Revealing the Unusual Boron-Pinned Layered Substructure in Superconducting Hard Molybdenum Semiboride

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ABSTRACT: Improving the poor electrical conductivity of hard materials is important, as it will benefit their application. High-hardness metallic Mo₂B was synthesized by high-pressure and high-temperature methods. Temperature-dependent resistivity measurements suggested that Mo₂B has excellent metallic conductivity properties and is a weakly coupled superconductor with a \( T_c \) of 6.0 K. The Vickers hardness of the metal-rich molybdenum semiboride reaches 16.5 GPa, exceeding the hardness of MoB and MoB₂. The results showed that a proper boron concentration can improve the mechanical properties, not necessarily a high boron concentration. First-principles calculations revealed that the pinning effect of light elements is related to hardness. The high hardness of boron-pinned layered Mo₂B demonstrated that the design of high-hardness conductive materials should be based on the structure formed by light elements rather than high-concentration light elements.

INTRODUCTION

In recent years, superconducting materials have been widely studied, and research on materials with high superconducting transition temperatures has further accelerated the application of superconducting materials. Simultaneously, the mechanical properties of superconducting materials have gradually gained popularity. Currently, many superconducting materials are brittle and expensive, which is unsuitable for processing, thus limiting their industrial applications.¹ Therefore, studies on higher-hardness superconducting materials to remove the unfavorable factors have garnered attention.² Research has been conducted on hard superconducting materials originating from the disclosure of the superconductivity properties of boron-doped diamond (BDD) by Japanese scientists.³ BDD has also attracted the interest of scientists in hard superconducting materials.⁴ However, BDD has some defects that make it unsuitable for use in special environments, such as brittleness, poor electrical conductivity, thermal stability, and processability. To address these difficulties, hard transition metal light element (TMLE) compounds with good conductivity have gradually become potential substitutes.⁵ Superconductivity can also be found in many TMLEs.⁶⁻⁷ The superconductivity emanates from the high Debye temperature \( (T_D) \) and electronic density of states (DOS) at the Fermi level \( (N(E_f)) \).¹⁰ These two points are perfectly matched by the TMLEs based on the high valence electron density (VED) of the transition metal (TM) and higher phonon frequencies provided by the light element.² Notably, the higher VED in the TM makes the electron gas show a strong repulsion when compressed by an external force, resulting in a higher bulk modulus to resist compression.¹¹,¹² Consequently, the combination of TM and LE guarantees high compression resistance and shear resistance simultaneously, which is good for excellent hardness.² TMLEs show superconducting properties and ensure proper hardness, thus enabling better understanding of their physical characteristics.

Compared with TM carbides and TM nitrides, TM borides are a better choice among TMLEs because the bonding conditions of boron and TM are milder and it is easy to produce abundant compounds.¹³ As a TM, molybdenum has abundant valence electrons from the d orbital and thus has good electrical conductivity. The valence electrons of Mo are arranged in a half-filled orbital according to the Hund rule,¹⁴ proving that Mo can form abundant valence and stable compounds. According to the hardness model, the compound formed by the two elements with a smaller difference in electronegativity is a potential superhard material, such as a
molybdenum boride system.\textsuperscript{15} In addition, excellent electrical conductivity and superconductivity characteristics exist in the abundant molybdenum boride system. Therefore, molybdenum borides, such as MoB\textsubscript{3}, MoB\textsubscript{2}, and MoB\textsubscript{4} have received considerable attention.\textsuperscript{6,16–18} Transition metal semiborides (TM\textsubscript{2}B) usually employ a tetragonal CuAl\textsubscript{2} type structure (I\textsubscript{4}/mcm), which are considered to be materials with different magnetic states.\textsuperscript{19} This indicates that metal-rich borides also have versatility. Moreover, many of these materials have high hardness, which is better than some boron-rich borides. For example, Cr\textsubscript{3}B is better than CrB\textsubscript{2} in hardness, and Ni\textsubscript{3}B is better than NiB as well.\textsuperscript{20–22} This clarifies that directional covalent bonds can promote an increase in hardness; however, it does not mean that a high concentration of B is necessarily beneficial for hardness. This is also confirmed by the material TaB\textsubscript{2}, which is harder than TaB\textsubscript{3}.\textsuperscript{23} A proper B content may help to increase the hardness and introduce dozens of electrons to promote conductivity.\textsuperscript{24,25} Therefore, adjusting the structure can change the hardness and adjusting the appropriate boron ratio can improve the electronic conductivity. Molybdenum semiboride has a high elastic modulus (310 GPa) from a diamond anvil cell experiment, which is appropriate for hardness. However, it lacks measurement to prove its hardness. In addition, Escamilla et al. found that paramagnetic Mo\textsubscript{2}B has superconducting properties with susceptibility versus temperature curves.\textsuperscript{27} It has been speculated that Mo\textsubscript{2}B may have good conductivity at room temperature, which requires resistivity measurement to verify. Mo\textsubscript{2}B may be a potential material with high hardness and excellent electrical conductivity.

In this work, metallic molybdenum and boron layers are pinned together via covalent and ionic chemical bonds to form dimolybdenum boride synthesized by a high-pressure and high-temperature (HPHT) method. Mechanical and electrical measurements were performed to determine their hardness and resistivity properties, respectively. X-ray photoelectron spectroscopy (XPS) measurements and first-principles calculation methods were combined to explore the chemical bond properties and electronic configuration as well as to show that this unusual structure can adjust its hardness and resistivity.

\section*{RESULTS AND DISCUSSION}

Figure 1 shows the XRD pattern of the Mo\textsubscript{2}B specimen under ambient conditions. This is nearly consistent with the existing ICSD crystal information, which demonstrates that the synthesized sample has a highly crystalline nature and no impurities. The Rietveld refinement fixes the crystal structure of Mo\textsubscript{2}B and clarifies that Mo\textsubscript{2}B adopts a tetragonal CuAl\textsubscript{2} type crystal structure, which is a member of no. 140 space group (I\textsubscript{4}/mcm). The crystal lattice parameters obtained from the Rietveld refinement are listed in Table 1. The crystal structure of Mo\textsubscript{2}B is shown in the top right diagram of Figure 1, where the Mo atomic layers sandwiched between every two B atomic layers along the c-axis are similar to a sandwich structure. The arrangement of contiguous Mo atomic layers was different. The substructures of the two adjacent B layer stacking sequences are regarded as the H layer, and next to the H layer is the K layer. This stack is arranged along the c-axis as “HKHK.” The Mo atoms in the H layer were rotated by 90° to obtain the Mo atoms in the K layers.

| Table 1. Crystal Lattice Parameter and Structure Details of Mo\textsubscript{2}B Gained from the Refined XRD Data |
|----------------|----------------|
| identification code | Mo\textsubscript{2}B |
| radiation | Cu Kα |
| wavelength (Å) | 1.5416 |
| formula weight | 202.69 |
| crystal system | tetragonal |
| space group | I\textsubscript{4}/mcm (no. 140) |
| unit cell dimensions (Å) | \(a = b = 5.5471(6)\), \(c = 4.7404(0)\) |
| density (g/cm\textsuperscript{3}) | 9.152 |
| Θ range (°) | 20–80 |
| residuals | \(R_m = 0.0757\), \(R_w = 0.0945\) |
| \(\chi^2\) | 4.957 |
| atomic position | Wyckoff |
| B1 | 4a |
| Mo1 | 8h |

From SEM images (Figure 2a), it can be observed that stomas and chasms are nearly nonexistent in the sample, and large crystal grains are approximately 1–5 μm in size. A piece of ultrasonically processed sample was observed by the bright-field TEM image in Figure 2b. The edge was selected to perform SAED measurements, which are shown in the bottom right image of Figure 2b. Each diffraction point is calibrated to a different crystal plane through calculations. The distance and angle of the diffraction points are indexed to the I\textsubscript{4}/mcm space group, and further HRTEM images (Figure 3c) indicate the crystal plane. The (110) crystal plane of Mo\textsubscript{2}B is indicated by a lattice distance of 0.389 nm, which confirms the tetragonal phase of Mo\textsubscript{2}B that corresponds well to the refined crystal structure.
To determine its conductivity, low-temperature resistivity measurements were conducted, and the resistivity curve of Mo\(_2\)B from 2 to 300 K is shown in Figure 3a. The curve shows a resistivity of \(3.1516 \times 10^{-7} \ \Omega\cdot\text{m}\) at room temperature, indicating that it is a good conductor, which is significantly better than the resistivity of diamond or cubic boron nitride. It can be favorably compared with many metals and metal alloy conductors, such as platinum metal, manganese copper alloy, and ZrB\(_{12}\). Low-temperature magnetic measurements show the complete diamagnetism of Mo\(_2\)B below the superconducting temperature, which is the typical Meissner effect of superconducting materials. Furthermore, the typical metallic conductivity is shown by the decrease in the resistivity of Mo\(_2\)B as the temperature decreases. Temperature-dependent resistivity shows a sharply descending line at 6.0 K, illustrating that 6.0 K is the superconducting transition temperature of the Mo\(_2\)B specimen. Appropriately, the power law, \(\rho = \rho_0 + aT^n\), was used to fit the electronic resistivity below 100 K, where \(a\) is the electron–electron interaction and \(\rho_0\) is the residual resistivity. The resistivity curve could be commendably depicted by \(\rho_0 = 4.1 \times 10^{-8} \ \Omega\cdot\text{m}\) and \(a = 9.4 \times 10^{-12} \ \Omega\cdot\text{m}/\text{K}^2\). A relatively low residual resistivity (7.12) was calculated. Thus, the impurities or defects have a sensitive impact on the conductivity of the Mo\(_2\)B samples. The resistivity measurements were conducted at 2–10 K using different magnetic fields, respectively. The temperature-dependent resistivity curves for different magnetic fields are shown in Figure 3b. The decrease in \(T_c\) with an increase in the magnetic field shows a typical trend, where superconductivity is restrained by the elevated magnetic field. The WHH fitting curve is shown at the bottom right of Figure 3b, presenting the upper critical magnetic field as 2.35 T. The Ginzburg–Landau (GL) coherence length \(\xi = 11.8 \ \text{nm}\) was calculated using the following formula with the calculated upper critical magnetic field value:

\[
H_{c2} = \frac{\Phi_0}{2\pi\xi^2}
\]

where \(\Phi_0\) is the magnetic flux quantum constant, which is \(2.068 \times 10^{-15} \ \text{T}\cdot\text{m}^2\). The GL coherence length of Mo\(_2\)B is compatible with that of Li\(_3\)Pd\(_3\)B (9.1 nm) and is greater than that of MgCNi\(_3\) (4.6 nm), which indicates that Mo\(_2\)B is a weakly coupled superconducting material.
Microindentation Vickers hardness measurements were conducted to determine the hardness of Mo$_2$B. As shown in Figure 4, when the applied load is 0.49 N, the highest hardness value is 33.5 GPa, which is significantly higher than the hardness of W$_2$B (23.73 GPa), Cr$_2$B (13.2 GPa), and Co$_2$B (11.3 GPa) at 0.49 N with the same structure.\textsuperscript{31} The hardness convergence value is 16.5 GPa at an applied load of 9.8 N, which represents the actual hardness of the Mo$_2$B sample. It is superior to the hardness convergence values of Fe$_2$B and Mn$_2$B (12.4 GPa and 14.1 GPa, respectively) with the same structure,\textsuperscript{32,33} indicating that the hardness of Mo$_2$B in TM$_2$B with an $I4/mcm$ structure is advantageous. Moreover, this hardness convergence value is significantly greater than that of traditional hard steel (approximately 3 GPa).\textsuperscript{34} The hardness is increased by 35% compared to that of orthorhombic molybdenum diboride and 9% compared to that of hexagonal molybdenum diboride. This hardness is equivalent to that of tetragonal molybdenum monoboride with a similar structure.\textsuperscript{11} Its hardness is 32% higher than that of no-pinning-layered MnB$_2$. The results show that materials with a low boron concentration have higher hardness. Therefore, a high concentration of light elements is no longer a necessary condition for designing high-hardness functional materials.

XPS measurements were performed to explore the characteristics and electronic configuration of the bonds. The B 1s spectrum and Mo 3d spectrum of Mo$_2$B are shown in Figure 5. The binding energies of 231.1 and 228.0 eV on the 3d orbital of metallic molybdenum represent the degenerate energy levels of Mo$^{5/2}$ and Mo$^{3/2}$, respectively. This proves that electrons have energy level degeneracy in the 3d orbitals of the Mo atoms. Thus, the electrons of Mo atoms correspond to different states when forming different bonds. The binding energies of 227.5 and 230.6 eV show the change in the valence state of Mo atoms from low to high, which clarifies the process of electron transfer from Mo atoms. The binding energy of boron (187.5 eV) is related to the binding energy to molybdenum boride. It indicates that the interaction between the electrons of Mo and B atoms, which reveals that the bonding process is accompanied by charge transfer between Mo and B. Therefore, the binding energy peaks of B and Mo indicate that the bonding process is partially hybridized by the Mo 3d orbital and the B 1s orbital.

The nature of chemical bonds can be further understood using theoretically calculated electronic configurations, which is beneficial for the analysis of hardness and resistivity. It can be observed in Figure 6 that the conduction band and the valence band overlap at the Fermi level, indicating the metallic properties of Mo$_2$B. In addition, the “flat band-steep band” mode appears in the band structure near the Fermi level, revealing that it can be an ideal superconductor. In Figure 7, the bonding information in Mo$_2$B can be obtained by calculated COHP. In the Mo$_2$B crystal structure, interatomic bonding can be divided into three types of chemical bonds: Mo−B, B−B, and Mo−Mo bonds. As shown in Figure 6, the Mo−Mo bond presents an antibonding state at the Fermi level, with a relatively weak bond. Moreover, the Mo−Mo bonds in the same layer can also be observed in the (110) slice of the electron localization function (ELF) (Figure 8e). The electrons between Mo and Mo mainly exist in the form of free electrons, and part of the ELF value between Mo and B is 0.5, which also confirms the existence of free charge in the ionic bond. The DOS diagram also shows that the Mo 4d orbital is hybridized with the B 2p orbital. Evidently, a good conductivity originates from Mo atoms at the Fermi level. In Figure 7, the left and middle figures show that B−B and Mo−B bonds are bonded at the Fermi level, and they are dominant. Combined with the calculated Bader charge, it can be determined that each B atom receives 0.834 electrons from the surrounding Mo atoms, indicating that the Mo−B bond has an ionic feature. Figure 8d shows the bonding of Mo and B. Combined with a population value of 0.19, it can be explained that the Mo−B bond has ionic characteristics as well as covalent characteristics. Figure 8a shows the three-dimensional (3D) ELF. There is a strong electronic localization of the B atom between the “HKH” layers along the c-axis. Figure 8b shows a slice along the diagonal (110), and Figure 8c presents the front (100) slice. The population value calculation shows that the population value of B−B is 0.32, which expounds that there is a strong directional covalent bond.
electronic localization between the layers of B–B on the c-axis in these situations.

For the calculated elastic constants, it can also be observed that the value of \( C_{33} \) is significantly close to that of \( C_{11} \) and \( C_{22} \), revealing that the strength along the c-axis is almost equivalent to the strength along the a-axis and b-axis (Table 2). Thus, the boron pinning effect significantly increases the strength between the layers. The effect results in the formation of a B–B pinned substructure of “HKH” layers, which is similar to inserting steel bars into Mo–Mo-bonded concrete to achieve a fixed effect. Thus, avoiding slippage between layers greatly improves the hardness. The covalent pinning effect of covalent bonds on the layers increases the strength of the sample. The bulk modulus (302.4 GPa) is consistent with the previous experimental value (310 GPa), indicating that its high hardness is related to its high elastic modulus. The indentation fracture toughness was estimated to be 4.23 MPa·m\(^{0.5}\) by the microindentation method, which is consistent with the toughness characteristics of ceramic materials. The ratio of the bulk modulus and shear modulus can determine the brittleness or ductility of materials. The calculated \( B/G \) (2.005) of Mo\(_2\)B was higher than the threshold (1.75) for the ductile material. In addition, Poisson’s ratio that shows the characteristics of the binding force of Mo\(_2\)B is 0.286, and the lateral expansion after compression is larger. Chen’s hardness model is valid for polycrystalline and metallic materials, which is in line with our polycrystalline and metallic Mo\(_2\)B samples.

The calculated Vickers hardness is found to be 15.8 GPa by Chen’s model. However, Chen’s model is a macroscopic model that does not consider chemical bonds and the crystal structure. Therefore, the hardness value of 16.8 GPa was calculated using the hardness model of Tian, which considers the influence of the crystal structure, chemical bonds, and ionicity on hardness.\(^{36}\) The results obtained using these two models are practically in line with the experimental results. This shows that Mo\(_2\)B has covalent, ionic, and metallic

\[ \text{Figure 6. Electronic band data and DOS for Mo}_2\text{B: electronic band structure data are shown on the left and total and partial DOS for Mo}_2\text{B are shown on the right.} \]

\[ \text{Figure 7. Crystal orbital Hamilton population (COHP) images of Mo}_2\text{B. The dotted lines at zero are the Fermi level.} \]
characteristics, and the covalent pinning effect of boron does exist in this substance.

■ CONCLUSIONS

A single-phase bulk Mo$_2$B sample was synthesized using a high-pressure apparatus by the HPHT method. Electrical measurements show that excellent electrical conductivity was present in the bulk Mo$_2$B sample, and superconductivity was exhibited when the temperature was lower than 6.0 K. The characterization analysis and first-principles calculations illustrate that the excellent electrical conductivity is attributed to the metallic Mo−Mo bond. This signifies that Mo$_2$B is a member of the “covalent metal” family. The excellent Vickers hardness of 16.5 GPa illustrates that Mo$_2$B is a high-hardness superconducting material. Its hardness is superior to that of traditional superconductors and can even be comparable to that of commonly used cemented carbides. The covalent pinning effect plays the role of “reinforced concrete,” proving that the pinned interlayer structure results in high hardness, which is better than the higher B concentration counterparts, MoB and MoB$_2$. This idea provides a possibility for the design of conductive or even superconducting hard materials, which weakens the concentration of light element atoms to strengthen the structure as well as to improve conductivity and hardness. This research has contributed to improving the mechanical properties of superconductors. There is a challenge that higher hardness and superconducting transition temperature coexist. The design of materials with higher hardness and superconducting transition temperature is the aim of the future research work.

■ EXPERIMENTAL SECTION

Molybdenum powder with a purity of 99.99% and boron powder with a purity of 99.95% were prepared as precursor materials. The raw materials were weighed and placed in an agate mortar according to the molar ratio of Mo/B = 2:1, followed by grinding and mixing for more than 2 h. Thereafter, they were processed into a cylindrical sample with a radius of 2 mm and a height of 2.5 mm for the HPHT experiment, which was stuffed into the h-BN capsule. The sample was synthesized using an SPD-6×600 cubic anvil HPHT synthetic device. A pressure of 5.0 GPa and temperature conditions of 2000−2300 K were configured and maintained for 30 min.

The sample was processed into powder, and the crystal structure was determined by X-ray diffraction with Cu Kα radiation ($\lambda = 1.5416$ Å and voltage $V = 40$ kV) using a Rigaku...
D/Max-2500 instrument. An FEI Magellan 400 SEM was used to examine the microstructure and morphology of the bulk samples. A Jeol JEM-2200FS TEM was used to generate SAED patterns and HRTEM images to obtain more crystal information. Four ultrathin copper wires were equally spaced and glued to the cut and polished cuboid sample to measure the electrical resistivity using the four-probe method. Temperature-dependent resistivity (R−T) measurements were performed with commercial Physical Property Measurement System equipment (Quantum Design) between 2 and 300 K. The magnetization properties of Mo2B were measured in the temperature range from 2 to 300 K using a Quantum Design MPMS. An MDY-2 densimeter was used to measure the density of Mo2B at ambient pressure and temperature. The Vickers hardness values corresponding to different load forces (50, 100, 200, 300, 500, and 1000 g) were measured using microindentation hardness equipment (HV-1000ZDT). XPS was performed under ultrahigh vacuum conditions using an ESCALAB 250 X-ray photoelectron spectrophotometer, which has an X-ray source with a magnesium anode.

To further analyze the electronic structure of Mo2B, first-principles calculations were carried out using the Vienna ab initio Simulation Package, which used the Perdew−Burke−Ernzerhof exchange-correlation functional for generalized gradient approximation. A dense Monkhorst−Pack grid with a reciprocal space resolution of \( \pi 	imes 0.03 \) Å\(^{-1}\) and an energy cutoff of 500 eV was chosen to ensure that the total energies would be less than 1 meV/atom. The DOS, ELF, and Bader analysis were performed to confirm the chemical bond characteristics. The mechanical properties were estimated using Voigt−Reuss−Hill approximations, and elastic constants were calculated using the strain−stress method. Chen’s model and Tian’s model were selected to calculate the theoretical Vickers hardness value to verify the experimental hardness value.

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**Notes**

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**REFERENCES**

(1) Bottura, L.; Godeke, A. Superconducting Materials and Conductors: Fabrication and Limiting Parameters. Rev. Accel. Sci. Technol. 2012, 05, 25–50.

(2) Ma, T.; Li, H.; Zheng, X.; Wang, S.; Wang, X.; Zhao, H.; Han, S.; Liu, J.; Zhang, R.; Zhu, P.; Long, Y.; Cheng, J.; Ma, Y.; Zhao, Y.; Jin, C.; Yu, X. Ultrasstrong Boron Frameworks in ZrB\(_2\): A Highway for Electron Conduction. Adv. Mater. 2017, 29, No. 1604003.

(3) Ekinov, E. A.; Sidorov, V. A.; Bauer, E. D.; Mel’nik, N. N.; Curro, N. J.; Thompson, J. D.; Stishov, S. M. Superconductivity in diamond. Nature 2004, 428, 542–545.

(4) Lee, K. W.; Pickett, W. E. Superconductivity in Boron-Doped Diamond. Phys. Rev. Lett. 2004, 93, No. 237003.

(5) Zou, Y.; Qi, X.; Zhang, C.; Ma, S.; Zhang, W.; Li, Y.; Chen, T.; Wang, X.; Chen, Z.; Welch, D.; Zhu, P.; Liu, B.; Li, Q.; Cui, T.; Li, B. Discovery of Superconductivity in Hard Hexagonal e-NaN. Sci. Rep. 2016, 6, No. 22330.

(6) Gu, Q.; Krauss, G.; Steuerer, W. Transition Metal Borides: Superhard versus Ultra-incompressible. Adv. Mater. 2008, 20, 3620–3626.

(7) Hardy, G. F.; Hulm, J. K. The Superconductivity of Some Transition Metal Compounds. Phys. Rev. 1954, 93, 1004–1016.

(8) Wang, S.; Antonio, D.; Yu, X.; Zhang, J.; Cornelius, A. L.; He, D.; Zhao, Y. The Hardest Superconducting Metal Nitride. Sci. Rep. 2015, 5, No. 13733.

(9) Ge, Y.; Ma, S.; Bao, K.; Tao, Q.; Zhao, X.; Feng, X.; Li, L.; Liu, B.; Zhu, P.; Cui, T. Superconductivity with high hardness in Mo\(_2\)C\(_2\). Inorg. Chem. Front. 2019, 6, 1282–1288.

(10) Bauer, E.; Rogl, G.; Chen, X-Q.; Khan, R. T.; Michor, H.; Hilscher, G.; Royanian, E.; Kumagai, K.; Li, D. Z.; Li, Y. Y.; Podloucky, R.; Rogl, P. Unconventional superconducting phase in the weakly correlated noncentrosymmetric Mo\(_2\)Al\(_2\)C Compound. Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 82, No. 064511.

(11) Young, A. F.; Sanloup, C.; Gregoryanz, E.; Scandolo, S.; Hemley, R. J.; Mao, H-K. Synthesis of Novel Transition Metal Nitrides IrN\(_2\) and OsN\(_2\). Phys. Rev. Lett. 2006, 96, No. 155501.

(12) Chung, H.-Y.; Weinberger, M. B.; Levine, J. B.; Kavner, A.; Yang, J.-M.; Tolbert, S. H.; Kaner, R. B. Synthesis of Ultra-Incompressible Superhard Rhenium Diboride at Ambient Pressure. Science 2007, 316, No. 436.
(13) Veprek, S.; Zhang, R. F.; Argon, A. S. Mechanical properties and hardness of boron and boron-rich solids. J. Superhard Mater. 2011, 33, 409–420.

(14) Khomskii, D.; Transition Metal Compounds; Cambridge University Press, 2014.

(15) Li, K.; Wang, X.; Zhang, F.; Xue, D. Electronegativity Identification of Novel Superhard Materials. Phys. Rev. Lett. 2008, 100, No. 235504.

(16) Zhang, M.; Wang, H.; Wang, H.; Cui, T.; Ma, Y. Structural Modifications and Mechanical Properties of Molybdenum Borides from First Principles. J. Phys. Chem. C 2010, 114, 6722–6725.

(17) Liang, Y.; Yuan, X.; Fu, Z.; Li, Y.; Zhong, Z. An unusual variation of stability and hardness in molybdenum borides. Appl. Phys. Lett. 2012, 101, No. 181908.

(18) Tao, Q.; Chen, Y.; Lian, M.; Xu, C.; Li, L.; Feng, X.; Wang, X.; Cui, T.; Zheng, W.; Zhu, P. Modulating Hardness in Molybdenum Monoborides by Adjusting an Array of Boron Zigzag Chains. Chem. Mater. 2019, 31, 200–206.

(19) Zhang, Y.; Liu, D.; Shi, Y.; Sun, Z.; Wu, L.; Gao, Y. Elastic anisotropy and physical properties of semi-transition-metal borides: First-principles calculation. Appl. Phys. Express 2019, 13, No. 015501.

(20) Cheng, S.; Yu, X.; Zhang, J.; Zhang, Y.; Wang, L.; Lin, X.; Li, Y.; Leineweber, K.; Xu, H.; Popov, D.; Park, C.; Yang, W.; He, D.; Zhao, Y. Crystal structures, elastic properties, and hardness of high-pressure synthesized CrB₂ and CrB₄. Phys. J. Superhard Mater. 2014, 36, 279–287.

(21) Zhong, M.-M.; Huang, C.; Tian, C.-L. The structural stabilities, mechanical properties and hardness of chromium tetraboride: Compared with low-B borides. Int. J. Mod. Phys. B 2016, 30, No. 1650201.

(22) Zhang, H. K.; Chen, J. S.; Zhang, L. X.; Yu, Z.; Zhang, P.; Zhang, Y. Z.; Yu, C.; Lu, H. Phase stability, elasticity, hardness and electronic structures for binary M₄B₈ (M = Ni, Cr, Mo, W, n = 23, S, 3, 1, m = 6, 3, 2, 1) borides: A comprehensive study using first principles. Phase Transitions 2020, 93, 158–174.

(23) Ma, S.; Bao, K.; Tao, Q.; Li, L.; Huang, Y.; Huang, X.; Zhao, Y.; Xu, C.; Zhu, P.; Cui, T. Revealing the Unusual Rigid Boron Chain Substructure in Hard and Superconductive Tantalum Monoboride. Chem. – Eur. J. 2019, 25, 5051–5057.

(24) Li, Q.; Zhou, D.; Zheng, W.; Ma, Y.; Chen, C. Anomalous Stress Response of Ultrahard WBₙ Compounds. Phys. Rev. Lett. 2015, 115, No. 185502.

(25) Wang, C. C.; Akbar, S. A.; Chen, W.; Patton, V. D. Electrical properties of high-temperature oxides, borides, carbides, and nitrides. J. Mater. Sci. 1995, 30, 1627–1641.

(26) Sekar, M.; Chandra Shekar, N. V.; Appalakondaiah, S.; Shwetha, G.; Valtheesswaran, G.; Kanchana, V. Structural stability of ultra-incompressible Mo₈B₄: A combined experimental and theoretical study. J. Alloys Compd. 2016, 654, 554–560.

(27) Secundilla, R.; Carvajal, E.; Cruz-Irion, M.; Morales, F.; Huerta, L.; Verdín, E. XPS study of the electronic density of states in the superconducting Mo₈B₄ and Mo₈BC Compounds. J. Mater. Sci. 2016, 51, 6411–6418.

(28) Powell, R.; Tye, R.; Woodman Margaret, J. Thermal conductivities and electrical resistivities of the platinum metals. Platinum Met. Rev. 1962, 6, 138–143.

(29) He, T.; Huang, Q.; Ramirez, A. P.; Wang, Y.; Regan, K. A.; Rogado, N.; Hayward, M. A.; Haas, M. K.; Slusky, J. S.; Inumara, K.; Zandbergen, H. W.; Ong, N. P.; Cava, R. J. Superconductivity in the non-oxide perovskite MgCNi₂. Nature 2001, 411, 54–56.

(30) Badica, P.; Kondo, T.; Kado, T.; Nakamori, Y.; Orimo, S.; Togano, K. Magnetization measurements on L₁₂PdₓB Superconductors. Appl. Phys. Lett. 2004, 85, 4433–4435.

(31) Akgul, G.; Yeung, M. T.; Kaner, R. B. Rediscovers the Crystal Chemistry of Borides. Adv. Mater. 2017, 29, No. 1604506.

(32) Zhao, X.; Li, L.; Bao, K.; Zhu, P.; Tao, Q.; Ma, S.; Liu, B.; Ge, Y.; Li, D.; Cui, T. Synthesis and characterization of a strong ferromagnetic and high hardness intermetallic compound Fe₄B₃. Phys. Chem. Chem. Phys. 2020, 22, 27425–27432.