

New Tungsten Borides, Their Stability and Outstanding Mechanical Properties

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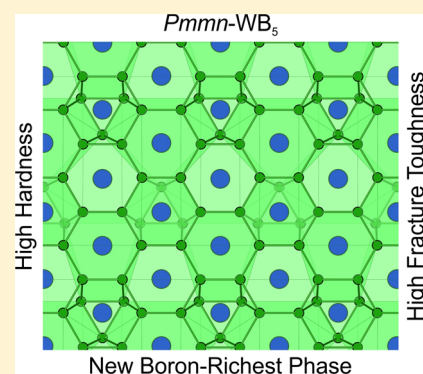
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Supporting Information

ABSTRACT: We predict new tungsten borides, some of which are promising hard materials that are expected to be stable in a wide range of conditions, according to the computed composition–temperature phase diagram. New boron-rich compound WB_5 is predicted to be superhard, with a Vickers hardness of 45 GPa, to possess high fracture toughness of $\sim 4 \text{ MPa}\cdot\text{m}^{0.5}$, and to be thermodynamically stable in a wide range of temperatures at ambient pressure. Temperature dependences of the mechanical properties of the boron-richest WB_3 and WB_5 phases were studied using quasiharmonic and anharmonic approximations. Our results suggest that WB_5 remains a high-performance material even at very high temperatures.



Superhard materials are important for many applications. A material can be called superhard if its Vickers hardness is higher than 40 GPa.^{1–3} Well-known hard and superhard materials include carbon allotropes,^{4–6} with the hardest possible material being diamond, followed by carbon nitrides, cubic boron nitride, boron allotropes, and borides, nitrides, and carbides of transition metals as such chromium,^{7–9} rhenium,¹⁰ molybdenum,^{11,12} tungsten,^{13–18} etc. Some of these carbides (WC) and nitrides (TiN) are widely used in machining tools and mining, e.g., in drilling equipment.

There are five stable tungsten boride phases known from experiments: W_2B ,^{13,19} WB (including α and β phases),^{19,20} WB_2 ,²¹ and WB_4 .^{13,14,16} Numerous theoretical investigations of the stability of new possible phases and their physical properties were published recently.^{10,15,22,23} Wide ranges of homogeneity of W – B phases were mentioned in theoretical and experimental works,^{13,18,24} and at least partly these may be caused by extensive polysomatism (for a discussion of polysomatism, see ref 25). This leads to big difficulties for synthesis of stoichiometric single-crystal phases. Quite often, this leads to inaccurate crystallographic descriptions of synthesized phases by experimental methods, especially given the difficulties in locating positions of light boron atoms using X-ray diffraction. Due to this, the originally claimed W_2B_3 phase¹⁹ was later identified as W_2B_4 with a $P6_3/mmc$ space group.^{24,26} For a discussion, we refer to ref 18. Given these

difficulties, recently developed crystal structure prediction methods can provide invaluable help.

Here we performed an evolutionary variable-composition search for new stable tungsten borides using the USPEX code.^{27–29} All experimentally synthesized phases were found during the search, together with three new stable phases (Cm - W_4B_3 , $C2$ - W_6B_5 , Pm - W_4B_7 , $Pmmn$ - WB_5). Thermodynamic stability at different temperatures was examined, Vickers hardness and fracture toughness were evaluated using recently developed models, and temperature-dependent elastic properties were studied for WB_3 and WB_5 ; these are of special interest, being the boron-richest tungsten borides.

Stable phases in the W – B system were predicted using a first-principles variable-composition evolutionary algorithm (EA) as implemented in the USPEX code.^{27–29} For each promising composition, fixed-composition searches were carried out. Here, evolutionary searches were combined with structure relaxations and total energy calculations using density functional theory (DFT)^{30,31} within the generalized gradient approximation (Perdew–Burke–Ernzerhof functional)³² and the projector augmented wave method^{33,34} as implemented in

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the VASP^{35–37} package. We used the plane-wave energy cutoff of 500 eV, and Γ -centered k -meshes of $2\pi \times 0.05 \text{ \AA}^{-1}$ resolution for Brillouin zone sampling, ensuring excellent convergence of total energies. During structure search, the first generation (120 structures) was produced randomly with up to 16 atoms (variable-composition search) and 36 atoms (fixed-composition search) in the primitive unit cell, and succeeding generations were obtained by applying heredity (40%), softmutation (20%), and transmutation (20%) operators, respectively, and 20 and 15% of each generation was produced using symmetric and topological random generators, respectively.

For the predicted crystal structures, we performed high-quality calculations of their physical properties. Crystal structures were relaxed until the maximum net force on atoms became less than 0.01 eV/Å. The Monkhorst–Pack scheme³⁸ was used to sample the Brillouin zone, using $10 \times 10 \times 10$ ($I4/m-W_2B$), $8 \times 8 \times 8$ ($Cm-W_4B_3$), $8 \times 8 \times 8$ ($C2-W_6B_5$), $8 \times 8 \times 8$ ($Cm-W_8B_7$), $10 \times 10 \times 8$ ($P4_21m-WB$), $10 \times 10 \times 4$ ($I4_1/amd-WB$), $6 \times 10 \times 4$ ($Cmcm-WB$), $10 \times 6 \times 4$ ($Pm-W_4B_7$), $8 \times 8 \times 4$ ($R\bar{3}m-WB_2$), $8 \times 8 \times 8$ ($P\bar{6}m2-WB_3$), $8 \times 8 \times 8$ ($P6_3/mmc-WB_4$), and $8 \times 8 \times 8$ ($Pmmn-WB_5$).

The elastic tensor was calculated using the stress–strain relations:

$$C_{ij} = \frac{\partial \sigma_i}{\partial \eta_j} \quad (1)$$

where σ_i is the i th component of the stress tensor and η_j is the j th component of the strain tensor. Equation 1 can be rewritten in terms of the Helmholtz free energy F as

$$C_{ij} = \frac{1}{V} \frac{\partial^2 F}{\partial \eta_i \partial \eta_j} \quad (2)$$

We compute the Helmholtz free energy as

$$F(T) = E_0(V) + F_{\text{vib}}(V, T) \quad (3)$$

where E_0 is the total energy from the DFT calculations and F_{vib} is vibrational Helmholtz free energy calculated from the following relation in the quasiharmonic approximation³⁹

$$F_{\text{vib}}(V, T) = k_B T \int_{\Omega} g(\omega(V)) \ln \left[1 - \exp \left(-\frac{\hbar \omega(V)}{k_B T} \right) \right] d\omega + \frac{1}{2} \int g(\omega(V)) \hbar \omega d\omega \quad (4)$$

Here $g(\omega(V))$ is the phonon density of states at the given volume, calculated using the finite displacements method as implemented in PHONOPY,^{40,41} with forces computed by VASP.^{35–37}

The high melting temperature (>3000 K)⁴² of tungsten and tungsten-based materials allows the use of these materials at extremely high temperatures, where the anharmonic part of the free energy is important³⁹

$$F(T) = E_0(V) + F_{\text{vib}}(V, T) + F_A(V, T) \quad (5)$$

Here we determined the anharmonic contribution as follows⁴³

$$F_A(V, T) \approx A_2 T^2 \quad (6)$$

where, empirically⁴³

$$A_2 = \frac{3k_B}{\Theta_H} (0.0078 \langle \gamma \rangle - 0.0154) \quad (7)$$

Here Θ_H is the high-temperature harmonic Debye temperature defined as³⁹

$$\Theta_H = \frac{\hbar}{k_B} \left(\frac{5}{3} \langle \omega^2 \rangle \right)^{1/2} \quad (8)$$

where $\langle \omega^2 \rangle$ is the average squared harmonic phonon frequency. In Debye theory, the average Grüneisen parameter $\langle \gamma \rangle$ can be calculated as

$$\langle \gamma \rangle = -\frac{d \ln(\Theta_H)}{d \ln(V)} \quad (9)$$

Using eqs 2 and 5 the temperature-dependent elastic tensor can be calculated as

$$C_{ij}(T) = \frac{1}{V(T)} \frac{\partial^2 F(T)}{\partial \eta_i \partial \eta_j} \quad (10)$$

The Grüneisen parameter can be calculated from the dependence of phonon frequencies on applied pressure using the following relation⁴⁴

$$\langle \gamma \rangle = \langle \gamma_i \rangle = \left\langle \frac{B_0}{\omega_i} \frac{d\omega_i}{dp} \right\rangle \quad (11)$$

where ω_i is the phonon frequency of the i th mode, B_0 is the bulk modulus, p is pressure.

Both eqs 9 and 11 give similar values of the Grüneisen parameter within ± 0.08 . For example, for pure tungsten, we obtain the average Grüneisen parameters of 1.755 (eq 9) and 1.68 (eq 11), both of which are in good agreement with the experimental value of 1.7 from ref 42. Grüneisen parameters calculated for h -BN (0.09) and c -BN (1.02) are also in agreement with reference data (0.1 and 0.95, respectively).³⁹

The Vickers hardness was estimated according to Chen's model⁴⁵ (H_V)

$$H_V = 2 \cdot (k^2 \cdot G)^{0.585} - 3 \quad (12)$$

where k is the Pugh ratio ($k = G/B$), G is the shear modulus, and B is the bulk modulus. The bulk and shear moduli were calculated in GPa via Voigt–Reuss–Hill averaging.^{46,47} Test calculations of the Vickers hardness for a number of materials using Chen's model agree well with the reference experimental data: diamond 98 (~ 96 ⁴⁸), TiN 22.6 (20.5⁴⁹), c -BN 56.9 (~ 55 ^{1,50}).

Fracture toughness was calculated using an empirical model from ref 51, where the fracture toughness can be estimated as follows

$$K_{IC} = \alpha \cdot V^{1/6} \cdot G \cdot \left(\frac{B}{G} \right)^{1/2} \quad (13)$$

where α is an enhancement factor accounting for the degree of metallicity, V is the volume per atom in m^3 , and G and B are shear and bulk moduli in MPa, respectively.⁵¹ For the case of insulators and semiconductors and also transition metal carbides, nitrides, and borides, $\alpha = 1$.⁵¹ The calculated values of the fracture toughness of diamond, WC, and c -BN are within the range of experimentally measured values and equal to 6.33 $\text{MPa} \cdot \text{m}^{0.5}$ (4–7 $\text{MPa} \cdot \text{m}^{0.5}$ ^{52–54}) for diamond, 5.37 $\text{MPa} \cdot \text{m}^{0.5}$

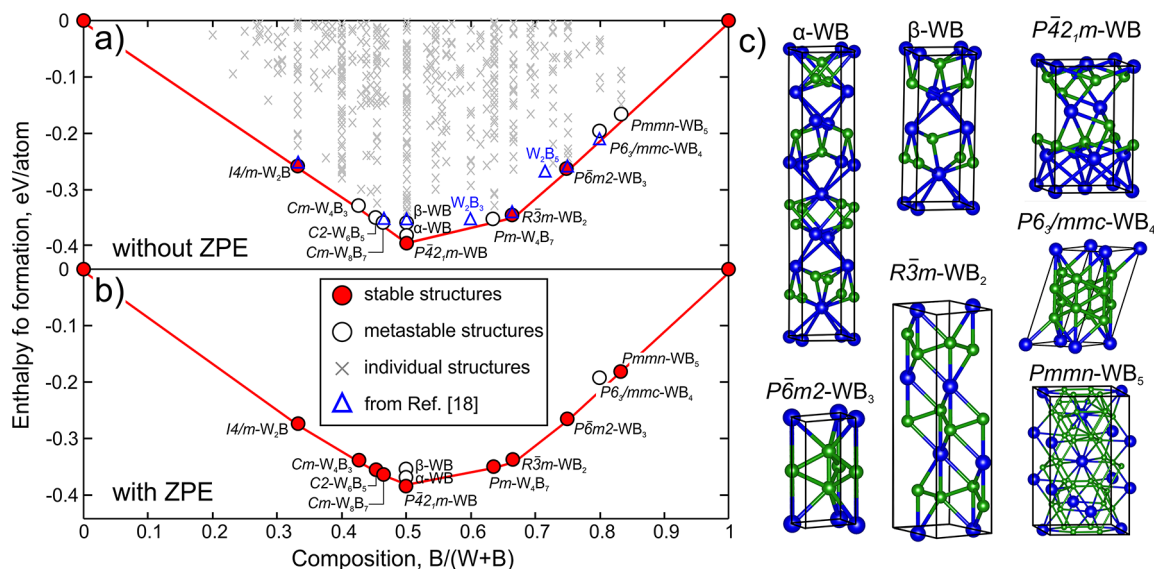


Figure 1. Thermodynamic convex hull of the W–B system (a) without and (b) with zero-point energy (ZPE) contribution. Filled circles are stable phases, open circles are metastable at 0 K, and open triangles are phases from ref 18. (c) Crystal structures of α -WB, β -WB, $P\bar{4}2_1m$ -WB, and boron-rich $R\bar{3}m$ -WB₂, $P\bar{6}m2$ -WB₃, $P6_3/mmc$ -WB₄, and $Pm\bar{m}n$ -WB₅ phases. Crystal structures of the predicted phases were visualized using VESTA.⁶⁰

Table 1. Mechanical Properties of Predicted W–B Phases at 0 K^a

phase	B	G	H_V	K_{IC}	phase	B	G	H_V	K_{IC}
$I4/m-W_2B$	337	153	12.1	3.45	WB ₂ (exp) ¹⁴	372		27.7	
W ₂ B ¹⁸	338	155	12.4		WB ₂ (exp) ²⁰			21.3	
$Cm-W_4B_3$	335	206	22.7	3.95	$P\bar{6}m2$ -WB ₃	308	226	30.1	3.79
$C2-W_6B_5$	337	203	21.7	3.91	WB ₃ ⁶¹	294	240	35.9	
$Cm-W_8B_7$	338	195	19.9	3.82	WB ₃ ⁶²	295	252	43.1	
α -WB	349	192	18.5	3.82	$P6_3/mmc$ -WB ₄	325	212	24.8	3.73
α -WB ¹⁸	352	199	19.8		WB ₄ ¹⁸	299	217	29.0	
α -WB (exp) ²⁰			25.3		WB ₄ ⁶²	300	102	16.8	
β -WB	300	192	22.7	3.55	WB ₄ (exp) ¹⁶	339		28.1–43.3	
β -WB ¹⁸	351	190	18		WB ₄ (exp) ¹⁴	304		31.8	
$P\bar{4}2_1m$ -WB	314	245	34.3	4.12	$Pm\bar{m}n$ -WB ₅	287	266	45.1	4.01
$Pm-W_4B_7$	325	250	34.3	4.16	$P\bar{6}m2$ -WB	383	292	29.6	5.37
$R\bar{3}m$ -WB ₂	313	248	35.8	4.06	WC ⁶³	383	291		
WB ₂ ¹⁸	318	266	39.7		WC (exp) ⁶⁴	439	302	30	
WB ₂ ⁶¹	321	274	41.3						

^aThe bulk (B) and shear (G) moduli and Vickers hardness (H_V) are in GPa, and the fracture toughness (K_{IC}) is in MPa·m^{0.5}. Experimental values are at room temperature.

(5–8 MPa·m^{0.555,56}) for WC, 3.3 MPa·m^{0.5} (4–5 MPa·m^{0.555}) for TiN, and 5.41 MPa·m^{0.5} (2–5 MPa·m^{0.550,54}) for c -BN.

With USPEX, we calculated the convex hull diagram of the W–B system (see Figure 1a), which displays all experimentally known phases, as well as several new phases ($Cm-W_4B_3$, $C2-W_6B_5$, $Pm-W_4B_7$, and $Pm\bar{m}n$ -WB₅). By definition, a thermodynamically stable phase has lower Gibbs free energy (or, at zero Kelvin, lower enthalpy) than any phase or phase assembly of the same composition. Phases that are located on the convex hull are thus by definition stable.

Let us first consider the case of $T = 0$ K. For WB, we found both known WB phases, namely, α and β , with a difference of enthalpy of about 15 meV/atom. Their crystal structures are in good agreement with experiment and so is the enthalpy difference, which is 13 meV/atom in experiment.⁵⁷ Moreover at zero Kelvin, the new $P\bar{4}2_1m$ -WB was found to be thermodynamically more stable than α -WB, with an enthalpy difference of 12 meV/atom. Some of the phases predicted in ref

18 are found to be metastable (W₂B₃, W₂B₅, WB₄). We also predicted several phases with W:B ratios (4:3, 6:5, and 8:7) close to WB, while W₄B₇ is stoichiometrically close to WB₂. We find strong similarities between crystal structures of $Cm-W_4B_3$, $C2-W_6B_5$, $Cm-W_8B_7$, and β -WB (see Figure S2a in the Supporting Information). There is an open question about the existence of boron-rich tungsten borides WB _{x} with $x > 3$. Previously, WB₃ and WB₄ were predicted.^{18,58} Here we predict that WB₄ found in ref 18 is metastable, being above the convex hull by 37 meV/atom if one neglects zero-point energy, and remains metastable when the zero-point energy is taken into account (see Figure 1a). Another new boron-rich phase, $Pm\bar{m}n$ -WB₅, seen both in our present calculations and in the calculations of the Guangzhou group,⁵⁹ was found to be metastable by 15 meV/atom (see Figure 1a) if one neglects the zero-point energy but becomes stable when the zero-point energy is taken into account (see Figure 1b).

Crystal structures of α -WB, β -WB, $P\bar{4}2_1m$ -WB, WB₂, WB₃, WB₄, and WB₅ are shown in Figure 1c. Structurally, α - and β -WB differ by the relative location of the layers. α -WB is made of AB-stacked WB layers, every other layer being rotated by 90°, while β -WB has AA' stacking, where every other layer is shifted by half of the lattice parameter a (see Figure S1 in the Supporting Information). In both phases, each W is coordinated by 7 B atoms and 10 W atoms, with a total coordination number of 17. New $P\bar{4}2_1m$ -WB has such layers as well, but each layer here is obtained by fusing of A and B layers of α -WB (see Figure S1 in the Supporting Information). Each layer consists of two tungsten atoms, one of which is coordinated by 8 B atoms and 8 W atoms, while the second one is coordinated by 6 B atoms and 10 W atoms. Crystal structures of all predicted phases are shown in Table S1 (see the Supporting Information). WB₃ has a hexagonal unit cell with one tungsten atom coordinated by eight boron atoms and six tungsten atoms. WB₅ has a very unusual structure, made of edge- and face-sharing WB₁₂ hexagonal prisms (i.e., each W atom is coordinated by 12 B atoms) and open B₁₅ clusters linked by B–B bonds into a 3D-structure (see Figure S3 in the Supporting Information for details).

Next we studied the mechanical properties of all predicted phases. We calculated the elastic constants tensor from which the hardness and fracture toughness were computed (see Table S2 in the Supporting Information). It is important to note that β -WB-based phases (Cm -W₄B₃, $C2$ -W₆B₅, and Cm -W₈B₇) display similar to β -WB elastic properties and hardness. This comes from the structural similarity of these phases (see Figure S2 in the Supporting Information). Boron-rich phases WB₂ and WB₃ have high hardness of 40 and 30 GPa, respectively, both of which are in good agreement with experimental data (see Table 1). The highest Vickers hardness is for WB₅ and equals 45.1 GPa, i.e., this is a superhard material.

Comparison of the mechanical properties of the predicted phases with WC (the most used hard phase) indicates that most of the new W–B phases surpass WC by Vickers hardness, while many have comparable fracture toughness. The unique combination of Vickers hardness and fracture toughness makes tungsten borides promising materials for widespread use.

The most interesting material for different industrial applications is superhard WB₅, which has an extremely high Vickers hardness along with good fracture toughness (see Table 1). In this case, addition of the metal atom does not lead to reduction of the hardness (in comparison with pure boron) but significantly increases fracture toughness.

On the basis of the obtained data, we constructed an Ashby plot of the Vickers hardness vs fracture toughness, which allows one to clearly find materials with an optimal combination of these properties (see Figure 2). Predicted phases are denoted by red circles, while blue ones are known superhard materials (diamond, α -B, c -BN) and hard alloys (WC, TiN). All predicted phases were divided into two groups; see Figure 2. It can be clearly seen that all materials that are in the red region have a Vickers hardness higher than that for WC (horizontal line) together with high fracture toughness comparable to that of WC and TiN. Phases in the blue region have Vickers hardness < 30 GPa and lower fracture toughness and will be of limited practical use.

The ideal tensile and shear strengths have also been proposed as a measure of hardness.^{65,66} We simulated the stress–strain curves for WB₃ and WB₅ (Figure 3). The lattice vectors of both phases were incrementally deformed in the

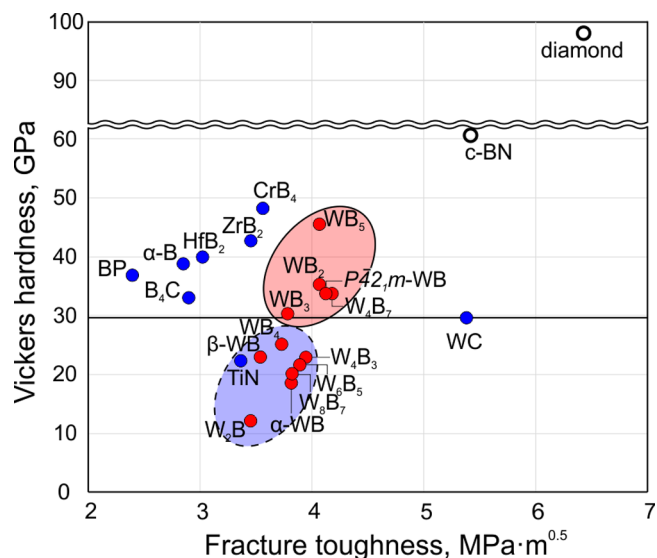


Figure 2. Ashby plot of Vickers hardness vs fracture toughness for predicted W–B phases (red points) compared with those of known superhard materials (blue points). The horizontal line is the value of the Vickers hardness of WC.

direction of applied strain. At each step, the structure was relaxed such that all components of the Hellmann–Feynman stress tensor orthogonal to the applied stress were less than 0.01 GPa. The minimum tensile and shear stresses in the stress–strain curves are taken as the ideal tensile and shear strength.

For tension of WB₃ (see Figure 3a), stress increases steeply with an ideal strength 52 GPa. Considering shear deformations of WB₃, the ideal shear strength corresponds to (1 $\bar{1}0$)[001] deformation with an ideal strength of 28 GPa (see Figure 3a). The ideal tensile strength of WB₅ was found along the [011] direction with a value of 54 GPa (see Figure 3b). Shear deformation shows lower values of ideal shear strength with an average value of 33 GPa (see Figure 3c). The minimum tensile and shear ideal strengths of WB₃ and WB₅ are thus 28 and 33 GPa, respectively.

As was mentioned above, WB₅ is thermodynamically stable at 0 K and zero pressure and is stabilized by the zero-point energy—a subtle effect; therefore, we performed a detailed study of the thermal stability of all predicted W–B phases along with WB₅ to see if this phase is stabilized by temperature or pressure.

First, we checked the effect of pressure and found that it destabilizes WB₅. A detailed study of the effect of pressure on the stability of tungsten borides will be reported elsewhere.⁵⁹ Then, we turned to investigating the effect of temperature by calculating the Gibbs free energy of each phase using both quasiharmonic (QHA) and anharmonic (AHA) approximations (see eqs 3 and 5). Gibbs free energies were calculated in the temperature range from 0 to 2500 K (melting temperatures of α -B and W are about 2400 and 3200 K,⁶⁷ respectively) with an increment of 100 K. It is generally accepted that the stable phase of boron at ambient pressure is the β -phase, but its structure is disordered and difficult to model; here we use α -B, which has practically indistinguishable energy.^{68,69} As a result, we constructed phase diagrams in the composition–temperature space; see Figure 4. Hitherto unobserved $P\bar{4}2_1m$ -WB turns out to be thermodynamically stable only at low temperatures from 0 to 300 K both within QHA and AHA

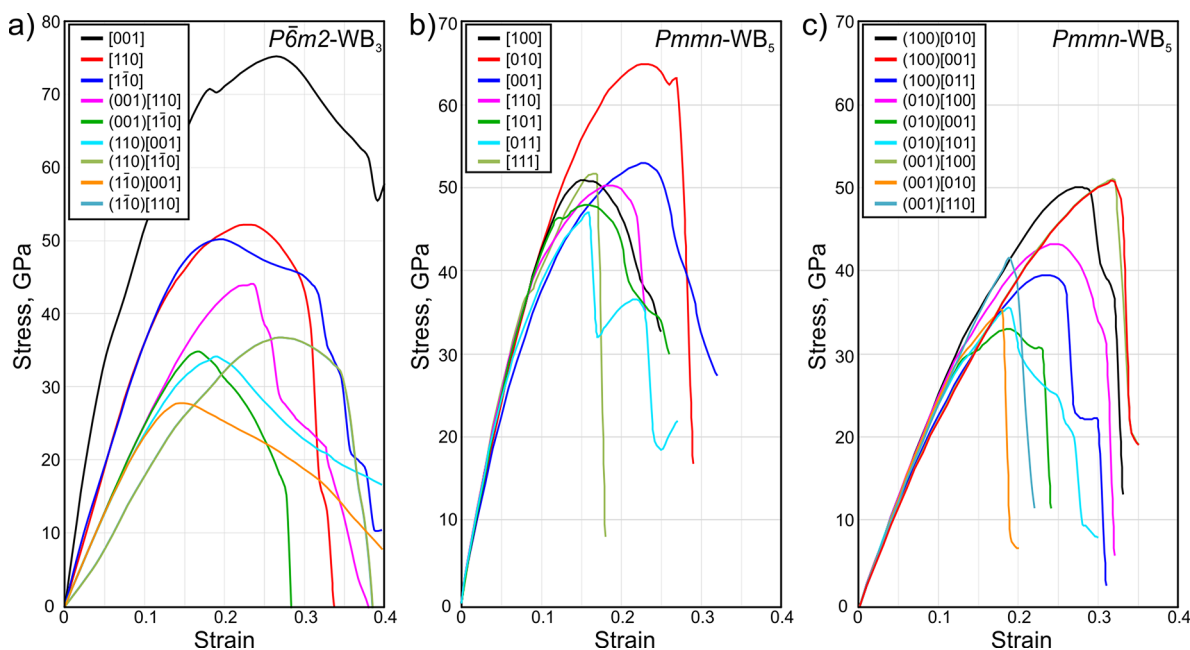


Figure 3. Ideal stress–strain curves of (a) $P\bar{6}m2$ -WB₃ and (b,c) $Pmmn$ -WB₅ along high-symmetry tensile and shear deformation directions.

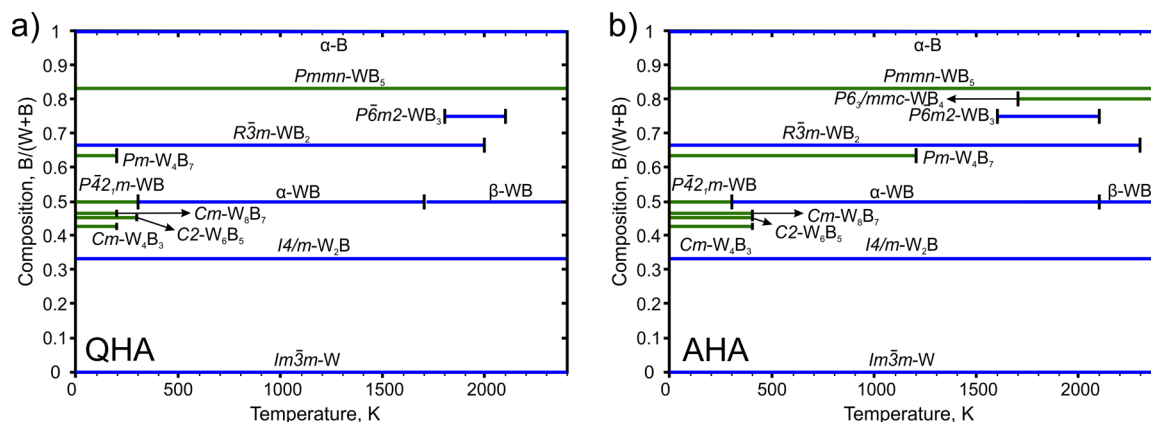


Figure 4. Temperature–composition phase diagrams calculated using (a) QHA and (b) AHA. New phases are shown by green color. These are simplified phase diagrams, not considering configurational entropy, finite homogeneity regions, and melting (congruent, incongruent, eutectic).

(see Figure 4). At temperatures above 300 K, α -WB is more stable. This low-temperature phase could not be observed in experiments because synthesis of WB is done at high temperatures (where α -B or β -B are stable), and at conditions where $P\bar{4}2_1m$ -WB is stable ($T < 300$ K), kinetics are prohibitively slow for the transition to take place. One can see from Figure 4a that within the QHA, α -WB transforms to β -WB at $T \approx 1700$ K, while within the AHA this transition occurs at 2100 K (see Figure 4b), which perfectly agrees with the experimental value of the transition temperature of 2110 K.⁵⁷

Phases related to β -WB (Cm -W₄B₃, $C2$ -W₆B₅, and Cm -W₈B₇) within the QHA are found to be stable only at temperatures below 300 K (see Figure 4a). AHA extends their temperature ranges of stability to 400 K (see Figure 4b). Similar stabilization due to anharmonicity is found for W₄B₇, which is a defective relative to $R\bar{3}m$ -WB₂. Configurational entropy will further stabilize defective versions of WB (W₄B₃, W₆B₅, and W₈B₇) and WB₂ (W₄B₇) and merge WB_{1-x} and WB_{2-x} into just two phases, and it is possible that samples of WB and WB₂ actually contain a significant concentration of boron vacancies.

WB₃ shows a very narrow stability region within QHA, from 1800 to 2100 K (1600–2100 K in AHA). Neither QHA nor AHA show the appearance of WB₄ at any temperature. Newly predicted WB₅ is thermodynamically stable in the whole temperature range studied here, i.e., this phase is stable at least up to 2400 K (see Figure 4), implying that WB₅ can be synthesized. This also allows the use of WB₅ at very high temperatures, while WB₂ and WB₃ become unstable at such high temperatures (~ 2000 K).

In addition to thermodynamic stability, an important issue related to temperature is the temperature dependence of the mechanical properties of hard W–B phases. In Figure 5a,b, the temperature dependences of the elastic constants C_{ij} for WB₃ and WB₅ (within both QHA and AHA) are shown. Here one can see that all elastic constants depend on temperature nonlinearly. The same behavior was observed previously for Al₂O₃,⁷⁰ Mo, and W.⁴² At 2000 K, WB₅ is predicted to have a hardness of 27 GPa, still a very high value.

In conclusion, we studied in detail the W–B system using global optimization algorithm USPEX and predicted new interesting materials. We found Cm -W₄B₃, $C2$ -W₆B₅, Pm -W₄B₇,

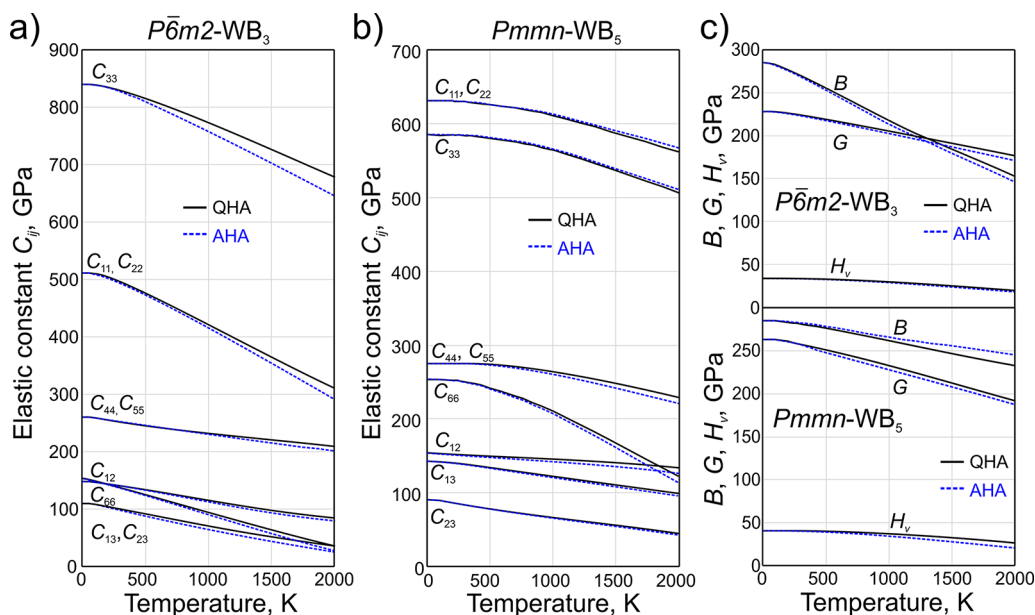


Figure 5. Temperature dependence of (a,b) C_{ij} and (c) bulk, shear moduli and the Vickers hardness of WB_3 and WB_5 . Data calculated by QHA and AHA are shown by solid black and dotted blue lines, respectively.

and $Pmmn-WB_5$ phases. Among the predicted new phases, WB_5 is superhard and has a Vickers hardness of 45 GPa and a very high fracture toughness ($4 \text{ MPa} \times \text{m}^{0.5}$). In addition to its phenomenal mechanical properties, WB_5 is thermodynamically stable at ambient pressure at all temperatures up to at least 2400 K. Even though the mechanical properties of WB_5 are predicted to naturally decrease with temperature, WB_5 will possess impressive mechanical properties even at very high temperatures. All obtained data allow one to consider WB_5 as a promising material for applications in different fields of industry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.8b01262](https://doi.org/10.1021/acs.jpclett.8b01262).

Crystal structure information of predicted phases, elastic constant tensors, and acoustic velocities (PDF)

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Notes

The authors declare no competing financial interest.

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