. However, the research of hard nature remains conundrum. Therefore, to search for novel superhard material and reveal the hard nature are necessary.

Owing to the outstanding physical properties of vanadium borides, they have been used in various applications such as high-temperature material, surface protection materials and wear-resistant materials et al[11, 12]. Moreover, the structures of vanadium borides with various stoichiometries are obtained at ambient pressure: VB_2 (space group: P6/mmm with AlB_2 structure)[13], V_2B_3 (space group: cmcm)[14], V_3B_4 (space group: Immm with Cr_3B_4)[12], V_5B_6 (space group: Ammm with Ti_5B_6)[15], VB (space group: cmcm with CrB structure)[16] and V_3B_2 (space group: P4/mbm with Ta_3B_2 structure)[17]. However, the structural, elastic modulus and electronic structure of only VB_2 have been studied by first-principles approach. They found that the bulk modulus of VB_2 is 308 GPa, which is close to the value of CrB_4 (306 GPa)[18, 19], indicating that these vanadium borides are expected to be potential

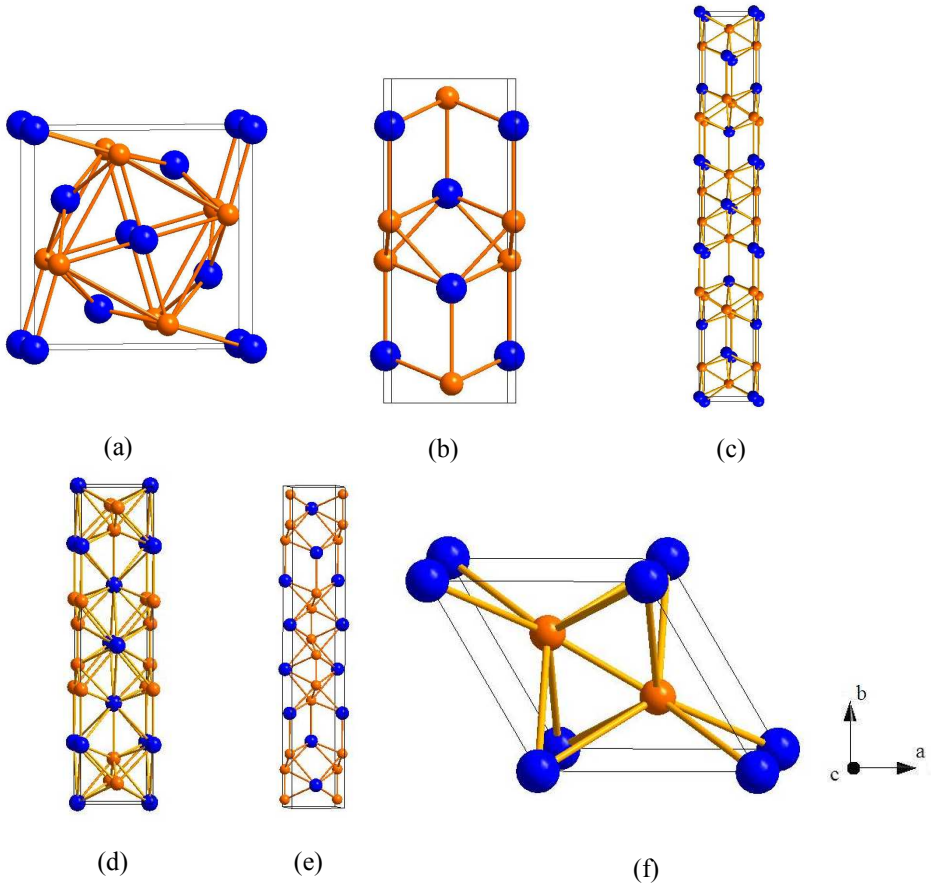

Fig. 1. Crystal structure of V-B system. (a) V_3B_2, (b) VB, (c) V_5B_6, (d) V_4B_5, (e) V_2B_3, (f) VB_2, respectively. The blue and orange spheres represent the V and B atoms.

candidate for superhard material. Unfortunately, the mechanical properties of other vanadium borides have seldom been reported.

In order to search for novel superhard materials and to reveal the correlation between hardness and bond characteristic, in the present work, the structural information, elastic modulus, hardness and electronic structure of vanadium borides include V_3B_2, VB, V_5B_6, V_3B_4, V_2B_3 and VB_2 are systematically studied by first-principles approach. We found that the vanadium borides are potential superhard materials and bond orientation plays an important role in hardness of TMBs. The main purpose of this work is to propose some helpful for studying of the novel transition metal borides superhard materials.

2. Computational details

Six different vanadium borides involve V_3B_2, VB, V_5B_6, V_3B_4, V_2B_3 and VB_2 are considered in this paper. The crystal structures are shown in Fig. 1, where the blue and orange spheres represent the V and B atoms. In order to obtain the mechanical and physical properties under ground state, all calculations were performed by density functional theory with CASTEP code[20]. To estimate our calculated results, the exchange-correlation function was taken into account through the local density approximation (LDA) with Ceperley-Alder (CA-PZ)[21] and the general gradient approximation (GGA) with

Perdew-Burke-Ernzerhof (PBE)[22]. The $3p^6 3d^3 4s^2$ and $2s^2 2p^1$ were considered as the valence electrons for V and B atoms, respectively. A plane-wave basis set for electron wave function with cutoff energy of 320 eV was used. Integrations in the Brillouin zone were performed using special *k*- points generated with 9×9×16, 11×4×11, 5×11×11, 11×5×11, 10×4×10 and 12×12×12 mesh grids for V_3B_2, VB, V_5B_6, V_3B_4, V_2B_3 and VB_2, respectively. During the structural optimization, no symmetry and no restriction were constrained for the unit-cell shape, volume and atomic positions. Elastic stiffness constants were calculated by strain-stress method. From the calculated elastic constants C_{ij}, the polycrystalline bulk modulus (B) and shear modulus (G) were estimated by using the Voigt -Reuss-Hill (VRH) approximation method[23].

3. Results and discussion

The calculated lattice parameters, densities and volumes of V-B system with LDA and GGA are listed in Table 1, together with corresponding experimental results. It can be seen that the calculated lattice parameters of six different vanadium borides and pure vanadium are in good agreement with experimental data. Moreover, the calculated lattice parameters of V, V_3B_2, VB, V_5B_6 V_2B_3 and VB_2 are smaller than that of experimental data whether LDA or GGA. However, we

Table 1 Calculated lattice parameters, *a* (Å), *b* (Å), *c* (Å), densities ρ (g/cm^3) and unit-cell volumes, V (Å^3) of V-B system, respectively.

Phase	Method	Space group	Structure type	*a*	*b*	*c*	ρ	V
V	LDA	Im-3m	cubic	2.930			6.724	25.16
	PBE			3.000			6.261	27.02
	Exp[24]			3.040			5.680	
V_3B_2	LDA	P4/mbm	tetra	5.637		2.962	6.155	94.13
	PBE			5.730		3.021	5.842	99.16
	Exp[17]			5.755		3.038	5.830	100.62
VB	LDA	cmcm	orthor	2.997	7.920	2.922	5.913	69.37
	GGA			3.053	8.044	2.965	5.632	72.83
	Exp[16]			3.100	8.170	2.980	5.434	75.47
V_5B_6	LDA	ammm	orthor	2.931	20.918	2.993	5.783	183.53
	GGA			2.974	21.225	3.050	5.512	192.54
	Exp[12]			3.058	21.250	2.974	5.492	193.26
V_3B_4	LDA	Immm	orthor	2.987	13.019	2.935	5.704	114.15
	GGA			3.044	13.207	2.977	5.440	119.70
V_2B_3	LDA	cmcm	orthor	2.983	18.148	2.937	5.611	158.99
	GGA			3.042	18.406	2.978	5.349	166.79
	Exp[14]			3.060	18.429	2.984	5.302	168.26
VB_2	LDA	P6/mmm	hexa	2.954		2.966	5.376	22.41
	GGA			2.993		3.029	5.127	23.50
	Exp[25]			2.997		3.056	5.060	
	Theo[26]			3.008		3.068		

Table 2 Calculated elastic constants C_{ij} (GPa) of V-B system, respectively.

Phase	Method	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
V_3B_2	LDA	596	105	147			501	228		199
	PBE	552	95	132			451	211		185
VB	LDA	545	141	168	701	89	672	237	304	240
	PBE	492	123	146	628	77	608	218	277	226
V_5B_6	LDA	700	94	145	674	153	530	295	253	249
	PBE	630	81	130	615	137	484	265	230	227
V_3B_4	LDA	529	149	157	698	101	677	254	291	255
	PBE	479	133	137	629	91	620	236	261	232
V_2B_3	LDA	544	139	148	706	112	694	272	283	262
	GGA	488	124	129	639	101	632	250	251	236
VB_2	LDA	740	115	135			538	254		
	PBE	680	107	120			478	222		
	Theo[18]	681	110	125			460	230		

found that the lattice parameters of V_3B_4 by LDA are also smaller than experimental data in contrast to the lattice parameters by GGA are bigger than experimental data. Compared with the calculated results, we conclude that the calculated lattice parameters by GGA are better than LDA at ground state.

In order to estimate structural stable, the formation enthalpy of V-B system as a function of B concentration is calculated and shown in Fig. 2. It can be seen that the VB displays a lowest negative formation enthalpy with minimum values of about -0.890 eV/atom with LDA and -0.849 eV/atom with GGA,

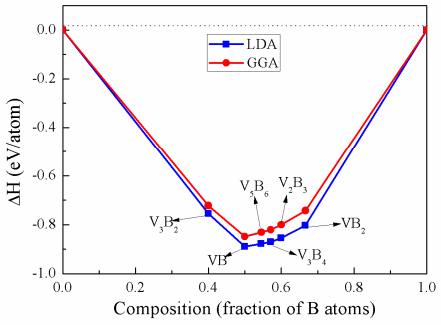

Fig. 2. Formation enthalpy of V-B system.

respectively, and the convex hull indicates that the VB is more stable than other vanadium borides. There is no doubt that the discrepancy is due to the localized hybridization and crystal structure.

The elastic modulus and plastic deformation of a solid are very estimated by elastic constants. Here, the elastic constants of these borides should be discussed. Table 2 summarizes the calculated elastic constants of V-B system, respectively. The calculated elastic constants of VB_2 are in good agreement with previous theoretical results. We observed that these borides are mechanically stable because their elastic constants obey the Born stability criteria[27]. Moreover, the calculated elastic constant C_{11} of V_3B_2, V_5B_6 and VB_2 is bigger than C_{33}, indicating that these borides have strong ultra-incompressible along the *a*-axis. Our previous work pointed out that the Vickers hardness is in the *a-c* plane and the direction of applied load is the *b*- direction. That is to say, the higher the C_{11} and C_{33}, the bigger the hardness. Therefore, the higher elastic constants C_{11} and C_{33} are the origin of the high elastic modulus and hardness. However, the calculated elastic constants C_{22}

and C_{33} of VB, V_3B_4 and V_2B_3 are bigger than C_{11}, implying that these borides exhibit excellent resistant to deformation along the *b*- and *c*- axis. On the other hand, the elastic constant C_{44} is related to resistant to shear deformation. As shown in Table 2, the calculated elastic constant C_{44} of V-B system is bigger than 200 GPa and the elastic constant C_{44} of V_5B_6 (295 GPa by LDA and 265 GPa by GGA) is bigger than other vanadium borides. There result shows that the V_5B_6 has strong resistant to shear deformation.

Low G means a low resistance to shear deformation, and hence ductility; while low 1/B indicates a weak resistance to fracture, and hence brittleness. Therefore, either ductile or brittle behavior of a solid is estimated by B/G ratio. According to the Pugh rule[28], the critical value of B/G ratio which separates ductile and brittle material has been evaluated to be equal to 1.75. If B/G > 1.75, a material behaves in a ductile manner, while if B/G < 1.75, a material does in a brittle manner. In fact, the value of B/G ratio indirectly determines the hardness of a solid. The general trend is: the lower the B/G ratio, the higher the hardness. For example, the B/G ratio of diamond is only about of 0.826[19].

As we known, the hard nature of solid is very complex, which is related to intrinsic factors such as electronic structure, bond orientation and crystal structure et al, and external factors such as defects and deformation et al. In order to obtain precious theoretical hardness, in this paper, the hard model of V-B system is adopted by intrinsic hard model[29] and semi-empirical hard model[30], respectively.

The calculated bulk modulus, shear modulus, Young′s modulus, Poisson′s ratio, B/G ratio and theoretical hardness of V-B system within both LDA and GGA are listed in Table 3. We observed that the calculated bulk modulus of these vanadium borides is 2.0 times higher than that of pure V, and the shear modulus is 4~5 times larger than the pure V, implying that these vanadium borides have strong resistant to shape and shear deformation. There is no doubt that the B-B and V-B covalent bonds in V-B system can enhance the resistance to deformation when the

Table 3 Calculated bulk modulus, B (GPa), shear modulus, G (GPa), Young′s modulus, E (GPa), Poisson′s ratio, σ, B/G ratio and hardness, H (GPa) of V-B system, respectively.

Phase	Method	B	G	E	σ	B/G	H_{Gao}	H_{chen}
V_3B_2	LDA	276	216	514	0.190	1.278	43.0	31.8
	PBE	252	200	474	0.186	1.260	40.7	30.9
VB	LDA	301	255	597	0.170	1.180	35.2	41.7
	PBE	269	234	544	0.163	1.149	36.9	38.3
V_5B_6	LDA	298	258	601	0.164	1.155	44.0	40.5
	PBE	269	234	544	0.163	1.150	47.6	38.3
V_3B_4	LDA	301	257	600	0.168	1.171	30.1	39.7
	PBE	271	235	547	0.164	1.153	32.0	38.2
V_2B_3	LDA	303	265	616	0.161	1.143	30.8	41.7
	PBE	273	240	557	0.160	1.137	33.5	39.5
VB_2	LDA	307	270	626	0.160	1.137	53.4	42.8
	PBE	278	242	563	0.163	1.149	50.0	39.5
	Theo[31]	175						
V	Theo[32]	155	54	144	0.340	2.870		

introduction of light element, B into the lattice of transition metal, and is expected to have profound influence on their chemical and mechanical properties.

Moreover, the calculated bulk modulus of these borides are close to the diborides in contrary to the shear modulus are very higher than that of diborides[33, 34]. In addition, the calculated bulk modulus of V-B system is not affected by B concentration. However, the shear and Young′s modulus are slightly increase with B concentration increases. It is worth to notice that the calculated bulk modulus, shear modulus and Young′s modulus of VB_2 are 307 GPa, 270 GPa and 626 GPa by LDA, respectively, which are higher than other vanadium borides. These results are very demonstrated by B/G ratio and Poisson′s ratio because the calculated B/G ratio and Poisson′s ratio of these borides follow the B concentration. The calculated B/G ratio of V-B systems is smaller than 1.75 whether LDA or GGA, indicating that these vanadium borides exhibit brittle behavior and have high hardness. Note that the B/G ratio and Poisson′s ratio of VB_2 are lower than other vanadium borides. We suggest that this discrepancy is related to bond covalency and atomic arrangement.

As shown in Table 3, the vanadium borides have high hardness whether intrinsic model or experimental model. We note that the hardness of V_3B_2, V_5B_6 and VB_2 by intrinsic model is bigger than 40 GPa and the hardness of VB_2 by semi-empirical model is bigger than 40 GPa. The hard discrepancy is determined by the choice of hard model. Based on the analysis of hardness, we predict that the V_5B_6 and VB_2 are potential superhard material. Furthermore, we suggest that the hardness of V-B system is determined by B-B and V-B covalent bonds, which are demonstrated by electronic structure (see Fig. 3 and Fig. 4).

To gain insight into the mechanical properties of V-B system, the total and partial density of states (DOS) of V_3B_2, VB, V_5B_6, V_3B_4, V_2B_3 and VB_2 are calculated and presented in Fig. 3, while the black vertical dashed of DOS represents the Fermi level (E_F). Clearly, the DOS profiles show that all vanadium borides exhibit metallic behavior due to their finite values at E_F. Moreover, the DOS profiles below E_F are mainly contributed by V-3*d* state, B-2*p* state and B-2*s* state, reflecting the significant hybridization between V and B atoms, and forming the V-B bond. In addition, the B-2*s* state stretches into the B-2*p* state below E_F so as to form B-B covalent bond. Obviously, the high elastic modulus and high hardness are derived from the strong B-B and V-B covalent bonds.

Moreover, the deep valley near E_F is named pseudogap, which separates the bonding and antibonding. As shown in Fig. 3, the deep valley of V_3B_2 above E_F in contrast to the valley of VB, V_5B_6, V_3B_4, V_2B_3 and VB_2 below E_F, indicating that the V(*d*)-B(*p*) bonding states of VB, V_5B_6, V_3B_4, V_2B_3 and VB_2 below stated to be saturated. The nearly full occupation of the bonding states and without filling on the antibonding state leads to high elastic modulus, smaller Poisson′s modulus and high hardness.

To further comprehend the bond mechanism and mechanical properties, the calculated charge density distribution on the (100) plane of V-B system within LDA are shown in Fig. 4. It can be seen that some electrons between V and B atoms, indicating a strong directional covalent V-B covalent bonds exist in these vanadium borides. Moreover, two neighbor B atoms form the B-B covalent bonds. It is emphasized that high elastic modulus and hardness are determined by bond strength and bonding direction.

The hardness of a solid is related to bond state in *a-c* plane. In order to reveal the hard nature, the bond state in *a-c* plane of V-B system should be discussed and analyzed, here.

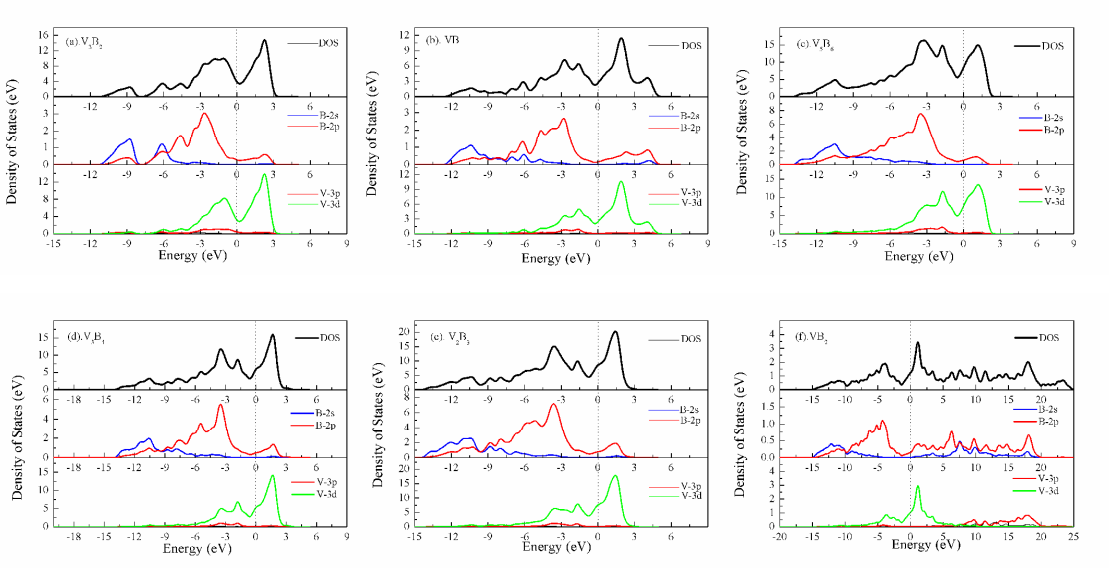

Fig. 3. The total and partial density of states of vanadium borides. (a) V_3B_2, (b) VB, (c) V_5B_6, (d) V_4B_5, (e) V_2B_3, (f) VB_2, respectively.

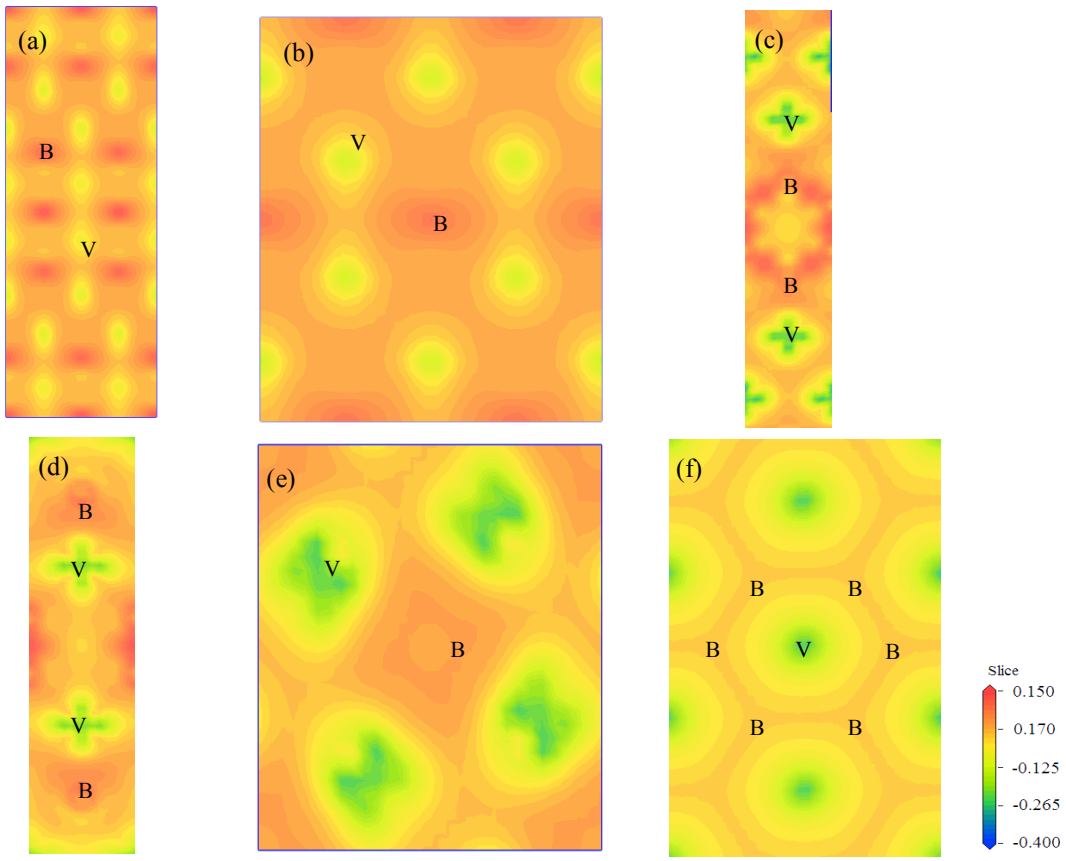

Fig. 4. The difference charge density contour plots of V-B system in (100) plane. (a) V_3B_2, (b) VB, (c) V_5B_6, (d) V_4B_5, (e) V_2B_3, (f) VB_2, respectively.

From Fig. 4 (a), the B atom of V_3B_2 locates at the octahedral interstitial site (OIS) and each B atom is surrounded by eight V atoms, which the V and B atoms form 3D- network structure (see Fig. 1(a)). On the other hand, it has one type of B-B covalent bond (1.761 Å) and two types of V-B bonds (2.237 Å and 2.282 Å). In particular, the weak V-B covalent bond is compensated by B-B covalent bond in *a-c* plane, which resist load applied.

The structural feature and bond states of VB, V_5B_6, V_3B_4 and V_2B_3 with orthorhombic structure are similar, and the slight discrepancy is the number of B-B and V-B covalent bonds in *a-c* plane. As seen in Fig. 4(b)-(e), the alternative stacked V and B layers can be viewed along the *b*- direction. In *a-c* plane, we observed that the VB has one type of B-B (1.762 Å) and V-B (2.200 Å) covalent bonds, respectively. The V_5B_6, V_3B_4 and V_2B_3 have one type of B-B (1.730 Å for V_5B_6, 1.733 Å for V_3B_4 and 1.736 Å for V_2B_3) covalent bond and two types of V-B (2.200 Å and 2.262 Å for V_5B_6, 2.198 Å and 2.261 Å for V_3B_4, 2.195 Å and 2.261 Å for V_2B_3), respectively. For VB_2 with hexagonal structure, it has one type of B-B (1.705 Å) and V-B (2.260 Å) covalent bonds. Obviously, the discrepancy about elastic modulus and hardness is the bond strength and bond orientation along *a-c* plane. Therefore, we conclude that the bond orientation also plays an important role in hardness of TMBs.

4. Conclusion

In summary, we have presented first-principle density functional theory to study the structural information, elastic modulus, hardness and electronic structure of V-B system. In order to estimate the calculation results, the exchange-correlation function is considered by LDA and GGA. The conclusions as following:

(1) The calculated lattice parameters and volumes of these borides are in good agreement with the experimental data, and the calculated results by GGA are better than LDA. The calculated formation enthalpy of VB is about of -0.890 eV/atom with LDA and -0.849 eV/atom with GGA, which is smaller than other vanadium borides.

(2) These borides all have high bulk modulus, high shear modulus, lower Poisson′s ratio, and smaller B/G ratio. The calculated bulk, shear modulus and Young′s of VB_2 are higher than other vanadium borides. The calculated B/G ratios of these borides are smaller than 1.75. Therefore, they exhibit brittle behavior. The B/G ratio of VB_2 is smaller than other vanadium borides, indicating that VB_2 maybe has high hardness.

(3) The calculated intrinsic hardness of V_3B_2, V_5B_6 and VB_2 is bigger than 40 GPa and the semi-empirical hardness of VB_2 is also higher than 40 GPa, indicating that the V_5B_6 and VB_2 are potential superhard materials.

(4) The high elastic modulus and hardness originate from the strong hybridization between V and B atoms. We found that the bond orientation plays an important role in hardness for these borides.

Acknowledgments

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