Structure, Stability, and Mechanical Properties of Boron-Rich Mo–B Phases: A Computational Study

Dmitry V. Rybkovskiy, Alexander G. Kvashnin,* Yulia A. Kvashnina, and Artem R. Oganov

ABSTRACT: Molybdenum borides were studied theoretically using first-principles calculations, parameterized lattice model, and global optimization techniques to determine stable crystal structures. Our calculations reveal the structures of known Mo–B phases, attaining close agreement with experiment. Following our developed lattice model, we describe in detail the crystal structure of boron-rich MoBx phases with 3 ≤ x ≤ 9 as the hexagonal P63/mmc-MoB3 structure with Mo atoms partially replaced by triangular boron units. The most energetically stable arrangement of these B3 units corresponds to their uniform distribution in the bulk, which leads to the formation of a disordered nonstoichiometric phase, with ordering arising at compositions close to x = 5 because of a strong repulsive interaction between neighboring B3 units. The most energetically favorable structures of MoBx correspond to the compositions 4 ≤ x ≤ 5, with MoB5 being the boron-richest stable phase. The estimated hardness of MoB5 is 37–39 GPa, suggesting that the boron-rich phases are potentially superhard.

Transition metal borides are often considered as possible replacements of traditional superhard materials in various technological applications. Unlike widely used diamond and cubic boron nitride, transition metal borides do not require high pressure for their synthesis, making their production cheaper and more readily scalable. The outstanding mechanical properties of these materials originate from the combination of high valence electron density of metal atoms, responsible for high incompressibility, and covalent bonds of light boron atoms, resulting elastic and plastic shape deformations.1–6 The borides of tungsten and molybdenum are of particular interest because of their capability to contain a significant amount of boron, resulting in high hardness. The W–B system has been extensively studied both experimentally1–3 and theoretically,4–9 whereas the exact crystal structure of higher Mo–B phases is still under debate.

Today, the experimental methods of structure determination are strongly supported by state-of-the-art computational techniques based on global optimization algorithms and robust quantum–chemical total energy computational methods.10 Such approaches have already been applied to the investigation of the Mo–B phase diagram, shedding light on some aspects of the crystal structure of molybdenum borides. Liang et al.11 computed the energies of the experimentally claimed and hypothetical crystal structures. Zhang et al.12 used the evolutionary global optimization algorithm USPEX for an unbiased study of Mo–B phases. The latter work was, however, restricted to specific chemical compositions. Despite the success of the existing theoretical studies, the structure of the molybdenum borides with compositions close to MoB4, which are particularly interesting for potential applications as hard materials, is still controversial. The experimentally proposed structures are mainly based on X-ray diffraction (XRD) experiments, where the largest part of the signal is determined by the positions of Mo atoms, and the correct placement of much lighter boron atoms is complicated. Total energy computations show that such structures have high energies of formation, indicating their instability.11,12 On the other hand, the theoretically predicted P63/mmc-MoB4 structure,12 although having a low energy of formation, has an X-ray diffraction (XRD) pattern that is incompatible with experiment. These contraventions motivate a further search for boron-rich Mo–B phases that would match the experimental XRD and exhibit an energetically preferable boron arrangement.

In this work we use a broad range of computational techniques, including the evolutionary crystal structure prediction to search for thermodynamically stable phases through all possible compositions, density-functional total energy computations, and a parameterized lattice model for the theoretical study of the boron-rich part of the Mo–B phase diagram. We show that within the compositional range between MoB4 and MoB5, the molybdenum borides may be described by a structural model similar to the one proposed by
Lech et al.\textsuperscript{6} for the highest tungsten boride. On the basis of total energy computations and relative stabilities, we describe the requirements that the structures have to satisfy to be energetically preferable.

Global optimization of Mo–B crystal structures was performed using the variable-composition evolutionary algorithm as implemented in the USPEX code.\textsuperscript{13–15} This approach makes it possible to perform an automatic structure search within the whole compositional range of a multicomponent system. During the structure search, the first generation of 120 structures was produced randomly with up to 24 atoms (for the variable-composition search) and 36 atoms (for the fixed-composition search) in the primitive cell. The succeeding generations were obtained by applying the heredity (40% of each generation), softmutation (20%), and transmutation (20%) operators.\textsuperscript{13–15} 20% of each generation were produced using random\textsuperscript{16} and random topological generators.\textsuperscript{17}

For the structure relaxations and total energy computations, the projector augmented-wave\textsuperscript{18,19} density functional theory (PAW-DFT) was used as implemented within the VASP\textsuperscript{20–22} package. The generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE)\textsuperscript{23} was used for the exchange–correlation functional. PAW data sets were used to describe the electron–ion interactions with Mo 4p, 4d, 5s and B 2s, 2p electrons treated as valence electrons. The plane-wave energy cutoff of 400 eV, the Methfessel–Paxton electronic smearing,\textsuperscript{24} and \(\Gamma\)-centered \(k\)-point meshes with a resolution of 2\(\times\)0.025 \(\text{Å}^{-1}\) for the Brillouin zone sampling ensured the convergence of total energies.

To investigate the boron-rich part of the Mo–B phase diagram, a lattice model for the total energy was developed. The \(\Gamma\) diffraction has been simulated with the VESTA software\textsuperscript{25} using 1.54059 Å wavelength.

Vickers hardness was estimated according to the Mazhnik–Oganov\textsuperscript{26} (\(H_{\text{VMO}}\)) and Chen\textsuperscript{27} (\(H_{\text{VC}}\)) models. Test calculations of Vickers hardness for a number of materials using Mazhnik–Oganov and Chen’s models agree well with the reference experimental data: diamond, 99 and 94 GPa (\(\sim 96\) GPa\textsuperscript{26}); TiN, 21 and 23 GPa (20.5 GPa\textsuperscript{26}); and c-BN, 71 and 63 GPa (\(\sim 66\) GPa\textsuperscript{30}).

Fracture toughness was calculated using the empirical Mazhnik–Oganov model\textsuperscript{26} (\(K_{\text{VMO}}\)) and Niu–Oganov model\textsuperscript{41} (\(K_{\text{VO}}\)). Calculated values of fracture toughness for well-studied materials nicely agree with experimental data. The Mazhnik–Oganov model gives 6.2, 7.7, 3.8, and 5.4 MPa·m\textsuperscript{0.5} for diamond, WC, TiN, and c-BN, respectively. The Niu–Oganov model gives fracture toughness of diamond, WC, TiN, and c-BN equal to 6.3, 5.4, 3.3, and 5.4 MPa·m\textsuperscript{0.5}, respectively. The experimental data are 4–7 MPa·m\textsuperscript{0.5} for diamond\textsuperscript{32–34} 5–8 MPa·m\textsuperscript{0.5} for WC\textsuperscript{35,36} and 3–5 MPa·m\textsuperscript{0.5} for TiN\textsuperscript{35} and 2–5 MPa·m\textsuperscript{0.5} for c-BN.\textsuperscript{33,37}

\textbf{Variable-Composition Evolutionary Structure Search.} A thermodynamically stable phase has a lower energy of formation than any phase or phase assemblage of the same composition and is located on the convex hull line. The calculated energies of formation, \(\Delta E_{\text{form}}\), of the stable and metastable structures, obtained during evolutionary search and proposed earlier for some Mo–B phases in refs 3 and 38–41 are shown in Figure 1 as a function of the atomic fraction of boron.

The only stable phases obtained using the evolutionary search were \(I4/m\text{-}amd\text{-MoB} (\alpha\text{-MoB}), R3m\text{-MoB}_2\), and \(Pmmn\text{-MoB}_3\). It should be mentioned, however, that vibrational effects might change the convex hull at high temperatures. Such vibrational contributions may result in stabilization of some phases close to the convex hull line. It is therefore important to consider not only systems lying on the convex hull in Figure 1, but also metastable phases, which are close to it. Such phases include \(I4/m\text{-}Mo_3B_2, I4/m\text{-}cm\text{-}Mo_3B_2, P4/m\text{bm}-\text{MoB}_3, Cmcn\text{-}MoB (\beta\text{-}MoB), P6_3/m\text{mc}\text{-}MoB_9, P6_3/m\text{mc}\text{-}MoB_9\), and \(P6_3/m\text{mc}\text{-}MoB_9\), and further discussion on the basis of available experimental and theoretical data from literature will show that some of them may indeed become stable at finite temperature. Crystal structures of the USPEX-obtained Mo–B phases are shown in Figure 2. Each of the phases is discussed separately, starting from those having a low boron content.

The Mo\textsubscript{5}B\textsubscript{5} phase is well known from experimental studies\textsuperscript{3,38,42,43} and global optimization predicts the \(I4/m\text{cm}\) space group for this composition. However, it has been shown theoretically\textsuperscript{44,45} that \(I4/m\text{cm}\) phase is dynamically unstable and transforms to \(I4/m\) phase. Total energy calculations of \(I4/m\text{cm}\text{-}MoB_3\) and \(I4/m\text{-}MoB_3\) show that they lie 20 and 16 meV/atom above the convex hull, respectively, which agrees with the previous theoretical findings.\textsuperscript{11,12} Both structures are therefore metastable at 0 K, and we conclude that vibrational effects are responsible for the stabilization of Mo\textsubscript{5}B\textsubscript{5}. Another metastable structure, which has been experimentally found at high temperatures \((T > 1550 \text{ K})\), is \(P4/m\text{bm}\text{-}MoB_3\), whose energy of formation lies 25 meV/atom above the convex hull. It was first reported by Steinitz et al. in 1952,\textsuperscript{38} though some later works doubted its existence.\textsuperscript{32}

We also obtained two known Mo\textsubscript{3}B\textsubscript{2} phases: \(I4/m\text{-}amd\text{-MoB} (\alpha\text{-MoB})\) and \(Cmcn\text{-}MoB (\beta\text{-}MoB)\). The energy of formation of \(\beta\text{-}MoB\) is higher than that of \(\alpha\text{-}MoB\) by 11 meV/atom. \(I4/m\text{-}amd\text{-MoB}\) undergoes a phase transition to the high-temperature \(Cmcn\text{-}MoB\) at \(\sim 1900 \text{ K}\), as known from experiment and predicted by theory.\textsuperscript{11,38,42}

The chemical compositions and crystal structures of boron-rich Mo–B phases were debated for a long time. We obtained
higher by 152 meV/atom compared to that of R3m-MoB2, which agrees with the previous theoretical studies. The structure of P63/mmc-MoB2 corresponds to the hP12-WB2 type proposed in ref 11 and lies 3 meV/atom above the lowest-energy R3m-MoB2.

Mo2B3 was reported in several experimental works3,38,42 and was first described by Kiesling3 as a derivative of the R3m-MoB2 structure with alternating planar hexagonal and puckered (with additional B atoms) hexagonal boron layers separated by Mo layers.3,43 The existence of this phase has been questioned by experiments46,47 and a conclusion has been made that it actually is identical to R3m-MoB2. Later, another metastable, lower-energy P63/mmc-MoB2 with a different structure was predicted theoretically.12 We found that R3m-MoB2 is unstable, having a positive energy of formation of 55 meV/atom, and P63/mmc-MoB2 is 25 meV/atom above the convex hull, which agrees with the previous theoretical results.11,12

We found that R3m-MoB3 is metastable, lying 12 meV/atom above the convex hull, which agrees with the previous theoretical results. In comparison, P63/mmc-MoB3 differs by the mutual position of the planar Mo layers, and its calculated energy is 7 meV/atom higher, but previous theoretical investigations have suggested that it becomes more stable than the R3m phase at high temperatures.11

The MoB4 structure with P63/mmc space group, which we denote as the P63/mmc-MoB4 phase, is metastable, lying 15 meV/atom above the convex hull. This phase is equivalent to those obtained in previous theoretical global optimization studies.12 It is composed of Mo layers sandwiched between puckered boron bilayers. Numerous experimental works reported the synthesis of boron-rich compounds with compositions close to MoB4.59,40,48 However, the structures proposed in these works have a different XRD pattern in comparison to the theoretical P63/mmc-MoB4 phase.

Our evolutionary structure search revealed a new stable boron-rich phase Pmnn-MoB5 with the same structure type as that of an earlier reported WB2.5 This phase is made of edge- and face-sharing MoB12 hexagonal prisms and open B15 clusters linked into a 3D structure by B–B bonds. The calculated phonon spectrum shows the dynamical stability of this phase (Supporting Information Figure S3). Crystal structures of all low-energy phases are presented in Table S1.

Because the main practical interest in boron-rich molybdenum borides is due to their potential for technological applications as hard materials, we estimated the mechanical properties of the obtained low-energy Mo–B phases. The results are summarized in Table 1. The Vickers hardness, estimated using the Chen (Hv) model and Mazhnik–Oganov (HM0) model, is in good agreement with the experimental results for MoB5, whereas the estimated hardness values for MoB3 are ~33–36 GPA. For the most boron-rich phase Pmnn-MoB5, we estimated the Vickers hardness as ~37–39 GPA, which is close to the lower bound for superhard materials, 40 GPA.53 Therefore, the highest borides of molybdenum are potentially superhard. It is worth noting that a recent experimental study of boron-rich molybdenum boride with the composition Mo0.77B3 reported anisotropic nanoindentation hardness of ~34–40 GPA.53 A comparison of mechanical characteristics with known materials is shown in Figure S1 (see the Supporting Information).

Higher Molybdenum Borides. Our variable-composition evolutionary search reproduced most of the experimentally observed phases and predicted the boron-richest phase MoB5 that has not been reported experimentally. There have been several experimental reports of Mo–B phases with the composition close to MoB4 and a controversial structure determination,59,40,48 whereas the evolutionary search did not find any structures of MoB4 that would match the experimentally observed XRD pattern.

![Crystal structures of the Mo–B phases obtained using the evolutionary crystal structure search.](image)

![Table 1. Mechanical Properties of the Low-Energy Mo–B Phases](table)

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Figure 2. Crystal structures of the Mo–B phases obtained using the evolutionary crystal structure search.

Table 1. Mechanical Properties of the Low-Energy Mo–B Phases

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Crystal structures in the boron-rich area of the Mo–B phase diagram are difficult to study experimentally because of a large difference in the X-ray scattering cross sections of boron and metal atoms which makes it hard to determine the exact positions of boron atoms and the boron content in the compound. Previous proposals for several structures of boron-rich Mo–B compounds have been made mainly on the basis of chemical intuition and limited experimental data. These structures usually consist of sequences of hexagonal graphene-like boron and molybdenum layers with partial Mo occupancies and additional boron fragments of different forms. However, theoretical total energy computations showed that these hypothetical structures have high energies of formation, indicating their instability. Galasso and Pinto proposed the $P6_3/mmc$-MoB$_3$ phase with boron dimers placed between the hexagonal boron layers and oriented along the $c$ axis of a unit cell. After relaxation of this structure, we obtained a positive energy of formation of 261 meV/atom, which agrees with previous theoretical works. Another structure, suggested by Lundström and Rosenberg, has Mo$_{1-x}$B$_3$ composition with $x \approx 0.20$ and $P6_3/mmc$ space group. This structure is similar to $P6_3/mmc$-MoB$_3$, obtained during the USPEX evolutionary search, but with a portion of Mo atoms removed. To simulate this structure, we constructed a $2 \times 2 \times 1$ supercell of $P6_3/mmc$-MoB$_3$ with three Mo vacancies in the Wycko position $2b$, which resulted in the composition Mo$_{0.8125}$B$_3$. Its energy of formation is negative, $-98$ meV/atom, but lying quite high above the convex hull (Figure 1), which makes this structure unstable. A recent experimental work considered a similar structure with Mo$_{0.757}$B$_3$ composition. We also examined the experiment-based structure of Novotny et al., for higher tungsten borides. This structure with the composition Mo$_{0.2-0.3}$B$_3$ features boron octahedra and lacks one of the two hexagonal graphene-like boron layers. After relaxation of Mo$_{0.3}$B$_3$ structure, the atoms significantly rearranged, but the resulting energy of formation remained positive at 114 meV/atom (Figure 1). We conclude that crystal structures proposed on the basis of the experimental measurements are unstable. Although the positions of metal atoms can be robustly determined from XRD, constructing an energetically favorable arrangement of light boron atoms is extremely complicated. Experiment-independent structure prediction approaches have also been used before to resolve the correct crystal structure of boron-rich phases. The computations have revealed the $P6_3/mmc$-MoB$_3$ phase that also appeared in our global optimization procedure. This structure has a low energy of formation and is located only 15 meV/atom above the convex hull. However, its XRD pattern is distinctly different from that of the experimentally synthesized highest molybdenum boride. Similar puzzle existed in the chemically similar W–B system. In 2015, Lech et al. carried out neutron diffraction studies of boron-rich W–B phases, partially replacing the tungsten atoms in the Wycko position $2b$ with boron trimers, which resulted in WB$_{4.2}$ chemical composition having $P6_3/mmc$ space group. It should be noted that recent theoretical work considered the equilibrium arrangement of these boron trimers within the WB$_{4.2}$ crystal. However, our global optimization procedure did not reveal such structures with partial atomic occupations because of the limited unit cell size used in the evolutionary search (up to 36 atoms per unit cell). At the same time, it is possible to construct the energetically favorable Mo–B phases that have the compositions between MoB$_3$ and MoB$_5$ by analyzing the structures of USPEX-predicted phases.

The crystal structures of $P6_3/mmc$-MoB$_3$ and $Pmmn$-MoB$_5$ (Figure 3a) have clear similarities: the alternation of graphene-like boron layers with the layers of Mo. The structure of MoB$_5$ can be produced from MoB$_3$ by replacing half of the Mo atoms in the Wycko position $2b$ by three boron atoms in a triangular arrangement (a B$_3$ unit), shown in orange in Figure 3a. This agrees with the structure proposed by Lech et al. We considered the possibility to construct stable MoB$_5$ phases having various compositions by replacing a different number of Mo atoms with boron triangles. We first focused on the preferable position and orientation of an individual boron triangle. In the $P6_3/mmc$-MoB$_3$ structure, such B$_3$ units may occupy three Wycko positions: $2b$, $2c$, and $2d$ (Figure 3b). To reveal the most favorable position and orientation of a B$_3$ unit, we constructed a $2 \times 2 \times 2$ supercell of $P6_3/mmc$-MoB$_3$ and placed a single B$_3$ unit at these Wycko positions, either replacing the molybdenum atom at the corresponding site or filling an empty space of the Wycko position $2d$ (Figure 3b). The two Mo layers in the...
$P6_3/mmc$-MoB$_3$ unit cell differ in rotation by $\frac{\pi}{3}$, therefore, we considered the B$_3$ units in only one of these layers, keeping in mind that a change of layer would require a proper rotation of the boron triangle. We also considered a supercell with a single Mo vacancy in the 2b position for comparison, because some of the experimentally suggested Mo–B phases have partial occupation of the Mo sublattice due to vacancies.\cite{S9,S2} We relaxed the atomic coordinates and lattice parameters of the resulting supercells and evaluated their total energies using DFT. The distance above the convex hull $\Delta H$ was used as a quantitative measure to compare the relative stabilities of the structures. The resulting energies of formation as a function of composition are shown in Figure 3c, and the energy values are summarized in Table 2. Most of the B$_3$ configurations, as well as a single Mo vacancy, have higher $\Delta H$ than the initial $P6_3/mmc$-MoB$_3$. The instability of the Mo vacancy is consistent with the high energy of formation of the Mo$_{0.33}B_3$ structure, discussed above. The most stable configuration was realized when a boron triangle replaced a Mo atom in the Wyckoff position 2b so as to maximize the distance to the closest in-plane Mo atoms (2b-1 configuration). This most preferred B$_3$ configuration results in the lowering of $\Delta H$ compared to pure $P6_3/mmc$-MoB$_3$ from 18 to 14 meV/atom. Therefore, there is a prospect for the structure stabilization by replacement of more Mo atoms in the Wyckoff positions 2b and a consequent increase in the B$_3$ content. Such increase in the boron concentration would bring the energies of formation of the resulting structures closer to the convex hull line. However, as the number of B$_3$ units increases, the distance between them becomes smaller, their mutual position starts to play a role, and the interaction between the individual B$_3$ units has to be considered.

The investigation of possible mutual arrangements of B$_3$ units requires consideration of many configurations with large supercells, complicating the computations that use the first-principles DFT approach. To approximate the DFT results, we developed a lattice model that is very accurate for the boron-rich Mo–B compounds. In this model, the Wyckoff positions 2b of $P6_3/mmc$-MoB$_3$ are considered as lattice sites that may be occupied by either Mo atoms or B$_3$ units in the 2b-1 configuration. The total energy of a supercell consisting of 2b-1 configuration results in the lowering of $\Delta H$ compared to pure $P6_3/mmc$-MoB$_3$ from 18 to 14 meV/atom. Therefore, there is a prospect for the structure stabilization by replacement of more Mo atoms in the Wyckoff positions 2b and a consequent increase in the B$_3$ content. Such increase in the boron concentration would bring the energies of formation of the resulting structures closer to the convex hull line. However, as the number of B$_3$ units increases, the distance between them becomes smaller, their mutual position starts to play a role, and the interaction between the individual B$_3$ units has to be considered.

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In this formula, $E_{\text{Mo}}$ is the energy of a single $P6_3/mmc$-MoB$_3$ unit cell. $\Delta E_{\text{B}}$ is the energy change produced by the replacement of a single Mo atom by a B$_3$ unit in its lowest-energy configuration, calculated as the total energy difference between a $2 \times 2 \times 2$ supercell of $P6_3/mmc$-MoB$_3$ with a B$_3$ unit in the 2b-1 configuration and a pristine $2 \times 2 \times 2$ $P6_3/mmc$-MoB$_3$ supercell. The first two energy terms serve as the definition of the absolute energy value and may differ depending on the particular DFT implementation used. The third term represents the interaction between the individual B$_3$ units located in the 2b sites $i$ and $j$, where $K_{ij}$ is a parameter whose value depends on the distance between the sites that are occupied by the B$_3$ units. The interactions up to the fourth nearest-neighbor site were taken into account. Each 2b site has two nearest neighbors located above and below along the $c$ axis. Six second-order neighbors are located in the same layer plane. Twelve third-order neighbors occupy the upper and lower planes of 2b sites. The two remaining neighbors of the fourth order are located along the $c$ axis at a distance twice as long as the first-order neighbors. The graphical representation of the neighbor map is shown in Figure S4.

Thus, six parameters completely describe our lattice model, with two of them, obtained from the energies of $2 \times 2 \times 2$ supercells, defining the absolute energy. Four remaining parameters, responsible for the B$_3$ interaction, were fit to reproduce the DFT total energies of supercells with multiple B$_3$ units. To do this, we constructed $18 \times 2 \times 2 \times 2$ and $14 \times 2 \times 2 \times 3$ supercells with randomly distributed B$_3$ units, having the compositions between MoB$_{1.5}$ and MoB$_{2.33}$. We calculated their total energies within the DFT approach and then minimized the squared difference between the DFT energies and lattice model energies from eq 1 with use of the random walk minimization procedure. The resulting set of parameters is presented in Table 3. All parameters responsible for the interaction have positive values, which indicates the repulsive nature of the B$_3$–B$_3$ interaction. For the supercells constructed for the fitting procedure, the largest absolute difference between the total energy calculated using the DFT and our lattice model was $\sim 1$ meV/atom. By construction, the highest accuracy of our lattice model is attained for boron-poor systems, diminishing as the boron content increases (the largest error in the total energy was 12 meV/atom for the MoB$_9$ structure).

Having accurately parameterized the lattice model, we searched for the most stable composition, corresponding to the optimal arrangement of the B$_3$ units, by considering the $2 \times 2 \times 3$ $P6_3/mmc$-MoB$_3$ supercell and performing a brute-force

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<td>-274</td>
<td>44</td>
</tr>
<tr>
<td>$Pmmn$-MoB$_3$</td>
<td>-233</td>
<td>0</td>
</tr>
</tbody>
</table>

$E_{\text{N},n} = NE_{\text{Mo}} + n\Delta E_{\text{B}} + \frac{1}{2} \sum_{i \neq j} K_{ij}\delta_{ij}$ (1)
search for lowest-energy structures, taking into account all possible arrangements of the $B\_3$ units. The energies of formation of the constructed nonstoichiometric structures are shown in Figure 4a, displaying only the boron-rich region of the convex hull diagram from Figure 1. An increase in the boron content leads to a decrease in the energy of formation,
which approaches the convex hull line at the composition close to MoB$_4$ (within the $2 \times 2 \times 3$ supercell approach, the obtained composition is MoB$_{2.02}$, lying just 2 meV/atom above the convex hull) and closely follows this line until the composition MoB$_3$ on the convex hull is reached. Taking into account the effects of lattice vibrations and configurational entropy will make this phase stable. Further increase in the boron content leads to a rapid decrease in stability (the energy of formation increases). The composition range between $4 \leq x \leq 5$ is therefore the most stable within the considered structure type, with MoB$_5$ being the most boron-rich among them. To verify the accuracy of the obtained results, we recalculated the energy of formation of some structures within DFT. The corresponding energies of formation, marked by squares in Figure 4a, show excellent agreement between the lattice model and DFT calculations (a direct comparison between the results of the lattice model and DFT is shown in Figure 4b). Figure 4c shows the dependence of the equilibrium lattice constants (per single $P6_3/mmc$ primitive cell) on the boron content of the lowest-energy MoB$_x$ phases. Such dependence could be used for experimental determination of the chemical composition of these compounds, by experimentally calibrating the dependence of the cell parameters on the composition. The plot clearly shows different behavior at different boron concentrations. In the range from MoB$_3$ to MoB$_{1.4}$, the addition of more B$_3$ units leads to a small increase of both lattice constants $a$ and $c$. For structures between MoB$_{1.4}$ and MoB$_9$, which correspond to the interval of the most stable compositions, the parameter $c$ increases from 6.31 to 6.37 Å with a small decrease of lattice constant $a$ from 5.21 to 5.20 Å. Further increase of the boron content results in an opposite trend, with a fast decrease of the $c$ parameter and increase of $a$.

During the brute-force search, we collected the data on the highest-energy structures to determine the origins of the energy penalty due to the arrangement of B$_3$ units. Crystal structures of the least and most stable phases are shown in Figure 4d,e to clearly see the structural difference between them. In the low-energy structures (Figure 4e), the B$_3$ units, shown in orange, are uniformly distributed within the considered cells, whereas in the high-energy structures (Figure 4d), the B$_3$ units tend to form vertical columns. The high energy of these structures is the consequence of the repulsion between the B$_3$ units, which also explains the jump in the energy for structures where the atomic fraction of boron is greater than $5/6$. MoB$_3$ is the boron richest phase where the B$_3$ units can be distributed without being placed in the adjacent sites. This is the highest theoretically achievable molybdenum boride within the proposed type. The lowest-energy B$_3$ arrangements, presented in Figure 4e, are not unique. Multiple different configurations, corresponding to the ground-state energies, were found during our brute-force search, which points at the disordered nature of this material. However, at the MoB$_3$ composition, the strong repulsive interaction between the nearest-neighbor B$_3$ units reduces the number of lowest-energy configurations and suggests the ordering of B$_3$ units at compositions close to MoB$_5$.

Our calculations show that the MoB$_x$ structures, constructed via partial replacement of the 2b-Mo atoms of the P6$_3$/mmc-MoB$_4$ phase by triangular B$_3$ units, are energetically more preferable than the previously proposed boron-rich Mo–B phases with compositions close to MoB$_4$, including P6$_3$/mmc-MoB$_{4.2}$ (see Figure 4a) and P6$_3$/mmc-Mo$_{4.2}$B$_3$ (see Figures 1 and 3c and ref 39). We compared the simulated X-ray diffraction patterns of these molybdenum borides (Figure 5). The XRD pattern of P6$_3$/mmc-MoB$_4$ (Figure 5a) is clearly different from the most widely accepted P6$_3$/mmc-Mo$_{0.85}$B$_3$ ($x = 0.20$) model (Figure 5b), proposed experimentally and closely reproducing experimental XRD pattern. Given that both lattice parameters and XRD peak intensities are very sensitive to the exact stoichiometry (see Figure 4d and Figure 5c,d), the agreement with experiment for both the XRD peak intensities and the predicted lattice parameters corresponding to the composition MoB$_{1.7}$ suggests that the actual chemical composition of samples studied in ref 39 is close to MoB$_{1.8}$. To obtain the XRD pattern of the MoB$_x$ phases within our suggested structure type, we considered a $12 \times 12 \times 10$ supercell of the P6$_3$/mmc-MoB$_4$ phase, with a partial replacement of the Mo atoms in the 2b-position by B$_3$ units.

![Figure 5. Simulated XRD spectra. (a) Previously theoretically proposed P6$_3$/mmc-MoB$_4$. (b) Experimentally proposed P6$_3$/mmc-Mo$_{0.85}$B$_3$ model with $x = 0.2$. (c) MoB$_4$ and (d) MoB$_{1.8}$ structures, constructed as $12 \times 12 \times 10$ supercells of the P6$_3$/mmc-MoB$_4$ phase, with a partial replacement of the Mo atoms in the 2b-position by B$_3$ units.](https://dx.doi.org/10.1021/acs.jpclett.0c00242)
intensity of this peak, bringing the resulting XRD spectrum in closer agreement with experiment. Further increase of boron content resulted in the appearance of additional peaks at around 18° in the simulated XRD pattern because of the B₃ units ordering. Such ordering appears because of the strong repulsive interaction between the B₃ units, located at the adjacent sites, which restricts the number of their possible arrangements.

Good agreement between the experimental XRD pattern and the XRD pattern of our proposed structure, together with its favorable thermodynamics, gives strong evidence in favor of this structure (which can be described as based on the P6₃/mmc -MoB₃ structure with partial replacement of Mo atoms in the 2b-position with triangular B₃ units). Our calculations show that the highest theoretically achievable molybdenum boride within this structure type is MoB₅.

In conclusion, the crystal structure of boron-rich Mo–B phases has been debated for a long time. The structural complexity of pure boron manifests itself in the boron-rich part of the transition metal boride phase diagram. In this work we used a range of computational approaches, including the evolutionary global optimization, first-principles total energy calculations, and a parameterized lattice model, to investigate the atomic structures of Mo–B phases in the whole compositional range. Beside the phases reported and characterized in previous experimental and theoretical studies, we found a new stable phase of MoB₁₀ having the same structure type as previously predicted WB₁₀.⁸ We showed that the appropriate mixing of structural fragments of MoB₁₀ and metastable P6₃/mmc-MoB₃ (the partial replacement of the molybdenum atoms in the Wyckoff position 2b by appropriately rotated boron triangles B₃) makes it possible to construct a broad range of structures with the compositions between MoB₃ and MoB₁₀. The development and application of a lattice model for total energy calculations allowed us to find energetically stable boron-rich phases with MoB₁₀–MoB₃ compositions. The energetically favorable MoB₁₀ phases correspond to a uniform distribution of the B₃ units within the hexagonal lattice, based on the tendency of these units to avoid each other in the bulk. The crystal structure of MoB₃ with low concentrations of B₁₀ units is disordered and similar to those proposed by Lech et al.⁴ for the W–B system. An increase in the boron content decreases spatial freedom for boron triangles because of the repulsive interaction neighboring B₃ units, resulting in their ordering at compositions close to MoB₁₀. The estimations of Vickers hardness show that higher borides have a high hardness of 33–39 GPa, indicating the possible superhardness of these materials. In addition, we showed that the computational structure prediction methods are powerful tools for determining the structure of systems in situations where an experimental crystal structure assessment is complicated.

ASSOCIATED CONTENT

Supporting Information

Crystal data, mechanical properties, physical properties of MoB₁₀, and lattice model neighbor map (PDF)


