Electronic structure, bonding characteristics, and mechanical behaviors of a new family of Si-containing damage-tolerant MAB phases $\text{M}_5\text{SiB}_2$ ($\text{M} = \text{IVB–VIB transition metals}$)

Na Ni$^{a,*}$, Hanchao ZHANG$^a$, Yanchun ZHOU$^{b,*}$

$^a$School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China  
$^b$Science and Technology on Advanced Functional Composite Laboratory, Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, China

Received: May 23, 2022; Revised: July 5, 2022; Accepted: July 17, 2022  
© The Author(s) 2022.

Abstract: MAB phases are layered ternary compounds with alternative stacking of transition metal boride layers and group A element layers. Until now, most of the investigated MAB phases are concentrated on compounds with Al as the A element layers. In this work, the family of $\text{M}_5\text{SiB}_2$ ($\text{M} = \text{IVB–VIB transition metals}$) compounds with silicon as interlayers were investigated by density functional theory (DFT) methods as potential MAB phases for high-temperature applications. Starting from the known $\text{Mo}_5\text{SiB}_2$, the electronic structure, bonding characteristics, and mechanical behaviors were systematically investigated and discussed. Although the composition of $\text{M}_5\text{SiB}_2$ does not follow the general formula of experimentally reported $(\text{MB})_{2z}\text{A}_x(\text{MB}_2)^y$ ($z = 1, 2; x = 1, 2; y = 0, 1, 2$), their layered structure and anisotropic bonding characteristics are similar to other known MAB phases, which justifies their classification as new members of this material class. As a result of the higher bulk modulus and lower shear modulus, $\text{Mo}_5\text{SiB}_2$ has a Pugh’s ratio of 0.53, which is much lower than the common MAB phases. It was found that the stability and mechanical properties of $\text{M}_5\text{SiB}_2$ compounds depend on their valence electron concentrations (VECs), and an optimum VEC exists as the criteria for stability. The hypothesized Zr and Hf containing compounds, i.e., $\text{Zr}_5\text{SiB}_2$ and $\text{Hf}_5\text{SiB}_2$, which are more interesting in terms of high-temperature oxidation/ablation resistance, were found to be unfortunately unstable. To cope with this problem, a new stable solid solution $(\text{Zr}_{0.6}\text{Mo}_{0.4})_5\text{SiB}_2$ was designed based on VEC tuning to demonstrate a promising approach for developing new MAB phases with desirable compositions.

Keywords: borides; MAB phases; density functional theory (DFT); thermodynamic stability; electronic structure; mechanical properties

1 Introduction

In the last two decades, a category of ternary-layered layered carbides and nitrides referred to as MAX phases has been proven to possess a unique combination of ceramic-like and metal-like properties such as good electrical conductivity, high strength and toughness, good thermal shock/oxidation/corrosion resistance, and damage tolerance, which is owing to their nano laminated crystal structure and diverse and anisotropic chemical
bondings [1–3]. Inspired by the unique properties of the MAX phases, a family of nano laminated ternary borides, named MAB phases (where M is a transition metal, A is a IIIA or IV A group element, and B is boron) were proposed by Ade and Hillebrecht [4] in 2015. MAB phases are anticipated to exhibit similar properties to the MAX phases, such as good electrical conductivity, damage tolerance [5,6], resistance to thermal shock [7] and oxidation [8] at high temperatures, as well as superior high-temperature strength [7] and self-healing capability of cracks [9].

According to Kota et al. [10], the experimentally prepared MAB phases can be represented by the general formula of \((\text{MB})_2\text{A}_x(\text{MB}_2)_z (z = 1, 2; x = 1, 2; y = 0, 1, 2)\), including MAIB, M2AlB2, M3AlB4, M4AlB6, and M4AlB8 with abbreviation of 222, 212, 314, 416, and 414 phases, respectively. In these compounds, MB sublattices are separated by two layers of Al in the MAB phases, such as MoAlB [11], or a single layer of Al in phases such as Fe2AlB2 [12], Cr3AlB2 [13], Cr4AlB6, Cr5AlB4 [14–16], and Mn2AlB2 [17]. Other than the initial MAB phases, new layered borides including Nb5SB [18], Y5Si2B5 [19], V2AlB [20], Zr5CdB4 [21], V6SiB [22], and Hf5PdB [23] have also been reported, which riches the family of MAB phases.

For applications in a high-temperature oxygen-containing environment, the choice of Si on the A site is interesting. It is well established that the compounds with Si as interlayers have been considered to be resistant to oxidation by forming a protective SiO2 scale [24–27]. To find new Si-containing MAB phases, Zhou et al. [19,26] theoretically predicted the intrinsic properties of Y5Si2B6, Cr5Si2B6, and Hf5Si2B6 using the density functional theory (DFT). In Y5Si2B6, YB4 layers are interleaved by the Y3Si2 layers, while in Cr5Si2B6 and Hf5Si2B6, face-shared BCr6 and BHf6 octahedra are interleaved by Si atoms on \{10\overline{1}0\} planes. These compounds are expected to demonstrate attractive properties such as damage tolerance for their low shear modulus and thermal shock resistance due to the moderate Young’s modulus. Intriguingly, it is noted that Cr5Si2B6, Hf5Si2B6, and Y5Si2B6 do not follow the general formula proposed by Kota et al. [10], indicating the possibility to expand the MAB phases beyond this compositional limitation.

A careful literature survey reveals that Si-containing ternary layered borides with a formula M2SiB2 (M = V, Nb, Mo, W), also known as the T2 phase, were proven to exist by Nowotny et al. [28] in 1957. These compounds crystallize in a D8h structure, which can be described by a body-centered tetragonal unit cell (I32, space group I4/mcm) with Si as interlayers [29]. Other ternary borides with the D8h structure have also been found experimentally in the Mo–Si–B [30–32], V–Si–B [33], Nb–Si–B [34], W–Si–B [35], Fe–Si–B [36], and Ta–Ge–B [37] systems. Therefore, it is clearly of interest to investigate whether M5SiB2 can be considered a new family of the MAB phases by its nature and exhibits the desirable damage-tolerant and thermally shock-resistant properties. First-principles studies of V5SiB2, Nb5SiB2, and Ta5SiB2 by Li et al. [29] have shown that they exhibit intrinsic brittleness. However, it is noted that the above three M5SiB2 compositions have the same valence electron concentration (VEC). Considering the significant effect of VEC on the elastic properties of binary borides [38], more work is needed to investigate the M5SiB2 compounds with different VECs.

In this work, first-principles calculations within the framework of DFT were carried out to systematically evaluate the thermodynamic stability, electronic structure, bonding characteristics, elastic properties, and damage tolerance of the known stable compounds M5SiB2 (M = Mo, W, V, Nb), and the effects of VEC on these aspects were discussed. We then extended the selection of M atoms to other IVB–VIB transition metals for potential high-temperature applications. Among them, the candidates containing desirable M elements for oxidation/ablation resistance, i.e., Zr and Hf, however, were found thermodynamically unstable. An approach based on the VEC tuning is then demonstrated by the stability of a newly designed composition of \((Zr_{0.6}Mo_{0.4})_5SiB_2\).

2 Calculation methods

The first-principles calculations were performed by the CASTEP code with the plane-wave method within the framework of DFT [39]. The exchange-correlation function was utilized with the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) [40]. The interaction between electrons and ion cores was treated in the reciprocal space by ultrasoft pseudopotentials [41]. The plane-wave basis set cutoff was 700 eV, and the k-points...
mesh separation was 0.04 Å\(^{-1}\) according to the Monkhorst-Pack method in the Brillouin zone. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme [42] was used in the geometry optimization with the tolerance of difference on total energy within \(5 \times 10^{-6}\) eV/atom, maximum ionic Hellmann–Feynman force within 0.01 eV/Å, maximum ionic displacement within \(5 \times 10^{-4}\) Å, and maximum stress within 0.02 GPa. The calculations were accomplished under zero pressure, allowing all atomic sites, lattice constants, and angles to fully relax. The spin–orbit coupling effect, the employment of GGA+U approach, and the spin–polarization effect have been checked with representative compositions and found to have little effect on the calculation results for the M\(_5\)SiB\(_2\) phases investigated in this work (Figs. S1–S3 in the Electronic Supplementary Material (ESM)).

The band structure, density of states (DOS), and elastic constants of the M\(_5\)SiB\(_2\) phases were extracted from the fully geometry optimized state. The elastic constants were determined from a linear fit of the calculated stress as a function of strain. Bulk modulus (\(B\)) and shear modulus (\(G\)) were calculated from the second-order elastic constants (\(c_{ij}\)) according to Voigt [43], Reuss [44], and Hill [45] (VRH) approximations. Meanwhile, Young’s modulus (\(E\)) was calculated from Hill’s bulk modulus (\(B_H\)) and shear modulus (\(G_H\)).

Thermodynamic stability assessed by formation energy (\(\Delta E\)) and formation enthalpy (\(\Delta H\)) was calculated by Eqs. (1) and (2) [46]:

\[
\Delta E = E_{\text{MAB}} - E_{\text{bin}(M)} - E_{\text{bin}(A)} - E_{\text{bin}(B)}
\]

\[
\Delta H = E_{\text{MAB}} - E_{\text{ES}}
\]

where \(E_{\text{MAB}}\), \(E_{\text{bin}}\), and \(E_{\text{ES}}\) are the total energy of the system, the energy of the atom in the bulk phase, and the energy of the equilibrium simplex, respectively. The equilibrium simplexes were selected from the stable compounds in the M–Si–B ternary system as competing phases, such as binary or ternary borides and silicides as listed in Table 1. Phonon calculations were performed with the supercell approach by the finite displacement method. The supercell was defined by the cutoff radius of 5 Å to ensure that the lattice constants of the supercell are larger than 10 Å. The \(k\)-points of \(4 \times 4 \times 2\) mesh was used for the phonon calculations. The bond stiffness was calculated using the model proposed by Bai et al. [15] at hydrostatic pressures of 0, 10, 20, 30, and 40 GPa.

Table 1  Identified equilibrium simplex for M\(_5\)SiB\(_2\)

| Compound            | Equilibrium simplex                  |
|---------------------|--------------------------------------|
| Ti\(_5\)SiB\(_2\)   | Ti\(_5\)SiB, TiB, Ti                 |
| Zr\(_5\)SiB\(_2\)   | ZrB\(_2\), Zr\(_2\)Si, Zr            |
| Hf\(_5\)SiB\(_2\)   | HfB\(_2\), Hf\(_2\)Si, Hf            |
| V\(_5\)SiB\(_2\)    | VB, V\(_2\)Si                        |
| Nb\(_5\)SiB\(_2\)   | Nb\(_2\)B\(_2\), Nb\(_2\)Si, Nb      |
| Ta\(_5\)SiB\(_2\)   | Ta\(_3\)B\(_2\), TaSi                |
| Cr\(_5\)SiB\(_2\)   | CrB, Cr\(_3\)Si                      |
| Mo\(_5\)SiB\(_2\)   | MoB, Mo\(_3\)Si                      |
| W\(_5\)SiB\(_2\)    | W\(_2\)B, W\(_2\)Si, W               |
| (Zr\(_{0.6}\)Mo\(_{0.4}\))\(_5\)SiB\(_2\) | ZrB\(_2\), ZrSiMo, ZrMo\(_2\), Zr\(_2\)Si |

3  Results

3.1  Crystal structure

Mo\(_5\)SiB\(_2\) crystallizes in a tetragonal structure with a space group of \(I4/mcm\) (No. 140). There are four formulas (32 atoms) per unit cell. Mo\(_1\), Mo\(_2\), Si, and B atoms are located at 16l, 4c, 4a, and 8h Wyckoff positions, respectively. Figure 1 illustrates the crystal structure and composition of Mo\(_5\)SiB\(_2\). As shown in Fig. 1(a), the crystal structure consists of alternating layers of four face-shared BMo\(_8\) tetrakaidecahedrons and Si atoms. The four face-shared BMo\(_8\) tetrakaidecahedrons and B coordination are illustrated in Figs. 1(b) and 1(c), respectively. Figure 1(d) shows that the B atoms are present in the same (001) plane as Mo\(_2\) atoms, and the B–B bond and Mo\(_2\)–B bond lengths are 2.121 and 2.371 Å, respectively. Interestingly, the B atoms in Mo\(_5\)SiB\(_2\) do not form chains as in the case of MoAlB\(_4\) [47] or networks as in Cr\(_3\)AlB\(_4\) [4]. The Mo\(_1\) atoms are all on the different (001) planes with B, as shown in Fig. 1(e), and the Mo\(_1\)–B bond length is 2.347 Å. The first nearest neighbor of Si is the Mo\(_1\) atom at a distance of 2.553 Å. The Si atomic layer is the most loosely arranged layer, and the atoms are relatively far apart, as shown in Fig. 1(f), i.e., the distance between the Si atoms is as far as 4.241 Å in Mo\(_5\)SiB\(_2\), which gives us a hint that the Si–Si in-plane interaction might be very weak in the Mo\(_5\)SiB\(_2\) structure. The above analyses of the crystal structure indicate that the nanolaminated structure of the Mo\(_5\)SiB\(_2\) phase is similar to those of the MAX and MAB phases.
The calculated lattice constants \(a\) and \(c\) of known \(M_5SiB_2\) (\(M = Mo, W, V, \) or \(Nb\)) are compared with the available experimental values as shown in Table 2. The agreement between the calculated and experimental data validates that the adopted calculation method is reliable. When \(M\) changes from 4d (Mo) to 5d (W), the \(c\)-axis decreases slightly due to the lanthanide contraction effect of the 5d transition metals, while along the same period \(Nb_5SiB_2\) has a larger lattice constant than \(Mo_5SiB_2\) since \(Nb\) has a larger atomic radius [48]. \(\Delta E\) and \(\Delta H\) are also calculated for these phases, which are all negative, indicating that these existing phases are indeed thermodynamically stable.

Table 3 shows the Mulliken bond population and bond lengths in these \(M_5SiB_2\) phases. The positive Mulliken bond populations of \(B–B\), \(M_1–B\), \(M_2–B\), and \(M_1–Si\) bonds indicate their covalent bonding nature. The \(B–B\) bonds have a short bond length with a large bond population, indicating a strong bonding. However, they are relatively scarce, especially compared to \(M–B\) bonds, which is consistent with the absence of the \(B\) chains or networks in the structure. The \(M–B\) bonds are considered to be ionic-covalent based on their positive populations and the difference in electronegativity, which results in the electron transfer from the transition metal to boron, as can be seen in Table 4. Meanwhile, the lower bond population and less significant electron transfer from \(M_1\) to \(Si\) indicate that the ionic-covalent interaction between \(M_1\) and \(Si\) is very weak.

The band structure and projected density of states (PDOS) of \(Mo_5SiB_2\) are shown in Fig. 2, and the Fermi level is set to 0 eV. The overlap of the energy bands with a high DOS at the Fermi energy level indicates a metal-like conductivity, and the anisotropy of the energy bands between high symmetry points shows the anisotropic electrical conductivity. The Fermi energy level lies above the bottom of the conduction bands, indicating that the excess valence electrons fill in the conduction bands. The DOS of \(Mo\) and \(B\) atoms overlap from \(-8.9\) eV and persist until near \(-2.0\) eV, in contrast to \(Mo_1\) atoms and \(Si\) atoms, which overlap only insignificantly between \(-6.0\) and \(-3.0\) eV. This phenomenon suggests that there is a stronger electronic interaction between \(Mo\) and \(B\) inside the BMo\(_8\) sublattice, while that between \(Mo_1\) and \(Si\) across the layers is weaker.

The charge density (Fig. 3) was employed to describe the charge accumulation in different energy ranges. Carbon-like electronic configuration \((2s^22p^1\rightarrow2s^22p^2)\) was generated in boron through the transition of electrons from \(Mo\) to \(B\). Figures 3(a) and 3(b) show that the states from \(-10.9\) to \(-8.9\) eV are mainly from the overlap of \(B\) sp\(_z\) orbitals, which form the strong \(\sigma\)-type covalent bonds. The states from \(-7.0\) to \(-2.0\) eV below the Fermi level are mainly from \(B\) 2p\(_z\), \(Mo_1\) 4d(t\(_{2g}\)), and \(Mo_2\) 4d(e\(_{g}\)) orbitals, as shown in Figs. 3(c) and 3(d). This phenomenon confers boron diversity in hybridization, which is prevalent in the MAB phases. According to Figs. 3(e) and 3(f), the states near the Fermi energy level are mainly from \(4d(t_{2g})\) orbitals of \(Mo_1\) and \(4d(e_{g})\) orbitals of \(Mo_2\), indicating that the main contribution to the conductivity is from \(Mo\). Figure 3(g) shows the charge density of the plane containing \(Mo_1\), \(Si\), and \(B\) atoms. It can be seen that the charge accumulation between \(Mo_1\) and \(B\) is closer to the \(B\) atom, which is typical of ionic-covalent bonding nature. However, the charge accumulation between \(Mo_1\) and \(Si\) is not obvious, suggesting a weaker interaction between them. In addition, no bonding is formed between \(Si\) atoms indicated by the absence of charge accumulation.

3.2 Electronic structure and chemical bonding

The band structure and projected density of states (PDOS) of \(Mo_5SiB_2\) are shown in Fig. 2, and the Fermi level is set to 0 eV. The overlap of the energy bands with a high DOS at the Fermi energy level indicates a metal-like conductivity, and the anisotropy of the energy bands between high symmetry points shows the anisotropic electrical conductivity. The Fermi energy level lies above the bottom of the conduction bands, indicating that the excess valence electrons fill in the conduction bands. The DOS of \(Mo\) and \(B\) atoms overlap from \(-8.9\) eV and persist until near \(-2.0\) eV, in contrast to \(Mo_1\) atoms and \(Si\) atoms, which overlap only insignificantly between \(-6.0\) and \(-3.0\) eV. This phenomenon suggests that there is a stronger electronic interaction between \(Mo\) and \(B\) inside the BMo\(_8\) sublattice, while that between \(Mo_1\) and \(Si\) across the layers is weaker.

The charge density (Fig. 3) was employed to describe the charge accumulation in different energy ranges. Carbon-like electronic configuration \((2s^22p^1\rightarrow2s^22p^2)\) was generated in boron through the transition of electrons from \(Mo\) to \(B\). Figures 3(a) and 3(b) show that the states from \(-10.9\) to \(-8.9\) eV are mainly from the overlap of \(B\) sp\(_z\) orbitals, which form the strong \(\sigma\)-type covalent bonds. The states from \(-7.0\) to \(-2.0\) eV below the Fermi level are mainly from \(B\) 2p\(_z\), \(Mo_1\) 4d(t\(_{2g}\)), and \(Mo_2\) 4d(e\(_{g}\)) orbitals, as shown in Figs. 3(c) and 3(d). This phenomenon confers boron diversity in hybridization, which is prevalent in the MAB phases. According to Figs. 3(e) and 3(f), the states near the Fermi energy level are mainly from \(4d(t_{2g})\) orbitals of \(Mo_1\) and \(4d(e_{g})\) orbitals of \(Mo_2\), indicating that the main contribution to the conductivity is from \(Mo\). Figure 3(g) shows the charge density of the plane containing \(Mo_1\), \(Si\), and \(B\) atoms. It can be seen that the charge accumulation between \(Mo_1\) and \(B\) is closer to the \(B\) atom, which is typical of ionic-covalent bonding nature. However, the charge accumulation between \(Mo_1\) and \(Si\) is not obvious, suggesting a weaker interaction between them. In addition, no bonding is formed between \(Si\) atoms indicated by the absence of charge accumulation.
| Compound | Mo₂SiB₂ | W₅SiB₂ | V₅SiB₂ | Nb₅SiB₂ |
|----------|---------|--------|--------|--------|
| Space group | I₄/mcm (No. 140) | — | — | — |
| Z formula unit | 4 | — | — | — |
| Density (g/cm³) | 8.69 | 13.61 | 5.63 | 7.50 |
| | Experimental | Ref. [23] | Ref. [26] | Ref. [24] | Ref. [25] |
| | a = 5.998 | a = 6.047 | a = 5.810 | a = 6.2660 |
| | c = 11.027 | c = 10.990 | c = 10.796 | c = 11.6400 |
| Lattice constant (Å) | Calculated | a = 6.0214 | a = 6.0557 | a = 5.7784 | a = 6.2528 |
| | c = 11.1642 | c = 11.1261 | c = 10.7654 | c = 11.6561 |
| | α/α = 1.854 | α/α = 1.837 | α/α = 1.863 | α/α = 1.864 |
| Δα = 0.39%, Δc = 1.24% | Δα = 0.14%, Δc = 1.24% | Δα = -0.54%, Δc = -0.25% | Δα = -0.22%, Δc = 0.14% |
| Experimental | | | | |
| | Mo₂ 16I (0.1653, 0.6653, 0.1388) | Mo₂ 16I (0.1653, 0.6653, 0.1388) | W₁ 16I (0.1660, 0.6660, 0.1430) | V₁ 16I (0.1660, 0.6660, 0.1430) | Nb₁ 16I (0.1641, 0.6641, 0.1398) |
| | Mo₂ 4c (0, 0, 0) | W₂ 4c (0, 0, 0) | Si 4a (0, 0, 0.25) | Si 4a (0, 0, 0.25) | Si 4a (0, 0, 0.25) |
| | B₈h (0.6250, 0.1250, 0) | B₈h (0.6250, 0.1250, 0) | B₈h (0.6250, 0.1250, 0) | B₈h (0.6250, 0.1250, 0) | B₈h (0.6250, 0.1250, 0) |
| | | | | | |
| Atomic position | Calculated | Mo₂ 16I (0.1656, 0.6653, 0.1386) | Mo₂ 16I (0.1653, 0.6630, 0.1402) | W₁ 16I (0.1669, 0.6699, 0.1366) | V₁ 16I (0.1693, 0.6693, 0.1371) |
| | | | | | |
| | Mo₂ 4c (0, 0, 0) | W₂ 4c (0, 0, 0) | Si 4a (0, 0, 0.2500) | Si 4a (0, 0, 0.2500) | Si 4a (0, 0, 0.2500) |
| | Si 4a (0, 0, 0.2500) | Si 4a (0, 0, 0.2500) | Si 4a (0, 0, 0.2500) | Si 4a (0, 0, 0.2500) | Si 4a (0, 0, 0.2500) |
| | B₈h (0.6187, 0.1187, 0) | B₈h (0.6235, 0.1235, 0) | B₈h (0.6148, 0.1148, 0) | B₈h (0.6129, 0.1129, 0) | B₈h (0.6129, 0.1129, 0) |
| ΔE (eV/atom) | -0.713 | -0.295 | -0.688 | -0.678 |
| ΔH (eV/atom) | -0.003 | -0.065 | -0.034 | -0.117 |
Table 3  Mulliken bond population and bond lengths of Mo₅SiB₂, W₅SiB₂, V₅SiB₂, and Nb₅SiB₂

| Compound | Bond | Bond length (Å) | Bond population | Number per unit cell |
|----------|------|-----------------|-----------------|----------------------|
| Mo₅SiB₂  | B–B  | 2.02231         | 0.41            | 4                    |
|          | Mo1–B | 2.32495         | 0.19            | 32                   |
|          | Mo1–B | 2.40190         | 0.25            | 16                   |
|          | Mo2–B | 2.40451         | 0.27            | 16                   |
|          | Mo1–Si | 2.56814        | 0.23            | 32                   |
| W₅SiB₂   | B–B  | 2.11548         | 0.25            | 4                    |
|          | W1–B | 2.34519         | 0.24            | 32                   |
|          | W2–B | 2.39948         | 0.25            | 16                   |
|          | W1–B | 2.40369         | 0.29            | 16                   |
|          | W1–Si | 2.57525        | 0.24            | 32                   |
| V₅SiB₂   | B–B  | 1.87674         | 0.63            | 4                    |
|          | V1–B | 2.23051         | 0.15            | 32                   |
|          | V1–B | 2.29277         | 0.33            | 16                   |
|          | V2–B | 2.32248         | 0.21            | 16                   |
|          | V1–Si | 2.46748        | 0.21            | 32                   |
| Nb₅SiB₂  | B–B  | 1.99684         | 0.51            | 4                    |
|          | Nb1–B | 2.40661         | 0.20            | 32                   |
|          | Nb1–B | 2.50211         | 0.30            | 16                   |
|          | Nb2–B | 2.52091         | 0.25            | 16                   |
|          | Nb1–Si | 2.66960        | 0.24            | 32                   |

Table 4  Mulliken charge of Mo₅SiB₂, W₅SiB₂, V₅SiB₂, and Nb₅SiB₂

| Species in Mo₅SiB₂ | Total charge (e) | Charge transfer (e) |
|-------------------|------------------|---------------------|
| B                 | 3.46             | −0.46               |
| Si                | 3.91             | 0.09                |
| Mo1               | 13.77            | 0.23                |
| Mo2               | 14.09            | −0.09               |

| Species in W₅SiB₂ | Total charge (e) | Charge transfer (e) |
|-------------------|------------------|---------------------|
| B                 | 3.48             | −0.48               |
| Si                | 3.86             | 0.14                |
| W1                | 13.79            | 0.21                |
| W2                | 14.03            | −0.03               |

| Species in V₅SiB₂ | Total charge (e) | Charge transfer (e) |
|-------------------|------------------|---------------------|
| B                 | 3.58             | −0.58               |
| Si                | 4.15             | −0.15               |
| V1                | 12.69            | 0.31                |
| V2                | 12.93            | 0.07                |

| Species in Nb₅SiB₂ | Total charge (e) | Charge transfer (e) |
|-------------------|------------------|---------------------|
| B                 | 3.55             | −0.55               |
| Si                | 4.13             | −0.13               |
| Nb1               | 12.70            | 0.30                |
| Nb2               | 12.97            | 0.03                |

Fig. 2  Band structure and PDOS of Mo₅SiB₂.

Fig. 3  Charge density for (a) (001) plane from −10.9 to −8.9 eV, (b) (110) plane from −10.9 to −8.9 eV, (c) (001) plane from −7.0 to −2.0 eV, (d) (110) plane from −7.0 to −2.0 eV, (e) (001) plane near the Fermi level, (f) (110) plane near the Fermi level of Mo₅SiB₂. The (001) plane passes through Mo2 and B atoms, and the (110) plane through Mo1 and B atoms. (g) Charge density for a plane containing Mo1, Si, and B atoms from −7.0 to −2.0 eV.
Figure 4 shows the band dispersion curves along with the high symmetry directions and PDOS of V$_5$SiB$_2$. Similar to Mo$_5$SiB$_2$, metallic bonding and electrical conductivity are confirmed by the overlap (crossing) of valence and conduction bands at the Fermi energy level. The DOS shifts to a higher energy than that of Mo$_5$SiB$_2$ due to the lower VEC of V$_5$SiB$_2$. As a result, the Fermi energy level lies closer to the pseudogap, which indicates a more stable electronic structure [38]. Similar to Mo$_5$SiB$_2$, the interaction energy between V and B is lower than that between V1 and Si, implying a stronger V–B bond and a weaker V1–Si bond.

Above we have analyzed the electronic structure based on two typical compounds Mo$_5$SiB$_2$ and V$_5$SiB$_2$. The variations of the electronic structure mainly derive from the valence electron of the M atom. V$_5$SiB$_2$ has a lower VEC = 4.375 compared to Mo$_5$SiB$_2$ with VEC = 5.000. By comparing the relative positions of the pseudogap and the Fermi energy level in the DOS of Mo$_5$SiB$_2$ and V$_5$SiB$_2$, a more stable electronic structure with the VEC near 4.375 is obtained for V$_5$SiB$_2$. To further verify the effect of VEC on the electronic stability, the PDOS of W$_5$SiB$_2$ (VEC = 5.000) and Nb$_5$SiB$_2$ (VEC = 4.375) are plotted and shown in Fig. 5, with the Fermi energy level of W$_5$SiB$_2$ being located in the conduction band and Nb$_5$SiB$_2$ close to the pseudogap. Thus, a simple criterion about the stability of the electron is obtained. A VEC value close to 4.375 is expected to enable a more stable electronic structure.

3.3 Lattice dynamics

The lattice vibrations were identified by phonon dispersion and DOS, and the lattice dynamics also reflect the anisotropy of the chemical bonds. The phonon dispersion curves are shown along the high-symmetry direction of the Brillouin zone (Figs. 6 and 7), where no negative vibrational frequencies appear, thereby confirming that Mo$_5$SiB$_2$ and V$_5$SiB$_2$ are dynamically stable to mechanical perturbations. It can also be seen that there are five band gaps in the range of optical phonons for both Mo$_5$SiB$_2$ and V$_5$SiB$_2$ due to the mass differences among the atoms and the weak interactions of the atoms.
The projected phonon density of states for different atoms M1, M2, Si, and B were calculated separately to investigate the contribution of different bonds to the total phonon density of states. In general, the low-frequency acoustic branch is mainly from M1 and M2, and the high-frequency optical branch is mainly from B–B and M–B. Also, there are mid-frequency optical branches between the high-frequency optical branch and the low-frequency acoustic branch. The mid-frequency optical branches are mainly from M–Si, which indicates a weaker interaction between them [19]. The combination of anisotropic bonds will be shown to affect the elastic properties as well as the mechanical behavior of the compounds in the next section.

### 3.4 Elastic properties and mechanical behaviors

The six independent second-order elastic constants (\(c_{11}\), \(c_{33}\), \(c_{44}\), \(c_{66}\), \(c_{12}\), and \(c_{13}\)) and anisotropic Young’s modulus (\(E_r\) and \(E_z\)) of Mo5SiB2 with the tetragonal system are listed in Table 5. Born–Huang criteria [49] suggested that the following conditions are necessary for tetragonal solids to be mechanically stable: \(c_{11} > \vert c_{12}\vert\); \(c_{33}(c_{11} + c_{22}) - 2c_{13}^2 > 0\); \(c_{44} > 0\). All the selected M5SiB2 satisfy the above-mentioned criteria, demonstrating their mechanical stability. The calculated elastic constants (\(c_{11}\) and \(c_{33}\)) representing the stiffness against compression/tension deformation in main crystalline directions are very large compared to other elastic constants, indicating that the M5SiB2 system is very rigid under uniaxial stress along with the directions of the \(a\)-axis and \(c\)-axis. Furthermore, the value of \(c_{11}\) is higher than that of \(c_{33}\), which signifies that the bonding along the crystallographic \(a\)-axis is stiffer than that along the \(c\)-axis. The stiffness along the \(a\)-axis is largely contributed by the B–B bonds. In contrast, the interlayered M–Si bonds along the \(c\)-axis are relatively weaker, which leads to a lower \(c_{33}\). Therefore, the anisotropy of chemical bonds also leads to that \(E_r\) being higher than \(E_z\). The \(c_{44}\) and \(c_{66}\) reflect the resistance of tetragonal crystals to shear deformation at the (100)/(010) and (001) planes, respectively, which are all smaller than \(c_{11}\) and \(c_{33}\), demonstrating a low shear deformation resistance of these new MAB phases. The anisotropic mechanical properties are like the well-investigated MAX and MAB phases, which are underpinned by the anisotropic chemical bonding.

The calculated elastic moduli including the bulk modulus (\(B\)), shear modulus (\(G\)), Young’s modulus (\(E\)), Pugh’s ratio (\(G/B\)), Cauchy pressure (\(P\)), and Poisson’s ratio (\(v\)) are listed in Table 6. The Voigt–Reuss–Hill approximations are employed to calculate the \(B\) and \(G\). Equations of \(E = (9G \times B)/(3B + G)\) and \(v = (3B - 2G)/(6B + 2G)\) are used to estimate \(E\) and \(v\), respectively [50]. For tetragonal compounds, \(P\) in three different directions can be defined as \(p_{a} = p_{b} = c_{13} - c_{44}\), \(p_{c} = c_{12} - c_{66}\) [51]. For \(B\), the calculated values of Mo5SiB2, W5SiB2, V5SiB2, and Nb5SiB2 were 267, 303, 223, and 216 GPa, respectively, which are higher when compared with other MAB phases such as MoAlB (207 GPa) [47] and Cr2AlB2 (259 GPa) [52], indicating that M5SiB2 demonstrates a strong resistance to volume deformation. However, it may deform easily when subjected to shear stress due to a lower \(G\). The combined higher \(B\) and \(G\), a lower ratio of 0.53 and 0.50, respectively [54], considered to possess a promising damage tolerance.

| Compound | \(c_{11}\) | \(c_{33}\) | \(c_{44}\) | \(c_{66}\) | \(c_{12}\) | \(c_{13}\) | \(E_r\) | \(E_z\) | Ref. |
|----------|---------|---------|---------|---------|---------|---------|-------|-------|------|
| Mo5SiB2  | 471     | 377     | 164     | 138     | 164     | 191     | 362   | 262   | This work |
| Mo5SiB2  | 480     | 415     | 174     | 143     | 166     | 197     | —     | —     | Exp. [32] |
| W5SiB2   | 504     | 438     | 182     | 133     | 186     | 227     | 375   | 289   | This work |
| V5SiB2   | 475     | 408     | 184     | 161     | 98      | 115     | 433   | 362   | This work |
| Nb5SiB2  | 431     | 386     | 157     | 138     | 105     | 123     | 381   | 330   | This work |

| Compound | \(G\) | \(E\) | \(B\) | \(P\) | \(v\) |
|----------|-------|------|-------|-------|------|
| Mo5SiB2  | 480   | 137  | 207   | 0.53  |
| Mo5SiB2  | 423   | 137  | 207   | 0.50  |
| W5SiB2   | 471   | 137  | 259   | 0.53  |
| V5SiB2   | 475   | 137  | 207   | 0.50  |
| Nb5SiB2  | 431   | 137  | 216   | 0.50  |

As a result of the combined higher \(B\) and \(G\), lower \(G/B\) and lower \(P\), Mo5SiB2, W5SiB2, V5SiB2, and Nb5SiB2 are 267, 303, 223, and 216 GPa, respectively, which are higher when compared with other MAB phases such as MoAlB [26] and Mo5SiB2 [47], and lower than Cr2AlB2 (197 GPa) [52], indicating that M5SiB2 demonstrates a strong resistance to volume deformation. However, it may deform easily when subjected to shear stress due to a lower \(G\). The combined higher \(B\) and \(G\), a lower ratio of 0.53 and 0.50, respectively [54], considered to possess a promising damage tolerance. In contrast, V5SiB2 yields the highest \(G/B\) of 0.78 among the investigated M5SiB2.
where $s_{ij}$ is the elastic compliance constant. For the tetragonal system, $G_{[100]}$ and $G_{[010]}$ are equivalents. The projections of the shear modulus of Mo$_5$SiB$_2$ are displayed in Figs. 8(a) and 8(b). The $G_{\min}$ of 113 GPa for Mo$_5$SiB$_2$ appears on the (100) plane along the [011] direction and on the (010) plane along the [101] direction, which demonstrates that the slip systems are related to (001) [011] and (001) [101]. The low $G_{\min}$ indicates a metal-like shear stress resistance and is the source of the local ductility of compounds [56]. Furthermore, the projections of the shear modulus deviate significantly from the round shape (sphere), confirming the presence of significant shear anisotropy.

Moreover, Mo$_5$SiB$_2$ and W$_5$SiB$_2$ show consistently positive $p$ and large $v$ in comparison to other MAB and MAX phases, as listed in Table 6. Positive $p$ means that the resistance to the shear stress is weaker than the normal stress and the large $v$ also indicates that the shape deformation is easier.

Based on the above results, some of the M$_5$SiB$_2$ materials, e.g., Mo$_5$SiB$_2$ have the potential to exhibit higher damage tolerance than most of MABs already investigated. Using Mo$_5$SiB$_2$ as an example, the bonding characteristics are further discussed to understand their effects on the mechanical properties.

There are three types of covalent bonds in Mo$_5$SiB$_2$ from strong to weak: (i) strongest B–B bonds distributed in the (001) plane; (ii) sublattice composed of BMo$_8$ face-shared tetrakaidecahedron with second strongest ionic-covalent bonds between the B and Mo atoms; and (iii) interlayer ionic-covalent bonds composed of Mo1 and Si, which are the weakest. In addition, no bonding is formed between the Si atoms. The weak Mo1–Si bonds contribute to low shear modulus and a lower $c_{33}$ (compared to $c_{11}$) due to that the Si layers are interspersed along the c-axis.

However, bond anisotropy is also present in other MAB phases and cannot fully explain the very low Pugh’s ratio value of Mo$_5$SiB$_2$. A more quantitative perspective in terms of the ratios among different types of bonding within a unit cell in Mo$_5$SiB$_2$ is given in Table 7 and compared to that of other typical MAB phases. It can be seen that, the number ratio of Mo–B to B–B bonds is the highest in Mo$_5$SiB$_2$, reaching 16, while it is only 2 in MoAlB. As a result of the small

Table 6  Bulk modulus ($B$), shear modulus ($G$), Young's modulus ($E$), Cauchy pressure ($p$), Pugh's ratio ($G/B$), and Poisson's ratio ($v$) of M$_5$SiB$_2$ and several typical MAB and MAX phases

| Compound    | $B$ (GPa) | $G$ (GPa) | $G/B$ (GPa) | $E$ (GPa) | $p$ (GPa) | $G/B$ | $v$  | Ref     |
|-------------|-----------|-----------|-------------|-----------|-----------|-------|------|---------|
| Mo$_5$SiB$_2$ | 267       | 142       | 0.53        | 363       | 27        | 26    | 0.27 | This work |
| Mo$_5$SiB$_2$ | 277       | 151       | 0.55        | 383       | 23        | 23    | 0.27 | Exp. [32] |
| W$_5$SiB$_2$  | 303       | 150       | 0.50        | 387       | 45        | 53    | 0.29 | This work |
| V$_5$SiB$_2$  | 223       | 174       | 0.78        | 414       | −69       | −63   | 0.19 | This work |
| Nb$_5$SiB$_2$ | 216       | 150       | 0.69        | 365       | −34       | −33   | 0.22 | This work |
| MoAlB        | 207       | 137       | 0.66        | 336       | −37       | −23   | 0.23 | Cal. [47] |
| Cr$_2$AlB$_2$| 259       | 197       | 0.76        | 471       | −65       | −72   | 0.20 | Cal. [52] |
| Mn$_3$AlB$_2$| 256       | 165       | 0.64        | 407       | −20       | 6     | 0.23 | Cal. [52] |
| Cr$_3$AlB$_4$| 237       | 182       | 0.74        | 440       | −10       | −78   | 0.20 | Cal. [5] |
| Y$_5$Si$_2$B$_8$ | 130        | 104       | 0.80        | 246       | −47       | −35   | 0.18 | Cal. [19] |
| Ti$_5$SiC$_2$ | 183       | 141       | 0.77        | 337       | −62       | −40   | 0.19 | Cal. [26] |

Fig. 8  (a) Planar projections of shear modulus of Mo$_5$SiB$_2$ along different directions. On (100)/(010) plane, A represents [010]/[100], and B represents [001]. On (001) plane, A represents [100], and B represents [010]. (b) 3D projection of shear modulus of Mo$_5$SiB$_2$. (c) Charge density of (001) plane containing B–B σ-bond from −10.9 to −8.9 eV, wherein a $2 \times 2 \times 1$ supercell is used.
Table 7  Number of covalent bonds within a unit cell of \( \text{Mo}_5\text{SiB}_2, \text{Y}_5\text{Si}_2\text{B}_8, \text{MoAlB}, \text{Cr}_2\text{AlB}_2, \text{and Cr}_3\text{AlB}_4 \)

| Bond   | \( \text{Mo}_5\text{SiB}_2 \) | \( \text{Y}_5\text{Si}_2\text{B}_8 \) | \( \text{MoAlB} \) | \( \text{Cr}_2\text{AlB}_2 \) | \( \text{Cr}_3\text{AlB}_4 \) |
|--------|-------------------------------|-------------------------------|--------------------|-----------------|------------------|
| B–B    | 4                             | 32                            | 2                  | 2               | 2                |
| M–B    | 64                            | 68                            | 4                  | 4               | 6                |
| M–A    | 32                            | 8                             | 4                  | 4               | 2                |
| Ratio of M–B/B–B | 16 | 2.125 | 2 | 2 | 3 |

quantity of B–B bonds, they are sparsely distributed on the (001) surface and do not form either chain as in \( \text{MoAlB} \) or a graphene-like network as in \( \text{Cr}_3\text{AlB}_4 \). This special structure has two consequences. On one hand, the fact remains that the B–B bond is still the strongest covalent bond within the crystal, which ensures the high \( c_{11} \) value and resistance to volume change. On the other hand, the channels between the B–B bonds, as seen in Fig. 8(c), increase the possibility of slip initiation, similar to what was suggested for the discrete Si–Si bonds in \( \text{Y}_5\text{Si}_2\text{B}_8 \) \[19\]. The calculated slip systems in \( \text{Mo}_5\text{SiB}_2 \), (001) [011] and (001) [101], also support this idea as they coincide with the directions of the channels between the B–B bonds.

4 Discussion

4.1 Damage tolerance and fracture toughness of \( \text{Mo}_5\text{SiB}_2 \)

In Section 3.4, \( \text{Mo}_5\text{SiB}_2 \) was judged to exhibit promising damage tolerance due to the low Pugh’s ratio, positive Cauchy pressure, and high Poisson’s ratio. On the other hand, Zhang \textit{et al.} [57] showed that the fracture toughness of polycrystalline \( \text{Mo}_5\text{SiB}_2 \) was not particularly high (3.34 MPa·m\(^{1/2}\)). To shed more light on this discrepancy, the criterion based on the bond stiffness model [58], which characterizes the chemical bond strength indirectly by measuring the elastic response of the chemical bonds between adjacent atoms under hydrostatic pressure, was adopted to assist the evaluation of the tough/brittle properties of \( \text{Mo}_5\text{SiB}_2 \).

Bai \textit{et al.} [15,47] have shown that MAX and some MAB phases are considered to have a higher fracture toughness when the ratio of the lowest bond stiffness (\( k_{\text{min}} \)) to the highest bond stiffness (\( k_{\text{max}} \)) is less than 0.5. The bond stiffness of \( \text{Mo}_5\text{SiB}_2 \) is calculated and listed in Table 8.

Table 8  Bond stiffness (\( k \)) of \( \text{Mo}_5\text{SiB}_2 \)

| Bond   | \( \text{Mo}_5\text{SiB}_2 \) | \( \text{Mo}_1\text{B} \) | \( \text{Mo}_2\text{B} \) | \( \text{Mo}_1\text{Si} \) | \( k_{\text{min}}/k_{\text{max}} \) |
|--------|-------------------------------|-----------------|-----------------|-----------------|------------------|
| B–B    | 820                           | 934             | 952             | 1010            | 741              | 0.73             |

\( \text{Mo}_5\text{SiB}_2 \) is greater than 0.5, which indicates that the bond stiffnesses within the crystal are similar, implying a low fracture toughness. Therefore, the experimentally measured fracture toughness appears to be consistent with the bond stiffness model for \( \text{Mo}_5\text{SiB}_2 \). However, it is worth noting that the damage tolerance characterizes the sensitivity of the material to contact damage, which is not equivalent to the fracture toughness. Polycrystalline graphite is an important example. The fracture toughness was only 0.73–0.85 MPa·m\(^{1/2}\) measured experimentally [59], but graphite exhibits insensitivity to notch geometry and is therefore considered a high damage tolerance material [60]. Therefore, in-depth studies are still needed in the future to study the damage tolerance and its correlation with fracture toughness in the MAB phase materials.

4.2 Extension to other \( \text{M}_5\text{SiB}_2 \) phases

When the choice of M is extended to the transition metals of group IVB–VIB, the effect of VEC on stability and elastic properties is more clearly demonstrated. We calculated and compared the enthalpies of formation \( \Delta H \) of \( \text{M}_5\text{SiB}_2 \) (\( \text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W} \)), which were naturally divided into three groups based on VEC, as shown in Fig. 9. Among them, \( \text{Ti}_5\text{SiB}_2, \text{Zr}_5\text{SiB}_2, \) and \( \text{Hf}_5\text{SiB}_2 \) have VEC = 3.750, which are thermodynamically unstable as predicted by the positive \( \Delta H \). The PDOS of \( \text{Ti}_5\text{SiB}_2, \text{Zr}_5\text{SiB}_2, \) and \( \text{Hf}_5\text{SiB}_2 \) are plotted in Figs. 10, S1, and S2 in the ESM. The Fermi energy level lies below the peak of the bonding state, indicating incomplete filling of the valence band consistent with the positive \( \Delta H \). With a higher VEC = 4.375, the three compounds of \( \text{V}_5\text{SiB}_2, \text{Nb}_5\text{SiB}_2, \) and \( \text{Ta}_5\text{SiB}_2 \) are thermodynamically stable in accordance with the location of the Fermi energy level close to the pseudogap (Figs. 3, 5(b), and S3 in the ESM). When VEC increased to 5.000, the filling of the \( d \)-orbital electron to the conduction band decreases the electronic stability (Figs. 2, 5(a), and S4 in the ESM). Although \( \text{Mo}_5\text{SiB}_2 \) and \( \text{W}_5\text{SiB}_2 \) remain thermodynamically stable, metastable phases like \( \text{Cr}_5\text{SiB}_2 \) [49] appear. The above results follow the VEC criterion for electronic structure stability described in Section 3.2.
Fig. 9 Enthalpy of formation ($\Delta H$) of $M_5\text{SiB}_2$.

The calculated lattice constants and elastic modulus of $M_5\text{SiB}_2$ ($M = \text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{Cr}$) are listed in Table 9. Combined with the data in Table 6, it can be seen that when VEC = 4.375, $\text{V}_5\text{SiB}_2$, $\text{Nb}_5\text{SiB}_2$, and $\text{Ta}_5\text{SiB}_2$ exhibit peak values of Pugh’s ratio among all $M_5\text{SiB}_2$ phases. The shear modulus is closely related to the $M\text{d}$–$\text{B}\text{p}(sp^2)$ bonding [38]. As the VEC decreases to 3.750, the reduction of the d-orbital electron leads to the decrease in the shear modulus and thus a reduction in $G/B$ of $\text{Ti}_5\text{SiB}_2$, $\text{Zr}_5\text{SiB}_2$, and $\text{Hf}_5\text{SiB}_2$. On the other hand, when VEC increases to 5.000, additional electrons saturate the $\text{p}(sp^2)$–d bonding state and fill the M d(t_{2g}) and d(eg) orbitals near the Fermi level, again reducing $G$ and correspondingly $G/B$ in $\text{Cr}_5\text{SiB}_2$, $\text{Mo}_5\text{SiB}_2$, and $\text{W}_5\text{SiB}_2$. It is found that the former effect is more significant, and therefore $\text{Ti}_5\text{SiB}_2$, $\text{Zr}_5\text{SiB}_2$, and $\text{Hf}_5\text{SiB}_2$ phases possess a low Pugh’s ratio of 0.52, 0.46, and 0.49, respectively. Considering Young’s modulus of 207, 158, and 192 GPa, these compounds would exhibit good damage tolerance and thermal shock resistance if they could be stabilized.

Overall, we confirmed the effect of VEC on the stability and elastic properties of the Mo$_5$SiB$_2$-type compounds. A relationship between the thermodynamic stability and the electronic stability was found, and it is hypothesized that otherwise unstable compounds could be stabilized if their VEC is optimized.

Table 9 Lattice constants, elastic modulus, and Pugh’s ratio ($G/B$) of Ti$_5$SiB$_2$, Zr$_5$SiB$_2$, Hf$_5$SiB$_2$, Ta$_5$SiB$_2$, and Cr$_5$SiB$_2$

| Compound   | $a = b$ (Å) | $c$ (Å) | $B$ (GPa) | $G$ (GPa) | $G/B$ | $E$ (GPa) |
|------------|-------------|---------|-----------|-----------|-------|-----------|
| Ti$_5$SiB$_2$ | 6.0890      | 11.6114 | 156       | 81        | 0.52  | 207       |
| Zr$_5$SiB$_2$ | 6.6114      | 12.4002 | 133       | 61        | 0.46  | 158       |
| Hf$_5$SiB$_2$ | 6.6776      | 12.0117 | 152       | 74        | 0.49  | 192       |
| Ta$_5$SiB$_2$ | 6.3054      | 11.7171 | 216       | 153       | 0.71  | 372       |
| Cr$_5$SiB$_2$ | 5.5854      | 10.3731 | 257       | 161       | 0.63  | 401       |

4.3 Composition optimization for Mo$_5$SiB$_2$

Our calculation shows that Mo$_5$SiB$_2$ is expected to be a damage-tolerant material with quasi-ductile characteristics. However, oxidation is a necessary consideration for high-temperature applications. Since the oxidation products of Mo are sparse and volatile, which is not favorable for oxidation resistance [51], the M elements forming high stability oxidation products, such as Zr and Hf, would be more ideal options. Unfortunately, as demonstrated in Section 4.2, although Zr$_5$SiB$_2$ and Hf$_5$SiB$_2$ show even lower Pugh’s ratios of 0.46 and 0.49 and adequate Young’s moduli of 158 and 192 GPa respectively, they are thermodynamically unstable since their $\Delta H$ are 1.348 and 1.579 eV/atom, respectively.

As discussed in Section 4.2, the instability of Zr$_5$SiB$_2$ and Hf$_5$SiB$_2$ is likely to be originated from the lack of sufficient valence electrons. Therefore, it is possible to stabilize them by optimizing the VEC to near 4.375, which is the minimum VEC value for the stabilization of Mo$_5$SiB$_2$ as found in Section 3.2. Thus, a crystal model of (Zr$_{0.6}$Mo$_{0.4}$)$_5$SiB$_2$ was built to represent the disordered solid solution using the Atomsk code [61]. As the ratio of Mo to Zr increases to 2 : 3, the VEC reaches 4.250, which is very close to 4.375 and expected to render a stable electronic structure. Depending on the designed chemical composition, 8 of the 20 Zr atoms were randomly replaced with the Mo atoms without human intervention. To ensure the reliability of the calculation, we constructed five random models, as shown in Fig. 11, and used the average values of the 5 models. $\Delta H$ was calculated according to Eq. (2), and the equilibrium simplexes are shown in Table 1. The calculated $\Delta H$ of $-1.226\pm0.009$ eV/atom indicates that the solid solution of (Zr$_{0.6}$Mo$_{0.4}$)$_5$SiB$_2$ is thermodynamically stable at 0 K. The small error among the five models also indicates that the results

Fig. 10 PDOS of Zr$_5$SiB$_2$. 

www.springer.com/journal/40145
are reliable. The calculated lattice constants are $a = 6.3338\pm0.0119$ Å, $b = 6.3349\pm0.0141$ Å, and $c = 12.0485\pm0.0647$ Å, which lie between those of $\text{Zr}_5\text{SiB}_2$ and $\text{Mo}_5\text{SiB}_2$. The PDOS of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$ is depicted in Fig. 12(a), where the Fermi energy level is located near the pseudogap, indicating a stable electronic structure of this solid solution. In addition, there is no imaginary frequency in phonon dispersion of this material, as shown in Fig. 12(b), suggesting that the lattice dynamics are stable. The elastic constants and moduli of the elasticity of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$ are listed in Tables 10 and 11, respectively. Firstly, the solid solution is mechanically stable according to the Born–Huang criteria [49]. Secondly, the elastic constants exhibit similar anisotropy as analyzed in Section 3.2. Finally, the large increase in the shear modulus is attributed to the solid solution effects, leading to an increase in the Pugh’s ratio to 0.61. However, it is much lower than that of $\text{V}_5\text{SiB}_2$ (Pugh’s ratio = 0.78) and lower than the typical MAB phases such as $\text{MoAlB}$ (Pugh’s ratio = 0.66). An attempt to evaluate the damage tolerance of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$ was done using the bond stiffness model (Tables S2, S3, and Fig. S4 in the ESM). The mean bond stiffness is 1194 GPa for the B–B bonds, 695 GPa for the M–B bonds, and 535 GPa for the M–Si bonds (M = Mo, Zr). Thus, $k_{	ext{min}}/k_{	ext{max}}$ is obtained as 0.45 if the average bond stiffness values are used. Moreover, the individual maximum and lowest bond stiffnesses occur for the B–B bond (1726 GPa) and Zr–Si bond (388 GPa), respectively, which would yield an even lower $k_{	ext{min}}/k_{	ext{max}}$ value of 0.22. The large difference in the bond stiffness can indicate a significant variation in the chemical bond strength within the crystal, and a good damage tolerance property may be present in $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$ according to the criteria suggested by the bond stiffness model [58].

![Fig. 11](image1)

**Fig. 11** Five randomly generated unit cells of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$.

![Fig. 12](image2)

**Fig. 12** (a) PDOS and (b) phonon dispersion of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$. 

### Table 10 Elastic constants ($c_{ij}$) of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$

| Model | $c_{11}$ (GPa) | $c_{33}$ (GPa) | $c_{44}$ (GPa) | $c_{66}$ (GPa) | $c_{12}$ (GPa) | $c_{13}$ (GPa) |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1     | 328            | 258            | 112            | 94             | 100            | 116            |
| 2     | 341            | 276            | 112            | 101            | 100            | 107            |
| 3     | 336            | 265            | 113            | 111            | 97.2           | 111            |
| 4     | 343            | 277            | 112            | 101            | 99.5           | 103            |
| 5     | 338            | 269            | 112            | 103            | 97.4           | 106            |
| Average | 337±5         | 269±7          | 112±0.4        | 102±5          | 98.8±1         | 109±4          |

### Table 11 Bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), Cauchy pressure ($p_c$), Pugh’s ratio ($G/B$), and Poisson ratio ($\nu$) of $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$

| Compound | $B$ (GPa) | $G$ (GPa) | $G/B$ | $E$ (GPa) | $p_c$ (GPa) | $\nu$ |
|----------|-----------|-----------|-------|-----------|-------------|-------|
| 1        | 174       | 102       | 0.59  | 255       | 4           | 6     | 0.26 |
| 2        | 175       | 108       | 0.62  | 269       | -5          | -1    | 0.24 |
| 3        | 174       | 107       | 0.61  | 267       | -2          | -13.8 | 0.24 |
| 4        | 174       | 108       | 0.62  | 268       | -9          | -1.5  | 0.24 |
| 5        | 174       | 107       | 0.61  | 267       | -6          | -5.6  | 0.24 |
| Average  | 174±0.4   | 106±2     | 0.61±0.01 | 265±5 | −3.6±4    | −3.2±6 | 0.24±0.01 |

In summary, the calculated results in $\Delta H$, electronic DOS, and phonon dispersion all consistently show that the proposed $(Zr_{0.6}Mo_{0.4})_5\text{SiB}_2$ could be a stable solid solution with potentially good damage tolerance properties. Similarly, the study on the M site ordered and disordered T2 phases by Dahlqvist et al. [46] has also shown that the VEC of the stabilizing phases is all above 4.000, such as $\text{Ti}_5\text{MoSiB}_2$ (VEC = 4.000), $\text{Ti}_4\text{MnSiB}_2$ (VEC = 4.125), and $(\text{V}_{0.8}\text{Mo}_{0.2})_5\text{SiB}_2$ (VEC = 4.500). In combination with our calculations, it appears that $\text{M}_5\text{SiB}_2$ is most likely to be unstable when VEC is
smaller than 4.000. On the other hand, the study by Dahlqvist et al. found that the ordered Zr₄MoSiB₂ and disordered (Zr₀.₆Mo₀.₄)₂SiB₂ are thermodynamically unstable even with a VEC value of 4.125, and the current work shows that further increasing VEC to 4.250 with the composition of (Zr₀.₆Mo₀.₄)₂SiB₂ is sufficient to stabilize the Zr containing compound.

5 Conclusions

1) M₅SiB₂ consists of alternating layers of four face-shared BM₈ tetrakaidecahedrons and Si atoms. The covalent B–B bonds with sp hybridization form a discrete distribution on the (001) plane, and large amounts of M 4d–B 2p bonds formed by the electron transfer are present in the BM₈ tetrakaidecahedron. A weak M 4d–Si 3p bonding is present between the BM₈ and Si layers. The anisotropy of the chemical bond and the slip channel between the B–B bonds combine to result in a particularly low Pugh’s ratio of 0.53 in Mo₅SiB₂. It is lower than other common MAB phases reported in the literature [5,19,47,52] and is therefore considered to potentially have a better damage tolerance.

2) The VEC plays a dominant role in the electronic stability and thermodynamic stability of M₅SiB₂. The M₅SiB₂ compounds containing the group VB M elements (V, Nb, and Ta) have an optimum VEC of 4.375, resulting in the most stable structure, while partial filling of the valence band or conduction band reduces the stability for M₅SiB₂, represented by Zr₅SiB₂ and Cr₅SiB₂.

To stabilize Zr₅SiB₂, which has an even lower Pugh’s ratio of 0.46 and the desirable M element for potential high-temperature applications, the solid solution (Zr₀.₆Mo₀.₄)₂SiB₂ was designed with the principle of VEC optimization and is predicted to be stable based on the calculated thermodynamic, electronic, mechanical, and lattice dynamics.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 52072238).

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at https://doi.org/10.1007/s40145-022-0636-9.

References

[1] Barsoum MW. The M₅VAₓ phases: A new class of solids. Prog Solid State Chem 2000, 28: 201–281.
[2] Zhou YC, Sun ZM. Temperature fluctuation/hot pressing synthesis of Ti₅SiC₂. J Mater Sci 2000, 35: 4343–4346.
[3] Peng MJ, Wang RF, Wu YJ, et al. Elastic anisotropies, thermal conductivities and tensile properties of MAX phases Zr₅AlC and Zr₅AlN: A first-principles calculation. Vacuum 2022, 196: 110715.
[4] Ade M, Hillebrecht H. Ternary borides Cr₂AlB₂, Cr₃AlB₄, and Cr₄AlB₆. The first members of the series (CrBₓ)ₙCrAl with n = 1, 2, 3 and a unifying concept for ternary borides as MAB-phases. Inorg Chem 2015, 54: 6122–6135.
[5] Zhou YC, Xiang HM, Dai FZ, et al. Electrical conductive and damage-tolerant nanolaminated MAB phases Cr₂AlB₂, Cr₃AlB₄ and Cr₄AlB₆. Mater Res Lett 2017, 5: 440–448.
[6] Zhang HL, Kim JY, Su RR, et al. Defect behavior and radiation tolerance of MAB phases (MoAlB and Fe₂AlB₂) with comparison to MAX phases. Acta Mater 2020, 196: 505–515.
[7] Bai YL, Sun DD, Li N, et al. High-temperature mechanical properties and thermal shock behavior of ternary-layered MAB phases Fe₂AlB₂. Int J Refract Met Hard Mater 2019, 80: 151–160.
[8] Kota S, Zapata-Solvas E, Chen YX, et al. Isothermal and cyclic oxidation of MoAlB in air from 1100 °C to 1400 °C. J Electrochem Soc 2017, 164: C930–C938.
[9] Lu XG, Li SB, Zhang WW, et al. Crack healing behavior of a MAB phase: MoAlB. J Eur Ceram Soc 2019, 39: 4023–4028.
[10] Kota S, Sokol M, Barsoum MW. A progress report on the MAB phases: Atomically laminated, ternary transition metal borides. Int Mater Rev 2020, 65: 226–255.
[11] Richardson PJ, Keast VJ, Cuskelley DT, et al. Theoretical and experimental investigation of the W–Al–B and Mo–Al–B systems to approach bulk WAlB synthesis. J Eur Ceram Soc 2021, 41: 1859–1868.
[12] Kota S, Verger L, Natu V, et al. Thermal stability of the nanolayered Fe₂AlB₂ in nitrogen and argon atmospheres. J Am Ceram Soc 2021, 104: 733–739.
[13] Zhang HM, Dai FZ, Xiang HM, et al. Phase pure and well crystalline Cr₅AlB₂: A key precursor for two-dimensional CrB. J Mater Sci Technol 2019, 35: 1593–1600.
[14] Hanner LA, Kota S, Barsoum MW. Formation mechanisms of Cr₅AlB₂, Cr₅AlB₄, and Fe₂AlB₂ MAB phases. Mater Res Lett 2021, 9: 323–328.
[15] Bai YL, Qi XX, He XD, et al. Phase stability and weak
metallic bonding within ternary-layered borides CrAlB, Cr₃AlB₅, Crl₂AlB₄, and Cr₂AlB₄. J Adv Ceram Soc 2019, 102: 3715–3727.

[16] Zhang HM, Dai FZ, Xiang HM, et al. Crystal structure of Cr₃AlB₅: A new MAB phase compound discovered in Cr–Al–B system. J Mater Sci Technol 2019, 35: 530–534.

[17] Kota S, Chen YX, Wang JY, et al. Synthesis and characterization of the atomic laminate Mn₂AlB₂. J Eur Ceram Soc 2018, 38: 5333–5340.

[18] Qin YR, Zhou YC, Fan LF, et al. Synthesis and characterization of ternary layered Nb₃SB ceramics fabricated by spark plasma sintering. J Alloys Compd 2021, 878: 160344.

[19] Zhou YC, Xiang HM, Dai FZ, et al. Y₂Si₃B₄: A theoretically predicted new damage-tolerant MAB phase with layered crystal structure. J Adv Ceram Soc 2018, 101: 2459–2470.

[20] Suurc G, Gencer A, Wang XT, et al. Lattice dynamical and thermo-elastic properties of M₂AlB (M = V, Nb, Ta) MAX phase borides. J Alloys Compd 2020, 819: 152526.

[21] Qureshi MW, Ali MA, Ma XX. Screen the thermomechanical and optical properties of the new ductile 314 MAX phase boride Zr₃CdB₄: A DFT insight. J Alloys Compd 2021, 877: 160248.

[22] Sun Y, Yang AC, Duan YH, et al. Electronic, elastic, and thermal properties, fracture toughness, and damage tolerance of TM₅SiB₂ (TM = V and Nb) MAB phases. Int J Refract Met Hard Mater 2022, 103: 105781.

[23] Hossain MS, Ali MA, Hossain MM, et al. Physical properties of predicted MAX phase borides Hf₅AB (A = Pb, Bi): A DFT insight. Mater Today Commun 2021, 27: 102411.

[24] Zhang WW, Li SB, Wu S, et al. Synthesis and properties of MoOAlB composites reinforced with SiC particles. J Adv Ceram 2022, 11: 495–503.

[25] Kane KA, Pint BA, Mitchell D, et al. Oxidation of ultrahigh temperature ceramics: Kinetics, mechanisms, and applications. J Adv Ceram Soc 2021, 41: 6130–6150.

[26] Zhou YC, Xiang HM, Dai FZ, et al. Cr₃Si₃B and Hf₃Si₃B: New MAB phases with anisotropic electrical, mechanical properties and damage tolerance. J Mater Sci Technol 2018, 34: 1441–1448.

[27] Yao BX, Li SB, Ma PF, et al. Oxidation behavior of MoAl₀.₆₅Si₀.₃₅B solid solution at 1200–1400 °C. Mater Today Commun 2020, 22: 100846.

[28] Nowotny H, Dimakopoulou E, Kudielka H. Untersuchungen in dem system: VSi₂-TaSi₂. Monatsh Chem Und Verwandte Teile Anderer Wissenschaften 1957, 88: 180–192.

[29] Li B, Duan YH, Shen L, et al. Insights of electronic structures, mechanical properties and thermal conductivities of TM₅SiB₂ (TM = V, Nb, and Ta) MAB phases. Philos Mag 2022, 102: 1628–1649.

[30] Rawn CJ, Schneibel JH, Hoffmann CM, et al. The crystal structure and thermal expansion of Mo₂SiB₂. Intermetallics 2001, 9: 209–216.

[31] Aronsson B, Tjomsland O, Perlmann P, et al. The crystal structure of Mo₂SiB₂. Acta Chem Scand 1958, 12: 31–37.

[32] Ihara K, Ito K, Tanaka K, et al. Mechanical properties of Mo₂SiB₂ single crystals. Mater Sci Eng A 2002, 329–331: 222–227.

[33] Kudielka H, Nowotny H, Findeisen G. Untersuchungen in dem system: V–B, Nb–B, V–B–Si und Ta–B–Si. Monatsh Chem Verw T 1957, 88: 1048–1055.

[34] Fernandes BB, Rodrigues G, Silva G, et al. On the T₂-phase formation in mechanically alloyed Nb–Si and Nb–Si–B powders. J Alloys Compd 2007, 434–435: 530–534.

[35] Fukushima M, Kawashima K, Maruyama M, et al. Superconductivity in W₃SiB₂ with the T₂ phase structure. J Phys Soc Jpn 2011, 80: 024702.

[36] Werwiński M, Kontos S, Gunnarsson K, et al. Magnetic properties of Fe₂SiB₂ and its alloys with P, S, and Co. Phys Rev B 2016, 93: 174412.

[37] Hadi MA, Nasir MT, Rokняzamman M, et al. First-principles prediction of mechanical and bonding characteristics of new T₂ superconductor Ta₅GeB₂. Phys Status Solidi B 2016, 253: 2020–2026.

[38] Zhou YC, Xiang HM, Feng ZH, et al. General trends in electronic structure, stability, chemical bonding and mechanical properties of ultrahigh temperature ceramics TMB₂ (TM = transition metal). J Mater Sci Technol 2015, 31: 285–294.

[39] Segall MD, Lindan PJD, Probert MJ, et al. First-principles simulation: Ideas, illustrations and the CASTEP code. J Phys: Condens Matter 2002, 14: 2717–2744.

[40] Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett 1996, 77: 3865–3868.

[41] Lin JS, Qteish A, Payne MC, et al. Optimized and transferable nonlocal separable ab initio pseudopotentials. Phys Rev B Condens Matter 1993, 47: 4174–4180.

[42] Pfornmerr B, Côté M, Louie SG, et al. Relaxation of crystals with the quasi-Newton method. J Comput Phys 1997, 131: 233–240.

[43] Voigt W. Lehrbuch der kristallphysik (mit ausschluss der Feld: Datasheet from condensed matter). In: Forbes RG. The prediction of zero-barrier evaporation. Berlin: Springer-Verlag GmbH Germany, 2018: 158.
[49] Born M, Huang K, Lax M. Dynamical theory of crystal lattices. *Am J Phys* 1955, 23: 474.

[50] Green DJ. *An Introduction to the Mechanical Properties of Ceramics.* Cambridge: Cambridge University Press, 1998.

[51] Farkas D. Interatomic potentials for Ti–Al with and without angular forces. *Modelling Simul Mater Sci Eng* 1994, 2: 975–984.

[52] Kádas K, Iuşan D, Hellsvik J, et al. AlM₂B₂ (M = Cr, Mn, Fe, Co, Ni): A group of nanolaminated materials. *J Phys: Condens Matter* 2017, 29: 155402.

[53] Zhou YC, Xiang HM, Dai FZ, et al. Electrical conductive and damage-tolerant nanolaminated MAB phases Cr₃AlB₂, Cr₃AlB₄ and Cr₄AlB₆. *Mater Res Lett* 2017, 5: 440–448.

[54] Kota S, Zapata-Solvas E, Ly A, et al. Synthesis and characterization of an alumina forming nanolaminated boride: MoAlB. *Sci Rep* 2016, 6: 26475.

[55] Zhou YC, Sun ZM. Microstructure and mechanism of damage tolerance for Ti₃SiC₂ bulk ceramics. *Mater Res Innov* 1999, 2: 360–363.

[56] Zhou YC, Dai FZ, Xiang HM, et al. Near-isotropic elastic properties and high shear deformation resistance: Making low symmetry and open structured YbAlB₁₄, LuAlB₁₄ and ScMgB₁₄ superhard. *Acta Mater* 2017, 135: 44–53.

[57] Zhang LQ, Pan KM, Lin JP. Fracture toughness and fracture mechanisms in Mo₅SiB₂ at ambient to elevated temperatures. *Intermetallics* 2013, 38: 49–54.

[58] Bai YL, He XD, Sun Y, et al. Chemical bonding and elastic properties of Ti₃AC₂ phases (A = Si, Ge, and Sn): A first-principle study. *Solid State Sci* 2010, 12: 1220–1225.

[59] Li M, Tsujimura M, Sakai M. Crack-face grain interlocking/bridging of a polycrystalline graphite: The role in mixed mode fracture. *Carbon* 1999, 37: 1633–1639.

[60] Berto F, Lazzarin P, Ayatollahi MR. Brittle fracture of sharp and blunt V-notches in isostatic graphite under torsion loading. *Carbon* 2012, 50: 1942–1952.

[61] Hirel P. *Atomsk*: A tool for manipulating and converting atomic data files. *Comput Phys Commun* 2015, 197: 212–219.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.