Formation criterion for binary metal diboride solid solutions established through combinatorial methods

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Abstract
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Keywords
solid-solution ceramics, metal diborides, high-throughput methods, first-principles calculations, machine learning

Disciplines
Materials Science and Engineering

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Formation criterion for binary metal diboride solid solutions established through combinatorial methods

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Abstract

Establishing formation criterion is urgent for accelerating the discovery and design of solid-solution materials with desirable properties. Previously reported formation criterion mainly focused on solid-solution alloys, while the formation criterion was rarely established in solid-solution ceramics. To solve this problem, herein, we take a class of solid-solution ceramics, namely binary metal diboride ((M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2}) solid solutions, as a prototype. Through combinatorial methods including high-throughput molten salt syntheses and high-throughput first-principles calculations combined with machine learning approach, the correlation between influential factors, including atomic size difference (δ), mixing enthalpy at 0 K and 0 Pa (Δ\textsubscript{H}\textsubscript{mix}\textsubscript{0K}), doping condition (ϕ), and valence electron concentration (VEC), and the formation ability of (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions was first studied systematically, and then their formation criterion was well established. The results showed that the influential degree of the aforementioned four factors on the formation ability of (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions could be described as follows: δ > Δ\textsubscript{H}\textsubscript{mix}\textsubscript{0K} > ϕ > VEC. In addition, a newly proposed parameter, β, could well reflect the formation ability of (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions: when β > 0, the single-phase (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions could be successfully synthesized in our work and \textit{vice versa}. This study may provide a theoretical guidance in the discovery and design of various solid-solution ceramics, such as the metal borides, carbides, nitrides, etc., with desirable properties.

\textbf{Keywords:} Solid-solution ceramics, metal diborides, high-throughput methods, first-principles calculations, machine learning.
1. Introduction

With the highly competitive development of material industries, the discovery and design of materials with desirable properties is becoming increasingly necessary.\textsuperscript{1,2} Owing to the huge composition space, unique microstructure and adjustable properties, solid-solution materials are considered as the optimal candidates for the selection and design of advanced engineering and functional materials exceeding conventional materials, which are of great interest for a wide range of applications.\textsuperscript{3,4} How to achieve the fast discovery and design of solid-solution materials with desirable properties is the key point to realize their extensive applications.\textsuperscript{5,6} An effective strategy to solve this issue is the establishment of formation criterion for solid-solution materials. Up to now, numerous attempts have been made to establish the formation criterion for solid-solution alloys,\textsuperscript{7,8} especially for high-entropy alloys.\textsuperscript{9-11} Extensive experimental studies have demonstrated that the dominating factors of the formation ability for solid-solution alloys involve atomic size difference ($\delta$), mixing enthalpy, and valence electron concentration ($VEC$), which have greatly accelerated the discovery and design of solid-solution alloys with desirable properties.\textsuperscript{7-11}

Solid-solution ceramics with binary,\textsuperscript{12-14} ternary,\textsuperscript{15-17} and quaternary or more-component (also named high-entropy) structures,\textsuperscript{18-22} as the new members of solid-solution materials, have been attracting growing attention in recent years for potential applications in the structural and functional fields, especially under extreme conditions of temperature, pressure and others. Extensive efforts have been devoted to exploring diverse composition space and microstructure in search of solid-solution ceramics with
desirable structural and functional properties.\textsuperscript{18-21} To date, however, the exploration of solid-solution ceramics with desirable properties has been limited. Establishing formation criterion for solid-solution ceramics is of significant importance to solve this problem. Recently, some formation criterions have been developed to predict the formation ability of the solid-solution ceramics. For example, Gild et al.\textsuperscript{19} proposed the $\delta$ parameter to predict the formation ability of five-metal diboride solid solutions, Zhou et al.\textsuperscript{23} proposed applying the $\delta$, mixing enthalpy, and VEC parameters to predict the formation ability of four or five-metal alumino solid solutions, and Sarker et al.\textsuperscript{24} proposed an entropy-forming-ability descriptor to predict the formation ability of the five-metal carbide solid solutions based on the high-throughput first-principles calculations, which all played a positive role. However, these proposed formation criterions are isolated from each other without considering their correlations, which greatly limits the practical application. Therefore, establishing accurate formation criterion based on various factors from different aspects is essential for accelerating the discovery and design of solid-solution ceramics with desirable properties, but it is still a great challenge for the scientific community.

In this work, we take a class of solid-solution ceramics, namely binary metal diboride ($\left(\text{M}_{x}\text{N}_{1-x}\right)\text{B}_2$ with M, N = Hf, Zr, Ta, Nb, or Ti) solid solutions, as a prototype to establish the formation criterion of solid-solution ceramics. The combinatorial methods, including high-throughput molten salt synthesis and high-throughput first-principles calculations combined with machine learning approach, were employed to establish the quantitative formation criterion. The effect of the aforementioned three
possible factors on the formation ability of \((M_xN_{1-x})B_2\) solid solutions was studied systematically, as well as doping condition \((\varphi)\) factor. The influential degree of these four possible factors on the formation ability of \((M_xN_{1-x})B_2\) solid solutions was described as follows: \(\delta > \Delta H_{mix}^{0K}\) (\(\Delta H_{mix}^{0K}\) represents the mixing enthalpy at 0 K and 0 Pa) > \(\varphi > VEC\). In the meantime, a dimensionless parameter, \(\beta\), was proposed to reflect the formation ability of \((M_xN_{1-x})B_2\) solid solutions: when \(\beta > 0\), the single-phase \((M_xN_{1-x})B_2\) solid solutions could be successfully synthesized in our work and \textit{vice versa}. This study will accelerate the discovery and design of the diverse solid-solution ceramics, such as the metal borides, carbides, nitrides, etc., with desirable properties under the theoretical guidance.

2. Theoretical and experimental methods

2.1 The first-principles calculations

The first-principles calculations were performed by Vienna Ab-Initio Simulation Package (VASP)\textsuperscript{25,26} based on the density functional theory (DFT). The core-valence electron interactions were described by the projected-augmented-wave method and the exchange-correlation functional was treated by using the generalized gradient approximation of Perdew-Burke-Ernzerhof\textsuperscript{27,28}. The energy cutoff of 600 eV and the valence electron configurations of 5p6s5d (Hf, valency: 10), 4s4p5s4d (Zr, valency: 12), 5p6s5d (Ta, valency: 11), 4p5s4d (Nb, valency: 13), 3p4s3d (Ti, valency: 12), and 2s2p (B, valency: 3) were adopted throughout the calculations.\textsuperscript{29} In addition, the electronic energy convergence criterion and the ionic force convergence criterion were set as \(10^{-6}\) eV and 0.01 eV/Å, respectively. On the basis of Materials Project database,\textsuperscript{30} the most
stable structures of the individual metal diborides, including HfB$_2$, ZrB$_2$, TaB$_2$, NbB$_2$, and TiB$_2$, belonged to the same space group of P6/mmm where the unit cell was occupied by one metal atom and two B atoms. The lattice parameters and energies of the individual metal diborides were first calculated with a k-mesh grid of $2\pi \times 1/60$ Å$^{-1}$ in VASP and the results were listed in Table 1. It can be found that the lattice parameters in descending order are as follows: ZrB$_2$, HfB$_2$, NbB$_2$, TaB$_2$, TiB$_2$. Meanwhile, the valency of the metal atoms utilized in the DFT calculations was taken as the corresponding $VEC$ of the metal atoms in this work (Table 1), where the $VEC$ of Hf and Nb is the smallest (10) and largest (13), respectively.

Owing to the similar structure of five individual metal diborides, the generated $(M_{x}N_{1-x})B_2$ solid solutions would maintain the similar hexagonal structure. To generate the random occupations of the metal atoms in the metal sublattice of $(M_{x}N_{1-x})B_2$ solid solutions, the special quasi-random structure (SQS) approach was performed via the Alloy Theoretic Automated Toolkit code.$^{31,32}$ From the one aspect, when $x = 0.25$, 0.5, and 0.75, the SQS supercell with 24 atoms (8 metal atoms and 16 B atoms) was first generated and then DFT calculations were carried out with a k-mesh grid of $2\pi \times 1/60$ Å$^{-1}$ in VASP. We have checked that the energy difference between the SQS supercell with 24 and 48 atoms for different compositions is around 1 meV/atom. In this case, the SQS supercell with 24 atoms should be large enough for the calculation of DFT energies and lattice parameters. From the other aspect, when $x = 0.1$, 0.2, 0.3, 0.4, 0.6, 0.7, 0.8, and 0.9, the SQS supercell with 60 atoms (20 metal atoms and 40 B atoms) was constructed and DFT calculations were performed with a k-mesh grid of $2\pi \times 1/40$ Å$^{-1}$ in VASP.
Å⁻¹. Based on the results of DFT calculations, the \( \Delta H_{\text{mix}}^{0K} \) of \((M_xN_{1-x})B_2\) solid solution could be calculated by the following equation:

\[
\Delta H_{\text{mix}}^{0K} = E_{(M_xN_{1-x})B_2} - xE_{MB_2} - (1-x)E_{NB_2}
\]  

(1)

where \( E \) represented the DFT energies of the different systems after relaxation at 0 K and 0 Pa. Meanwhile, the \( \delta \) of \((M_xN_{1-x})B_2\) solid solutions could be expressed as follows:¹⁵

\[
\delta = \sqrt{\frac{x}{2} \left[ \left(1 - \frac{a_M}{\bar{a}} \right)^2 + \left(1 - \frac{c_M}{\bar{c}} \right)^2 \right] + \frac{1-x}{2} \left[ \left(1 - \frac{a_N}{\bar{a}} \right)^2 + \left(1 - \frac{c_N}{\bar{c}} \right)^2 \right]}
\]  

(2)

where \((a_M, c_M)\) and \((a_N, c_N)\) were the lattice parameters of MB₂ and NB₂, respectively, and \( \bar{a} = xa_M + (1-x)a_N \) and \( \bar{c} = xc_M + (1-x)c_N \) were the average lattice parameters. In addition, the \( VEC \) was the most common phase selection criterion in the solid-solution alloy⁹ and here we only considered the \( VEC \) of the metal elements. In this case, the \( VEC \) of \((M_xN_{1-x})B_2\) solid solutions could be expressed as:¹¹

\[
VEC = xVEC_M + (1-x)VEC_N
\]  

(3)

where \( VEC_M \) and \( VEC_N \) were the valency of M and N metal elements, respectively, as listed in Table 1.

2.2 High-throughput molten salt synthesis of \((M_xN_{1-x})B_2\) solid-solution powders

To improve the synthesis efficiency of \((M_xN_{1-x})B_2\) solid-solution powders, the high-throughput apparatus was designed and developed, as shown in Fig. 1. Fig. 1(a) displayed the longitudinal section of the apparatus with a large alumina tube. The large alumina tube was heated at the central zone where two sets of alumina crucible were placed inside each small alumina tube with the flowing Argon gas. The cross section of the large alumina tube was plotted in Fig. 1(b) where a large alumina tube consisted of
7 small alumina tubes. Fig. 1(c) exhibited the longitudinal section of a small alumina tube in which the starting raw materials were placed inside an alumina crucible with a graphite lid. In the heating process, 7 small alumina tubes were heated homogeneously, which ensured that the synthesis conditions were completely the same for the starting materials. That is to say, 14 different experiments could be performed simultaneously under the same synthesis conditions. Commercially-available HfO2, Nb2O5, and Ta2O5 powders (purity: 99.9%, particle size: 1-3 μm, Shanghai ChaoWei Nanotechnology Co. Ltd., Shanghai, China), ZrO2 and TiO2 powders (purity: 99.9%, particle size: 100-300 nm, Shanghai ChaoWei Nanotechnology Co. Ltd., Shanghai, China), and amorphous B powders (purity: 99.9%, particle size: 1-3 μm, Shanghai ChaoWei Nanotechnology Co. Ltd., Shanghai, China) were used as the starting materials to synthesize (MxN1-x)B2 solid-solution powders. The NaCl and KCl (molar ratio: 1:1, eutectic point: 931 K) were utilized as the molten salt medium. The starting materials including two types of metal oxides with the molar ratios of the metal elements, M and N, being \(x/(1-x)\), amorphous B, and NaCl/KCl were first milled by hand for 40 min in an agate mortar. To remove the possible residual oxides in the products, 20% excessive B precursor in stoichiometry was used. The weight ratio of (NaCl, KCl)/(two types of metal oxides, B) was kept as 10:1 for all the starting materials. Afterwards, they were put into the alumina crucibles with graphite lids and the whole assembly was placed into the high-throughput apparatus. The whole system was first heated with a rate of 10 K/min from room temperature to 1423 K and then maintained for 1 h. After naturally cooling down to room temperature, the as-synthesized powders were taken out and immersed in the
deionized water at 363 K and the absolute ethanol at 273 K followed by a filtering
procedure with Nuclepore filters (0.2-pm pore size) to remove the residual NaCl/KCl
salts and B₂O₃ product. Finally, the as-synthesized powders were repeatedly washed,
filtered, and dried at 333 K. During the heating and cooling processes, Argon gas
(99.99%, purity) with flowing rate of 200 sccm was injected into the whole system to
prevent oxidation.

2.3 Characterization

The phase composition of the as-synthesized powders was analyzed by X-ray
diffraction (XRD, X’pert PRO; PANalytical, Almelo, Netherlands). The equivalent
counting time for a conventional point detector would be 30 s per point at 0.01° 2θ
increments. The microstructure and compositional uniformity of the as-synthesized
powders were characterized by scanning electron microscopy (SEM, supra-55; Zeiss,
Oberkochen, Germany) with energy dispersive spectroscopy (EDS) and transmission
electron microscopy (TEM, JEM 2100, JEOL, Tokyo, Japan) equipped with EDS.

3. Results and discussion

3.1 (MₓN₁₋ₓ)B₂ solid solutions with x = 0.5

Here we first focus on the synthesis of C² = 10 types of (M₀.₅N₀.₅)B₂ solid-
solution powders. To analyze the formation ability of (M₀.₅N₀.₅)B₂ solid-solution
powders, their lattice parameters and energies were first calculated by VASP, as listed
in Table S1 of the Supplemental Material. On the basis of these results, their ΔH₀₉₉K,
δ, and VEC were calculated by Eqs. (1) - (3), respectively, as shown in Table 2. From the
aspect of ΔH₀₉₉K, a negative ΔH₀₉₉K indicates that (MₐN₁₋ₐ)B₂ solid solutions are more
stable with respect to their individual metal diborides in thermodynamics. In other words, the \((M_{0.5}N_{0.5})B_2\) solid solutions from No. 1 to 6 are more stable with respect to the constituent individual metal diborides. In contrast, the \((M_{0.5}N_{0.5})B_2\) solid solutions from No. 7 to 10 are not stable and may decompose into the individual metal diborides. In particular, the value of \(\Delta H^0_{mix}\) is the smallest when TiB\(_2\) reacts with TaB\(_2\) to form solid solutions, while the value of \(\Delta H^0_{mix}\) is the largest when TiB\(_2\) forms solid solutions with ZrB\(_2\). From the aspect of \(\delta\), \((Ta_{0.5}Nb_{0.5})B_2\) solid solution has the smallest \(\delta\) value among \((M_{0.5}N_{0.5})B_2\) solid solutions due to the similar lattice parameters between TaB\(_2\) and NbB\(_2\). On the contrary, \((Zr_{0.5}Ti_{0.5})B_2\) solid solution possesses the largest \(\delta\) value among \((M_{0.5}N_{0.5})B_2\) solid solutions because of the significant lattice mismatch between ZrB\(_2\) and TiB\(_2\). In addition, when the value of \(\Delta H^0_{mix}\) is more than zero, there is a positive relationship between \(\Delta H^0_{mix}\) and \(\delta\). That is to say, \(\Delta H^0_{mix}\) increases with the increase of \(\delta\), which suggests a decrease in the stability of \((M_{0.5}N_{0.5})B_2\) solid solutions. However, from the aspect of \(VEC\), its value is randomly distributed with respect to \(\Delta H^0_{mix}\) and \(\delta\), which reveals that the correlation between \(VEC\) and \(\Delta H^0_{mix}\) or \(\delta\) is not significant.

Following the theoretical analyses, the aforementioned 10 types of \((M_{0.5}N_{0.5})B_2\) solid-solution powders were attempted to be synthesized by the high-throughput molten salt method. It is worth mentioning that \((Hf_{0.5}Zr_{0.5})B_2\) solid-solution powders have been successfully synthesized by molten salt method at 1423 K in our previous work\(^{12}\). In our present work, the phase compositions of other 9 types of the as-synthesized \((M_{0.5}N_{0.5})B_2\) solid-solution powders are characterized by XRD and the results are
displayed in Fig. 2. The XRD patterns in Fig. 2 are plotted on a logarithmic scale to investigate the phase composition more clearly. It can be clearly seen that only as-synthesized (Ta0.5Ti0.5)B2 and (Ta0.5Nb0.5)B2 solid-solution powders consist of single phase of metal diborides, while other 7 types of the as-synthesized (M0.5N0.5)B2 solid-solution powders are composed of multiple phases of metal diborides. These experimental results are further summarized in Table 2. Clearly, in our work, only 3 types of (M0.5N0.5)B2 solid solutions, namely (Ta0.5Ti0.5)B2, (Hf0.5Zr0.5)B2, and (Ta0.5Nb0.5)B2, can be successfully synthesized, while other 7 types of (M0.5N0.5)B2 solid solutions cannot be synthesized. In combination with the calculated $\Delta H^0_{\text{mix}}$, $\delta$, and VEC of (M0.5N0.5)B2 solid solutions, a qualitative conclusion can be drawn from these experimental results that (M0.5N0.5)B2 solid solutions with more negative $\Delta H^0_{\text{mix}}$ and smaller $\delta$ are more likely to be successfully synthesized, but no obvious correlation between VEC and formation ability can be found. However, more theoretical and experimental analyses of (M$_x$N$_{1-x}$)B2 solid solutions with other compositions still need to be done to draw a more convincing and quantitative conclusion.

### 3.2 $\Delta H^0_{\text{mix}}$ and $\delta$ of (M$_x$N$_{1-x}$)B2 solid solutions with different $x$

To quantify the effect of $\Delta H^0_{\text{mix}}$ and $\delta$ on the formation ability of (M$_x$N$_{1-x}$)B2 solid solutions, the $\Delta H^0_{\text{mix}}$ and $\delta$ of (M$_x$N$_{1-x}$)B2 solid solutions with different $x$ are further calculated and the results are depicted in Fig. 3. Fig. 3(a) displays the values of $\Delta H^0_{\text{mix}}$ of (M$_x$N$_{1-x}$)B2 solid solutions as a function of $x$. It can be obviously observed that almost all the curves exhibit the shape of “convex hull”. In other words, with the value of $x$ increasing from 0 to 1, the absolute values of $\Delta H^0_{\text{mix}}$ first show a gradual increase
trend with the value of \( x \) increasing from 0 to 0.5 and then exhibit a continuous decrease trend with the value of \( x \) increasing from 0.5 to 1. Furthermore, it should be noted that the smallest and largest values of \( \Delta H_{mix}^{0K} \) among all \((M_xN_{1-x})B_2\) solid solutions are \((Ta_xTi_{1-x})B_2\) solid solutions and \((Zr_xTi_{1-x})B_2\) solid solutions, respectively. The calculated values of \( \delta \) of \((M_xN_{1-x})B_2\) solid solutions as a function of \( x \) are shown in Fig. 3(b).

Interestingly, all the curves also exhibit the similar “convex hull” shape where the values of \( \delta \) first gradually increase from zero at \( x = 0 \) to the maximum at \( x = 0.5 \) and then continuously decreases to zero at \( x = 1 \). The similar “convex hull” shape of \( \Delta H_{mix}^{0K} \) and \( \delta \) suggests the presence of an intrinsic correlation between them. Meanwhile, all the curves for \( \Delta H_{mix}^{0K} \) and \( \delta \) are almost symmetrical with respect to \( x = 0.5 \). That’s to say, the value of \( \Delta H_{mix}^{0K} \) and \( \delta \) at \( x = x_0 (0 < x_0 < 1) \) is close to that of \( \Delta H_{mix}^{0K} \) and \( \delta \) at \( x = 1-x_0 \), respectively. Moreover, the \( \delta \) values of \((Ta_xN_{1-x})B_2\) and \((Nb_xN_{1-x})B_2\) with \( N = Hf, Zr, \) or \( Ti \) are almost the same, which can be attributed to the similar lattice parameters of \( TaB_2 \) and \( NbB_2 \).

On the basis of the variation curves of \( \Delta H_{mix}^{0K} \) and \( \delta \) of \((M_xN_{1-x})B_2\) solid solutions as a function of \( x \), more theoretical and experimental analyses can be carried out to quantify the effect of \( \Delta H_{mix}^{0K} \), \( \delta \), and \( VEC \) of \((M_xN_{1-x})B_2\) solid solutions on their formation ability. Therefore, the effect of \( \Delta H_{mix}^{0K} \), \( \delta \), and \( VEC \) of \((M_xN_{1-x})B_2\) solid solutions with different \( x \) on their formation ability is further studied. As for the formation ability of \((M_xN_{1-x})B_2\) solid solutions with different \( x \), a factor \( \varphi \) should also be considered, except for \( \Delta H_{mix}^{0K} \), \( \delta \), and \( VEC \). To be specific, one individual metal diboride doped by another individual metal diboride with larger or smaller lattice
parameters should play a role in the formation ability of solid solutions. In our work, if
the molar fraction of the individual metal diborides with smaller lattice parameters is
more than 0.5, \( \varphi = 0 \) (“Small doped by Large”); else, \( \varphi = 1 \) (“Large doped by Small”).

3.3 Different \( \varphi \) of \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions

In our previous work, the \((\text{Hf}_{x}\text{Zr}_{1-x})\text{B}_2\) solid-solution powders with \( x = 0.2, 0.5, \) and 0.8 have been successfully synthesized by molten salt method at 1423 K under both \( \varphi = 0 \) and \( \varphi = 1 \) conditions.\(^{12}\) At the same time, combined with the theoretical and experimental results mentioned above, some \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions with negative \( \Delta H_{\text{mix}}^{0} \) or small \( \delta \), namely \((\text{Hf}_{x}\text{Ta}_{1-x})\text{B}_2\), \((\text{Hf}_{x}\text{Nb}_{1-x})\text{B}_2\), \((\text{Nb}_{x}\text{Ti}_{1-x})\text{B}_2\), and \((\text{Ta}_{x}\text{Ti}_{1-x})\text{B}_2\), are selected to quantify the effect of \( \Delta H_{\text{mix}}^{0} \), \( \delta \), and \( VEC \) on the formation ability of \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions and simultaneously study the effect of \( \varphi \) on the formation ability of \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions. As a result, the \( \Delta H_{\text{mix}}^{0} \), \( \delta \), and \( VEC \) of the chosen \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions from No. 11 to 17, under \( \varphi = 1 \) condition are first calculated and the results are listed in Table 3. Subsequently, the \( \Delta H_{\text{mix}}^{0} \), \( \delta \), and \( VEC \) of the chosen \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions from No. 18 to 22, under \( \varphi = 0 \) condition are also calculated, as listed in Table 4. It’s worth mentioning that the compositions of No. 18-22 in Table 4 are the counterparts of No. 11-17 in Table 3. Meanwhile, the values of \( \Delta H_{\text{mix}}^{0} \) and \( \delta \) of No. 18-22 in Table 4 are very close to that of their counterparts of No. 11-17 in Table 3, respectively, which are in good agreement with the aforementioned curves of \( \Delta H_{\text{mix}}^{0} \) and \( \delta \) of \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions as a function of \( x \) (Fig. 3).

Following the calculated \( \Delta H_{\text{mix}}^{0} \), \( \delta \), and \( VEC \) of the chosen \((\text{M} \text{xN}_{1-x})\text{B}_2\) solid solutions with different \( x \), the high-throughput molten salt syntheses of the
corresponding solid-solution powders are carried out at 1423 K. XRD patterns of the as-synthesized powders are displayed on logarithmic scale in Fig. 4. Fig. 4(a) demonstrates XRD patterns of the chosen (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions under $\varphi = 1$ condition in Table 3. It can be found that only (Nb\textsubscript{0.9}Ti\textsubscript{0.1})B\textsubscript{2}, (Nb\textsubscript{0.8}Ti\textsubscript{0.2})B\textsubscript{2}, (Ta\textsubscript{0.8}Ti\textsubscript{0.2})B\textsubscript{2}, and (Ta\textsubscript{0.6}Ti\textsubscript{0.4})B\textsubscript{2} solid-solution powders can be successfully synthesized at 1423 K, while the other solid-solution powders cannot be synthesized at 1423 K in that their as-synthesized powders involve multiple phases of metal diborides. It is worth noting that although the XRD pattern of (Nb\textsubscript{0.7}Ti\textsubscript{0.3})B\textsubscript{2} seems to be very similar to that of (Nb\textsubscript{0.8}Ti\textsubscript{0.2})B\textsubscript{2}, a small peak of other metal diborides can be observed for (Nb\textsubscript{0.7}Ti\textsubscript{0.3})B\textsubscript{2} (indicated by red arrow in Fig. 4(a)). This suggests that (Nb\textsubscript{0.7}Ti\textsubscript{0.3})B\textsubscript{2} solid-solution powders cannot be synthesized at 1423 K. When $\varphi = 0$, only (Ta\textsubscript{0.5}Ti\textsubscript{0.5})B\textsubscript{2} and (Ta\textsubscript{0.4}Ti\textsubscript{0.6})B\textsubscript{2} solid-solution powders can be successfully synthesized, as shown in Fig. 4(b). To quantify the effect of $\Delta H_{\text{mix}}^0$, $\delta$, and $VEC$ on the formation ability of (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions and simultaneously study the effect of $\varphi$ on the formation ability of (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions, the above-mentioned XRD results are further summarized in Tables 3 and 4. The theoretical and experimental results from Tables 3 and 4 further confirm that the (M\textsubscript{x}N\textsubscript{1-x})B\textsubscript{2} solid solutions with more negative $\Delta H_{\text{mix}}^0$ and smaller $\delta$ are more prone to being successfully synthesized. However, the obvious correlation between $VEC$ and formation ability is still difficult to be found. In addition, it is obvious that the (Nb\textsubscript{x}Ti\textsubscript{1-x})B\textsubscript{2} solid solutions with $x > 0.7$ (No. 13 and 14 in Table 3) can be successfully synthesized under $\varphi = 1$ condition (NbB\textsubscript{2} doped by TiB\textsubscript{2}). Nevertheless, even though $x = 0.1$, the (Nb\textsubscript{x}Ti\textsubscript{1-x})B\textsubscript{2} solid solution (No. 20 in Table 4)
still cannot be synthesized under $\varphi = 0$ condition (TiB$_2$ doped by NbB$_2$). As a result, combining with the results that the values of $\Delta H_{mix}^{0K}$ and $\delta$ at $x = x_0 \ (0 < x_0 < 1)$ are closed to that of $\Delta H_{m}^{0K}$ and $\delta$ at $x = 1-x_0$ for $(M_{x}N_{1-x})B_2$ solid solutions, we can draw a conclusion that $\varphi$ plays a role in the formation ability of $(M_{x}N_{1-x})B_2$ solid solutions. From the perspective of atomic packing, when a larger metal diboride dopes into a smaller one, there is not enough room in the smaller solvent lattice to incorporate the larger solute lattice and it would normally take higher activation energy than vice versa.\textsuperscript{33} In this case, $\varphi = 0$ (“Small doped by Large”) has lower solubility than $\varphi = 1$ (“Large doped by Small”).

3.4 Microstructure and compositional uniformity of the as-synthesized powders

To investigate the microstructure and compositional uniformity of the as-synthesized powders, we take two typical as-synthesized powders, namely single-phase (Ta$_{0.5}$Nb$_{0.5}$)B$_2$ and multiple-phase (Hf$_{0.5}$Ti$_{0.5}$)B$_2$, as examples. Fig. 5 shows the SEM images and the corresponding EDS compositional maps of the as-synthesized (Ta$_{0.5}$Nb$_{0.5}$)B$_2$ and (Hf$_{0.5}$Ti$_{0.5}$)B$_2$ solid-solution powders. From Fig. 5(a), it can be clearly seen that the as-synthesized (Ta$_{0.5}$Nb$_{0.5}$)B$_2$ solid-solution powders involve a large number of the nanorods with the typical diameter of 20-30 nm and length of 100-200 nm, as shown in high-magnification SEM image (top-right corner in Fig. 5(a)). Fig. 5(b) shows the corresponding EDS compositional maps of Fig. 5(a), from which it can be found that the distribution of Ta and Nb elements is highly uniform without localization of any Ta or Nb element at micrometer scale. Fig. 5(c) displays SEM image of the as-synthesized (Hf$_{0.5}$Ti$_{0.5}$)B$_2$ solid-solution powders, it can be seen that the as-
synthesized \((\text{Hf}_{0.5}\text{Ti}_{0.5})\text{B}_2\) solid-solution powders are composed of numerous irregular particles with the particle size of more than 1 \(\mu\text{m}\). The corresponding EDS compositional maps of Fig. 5(c) (Fig. 5(d)) present that the distribution of Hf and Ti elements is not uniform and there are some segregations of Ti element at micrometer scale, as indicated by yellow arrow in Fig 5(d). It's interesting to note that the segregation locations of Ti element are consistent with that of the particles indicated by yellow arrow in Fig. 5(c). Therefore, it can be concluded that the composition of the particles indicated by yellow arrow in Fig. 5(c) is different from that of irregular particles in the as-synthesized \((\text{Hf}_{0.5}\text{Ti}_{0.5})\text{B}_2\) solid-solution powders. In summary, the SEM-EDS analysis results of the as-synthesized \((\text{Ta}_{0.5}\text{Nb}_{0.5})\text{B}_2\) and \((\text{Hf}_{0.5}\text{Ti}_{0.5})\text{B}_2\) solid-solution powders are in good agreement with their XRD analysis results.

TEM characterization was further performed to investigate the microstructure and compositional homogeneity at nanoscale of the as-synthesized \((\text{Ta}_{0.5}\text{Nb}_{0.5})\text{B}_2\) and \((\text{Hf}_{0.5}\text{Ti}_{0.5})\text{B}_2\) solid-solution powders. Fig. 6(a) is a typical TEM image of the as-synthesized \((\text{Ta}_{0.5}\text{Nb}_{0.5})\text{B}_2\) solid-solution powders, which clearly exhibits that the as-synthesized powders involves numerous nanorods with the typical diameter of 20-30 nm and length of 100-200 nm. The high-resolution TEM (HRTEM) image (Fig. 6(b)) displays a clear periodic lattice structure with a set of fringes of about 3.27 Å, corresponding to the \(d\)-space of (001) planes of the metal diborides, which is in good agreement with the value (3.321 Å) from the first-principles calculations (Table S1 of the Supplemental Material). The corresponding Fast Fourier transform pattern (bottom-right corner in Fig. 6(b)) shows that these nanorods are the single crystal with a
hexagonal structure of (Ta<sub>0.5</sub>Nb<sub>0.5</sub>)B<sub>2</sub>. The distribution of Ta and Nb elements at nanoscale is presented in Fig. 6(c). Obviously, their distributions are highly uniform at nanoscale without any segregation or aggregation being observed. Figs. 6(d) is a representative TEM image of the as-synthesized (Hf<sub>0.5</sub>Ti<sub>0.5</sub>)B<sub>2</sub> solid-solution powders, from which a big irregular particle with some small regular particles (indicated by yellow arrow in Fig. 6(d)) can be observed. The corresponding STEM-EDS analysis shows that the composition of the as-synthesized (Hf<sub>0.5</sub>Ti<sub>0.5</sub>)B<sub>2</sub> solid-solution powders is not very uniform and the segregation of Ti element is very evident at nanoscale, especially in small regular particles. Consequently, in combination of XRD, SEM, and TEM analyses, it can be concluded that (Ta<sub>0.5</sub>Nb<sub>0.5</sub>)B<sub>2</sub> solid-solution powders can be successfully synthesized, while (Hf<sub>0.5</sub>Ti<sub>0.5</sub>)B<sub>2</sub> solid-solution powders cannot be synthesized in our work. In other words, XRD analysis can well demonstrate whether (M<sub>x</sub>N<sub>1-x</sub>)B<sub>2</sub> solid solutions have been successfully synthesized in our work.

3.5 Establishing formation criterion for (M<sub>x</sub>N<sub>1-x</sub>)B<sub>2</sub> solid solutions by machine learning approach

On the basis of the aforementioned theoretical and experimental results, the formation criterion for (M<sub>x</sub>N<sub>1-x</sub>)B<sub>2</sub> solid solutions can be well established by machine learning approach. It’s critical to elaborately quantify the aforementioned four factors, namely $\Delta H^0_{\text{mix}}$, $\delta$, VEC, and $\phi$, to depict the formation ability, which is the essence and the most challenging step in the high-throughput methods. By applying the logistic regression approach in supervised machine learning, the formation ability ($p$) of (M<sub>x</sub>N<sub>1-x</sub>)B<sub>2</sub> solid solutions can be expressed as:34
\[ p = \frac{1}{1 + \exp(-\beta)} \]  
(4)

\[ \beta = [1, \Delta H_{\text{mix}}^{0K}, \delta, VEC, \varphi] \times [\theta_0, \theta_1, \theta_2, \theta_3, \theta_4]^T \]  
(5)

where \( \beta \) is the dimensionless parameter, \( \Delta H_{\text{mix}}^{0K} \), \( \delta \), and \( VEC \) are the normalized values in the range of 0 to 1 of \( \Delta H_{\text{mix}}^{0K} \), \( \delta \), and \( VEC \), respectively. \( \theta_0 - \theta_4 \) are the parameters that represent the influence of the aforementioned four factors on the formation ability, which can be determined by the theoretical and experimental data.

The 22 types of \((\text{M}_{x}\text{N}_{1-x})\text{B}_2\) solid solutions in Tables 2-4 are first divided into two groups: No.1-12, 14, 18, 20, 21 are training data and the rest is validating data. The conventional gradient descent optimization algorithms are applied and \( \theta_0 - \theta_4 \) can be determined as 56.502, -84.096, -152.517, 7.374, and 12.884, respectively. In this light, the influential degree of the aforementioned four factors on the formation ability of \((\text{M}_{x}\text{N}_{1-x})\text{B}_2\) solid solutions can be described as follows: \( \delta > \Delta H_{\text{mix}}^{0K} > \varphi > VEC \). By using the optimized parameters \( \theta_0 - \theta_4 \), the formation ability of \((\text{M}_{x}\text{N}_{1-x})\text{B}_2\) solid solutions in the validating data (No. 13, 15-17, 19, 22) can be predicted, as displayed in Table 5. In our case, when \( p > 0.5 \), \((\text{M}_{x}\text{N}_{1-x})\text{B}_2\) solid solutions should be theoretically synthesized in our work and vice versa. As a result, it can be clearly seen from Table 5 that the predicted formation ability is in good agreement with the experimental results, so the model’s predictive accuracy is 100%. In addition, the leave-one-out cross validation accuracy of the model \((20/22 = 90.91\%)\) can be derived from Table S2 in the Supplemental Material, which further validates the robustness of the proposed model and shows that the sequence of the influential degree of the aforementioned four factors almost stays the same. Subsequently, the values of \( \beta \) parameter for 22 types of \((\text{M}_{x}\text{N}_{1-x})\text{B}_2\) solid solutions can
be calculated by Eq. (5) and the results are depicted in Fig. 7. Clearly, when \( \beta > 0 \), the single-phase \((M_xN_{1-x})B_2\) solid solutions can be successfully synthesized in our work and vice versa. Therefore, the values of \( \beta \) parameter can well reflect the formation ability of \((M_xN_{1-x})B_2\) solid solutions. What’s more, the upper limit of \( \Delta H_{mix}^{0K} \) and \( \delta \) for forming single-phase \((M_xN_{1-x})B_2\) solid solutions with different \( \varphi \) can also be estimated by the current model when the value of \( \overline{VEC} \) is considered as zero. The calculated results are listed in Table 6. In general, the upper limit of \( \Delta H_{mix}^{0K} \) and \( \delta \) means that \((M_xN_{1-x})B_2\) solid solutions cannot be synthesized in our work when either of \( \Delta H_{mix}^{0K} \) and \( \delta \) exceeds their upper limit. It can be noted that the upper limit of \( \Delta H_{mix}^{0K} \) and \( \delta \) for forming single-phase \((M_xN_{1-x})B_2\) solid solutions under \( \varphi = 1 \) condition is much higher than that under \( \varphi = 0 \) condition. This quantitatively suggests that the synthesis of \((M_xN_{1-x})B_2\) solid solution under \( \varphi = 0 \) condition (“Small doped by Large”) is more difficult than that under \( \varphi = 1 \) condition (“Large doped by Small”).

4. Conclusion

In conclusion, the formation criterion of \((M_xN_{1-x})B_2\) solid solutions has been well established through high-throughput experimental and theoretical methods combined with machine learning approach. The influential degree of four factors, namely \( \Delta H_{mix}^{0K} \), \( \delta \), \( VEC \), and \( \varphi \), on the formation ability of \((M_xN_{1-x})B_2\) solid solutions can be described as follows: \( \delta > \Delta H_{mix}^{0K} > \varphi > VEC \). In particular, \( \delta \) and \( \Delta H_{mix}^{0K} \) are two dominant factors in determining the formation ability of \((M_xN_{1-x})B_2\) solid solutions. Meanwhile, there are negative correlations between formation ability and \( \delta \) or \( \Delta H_{mix}^{0K} \) but positive correlations between formation ability and \( \varphi \) or \( VEC \) for \((M_xN_{1-x})B_2\) solid solutions. In
addition, the proposed parameter, $\beta$, which correlates linearly with four factors, is in good agreement with the experimental results. That’s to say, only when $\beta > 0$, the single-phase $(M_{x}N_{1-x})B_2$ solid solutions can be successfully synthesized in our work. This work will guide us to discover and design a variety of solid-solution ceramics with desirable properties, such as metal borides, carbides, nitrides, etc.
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Author Contributions

Y. Chu conceived and designed this work. T. Wen and C.Z. Wang performed the theoretical calculations and analyses. Y. Chu, B. Ye, H. Liu, and S. Ning performed the experiments. Y. Chu, T. Wen, and B. Ye analyzed the data. All authors commented on the manuscript.

Notes

The authors declare no competing financial interest.
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### Tables

**Table 1.** Calculated equilibrium lattice parameters \((a\) and \(c\)) and energies \((E)\) of five individual metal diborides at 0 K and 0 Pa and the \(VEC\) of the metal elements.

<table>
<thead>
<tr>
<th>Systems</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(E) (eV/atom)</th>
<th>(VEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB(_2)</td>
<td>3.143</td>
<td>3.486</td>
<td>-8.801</td>
<td>10</td>
</tr>
<tr>
<td>ZrB(_2)</td>
<td>3.171</td>
<td>3.540</td>
<td>-8.326</td>
<td>12</td>
</tr>
<tr>
<td>TaB(_2)</td>
<td>3.103</td>
<td>3.323</td>
<td>-9.053</td>
<td>11</td>
</tr>
<tr>
<td>NbB(_2)</td>
<td>3.110</td>
<td>3.321</td>
<td>-8.609</td>
<td>13</td>
</tr>
<tr>
<td>TiB(_2)</td>
<td>3.036</td>
<td>3.224</td>
<td>-8.144</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 2. Calculated $\Delta H_{mix}^{0K}$, $\delta$, and $VEC$ of (M$_{0.5}$N$_{0.5}$)B$_2$ solid solutions and the phase composition of the as-synthesized powders.

<table>
<thead>
<tr>
<th>No.</th>
<th>(M$<em>{0.5}$N$</em>{0.5}$)B$_2$</th>
<th>$\Delta H_{mix}^{0K}$ (kJ/mol)</th>
<th>$\delta$ (%)</th>
<th>$VEC$</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Ta$<em>{0.5}$Ti$</em>{0.5}$)B$_2$</td>
<td>-3.198</td>
<td>1.317</td>
<td>11.5</td>
<td>Single Phase</td>
</tr>
<tr>
<td>2</td>
<td>(Nb$<em>{0.5}$Ti$</em>{0.5}$)B$_2$</td>
<td>-1.382</td>
<td>1.349</td>
<td>12.5</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>3</td>
<td>(Zr$<em>{0.5}$Ta$</em>{0.5}$)B$_2$</td>
<td>-0.873</td>
<td>2.367</td>
<td>11.5</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>4</td>
<td>(Hf$<em>{0.5}$Ta$</em>{0.5}$)B$_2$</td>
<td>-0.760</td>
<td>1.755</td>
<td>10.5</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>5</td>
<td>(Ta$<em>{0.5}$Nb$</em>{0.5}$)B$_2$</td>
<td>-0.363</td>
<td>0.085</td>
<td>12</td>
<td>Single Phase</td>
</tr>
<tr>
<td>6</td>
<td>(Hf$<em>{0.5}$Zr$</em>{0.5}$)B$_2$</td>
<td>0.002</td>
<td>0.627</td>
<td>11</td>
<td>Single Phase$^{12}$</td>
</tr>
<tr>
<td>7</td>
<td>(Hf$<em>{0.5}$Nb$</em>{0.5}$)B$_2$</td>
<td>0.182</td>
<td>1.757</td>
<td>11.5</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>8</td>
<td>(Zr$<em>{0.5}$Nb$</em>{0.5}$)B$_2$</td>
<td>0.296</td>
<td>2.363</td>
<td>12.5</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>9</td>
<td>(Hf$<em>{0.5}$Ti$</em>{0.5}$)B$_2$</td>
<td>2.370</td>
<td>3.023</td>
<td>11</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>10</td>
<td>(Zr$<em>{0.5}$Ti$</em>{0.5}$)B$_2$</td>
<td>3.812</td>
<td>3.647</td>
<td>12</td>
<td>Multiple Phases</td>
</tr>
</tbody>
</table>
Table 3. Calculated $\Delta H_{mix}^{0K}$, $\delta$, and $VEC$ of the chosen $(M_{x}N_{1-x})B_{2}$ solid solutions with different $x$ and the phase composition of the as-synthesized powders. Herein $\varphi = 1$ ("Large doped by Small") indicates that the individual metal diborides with larger lattice parameters are doped by that with smaller lattice parameters.

<table>
<thead>
<tr>
<th>No.</th>
<th>$(M_{x}N_{1-x})B_{2}$</th>
<th>$\Delta H_{mix}^{0K}$ (kJ/mol)</th>
<th>$\delta$ (%)</th>
<th>$VEC$</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>$(\text{Hf}<em>{0.9}\text{Ta}</em>{0.1})B_{2}$</td>
<td>-0.403</td>
<td>1.034</td>
<td>10.1</td>
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<tr>
<td>12</td>
<td>$(\text{Hf}<em>{0.9}\text{Nb}</em>{0.1})B_{2}$</td>
<td>-0.038</td>
<td>1.035</td>
<td>10.3</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>13</td>
<td>$(\text{Nb}<em>{0.9}\text{Ti}</em>{0.1})B_{2}$</td>
<td>-0.375</td>
<td>0.801</td>
<td>12.9</td>
<td>Single Phase</td>
</tr>
<tr>
<td>14</td>
<td>$(\text{Nb}<em>{0.8}\text{Ti}</em>{0.2})B_{2}$</td>
<td>-0.796</td>
<td>1.071</td>
<td>12.8</td>
<td>Single Phase</td>
</tr>
<tr>
<td>15</td>
<td>$(\text{Nb}<em>{0.7}\text{Ti}</em>{0.3})B_{2}$</td>
<td>-1.108</td>
<td>1.230</td>
<td>12.7</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>16</td>
<td>$(\text{Ta}<em>{0.8}\text{Ti}</em>{0.2})B_{2}$</td>
<td>-1.858</td>
<td>1.045</td>
<td>11.2</td>
<td>Single Phase</td>
</tr>
<tr>
<td>17</td>
<td>$(\text{Ta}<em>{0.6}\text{Ti}</em>{0.4})B_{2}$</td>
<td>-2.958</td>
<td>1.287</td>
<td>11.4</td>
<td>Single Phase</td>
</tr>
</tbody>
</table>
Table 4. Calculated $\Delta H_{mix}^{0K}$, $\delta$, and $VEC$ of the chosen $(\text{M}_x\text{N}_{1-x})\text{B}_2$ solid solutions with different $x$ and the phase composition of the as-synthesized powders. Herein $\varphi = 0$ (“Small doped by Large”) indicates that the individual metal diborides with smaller lattice parameters are doped by that with larger lattice parameters.

<table>
<thead>
<tr>
<th>No.</th>
<th>$(\text{M}<em>x\text{N}</em>{1-x})\text{B}_2$</th>
<th>$\Delta H_{mix}^{0K}$ (kJ/mol)</th>
<th>$\delta$ (%)</th>
<th>$VEC$</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>$(\text{Hf}<em>{0.1}\text{Ta}</em>{0.9})\text{B}_2$</td>
<td>-0.228</td>
<td>1.072</td>
<td>10.9</td>
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<tr>
<td>19</td>
<td>$(\text{Hf}<em>{0.1}\text{Nb}</em>{0.9})\text{B}_2$</td>
<td>0.047</td>
<td>1.074</td>
<td>12.7</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>20</td>
<td>$(\text{Nb}<em>{0.1}\text{Ti}</em>{0.9})\text{B}_2$</td>
<td>-0.573</td>
<td>0.818</td>
<td>12.1</td>
<td>Multiple Phases</td>
</tr>
<tr>
<td>21</td>
<td>$(\text{Ta}<em>{0.2}\text{Ti}</em>{0.8})\text{B}_2$</td>
<td>-2.176</td>
<td>1.063</td>
<td>11.8</td>
<td>Single phase</td>
</tr>
<tr>
<td>22</td>
<td>$(\text{Ta}<em>{0.4}\text{Ti}</em>{0.6})\text{B}_2$</td>
<td>-3.137</td>
<td>1.294</td>
<td>11.6</td>
<td>Single phase</td>
</tr>
</tbody>
</table>
Table 5. The predicted formation ability ($p$) of (M$_x$N$_{1-x}$)B$_2$ solid solutions in the validating data and the phase composition of the as-synthesized powders.

<table>
<thead>
<tr>
<th>No.</th>
<th>(M$<em>x$N$</em>{1-x}$)B$_2$</th>
<th>$p$</th>
<th>Phase Composition</th>
<th>Match (yes or no)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>(Nb$<em>{0.9}$Ti$</em>{0.1}$)B$_2$</td>
<td>1.000</td>
<td>Single phase</td>
<td>yes</td>
</tr>
<tr>
<td>15</td>
<td>(Nb$<em>{0.7}$Ti$</em>{0.3}$)B$_2$</td>
<td>0.380</td>
<td>Multiple Phases</td>
<td>yes</td>
</tr>
<tr>
<td>16</td>
<td>(Ta$<em>{0.8}$Ti$</em>{0.2}$)B$_2$</td>
<td>1.000</td>
<td>Single phase</td>
<td>yes</td>
</tr>
<tr>
<td>17</td>
<td>(Ta$<em>{0.6}$Ti$</em>{0.4}$)B$_2$</td>
<td>1.000</td>
<td>Single phase</td>
<td>yes</td>
</tr>
<tr>
<td>19</td>
<td>(Hf$<em>{0.1}$Nb$</em>{0.9}$)B$_2$</td>
<td>0.000</td>
<td>Multiple Phases</td>
<td>yes</td>
</tr>
<tr>
<td>22</td>
<td>(Ta$<em>{0.4}$Ti$</em>{0.6}$)B$_2$</td>
<td>0.996</td>
<td>Single phase</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 6. The estimated upper limit of $\Delta H_{\text{mix}}^{0K}$ and $\delta$ for forming single-phase (M$_x$N$_{1-x}$)B$_2$ solid solutions with different $\varphi$.

<table>
<thead>
<tr>
<th>$\varphi$</th>
<th>$\Delta H_{\text{mix}}^{0K}$ (kJ/mol)</th>
<th>$\delta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.586</td>
<td>1.659</td>
</tr>
<tr>
<td>0</td>
<td>1.512</td>
<td>1.351</td>
</tr>
</tbody>
</table>
Figure Captions

**Fig. 1.** Schematic illustration of the high-throughput apparatus. (a) The longitudinal section of the apparatus showing a large alumina tube with two sets of alumina crucible at the central heating zone and the flowing Argon gas, (b) the cross-section of the large alumina tube showing the presence of 7 small alumina tubes inside, (c) the longitudinal section of a small alumina tube showing the presence of two sets of alumina crucible inside.

**Fig. 2.** XRD patterns of the as-synthesized (M0.5N0.5)B2 solid-solution powders.

**Fig. 3.** The calculated (a) $\Delta H_{mix}^{0K}$ and (b) $\delta$ of (M$_{x}$N$_{1-x}$)B$_{2}$ solid solutions as a function of $x$.

**Fig. 4.** XRD patterns of the as-synthesized (M$_{x}$N$_{1-x}$)B$_{2}$ solid-solution powders with different $\phi$. (a) $\phi = 1$ (“Large doped by Small”), (b) $\phi = 0$ (“Small doped by Large”).

**Fig. 5.** SEM characterization of the as-synthesized (Ta0.5Nb0.5)B$_2$ and (Hf0.5Ti0.5)B$_2$ solid-solution powders. (a) SEM image of (Ta0.5Nb0.5)B$_2$, (b) the corresponding EDS compositional maps of (a), (c) SEM image of (Hf0.5Ti0.5)B$_2$, (d) the corresponding EDS compositional maps of (c).

**Fig. 6.** TEM analysis of the as-synthesized (Ta0.5Nb0.5)B$_2$ and (Hf0.5Ti0.5)B$_2$ solid-solution powders. (a) TEM image of (Ta0.5Nb0.5)B$_2$, (b) HRTEM image of (Ta0.5Nb0.5)B$_2$, (c) STEM image and the corresponding EDS compositional maps of (Ta0.5Nb0.5)B$_2$, (d) TEM image of (Hf0.5Ti0.5)B$_2$, (e) STEM image and the corresponding EDS compositional maps of (Hf0.5Ti0.5)B$_2$.

**Fig. 7.** The calculated values of $\beta$ parameter for (M$_{x}$N$_{1-x}$)B$_2$ solid solutions. The orange
diamond and blue circle denote the single-phase and multiple-phase composition, respectively.