Stable and hard hafnium borides: A first-principles study

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ABSTRACT
We investigate the stability of hafnium borides at zero pressure via the evolutionary crystal structure prediction and first-principles calculations. Our results indicate that the well-known \( P_6/mmm \)-HfB\(_2\) is the only thermodynamically stable phase at zero temperature and pressure, and two more phases (\( Pnma \)-HfB and \( Fm\overline{3}m \)-HfB\(_{12}\)) become thermodynamically stable at higher temperatures. We compute the mechanical properties including bulk, shear and Young’s moduli, Vickers hardness, and fracture toughness for all stable and metastable hafnium borides (\( \sim 30 \) phases) and then study in detail the effect of boron concentration and topology of B-sublattice on their mechanical properties. We show that not only the concentration of boron, but also the topology of the boron sublattice is important for the mechanical properties of hafnium borides. Among the predicted stable and low-energy metastable hafnium borides, the highest possible hardness is exhibited by \( P6/mmm \)-HfB\(_2\) with graphenelike boron sheets and by phases with 3D boron networks and high B/Hf ratios (e.g., \( Pnm\overline{m} \)-HfB\(_3\) and \( Fm3m \)-HfB\(_{12}\)).

I. INTRODUCTION
Transition metal borides (TMBs) are important materials for many practical applications due to their high strength and hardness, 1–3 high melting temperature, 4,5 good corrosion and oxidation resistance, 4,6 electrical conductivity, 7 and other properties. Like most TMBs, they share common features like a facile synthesis at ambient pressure, diverse stoichiometries, and tunable properties changing with the B/TM ratio. Motivated by these features, many studies have been performed to discover/design novel TMBs with superior properties (e.g., potentially superhard CrB\(_4\) 8 and W\(_4\)B\(_6\) 9 high strength highly conductive ZrB\(_2\) 10 etc.). Among TMBs, hafnium borides are known as ultrahigh-temperature structural ceramics. 11–13 Experimentally, besides the well-known \( P6/mmm \)-HfB\(_2\), two more Hf\(_x\)B\(_y\) phases (\( Pnma \)-HfB and \( Fm\overline{3}m \)-HfB\(_{12}\)) have been synthesized at high temperatures. Several experimental and theoretical studies argued that HfB has
the $Fm\bar{3}m$ space group.$^{11,12}$ However, there are theoretical studies where the correct symmetry was determined as $Pnma$.$^{15-17}$ Theoretically, several other Hf$_x$B$_y$ structures, such as $I4/mcm$-Hf$_x$B$_y$,$^{12}$ $Cmcm$-Hf$_2$B$^6$,$^{13}$ $P6m2$-Hf$_y$B$^6$,$^{19}$ $R3m$-Hf$_2$B$^6$,$^{19}$ $Immm$-Hf$_2$B$^6$,$^{20}$ $C2/m$-Hf$_2$B$_6$,$^{31}$ and $Cmcm$-Hf$_5$B$_{12}$,$^{22,23}$ have been studied. Although the structures of hafnium borides have been discussed for many decades, a comprehensive study of their thermodynamic stability is still lacking.

The mechanical properties of hafnium borides have been widely investigated.$^{15,19,23,24,25}$ Hafnium borides with high B contents (HfB$_2$, HfB$_3$, HfB$_4$, and HfB$_5$) were found to have high strength and hardness.$^{22}$ HfB$_3$, HfB$_4$, and HfB$_5$ were suggested to be potentially superhard materials as indicated by their very high theoretical hardness (more than 40 GPa). We note that boron content is not the only factor that determines the mechanical properties of TMBs: boron motifs (ranging from 0D isolated boron atoms and boron dimers to 1D boron chains and ribbons and to 2D/3D boron frameworks) in TMBs also affect the mechanical properties drastically.$^{26-28}$

In the present study, we use the variable-composition evolutionary crystal structure prediction algorithm USPEX$^{29-31}$ to explore the thermodynamically stable and metastable hafnium borides. Diverse stoichiometries (Hf$_x$B$_y$, Hf$_2$B$_y$, Hf$_3$B$_y$, Hf$_4$B$_y$, Hf$_5$B$_y$, Hf$_6$B$_y$, HfB$_3$, HfB$_4$, HfB$_5$, HfB$_6$, and HfB$_{12}$) and many types of boron configurations (zigzag chain, ribbon, graphene-like sheet, double layer, triple layer, and 3D framework) were found. We have updated the ground-state structures for Hf$_2$B$_3$ and HfB$_4$ and several newly predicted hafnium borides (Hf$_4$B$_2$, Hf$_6$B$_2$, Hf$_7$B$_6$, HfB$_5$, and HfB$_6$). Based on ∼30 stable and low-energy metastable hafnium borides, we defined the correlation between B content, configuration of the B-sublattice, and computed mechanical properties. We show that not only the concentration of boron but also the topology of the boron sublattice has a strong effect on the mechanical properties of hafnium borides.

II. COMPUTATIONAL METHODS

To explore stable and metastable hafnium borides, we performed a variable-composition evolutionary crystal structure prediction for the Hf–B system. The maximum number of atoms in a primitive cell of the generated Hf$_x$B$_y$ structures was set at 28. During the structure search, the first generation (120 structures) was produced randomly, while the succeeding generations were obtained using heredity (40%), softmutation (20%), and transmutation (20%) operators, and the remaining 20% of each generation was randomly produced.

The VASP code$^{32,33}$ was used for structure relaxations and total energy calculations in the framework of the density functional theory.$^{34}$ The Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE$^{35}$) was used to treat the exchange-correlation energy, and the projector-augmented wave (PAW) method$^{36}$ was employed to describe core–valence interactions with $[Xe]f^{14}$ and $[He]$ core configurations for Hf and B, respectively. We chose the plane-wave kinetic cut-off energy of 500 eV and uniform k-point meshes for sampling the Brillouin zone with a reciprocal-space resolution of $2\pi \times 0.05$ Å$^{-1}$.

Stable hafnium borides were identified by the thermodynamic convex hull construction, which compactly presents the thermodynamic information about all possible formation and decomposition reactions. Stable compounds are located on the convex hull, while metastable ones are located above the convex hull at a given temperature and pressure. To construct the thermodynamic convex hull, the enthalpy of formation $\Delta H$ (normalized per atom) of each generated Hf$_x$B$_y$ structure was computed in the following way:

$$\Delta H_{f}(Hf_{x}B_{y}) = [H(Hf_{x}B_{y}) - xH(Hf) - yH(B)]/(x+y),$$

where $H(Hf_{x}B_{y})$, $H(Hf)$, and $H(B)$ are the enthalpies of Hf$_x$B$_y$ structure and ground-state structures of hafnium (hcp-Hf, $P6_3/mmc$) and boron (we used α-B, which is energetically degenerate with disordered ground-state β-boron), respectively.

For all stable Hf$_x$B$_y$ structures and low-energy metastable structures, we have performed the phonon calculations using the finite displacement method as implemented in the PHONOPY code$^{37}$ to confirm their dynamical stability. To check the mechanical stability of these Hf$_x$B$_y$ structures, the single-crystal elastic constants $C_{ij}$ were calculated by the stress–strain approach$^{38}$ using the VASP code.$^{32,33}$ The elastic constants of a mechanically stable crystal satisfy the Born–Huang criteria.$^{39}$ To calculate the phonon dispersion curves and mechanical properties, a denser k-points mesh with a reciprocal-space resolution of $2\pi \times 0.03$ Å$^{-1}$ was used.

By utilizing the computed $C_{ij}$ of predicted Hf$_x$B$_y$ structures, using the Voigt–Reuss–Hill averaging,$^{40}$ we derived their bulk moduli (B), shear moduli (G), Young’s moduli (Y), Pugh’s ratios ($k = G/B$), and Poisson’s ratios ($v$). We used the Chen–Niu empirical model$^{41}$ to estimate the Vickers hardness $H_V$ of the predicted Hf$_x$B$_y$ phases,

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

where $H_V$ and $G$ are expressed in GPa. The fracture toughness $K_{IC}$ was estimated by the Niu–Niu–Oganov empirical model,$^{42}$

$$K_{IC} = V_0^{1/6} \cdot G \cdot (B/G)^{1/2},$$

where $V_0$ is the volume per atom. For several Hf$_x$B$_y$ structures, we have also computed their ideal tensile ($\sigma$, in GPa) and shear ($\tau$, in GPa) strengths which are the maximum stresses reached in the stress–strain curves for a given direction and slip system.

III. RESULTS AND DISCUSSIONS

A. Stability of hafnium borides

1. Zero-temperature stability

Our variable-composition evolutionary crystal structure prediction calculations immediately give the information about stable and metastable hafnium borides at ambient pressure and $T = 0$ K. Figure 1 shows the thermodynamic convex hull of the Hf–B system, and it shows that the well-known $P6_3/mmc$-HfB$_2$ is the only thermodynamically stable hafnium boride at ambient pressure and zero temperature. For the other two experimentally reported hafnium borides ($Pmmn$-HfB and $Fm\bar{3}m$-HfB$_2$), our prediction shows that they are metastable at zero temperature, in agreement with the previous theoretical studies.$^{19}$
Besides recovering these three experimentally reported hafnium borides, we have also predicted many metastable hafnium borides which are close to the thermodynamic convex hull: Hf₂B, Hf₃B₂, Hf₆B₆, HfB, Hf₂B₄, HfB₃, HfB₄, HfB₅, and HfB₆, as shown in Fig. 1. Our predicted lowest-energy structures for HfB (P6₃m2) and HfB₆ (C2/m) are the same as those reported in the previous studies. For Hf₂B, Hf₃B₄, and HfB₄, previous works suggested space groups I4/mcm, Immm, and Cmcm, respectively. Now, I4/mcm-Hf₂B is replaced by the more stable R̅3m-Hf₂B, Immm-Hf₃B₄ by P6₃m2-Hf₃B₄, and Cmcm-HfB₄ by Amm2-HfB₄. Hf₂B₂ (P6₃m2), Hf₇B₆ (P6₃m2), Hf₂B₃ (R̅3m), HfB₅ (C2/m), and HfB₆ (Amm2) are newly predicted structures. For most of these metastable hafnium borides, besides the lowest-energy structures at zero temperature, we report several other low-energy structures for each composition (see Fig. 1).

Crystal structures of the predicted stable and metastable hafnium borides are listed in Table I and Table SI in the supplementary material. For the known structures, we give both experimental and theoretical values for comparison, and one can see a very good agreement.

### TABLE I. Computed formation enthalpy ΔH and thermodynamical stability for all the predicted hafnium borides at zero temperature and pressure along with B motifs in their structures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>B motif</th>
<th>ΔH (eV/atom)</th>
<th>Instability (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf₂B</td>
<td>R̅3m</td>
<td>Graphenelike layer</td>
<td>−0.496</td>
<td>0.022</td>
</tr>
<tr>
<td>Hf₃B₂</td>
<td>C2/m</td>
<td>Zigzag chain</td>
<td>−0.486</td>
<td>0.033</td>
</tr>
<tr>
<td>Hf₆B₆</td>
<td>P6₃m2</td>
<td>Graphenelike layer</td>
<td>−0.610</td>
<td>0.013</td>
</tr>
<tr>
<td>Hf₂B₄</td>
<td>Cmcm</td>
<td>Graphenelike layer</td>
<td>−0.589</td>
<td>0.033</td>
</tr>
<tr>
<td>HfB</td>
<td>P6₃m2</td>
<td>Graphenelike layer</td>
<td>−0.558</td>
<td>0.064</td>
</tr>
<tr>
<td>Hf₃B₃</td>
<td>R̅3m</td>
<td>Zigzag chain</td>
<td>−0.708</td>
<td>0.009</td>
</tr>
<tr>
<td>Hf₇B₆</td>
<td>P6₃m2</td>
<td>Graphenelike layer</td>
<td>−0.749</td>
<td>0.028</td>
</tr>
<tr>
<td>Hf₆B₅</td>
<td>Cmcm</td>
<td>Zigzag chain</td>
<td>−0.747</td>
<td>0.030</td>
</tr>
<tr>
<td>HfB₇</td>
<td>I4/mcm</td>
<td>Graphenelike layer</td>
<td>−0.734</td>
<td>0.043</td>
</tr>
<tr>
<td>Hf₆B₅</td>
<td>R̅3m</td>
<td>Zigzag chain</td>
<td>−0.878</td>
<td>0.010</td>
</tr>
<tr>
<td>Hf₂B₄</td>
<td>Immm</td>
<td>Ribon</td>
<td>−0.868</td>
<td>0.020</td>
</tr>
<tr>
<td>Hf₇B₆</td>
<td>Cmcm</td>
<td>Graphenelike layer</td>
<td>−0.926</td>
<td>0.007</td>
</tr>
<tr>
<td>Hf₂B₄</td>
<td>Immm</td>
<td>3D framework</td>
<td>−0.919</td>
<td>0.014</td>
</tr>
<tr>
<td>Hf₆B₅</td>
<td>P6/mmm</td>
<td>Graphenelike layer</td>
<td>−1.037</td>
<td>0</td>
</tr>
<tr>
<td>Hf₇B₆</td>
<td>C2/m</td>
<td>Graphenelike layer and Bilayer</td>
<td>−0.690</td>
<td>0.087</td>
</tr>
<tr>
<td>Hf₈B₇</td>
<td>Pmcm</td>
<td>3D framework</td>
<td>−0.600</td>
<td>0.177</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Amm2</td>
<td>Graphenelike layer and Trilayer</td>
<td>−0.497</td>
<td>0.125</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Cmcm</td>
<td>Bilayer</td>
<td>−0.489</td>
<td>0.133</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Ima2</td>
<td>3D framework</td>
<td>−0.480</td>
<td>0.142</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Pmcm</td>
<td>3D framework</td>
<td>−0.351</td>
<td>0.271</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>C2/m</td>
<td>3D framework</td>
<td>−0.419</td>
<td>0.099</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Pmcm</td>
<td>3D framework</td>
<td>−0.324</td>
<td>0.194</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Amm2</td>
<td>Trilayer</td>
<td>−0.272</td>
<td>0.172</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>P6/mmc</td>
<td>3D framework</td>
<td>−0.236</td>
<td>0.249</td>
</tr>
<tr>
<td>Hf₉B₈</td>
<td>Fm3m</td>
<td>3D framework</td>
<td>−0.191</td>
<td>0.049</td>
</tr>
</tbody>
</table>
To verify the dynamical stability of the predicted stable and metastable hafnium borides, we have calculated their phonon dispersion curves (see Fig. S1 in the supplementary material). There are no imaginary phonon frequencies, which indicates dynamical stability. We computed the elastic constants of all the predicted hafnium borides to check their mechanical stability (see Table SII in the supplementary material). All hafnium borides were found to be mechanically stable because their elastic constants fulfill the Born–Huang criteria.19

2. High-temperature stability

Compounds that are metastable at zero temperature may become stable and possible to synthesize as the environmental conditions (e.g., pressure and temperature) change. We have performed a detailed study of the thermodynamic stability of all predicted low-energy HfB phases to see whether any phases are stabilized by temperature. We computed Gibbs free energies at zero pressure and temperatures in the range from 0 to 2000 K using the quasiharmonic approximation (QHA).43 We constructed convex hulls at different temperatures (see Fig. S2 in the supplementary material) and composition-temperature phase diagram (see Fig. 2). We see that Pnma-HfB and Fm3m-HfB12, metastable at zero temperature, become thermodynamically stable at high temperatures, in agreement with the experiment.11 According to the computed composition-temperature diagram (Fig. 2), Pnma-HfB and Fm3m-HfB12 are thermodynamically stable at temperatures above 1850 K and 1840 K, respectively.

Temperature also induces a phase transition in HfB: as shown in Fig. 2, P6m2-HfB has slightly lower energy than Pnma-HfB at low temperatures (T < 780 K); however, at high temperatures (>780 K), Pnma-HfB has lower Gibbs free energy than P6m2-HfB. Similar temperature-induced phase transitions are also predicted for metastable HfB3 and HfB2 (see Fig. 2). Clearly, one has to consider not only the lowest-energy structures but also low-energy metastable structures when studying phase stability at nonzero temperatures.

B. B configurations in hafnium borides

Table I lists the phases studied here and provides the types of boron sublattices for them. We found 6 main types of boron sublattices: zigzag chain, ribbon, graphene-like sheet, bilayer, trilayer, and 3D framework in predicted hafnium borides. Crystal structures of hafnium borides with mentioned configuration types are shown in Fig. 3.

Let us consider HfB phases with the B/Hf ratio less than or equal to 1. Boron atoms in these structures mainly adopt two types of configurations: 2D graphene-like sheet and 1D zigzag chain. The former configuration is more favorable at ambient pressure and zero temperature, while the latter may become favorable at high temperatures, as suggested by the cases of P6m2- and Pnma-Hf2B.

At 1 < B/Hf ≤ 2, the graphene-like B-sheet is also adopted by the lowest-energy structures of HfB6, HfB5, and HfB4 (P6m2-Hf3B4, R3m-Hf3B4, and P6/mmm-HfB2) at zero temperature. Besides the 2D graphene-like B-sheet, we also found 1D B-ribbons in metastable Immm-HfB2 and Cmcm-HfB2, and a 3D B-framework in metastable Immm-HfB3. This is the first time that B atoms were found in 3D connectivity in a boride with such a low B content.


C. Mechanical properties of hafnium borides

The mechanical properties including elastic moduli (bulk B, shear G, and Young’s modulus Y), Pugh’s ratio (G/B), Poisson’s ratio (ν), Vickers hardness (Hv), and fracture toughness (KIC) of all predicted stable and metastable hafnium borides are summarized in Table II. Whenever possible, we also list the previously reported theoretical or experimental values,12,16,18,20 and one can see a good agreement with the previous studies.12,16,18,20

For a well-known high-temperature structural material HfB2 (P6/mmm), our calculation confirms the superior mechanical properties (B: 262 GPa, G: 248 GPa, E: 565 GPa, Hv: 44.1 GPa). Previous theoretical studies12 suggest that the elastic moduli and hardness of P6/mmm-HfB2 are higher than those of other hafnium borides. From Table II we can find that there are several newly predicted hafnium borides (HfB6, HfB5, HfB4, and HfB3) with elastic moduli and hardness comparable to HfB2, suggesting that boron-rich hafnium borides are promising structural materials. These boron-rich phases have lower density compared to HfB2 (e.g., 7.15 g/cm3 for Amm2-HfB2 vs 11.13 g/cm3 for P6/mmm-HfB2) and higher fracture toughness (e.g., 3.57 MPa m1/2 for Amm2-HfB2 vs 3.03 MPa m1/2 for P6/mmm-HfB2).

Besides the boron content, we can also find that the topology (more specifically, dimensionality) of the boron sublattice has a strong effect on the mechanical properties. HfB phases with the same boron content show wide variation in the elastic moduli and Vickers hardness (see Table II and Fig. 4). Interestingly, the mechanical properties of boron-rich HfB phases with y/x = 1.5–12 and with 3D boron networks do not show a dependence on boron...
FIG. 3. Crystal structures of several hafnium borides: Hf atoms are shown as blue spheres, B atoms as green spheres.
content (see Table II and green squares in Fig. 4). A general rule is
that structures with strong and isotropic three-dimensional covalent
boron networks, which withstand large tensile/shear strain, should have high mechanical strength and hardness.46

**D. Are hafnium borides intrinsically superhard materials?**

According to the Chen–Niu empirical model, a number of
HfB, phases studied here exhibit Vickers hardness \( H_v \) exceeding
40 GPa (a threshold for defining superhard materials). However,
perfect models of materials hardness do not exist, and we resort to a
double-check. We consider a material unquestionably superhard if its
estimated Vickers hardness and computed ideal tensile and shear
strengths are both above 40 GPa—we note that most of the known
intrinsically superhard materials possess very high ideal tensile
strength \( \sigma \) and shear strength \( \tau \) together with high Vickers hardness;
see the cases of diamond \( [H_v : 96 \text{ GPa}], \) c-BN \( [H_v : 66 \text{ GPa}], \)
\( \min (\sigma, \tau) ; 92.8 \text{ GPa}] \), B\(_2\)O \( [H_v : > 40 \text{ GPa}], \) \( \min
(\sigma, \tau) ; 38 \text{ GPa}] \), etc. For this reason, we have computed the ideal
tensile and shear strengths for 12 predicted HfB, phases (including
all stable structures and several metastable structures with computed
$H_f$, higher than 30 GPa), as listed in Table III; stress–strain curves are shown in Fig. S3 in the supplementary material. For the known \( P_6/mmm \)-HfB\(_2\), we have also listed the previously reported values\(^4\) for comparison. Our calculations agree well with the previous work.

According to Table III, \( P_6/mmm \)-HfB\(_2\) and \( Fm\bar{3}/C\bar{2}2m \)-HfB\(_{12}\) are the only two phases with ideal strengths higher than 30 GPa, which confirms that they are very hard and possibly superhard materials. The experimentally determined hardness for \( P_6/mmm \)-HfB\(_2\) is much lower than the predicted value, in the range from 20 to 32 GPa.\(^{44,45}\) For \( Fm\bar{3}m \)-HfB\(_{12}\), there is no experimentally measured hardness. Recently, Akopov et al.\(^{14}\) synthesized five \( Fm\bar{3}m-Y_xHf_{1-x}B_{12} \) (\(x = 0, 0.05, 0.25, 0.5, \) and 0.75) samples. The experimentally measured Vickers hardness for all those samples at high load (4.9 N) is in the range of 28–32 GPa.\(^{14}\) Based on their data, the derived Vickers hardness for pure \( Fm\bar{3}m \)-HfB\(_{12}\) should be around 30 GPa, which is close to the ideal strength, but below 40 GPa (the threshold for defining superhard materials).

Both the predicted hardness of \( Pm\bar{m}m-HfB_5 \) (34 GPa) and its ideal strength (25 GPa) suggest that \( Pm\bar{m}m-HfB_5 \) should be a hard material. Except for \( P_6/mmm-HfB_2\), \( Fm\bar{3}m-HfB_{12}\), and \( Pm\bar{m}m-HfB_5\), the calculated ideal strengths for other phases are lower than their predicted hardness, and none of these phases has an ideal strength higher than 21 GPa.

The diverse values of ideal strength and hardness of hafnium borides can be explained by the chemical bonding in their structures. The well-known \( P_6/mmm-HfB_2 \) has high ideal strength and hardness because of strong Hf–B bonds linking the two-dimensional covalently bonded graphenelike boron sheets and making the material withstand large tensile/shear strains. We remind that Hf–B bonds in Hf\(_{x}\)B\(_y\) compounds should be partially covalent because of the significant hybridization between Hf-5d and B-2p orbitals and large ELF values between Hf atoms and their neighboring B atoms.\(^{21,22}\) For Hf\(_{x}\)B\(_y\) phases with low B contents (e.g., \( P6m2-HfB \)), the hardness is low because of the presence of
TABLE III. Calculated ideal tensile $\sigma$ (GPa) and shear $\tau$ (GPa) strength of hafnium borides.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Tensile $\sigma_{\text{min}}$</th>
<th>Shear $\tau_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB</td>
<td>P6m2</td>
<td>21.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Hf$_2$B$_3$</td>
<td>Pnma</td>
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<td>10.4</td>
</tr>
<tr>
<td>Hf$_2$B$_5$</td>
<td>Immm</td>
<td>18.8</td>
<td>25.1</td>
</tr>
<tr>
<td>HfB$_4$</td>
<td>Cmcm</td>
<td>20.7</td>
<td>26.4</td>
</tr>
<tr>
<td>HfB$_5$</td>
<td>Imm</td>
<td>21.8</td>
<td>16.8</td>
</tr>
<tr>
<td>HfB$_6$</td>
<td>P6/mmm</td>
<td>34.9</td>
<td>36.2</td>
</tr>
<tr>
<td>HfB$_7$</td>
<td>Amm$2$</td>
<td>27.3</td>
<td>15.2</td>
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<tr>
<td>HfB$_8$</td>
<td>Cmcm</td>
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<td>9.5</td>
</tr>
<tr>
<td>HfB$_{12}$</td>
<td>Pmmm</td>
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<td>24.7</td>
</tr>
<tr>
<td>HfB$_{12}$</td>
<td>Amm$2$</td>
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<tr>
<td>HfB$_{12}$</td>
<td>Fm3m</td>
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<td>32.1</td>
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Using the evolutionary crystal structure prediction method USPEX combined with first-principles calculation, we investigated the stability of hafnium borides at zero pressure. We confirmed that the well-known $P6/mmm$-HfB$_2$ is the only thermodynamically stable phase at zero temperature and pressure. With an increase in temperature, two more phases ($Pnma$-HfB$_2$ and $Fm3m$-HfB$_{12}$) become thermodynamically stable at 1850 K and 1840 K, respectively. Besides these three stable Hf$_x$B$_y$ phases, we also discovered many metastable phases with rich stoichiometries (Hf$_x$B$_y$, Hf$_2$B$_3$, HfB$_y$, Hf$_x$B$_{12}$, HfB$_5$, and HfB$_6$) and diverse boron configurations (zigzag chain, ribbon, graphenelike sheet, double layer, triple layer, and 3D framework). We defined the correlation between boron content, boron sublattice type, and mechanical properties by considering both stable and metastable hafnium borides (~30 phases). For boron-poor Hf$_x$B$_y$ phases, the highest possible hardness is exhibited by $P6/mmm$-HfB$_2$ with graphenelike B-sheet and boron-rich structures with 3D boron networks, namely $Pnma$-HfB$_2$ and $Fm3m$-HfB$_{12}$. There are also several boron-rich phases such as HfB$_p$, HfB$_q$, and HfB$_r$ with 2D boron multilayered sublattice that are comparable to $P6/mmm$-HfB$_2$ by their elastic moduli, but their hardness is much lower because they undergo phase transitions under small strains.

SUPPLEMENTARY MATERIAL
The supplementary material includes data on the crystal structure of the predicted stable and metastable hafnium borides together with data on the elastic constants, phonon dispersion curves, thermodynamic convex hulls at finite temperatures, and stress–strain curves.

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