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Structural Modifications and Mechanical Properties of Molybdenum Borides from First Principles

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Received: January 10, 2010; Revised Manuscript Received: March 3, 2010

On the basis of the evolutionary methodology for crystal structure prediction, we have clarified the long-standing debates on the ground state structures of technically important molybdenum borides: MoB₂, Mo₂B₅, and MoB₄. The earlier proposed rhombohedral structure for Mo₂B₅ and WB₄-type structure for MoB₄ are ruled out. Instead, two novel hexagonal *P6₃/mmc* structures are proposed. Moreover, the yet synthesized MoB₃ was found to adopt the intriguing rhombohedral *R3m* structure and was suggested to be experimentally synthesizable by the calculation of convex hull. Density of states calculation revealed that the strong covalent bonding between Mo and B atoms is the driving force for the high bulk and shear modulus as well as small Poisson's ratio of the studied borides. The hardness calculations suggest that these borides are all hard materials, among which MoB₃ exhibits the largest Vickers hardness of 31.8 GPa, exceeding the hardness of α -SiO₂ (30.6 GPa) and β -Si₃N₄ (30.3 GPa).

Introduction

Superhard materials (Vickers hardness, $H_v \geq 40$ GPa) are of fundamental interest and practical importance because of their excellent mechanical, thermal, and chemical properties. It is known that superhard materials are often formed by the light elements B, C, N, and O, such as diamond,¹ c-BN,² B₆O,³ BC₂N,⁴ and BC₅.⁵ Recently, it has been proposed that the intercalation of these light elements into transition metals might be a good strategy for search of potential superhard materials.^{6–8} A promising material, ReB₂, has been synthesized at ambient pressure and was proposed to be superhard with claimed hardness of 36.4–48 GPa,^{8,9} though extensive debate exists.^{10–15} The element to the left and one row above Re in the periodic table is molybdenum (Mo), which also possesses a low compressibility, and the exploration of mechanical properties of its borides is greatly demanded.^{16,17}

In the Mo–B binary phase diagram,¹⁸ Mo borides have five known compositions: Mo₂B, MoB, MoB₂, Mo₂B₅, and MoB₄. It is known that crystal structures are the key for the understanding of mechanical properties of materials. Thus the crystal structures of these five compounds have been extensively studied. Consensus has been reached on that Mo₂B adopts the tetragonal Al₂Cu-type structure (*I4/mcm*, $Z = 4$),¹⁹ while MoB exists in two forms: the low-temperature tetragonal α -MoB (*I4₁/amd*, $Z = 8$)¹⁹ and the high-temperature orthorhombic β -MoB (*Cmcm*, $Z = 4$).¹⁶ However, crystal structures of MoB₂, Mo₂B₅, and MoB₄ are the subject of continuing debate. MoB₂ was first thought to have the hexagonal AlB₂-type structure (*P6₃/mmm*, $Z = 1$),^{16,20} but later argued to adopt the rhombohedral structure (*R3m*, $Z = 6$, hereafter denoted as RS_A).^{17,21} Mo₂B₅ was proposed to have the rhombohedral structure (*R3m*, $Z = 6$, hereafter denoted as RS_B),¹⁹ while recently it was experimentally suggested to be unstable.²¹ MoB₄ was reported to have a hexagonal WB₄-type structure (*P6₃/mmc*, $Z = 4$),²² in which,

however, our calculated phonon spectrum shows some large imaginary frequencies, signaling structural instability. Therefore, in order to better understand these technically important borides, there is a strong request to clarify the ground state structures of MoB₂, Mo₂B₅, and MoB₄. Moreover, it is of fundamental interest to explore other compositions beyond these five in the structure-rich family of the Mo–B system.

In the present work, we report a systematic study on the crystal structures of stoichiometric Mo borides by using the genetic algorithm for crystal structure prediction.^{23–29} We resolve an old controversy about the ground state structures of MoB₂, Mo₂B₅, and MoB₄ and suggest a synthesizable new composition MoB₃ with large calculated hardness 31.8 GPa. We have constructed the phase diagram of the Mo–B system at zero temperature, which could be extremely helpful for future experiments.

Computational Approach

The evolutionary variable-cell simulations for MoB₂, Mo₂B₅, MoB₃, and MoB₄ were performed at ambient pressure with systems containing one to four formula units (fu) in the simulation cell by using the USPEX code.^{23–25} The underlying ab initio calculations were performed with the density functional theory within the generalized gradient approximation (GGA),³⁰ as implemented in the VASP package.³¹ The all-electron projector augmented wave method^{32,33} was adopted with 2s²p¹ and 4p⁶4d⁵5s¹ treated as valence electrons for B and Mo, respectively. The cutoff energy (440 eV) for expansion of the wave function into plane waves was set for all cases, and the special points sampling integration over the Brillouin zone was employed by using the Monkhorst–Pack method³⁴ with a grid of 0.025 Å^{−1} to obtain well converged total energy within 1 meV/fu. The phonon frequencies were calculated by the direct supercell approach, which uses the forces obtained by the Hellmann–Feynman theorem calculated from the optimized supercell.³⁵ The elastic constants were calculated from evaluation of stress tensor generated small strain, and the bulk modulus,

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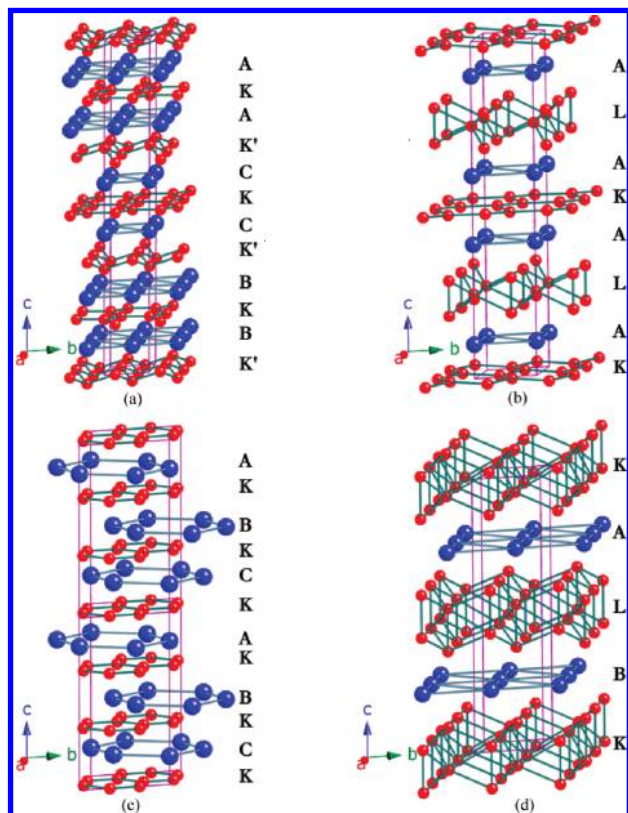


Figure 1. Crystal structures of the predicted Mo borides. The large and small spheres represent Mo and B atoms, respectively. (a) RS_A -type MoB_2 : the lattice parameters are $a = 3.019$ Å and $c = 20.961$ Å with B1 at 6c (0, 0, 0.6817), B2 at 6c (0, 0, 0.1677), and Mo at 6c (0, 0, 0.5758). (b) PS_A -type Mo_2B_5 : the lattice parameters are $a = 3.015$ Å and $c = 4.795$ Å with B1 at 4f (0.3333, 0.6667, 0.3023), B2 at 2b (0, 0, 0.25), and Mo at 4e (0, 0.25, 0.3981). (c) RS_C -type MoB_3 : the lattice parameters are $a = 5.224$ Å and $c = 9.363$ Å with B and Mo atoms occupying 18f (0.6651, 0, 0) and 6c (0, 0, 0.1649) sites, respectively. (d) PS_B -type MoB_4 : the lattice parameters are $a = 2.951$ Å and $c = 10.983$ Å with B1 at 4f (0.3333, 0.6667, 0.5449), B2 at 4f (0.3333, 0.6667, 0.1114), and Mo at 2d (0.6667, 0.3333, 0.25).

shear modulus, Young's modulus, and Poisson's ratio were thus derived from the Voigt–Reuss–Hill approximation.³⁶ Furthermore, the theoretical Vickers hardness was estimated by using the Šimůnek model.¹²

Results and Discussion

For MoB_2 , our variable cell simulation revealed the RS_A structure as the most stable phase as shown in Figure 1a, in excellent agreement with the recent experimental suggestion,^{17,21} but in contrast to the proposed AlB_2 -type structure.^{16,20,37} The RS_A was evidently ~ 153 meV/atom lower in enthalpy than that of the AlB_2 -type structure at ambient pressure. This suggests that MoB_2 is beyond the upper stable limit of hexagonal 4d transition metal diborides, for which the boron-deficient compound MoB_{2-x} ($0 < x < 1$) with AlB_2 -type structure can be easily obtained.^{21,38} In RS_A (as Figure 1a), the stacking sequence of Mo layers is $AABBCCAABBCC...$ along the crystallographic c axis, A, B and C layers are close-packed and layers B and C are shifted by ($a/3$, $2a/3$; here a is the lattice parameter) and ($2a/3$, $a/3$) with reference to A, respectively. The boron layers between the Mo layers form two kinds of hexagonal networks: K and K' . The K type is a planar graphite-like sheet and is sandwiched between AA (or BB or CC) Mo layers, similar to the packing of boron in the AlB_2 -type structure. However, the K' type is more densely puckered sitting in between AB (or BC

or CA) Mo layers. Interestingly, the Mo trigonal pyramids, being centered by B atoms of K' type, are pointing alternately upward and downward. Therefore the RS_A structure in MoB_2 can be described with the stacking order $AKAK'BKBK'CKCK'AKA...$

For Mo_2B_5 , we predicted a hexagonal ($P6_3/mmc$, $Z = 2$, hereafter denoted as PS_A) structure from evolutionary structural search as depicted in Figure 1b. Enthalpy calculations suggest that the predicted PS_A structure is energetically much more (~ 418 meV/atom lower in enthalpy) stable than the previously proposed RS_B structure. The Mo–B–Mo sandwich structural packing is similar to that of the RS_A structure in MoB_2 . The Mo atoms adopt a simple hexagonal arrangement $AAA...$ as shown in Figure 1b, and the distances between two adjacent Mo layers are 4.64 and 3.19 Å, respectively. The B layers also adopt two different types: K and L . K layers possess coplanar hexagonal nets and their B–B distance is 1.74 Å. L layers are more complex and can be viewed as two strongly puckered networks of titled hexagons connected by the common B atoms along the b axis.

Although metal-deficient compound $Mo_{1-x}B_3$ ($0 < x < 1$) has been synthesized,^{38,39} the lower limit compound MoB_3 so far has not been synthesized. We have also performed structural predication for MoB_3 and uncovered an intriguing rhombohedral structure ($R\bar{3}m$, $Z = 6$, hereafter denoted as RS_C), as illustrated in Figure 1c. The RS_C structure is constructed by graphite-like Mo and B layers with a clear sliding between two adjacent Mo layers. However, it should be pointed out that the interlayer distance (1.52 Å) is shorter than the B–B bond lengths (1.73 Å) indicating a strong interlayer interaction. The RS_C structure consists of a fundamental building block: a hexagonal prism with one Mo atom at the center and twelve B atoms at corners, i.e., each Mo atom has twelve nearest neighbors. As a new kind of B-rich composition in the Mo–B system, one might expect excellent mechanical properties.

MoB_4 has the largest B contents and was assumed to be a hexagonal WB_4 -type structure by X-ray powder diffraction.²² However, our phonon calculations for this structure have revealed some large imaginary frequencies, indicating structural instability. We therefore have performed an extensive structural search and predicted a hexagonal structure ($P6_3/mmc$, $Z = 2$ hereafter denoted as PS_B) [Figure 1d] that is energetically much superior to (~ 522 meV/atom lower in enthalpy) the WB_4 -type structure. In this structure, the Mo atoms are packed in a hexagonal close-packed (hcp) structure with the stacking order of $ALBKALBKA...$ along the crystallographic b axis. Here L and K denote the two different types of hexagonal boron networks, which can be viewed as three strongly puckered networks of titled hexagon layers connected by the common B atoms along the b axis. The basic building block of the PS_B structure is composed of two kinds of polyhedrons: the trigonal prism with one Mo at the center bonded with six B atoms at corners and two B tetrahedrons on its two basal faces.

It is known that phonons are a strict measure for structural stability. We thus have carefully performed the phonon calculations for the predicted RS_A , PS_A , RS_C , and PS_B structures for MoB_2 , Mo_2B_5 , MoB_3 , and MoB_4 , respectively, at ambient pressure. There are no imaginary phonons for these structures, supporting their structural stabilities.

Thermodynamic stability of a compound can be described by the knowledge of its ground state energies (enthalpies) which are a good approximation of the phase diagram. To determine the ground states of a system one needs to find, as a function of composition, the structures that have an enthalpy of formation lower than that of any other structures. The formation enthalpy

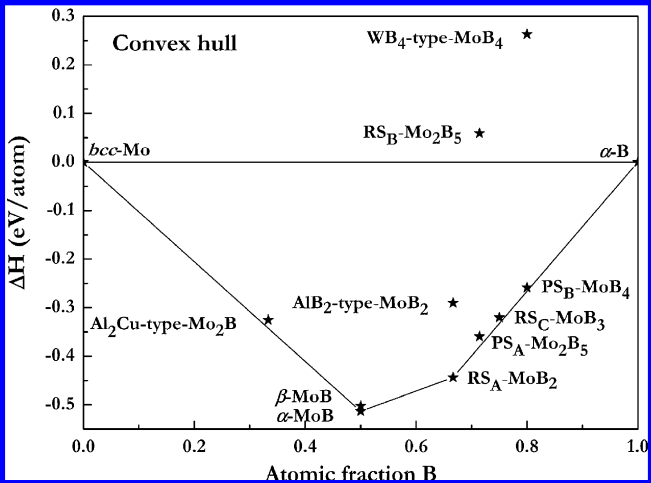


Figure 2. The formation enthalpy vs composition curves for stoichiometric Mo borides with *bcc*-Mo and α -B as reference states. The solid line denotes the ground state convex hull.

vs composition plot, called a convex hull, is the set of lines connecting the lowest energy structures. And any structure whose formation enthalpy lies on the convex hull is deemed stable and synthesizable in principle.^{40,41} Figure 2 presents the calculated convex hull for the studied Mo–B system. It can be clearly seen that the calculated formation enthalpies of Al₂Cu-type Mo₂B and RS_A-type MoB₂ sit nearly right on the curves of convex hull, in excellent agreement with the actual experi-

mental syntheses. These results support the reliability of our predictions and calculations. Strikingly, the predicted RS_C structure for MoB₃ matches evidently with the convex hull and this suggests the possible synthesis of this composition in real experiment. We suppose that the synthetic conditions of MoB₃ may be similar to those observed for the formation of Al₂Cu-type Mo₂B and RS_A-type MoB₂,^{17,18,21} i.e., ambient pressure and above 1400 °C. The earlier proposed RS_B-type Mo₂B₅ and WB₄-type MoB₄ lie well above the convex hull with large positive formation enthalpies, and thus can be ruled out as existing. For monoborides MoB, we found β -MoB is slightly less stable than that of α -MoB. This provides a natural explanation on why β -MoB can be synthesized only at high temperature, while α -MoB is ready for synthesis at low temperature.

As important engineering materials, Table 1 lists the theoretical results on the mechanical properties of the studied borides. It is found that the bulk moduli of these borides are evidently higher than that of pure Mo metal (230 GPa). It was previously suggested that bulk modulus might have a direct correlation with valence electron densities.^{7,8,42,43} However, the Mo borides studied do not follow this tendency and we find that valence electron densities change irregularly with the bulk modulus as shown in Table 1. To our knowledge, these mechanical constants are reported for the first time and are good references for future experiments. In addition, the calculated bulk moduli agree well with those directly obtained from the fitting of the third-order Birch–Murnaghan equation of state⁴⁴ (EOS), which underlines the accuracies of our calculations.

TABLE 1: The Calculated Elastic Constants C_{ij} , Bulk Modulus B , Shear Modulus G , Young’s Modulus E , EOS Fitted Bulk Modulus B_{EOS} , and Hardness H_V (in units of GPa)^c

compd	C_{11}	C_{22}	C_{33}	C_{12}	C_{23}	C_{13}	C_{44}	C_{55}	C_{66}	B	G	E	ν	B_{EOS}	VED	G/B	H_V	H_{Exp}
Mo ₂ B	500		515	202	199		152		151	301	151	389	0.28	309	0.4104	0.50	18.9	24.5 ^a
α -MoB	574		564	203	198		222		242	324	210	519	0.23	324	0.4335	0.61	21.3	23.0 ^a
β -MoB	546	539	572	219	211	194	209	240	212	324	199	496	0.24	324	0.4332	0.65	21.3	24.5 ^a
MoB ₂	609		718	123		152	239			310	238	569	0.19	313	0.4349	0.77	24.4	24.2 ^b
Mo ₂ B ₅	582		679	110		169	230			302	232	554	0.19	305	0.4375	0.77	22.8	
MoB ₃	602		420	106		166	247			276	222	526	0.18	277	0.4066	0.80	31.8	
MoB ₄	505		936	141		103	189			285	210	506	0.20	282	0.4347	0.74	24.8	

^a Reference 16. ^b Reference 17. ^c Also shown are Poisson’s ratio ν , B/G ratio, valence-electron density VED (electrons /Å³), and experimental hardness H_{Exp} (GPa).

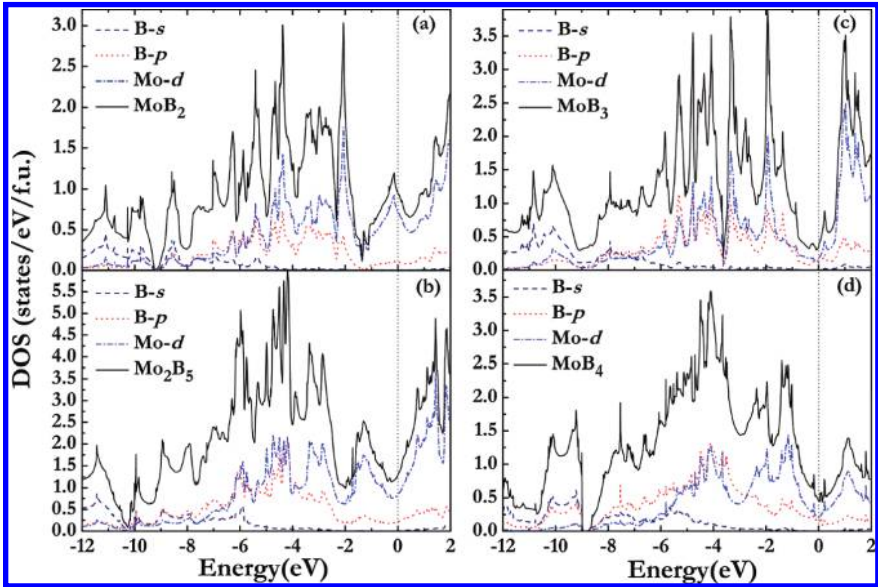


Figure 3. Total and partial densities of states for (a) RS_A-type MoB₂, (b) PS_A-type Mo₂B₅, (c) RS_C-type MoB₃, and (d) PS_B-type MoB₄. The vertical dashed line denotes the Fermi level.

In view of the high bulk and shear moduli of these borides, the hardness calculations are of great interest. The estimated theoretical Vickers hardness H_V of these borides in comparison with experiments is listed in Table 1. Our predicted H_V values for Mo_2B , $\alpha\text{-MoB}$, $\beta\text{-MoB}$, and MoB_2 are in satisfactory agreement with the experimental values. The relative directionality of the bonding in the material also has an important effect on its hardness and can be determined by the G/B ratio.⁴⁵ Among these borides, MoB_3 has the largest G/B ratio of 0.80, which suggests the strongest directional bonding between Mo and B atoms. Indeed, the estimated H_V for MoB_3 is 31.8 GPa, the largest one among the studied borides and beyond the hardness values of $\alpha\text{-SiO}_2$ (30.6 GPa) and $\beta\text{-Si}_3\text{N}_4$ (30.3 GPa).⁴⁶ Future synthesis of this boride is thus of great interest and important for utility of this excellent mechanical property.

To understand the bonding mechanism of these Mo borides on a fundamental level, the total and site projected electronic densities of states (DOS) of the predicted structures were plotted in Figure 3. It is clear that all borides are metal. The typical feature of the total DOS for these compounds is the presence of so-called “pseudogap”, a borderline between the bonding and antibonding orbital.⁴⁷ The major orbital occupancy near Fermi level stems from Mo 4d electrons which are the principal cause for the metallicity. It is noteworthy that for all the compounds, the Mo 4d orbital has a significant hybridization with the B 2p orbital, indicating the strong Mo–B covalent bonding nature. We also performed the Mulliken population analysis of these borides and found a charge transfer from Mo to B, implying an ionic contribution to the Mo–B bonding. We thus conclude that the chemical bonding in these molybdenum borides is a complex mixture of covalent, ionic, and metallic characters. Such a conclusion was also found in other transition metal borides.^{47–49} Clearly, the strong covalent Mo–B bonds are the driving force for the larger bulk modulus of these Mo borides compared to that of parent metal Mo, similar to those in chromium carbides.⁵⁰

Conclusions

In conclusion, we have extensively explored the ground state structures of stoichiometric Mo borides in the Mo–B system by ab initio evolutionary crystal structure prediction. We uncovered three intriguing structures: RS_A , PS_A , and PS_B for MoB_2 , Mo_2B_5 , and MoB_4 , respectively, ruling out the previously proposed AlB_2 -type, RS_B , and WB_4 -type structures. Moreover, the yet synthesized MoB_3 was predicted to take the rhombohedral RS_C structure, which possesses the largest calculated Vickers hardness of 31.8 GPa among these borides and could be possibly synthesized as suggested by the calculation of convex hull. The established enthalpy vs composition phase diagram of the Mo–B binary system is of fundamental interest and important for future experimental syntheses. The calculated phonon dispersion relations show that the predicted structures of MoB_2 , Mo_2B_5 , MoB_3 , and MoB_4 are all dynamically stability. We hope that these calculations will stimulate extensive experimental work on these technologically important molybdenum borides.

Acknowledgment. We are thankful for financial support from the China 973 Program under Grant No. 2005CB724400, the National Natural Science Foundation of China under Grant No. 10874054, the National Fund for Fostering Talents of Basic Science (Grant No. J0730311), and the 2007 Cheung Kong Scholars Programme of China. M.Z. thanks the Baoji University of Arts and Sciences Key Research Grant No. ZK08112.

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