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Investigation of out-of-plane ordered Ti$_4$MoSiB$_2$ from first principles

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Abstract

The laminated ternary boride Mo$_5$SiB$_2$ of T2 structure have two symmetrically inequivalent metallic sites, 16l and 4c, being occupied in a 4:1 ratio. The phase was recently shown to be stable for 80% substitution of Mo for Ti, at the majority site, forming an out-of-plane chemically ordered quaternary boride: Ti$_4$MoSiB$_2$. Considering that the hypothetical Ti$_5$SiB$_2$ is theoretically predicted as not stable, a key difference in bonding characteristics is indicated for full substitution of Mo for Ti at the metallic sites. To explore the origin of formation of Ti$_4$MoSiB$_2$, we here investigate the electronic properties and bonding characteristics of Mo$_5$SiB$_2$, Ti$_4$MoSiB$_2$ and Ti$_5$SiB$_2$ through their density of states, projected crystal orbital Hamilton population (pCOHP), Bader charge partitioning and second order force constants. The bond between the two different metallic sites is found to be key to the stability of the compounds, evident from the pCOHP of this bond showing a peak of bonding states close to the Fermi level, which is completely filled in Mo$_5$SiB$_2$ and Ti$_4$MoSiB$_2$, while only partially filled in Ti$_5$SiB$_2$. Furthermore, the lower electronegativity of Ti compared to Mo results in charge accumulation at the Si and B sites, which coincides with a reduced bond strength in Ti$_5$SiB$_2$ compared to Mo$_5$SiB$_2$ and Ti$_4$MoSiB$_2$. Bandstructure calculations show that all three structures are metallic. The calculated mechanical and elastic properties show reduced bulk ($B$) and elastic ($E$) moduli when introducing Ti in Mo$_5$SiB$_2$, from 279 and 365 GPa to 176 and 258 GPa, respectively. The Pugh criteria indicates also a slight reduction in ductility, with a $G/B$ ratio increasing from 0.51 to 0.59.

Keywords: chemical bonding, MAB, electronic structure, mechanical properties, quaternary laminated boride, transition metal boride, T2 phase

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
on the magnetic properties of Fe₅SiB₂ upon alloying of Fe material properties. These investigations are primarily focused through alloying on the M or A sites, as a mean of tailoring respectively.

16l and 4c, indicated in figure 1(b) by light and dark blue. The sites participating in each bond are also indicated, where sites populated by metals are labeled by their Wyckoff positions 16l and 4c, indicated in figure 1(b) by light and dark blue respectively.

Compositional expansion of T2 phases has been realized through alloying on the M or A sites, as a mean of tailoring material properties. These investigations are primarily focused on the magnetic properties of Fe₅SiB₂ upon alloying of Fe with Co and Mn at the M site and of P with Si or S at the A site [12–14], but also extend to the observation of alloying at the M site of Mo₅SiB₂ with Ti, Zr and Hf [18–20]. However, none of these studies have considered ordered structures, but either explicitly assumed solid solution or not mentioned it at all. It was only recently that an extensive first principles study was made to expand and identify novel quaternary T2 phases, through alloying by considering both solid solution and ordered distribution on the two metal sites. This quaternary T2 phase was coined out-of-plane ordered MAB phase (o-MAB), where M stands for a transition metal, A for an A-element and B for boron, in analogy with the so-called o-MAX phases [21]. One of the predicted structures, Ti₄MoSiB₂, was realized experimentally and successfully derived into a 2D titanium oxide [22]. The Ti₄MoSiB₂ o-MAB phase is depicted in figure 1(b), where Ti occupy the 16l sites and Mo occupy the 4c sites. Detailed structural information including the Wyckoff positions of Ti₄MoSiB₂ and the corresponding ternary phases Ti₅SiB₂ and Mo₅SiB₂ can be found in table S1 in the SM.

The Mo₅SiB₂ phase has thus been observed experimentally with up to 80% substitution of Mo for Ti, adopting a chemically ordered structure. This in contrast to the ternary phase Ti₅SiB₂ which has not been observed nor is found theoretically stable [23]. This indicates a key change in bonding characteristics and stability of Ti₅SiB₂ as compared to Ti₄MoSiB₂ and Mo₅SiB₂. The theoretical thermodynamic stability analysis performed in [22] are in complete agreement with experimental observations regarding Mo₅SiB₂, Ti₄MoSiB₂ and Ti₅SiB₂. In this work, we theoretically investigate the bonding properties of Ti₄MoSiB₂ and compare the results to those of Mo₅SiB₂ and Ti₅SiB₂, in order to understand why up to 80% of Mo can be substituted for Ti in Mo₅SiB₂. We also present the electronic and mechanical properties of Ti₄MoSiB₂ [22], and compare these results to those of the well known Mo₅SiB₂, and the hypothetical Ti₅SiB₂.

2. Computational details

The electronic structure of Ti₄SiB₂, Ti₄MoSiB₂ and Mo₅SiB₂ was determined using density functional theory [24, 25] as implemented in the Vienna ab initio simulation package (vasp) [26–29]. This implementation uses a plane wave basis set, and the plane wave energy cutoff was set to 400 eV. The Perdew–Burke–Ernzerhof formulation of the generalized gradient approximation (GGA) was used for the exchange–correlation potential [30]. The crystal potential was treated through the projector augmented wave method [31, 32], with the semicore p- and s-electrons for the transition metals Ti and Mo treated as valence electrons (i.e. 4d, 4p, 4s and 5s for Mo, 3d, 3p, 3s and 4s for Ti). The 3p and 3s electrons were considered valence electrons for Si, and the 2p and 2s for B.
The Brillouin zone was sampled with a \( k \)-point density of at least 10 Å\(^{-1} \), corresponding to a \( k \)-point mesh of 11 \times 11 \times 6. The elastic constants were determined using a denser \( k \)-point mesh of 16 \times 16 \times 8. The structures were relaxed until forces between atoms had converged to within 5 meV Å\(^{-1} \), and the total free energy to within 0.01 meV per atom.

The electronic bonding properties of the structures were analyzed using projected crystal orbital Hamilton population (pCOHP), as implemented in the LOBSTER code using the pbeVaspFit2015 basis set\(^{[33–35]} \). The density of states (DOS) was also attained via LOBSTER. The pCOHP and DOS contrast to each other in that the DOS shows the number of available states as a function of electron energy for a structure or a subset of atoms in a structure, while the pCOHP shows a ‘bond-weighted’ DOS of two atoms in a structure. By convention, \( -pCOHP \) is considered for analysis, and in analogy with COOP bonding states are thus represented by positive \( -pCOHP \), non-bonding by zero \( -pCOHP \) and anti-bonding by negative \( -pCOHP \). Integration of the \( -pCOHP \) (\( -ipCOHP \)) up to the Fermi level gives a qualitative measure of the bond strength.

Electronic properties were also considered by Bader partitioning of the electronic charge distribution\(^{[36–39]} \). Bader charge partitioning defines each point in the charge distribution as belonging to a charge maxima, which usually correlates with the crystal atoms, as is the case for all structures considered in this work. In this manner, the electronic charge is associated with the atoms, and the net charge of the atoms in the structure can be estimated.

The force constants of Ti\(_5\)SiB\(_2\), Ti\(_4\)MoSiB\(_2\) and Mo\(_5\)SiB\(_2\) were attained for bonding analysis through dynamical structure simulations, using the finite displacement method and phonopy\(^{[40]} \) with a \( 2 \times 2 \times 1 \) super cell. The force constants are 3 by 3 matrices corresponding to the second derivative of the crystal energy with respect to each of the three Cartesian coordinates of any two atoms in the crystal. In order to apply a scalar value toward the interaction strength between any two atoms we used the projection of each force constant matrix along the direction of the bond. This is equivalent to choosing a coordinate system where the bond is aligned with e.g. the x-axis, rotating the force constant matrices to this coordinate system and examining the element corresponding to displacements of the involved atoms along the bonding axis\(^{[41]} \).

The elastic constants were determined by straining the relaxed equilibrium structure along several different directions using a selection of strain tensors \( \varepsilon \). The stress \( \sigma \) was obtained from the vasp output and the elastic constant tensor \( C \) was obtained through the relation \( \sigma = C \varepsilon \). Details toward these calculations can be found in the SM.

## 3. Results and discussion

### 3.1. Structural characteristics

In this section we present the structural parameters of Ti\(_5\)SiB\(_2\), Ti\(_4\)MoSiB\(_2\) and Mo\(_5\)SiB\(_2\), out of which only the latter two have been successfully synthesized\(^{[9, 22]} \). In table 1, the theoretically calculated volumes, lattice parameters \( a \) and \( c \) and \( c/a \)-ratios are given, along with experimental parameters for Ti\(_4\)MoSiB\(_2\)\(^{[22]} \) and Mo\(_5\)SiB\(_2\)\(^{[17, 42, 43]} \). Note that for Mo\(_5\)SiB\(_2\) in\(^{[42]} \), a range for the measured lattice parameters were presented, corresponding to Mo\(_5\)SiB\(_2\) crystals formed in the Mo–Si–B system at different stoichiometries. The variations were suggested to be related to a substitution of Si for B.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( V ) (Å(^3)/f.u.)</th>
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<td>Ti(_5)SiB(_2)</td>
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<td>Mo(_5)SiB(_2)</td>
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<td>Mo(_5)SiB(_2)(^{[42]})</td>
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<td>Mo(_5)SiB(_2)(^{[43]})</td>
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The calculated lattice parameters for Ti\(_5\)MoSiB\(_2\) and Mo\(_5\)SiB\(_2\) are slightly overestimated as compared to experimentally reported values (within 1%). This is common and expected when using a GGA functional. Mo\(_5\)SiB\(_2\) has the smallest unit cell, and the shortest lattice parameters. The lattice parameters increase when Mo is substituted for Ti. The parameter \( a \) is qualitatively the same between Ti\(_5\)SiB\(_2\) and Ti\(_4\)MoSiB\(_2\), while Ti\(_5\)SiB\(_2\) is more elongated (larger value for \( c \)) resulting in a larger unit cell volume for Ti\(_5\)SiB\(_2\) than for Ti\(_4\)MoSiB\(_2\).

### 3.2. Electronic bonding characteristics and electronic structure

The electronic structure and electronic bonding properties of Ti\(_5\)SiB\(_2\), Ti\(_4\)MoSiB\(_2\) and Mo\(_5\)SiB\(_2\) have been investigated in\(^{[9, 22]} \), and results are presented, corresponding to Mo\(_5\)SiB\(_2\) crystals formed in the Mo–Si–B system at different stoichiometries. The variations were suggested to be related to a substitution of Si for B.

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Figure 2. Partial and total DOS and total $-p\text{COHP}$s for (a) Ti$_5$SiB$_2$, (b) Ti$_4$MoSiB$_2$, and (c) Mo$_5$SiB$_2$. In each panel, the horizontal dashed line indicates a peak in the DOS coming from the 16l and 4c sites, and the horizontal dotted line indicates where the total $-p\text{COHP}$ goes from being positive (bonding) to negative (antibonding). The solid horizontal line at zero energy indicates the Fermi level. The total $-p\text{COHP}$s consider the 12 shortest bonds (shown in green), and bonds up until a cutoff of 4.5 Å (shown in black). The latter corresponds to the 24 shortest bonds.

bonds in green, and for bonds up until a cutoff of 4.5 Å in black, corresponding to the 24 shortest bonds. Qualitatively, the total $-p\text{COHP}$s are not affected by including bonds beyond the 12 shortest bonds, and the 6 shortest bonds account for the main contributions the total $-p\text{COHP}$. The 12 shortest bonds are illustrated in figure 1(b), in order of increasing length with the left column containing the 6 shortest bonds and the right column the 6 longer bonds.

The horizontal dashed line in each panel of figure 2 indicates a peak in the partial DOS of the 16l and 4c sites, and the horizontal, dotted line separates the bonding (positive $-p\text{COHP}$) and anti-bonding (negative $-p\text{COHP}$) regions. At energies close to this separation energy, the corresponding states contribute negligibly to bonding implied by the $-p\text{COHP}$ being close to zero. Thus, the structure is most stable when the Fermi level lies close to the dotted line, populating all bonding states, but no anti-bonding states. Among the considered structures, Ti$_4$MoSiB$_2$ comes closest to fulfilling this criteria, while for Mo$_5$SiB$_2$ some anti-bonding states are populated, and for Ti$_5$SiB$_2$ some bonding states are empty just above the Fermi level. The DOS peak from the 16l and 4c sites are prominent also in the total $-p\text{COHP}$, and corresponds to a region of bonding states. This peak is well below the Fermi level for Ti$_4$MoSiB$_2$ and Mo$_5$SiB$_2$, while it is at the Fermi level and thus not completely filled for Ti$_5$SiB$_2$.

Table S2 presents a complete list of all bonds up to 4.5 Å, where it can be seen that most bonds are shorter in Mo$_5$SiB$_2$ than in the other two structures, making the B–B bond an exception to this trend. At the Fermi level the contribution from the B–B interaction in figure 3(a) is close to zero for all three structures. Additionally, some anti-bonding states are populated, most clearly seen in Ti$_5$SiB$_2$ which shows two anti-bonding peaks: a smaller peak just below the Fermi level and a larger at $-1.2$ eV. These peaks are present also in the other two structures, making the B–B bond an exception to this trend. At the Fermi level the contribution from the B–B interaction in figure 3(a) is close to zero for all three structures. Additionally, some anti-bonding states are populated, most clearly seen in Ti$_5$SiB$_2$ which shows two anti-bonding peaks: a smaller peak just below the Fermi level and a larger at $-1.2$ eV. These peaks are present also in the other two structures, making the B–B bond an exception to this trend.

Figures 3(a)–(g) show bond specific $-p\text{COHP}$s for the 7 shortest bonds of Ti$_5$SiB$_2$, Ti$_4$MoSiB$_2$ and Mo$_5$SiB$_2$, including the multiplicity of each bond per unit cell. In (b) the total $-p\text{COHP}$ is shown for all the remaining 5 bonds indicated in figure 1(b)—which are all different 16l–16l bonds—with the total number of bonds implied. Here we choose to focus on these 12 shortest bonds, since longer bond lengths only have a minor contribution to the total $-p\text{COHP}$.
Figure 3. Bond-specific $-p\text{COHP}$ for the three considered structures Ti$_5$SiB$_2$, Ti$_4$MoSiB$_2$ and Mo$_5$SiB$_2$ shown in orange, dark blue and light blue respectively, for the 24 shortest bonds: (a) B–B, (b) 16l–B, (c) 16l–B, (d) 16l–Si, (e) 4c–B, (f) 16l–4c, (g) 4c–Si and (h) 16l–16l (5 different). The legend color in each panel corresponds to the bonds in figure 1, besides (h) which includes all 16l–16l bonds in figure 1. The participating sites are specified in the legend text along with the multiplicity per unit cell of each bond, which is included in the shown $-p\text{COHP}$s. In (h) the total number of considered 16l–16l interactions is shown. The Fermi level is indicated by the vertical gray line. Note the different scale of the y-axis in the left and right column.

states in this bond, but it also has larger contributions from bonding states, so that the total contribution from this bond is comparable to that of Ti$_4$MoSiB$_2$. Mo$_5$SiB$_2$ has, however, a considerably smaller contribution from the B–B bond. The total contributions are shown by the $-p\text{COHP}$ in figure S2.

Figures 3(b) and (c) show the two 16l–B bonds (corresponding to orange and green bonds in figure 1). Note the larger range of the y-axis in figures 3(b), (d), (f) and (h) (panels in right column), which is related to the higher multiplicity of these bonds. Figure 3(b) corresponds to the 16l–B bond of higher multiplicity (orange in figure 1), which gives a larger $-p\text{COHP}$ than the bond in figure 3(c) with lower multiplicity (green in figure 1). Figures 3(d), (e) and (g) correspond to the 16l–Si, 4c–B and 4c–Si bonds, (shown in purple, red and pink in figure 1, respectively).

Some anti-bonding orbitals are filled for the 16l–B bond of lower multiplicity (green) in Mo$_5$SiB$_2$, seen in figure 3(c), and for the 4c–B bond (red) in Ti$_4$MoSiB$_2$, seen in figure 3(e). The magnitude of these anti-bonding contributions is comparable in size to that of the B–B bond in Ti$_5$SiB$_2$, seen in figure 3(a), implying neither of these anti-bonding contributions are decisive for the structural stability. Besides these anti-bonding contributions, all interactions in figures 3(a)–(e) are well optimized with the Fermi level located where the $-p\text{COHP}$s are non-bonding, thus separating bonding states below the Fermi level from anti-bonding states above the Fermi level. These bonds are therefore not very informative in our quest to understand why Ti$_4$MoSiB$_2$ is stable while Ti$_5$SiB$_2$ is not (or metastable at best).

Of more interest is the $-p\text{COHP}$ for the metal–metal 16l–4c bond (brown bond in figure 1) shown in figure 3(f), where a clear qualitative difference is found for the three different structures. The large bonding peak is successively shifted closer to the Fermi level upon substitution of Mo for Ti. This peak corresponds to the DOS/$-p\text{COHP}$ peak indicated by the dashed gray line in each panel of figure 2. For the stable Mo$_5$SiB$_2$, the peak is completely filled, with minor population of anti-bonding states just below the Fermi level. For Ti$_4$MoSiB$_2$, the peak is closer to the Fermi level, completely filled and with no anti-bonding states below or at the Fermi level, rendering the 16l–4c bond better optimized for Ti$_4$MoSiB$_2$ than for Mo$_5$SiB$_2$. For Ti$_5$SiB$_2$, however, the number of valence electrons are too few to completely fill the peak in the 16l–4c bond, leaving some bonding states above the Fermi level. This, in turn, has a negative impact on the bond strength and the overall stability, making the Ti$_5$SiB$_2$ stoichiometry unfavorable. Considering the total of the five 16l–16l bonds (gray, olive, cyan, yellow and salmon color in figure 1) shown in figure 3(h), they also show a considerable amount of empty bonding states above the Fermi level for both Ti$_4$MoSiB$_2$ and Ti$_5$SiB$_2$. The characteristics of these bonds are very similar between the two structures, indicating that the interaction between the 16l sites are barely affected by the substitution of Mo for Ti at the 4c site. Since these
bonds are so similar between Ti$_4$MoSiB$_2$ and Ti$_5$SiB$_2$ they are, however, not the key difference rendering Ti$_5$SiB$_2$ unstable while Ti$_4$MoSiB$_2$ is stable, although they will further add to why Ti$_4$MoSiB$_2$ is an unfavored structure. The last panel, figure 3(g), shows the 4c–Si bond (pink bond in figure 1). This bond is clearly the smallest contribution of those discussed, mainly because of it is low multiplicity (8). It is however included for completeness. Hence, based on the detailed bonding analysis in figure 3 we find that the metal–metal 16l–4c bond is the key to explaining why such a large proportion as 80% of the Mo atoms can be substituted for Ti in Mo$_5$SiB$_2$.

Studying figure 2 again, we can see that upon substitution of Mo for Ti at the 16l sites, both the DOS peak—indicated by the dashed line—and the separation between bonding and anti-bonding regions of the −pCOHP—indicated by the dotted line—are moved up in energy relative to the Fermi level. This can be understood from the decrease in valency upon substitution of Mo for Ti. Both lines are moved roughly the same amount, although the dotted line is moved slightly further than the dashed line, coming from the contribution of the 16l–16l states in figure 3(h). Upon substitution of Mo for Ti at the 4c site we can instead see that the DOS peak is almost to the Fermi level. That the DOS peak is affected more by this substitution than the rest of the DOS implies that the valence difference between Ti$_4$MoSiB$_2$ and Ti$_5$SiB$_2$ is concentrated to the 4c–16l bond. This same conclusion is inferred by studying the DOS minimum just below the DOS peak: the minimum widens upon substitution of Mo at the 4c site, implying that the states at the DOS peak, i.e. states assigned to the 16l–4c bond, loose relatively more electrons upon this substitution than those contributing to the DOS and −pCOHPs just below the gap coming primarily from the 16l–B interactions.

The band structure of Mo$_5$SiB$_2$, Ti$_4$MoSiB$_2$ and Ti$_5$SiB$_2$ has also been evaluated, showing a clearly metallic behavior for all three structures. The band plots are shown in figure S4.

3.3. Bader charge analysis

The reason for the successful substitution of Mo for Ti in Mo$_5$SiB$_2$ may be related to the elements’ different valence, but also to their significantly different electronegativity, being 1.54 for Ti and 2.16 for Mo. For reference, the electronegativity of B and Si are 2.04 and 1.90, respectively. To consider the effect of electronegativity, a Bader analysis on the three structures was performed to obtain the net charge associated with each atom in the structures. The results are shown in figure 4(a).

The metal sites 16l and 4c have in general a positive net charge, while the metalloids Si and B have a negative net charge. The only exception is the 4c metal sites in Ti$_4$MoSiB$_2$, occupied by Mo, which have a negative net charge. Mo$_5$SiB$_2$ has a more evenly distributed charge than the two other structures, leading to smaller electrostatic interactions. Ti$_5$SiB$_2$, on the other hand, has large net charges of about $1|e|$ on all metal sites, causing a stronger repulsion between the metal atoms. The fact that the bond lengths in general are longer...
in \(\text{Ti}_5\text{SiB}_2\) than in \(\text{Mo}_5\text{SiB}_2\) is not enough to negate the increased electrostatic repulsion between the metal atoms, and the same argument carries over to the negatively charged metalloids.

In \(\text{Ti}_4\text{MoSiB}_2\), the 16l sites have a slightly larger positive charge than in \(\text{Ti}_5\text{SiB}_2\), while the bonds are similar and often somewhat shorter than in \(\text{Ti}_5\text{SiB}_2\). However, the 4c sites are negatively charged, leading to an attractive electrostatic force between the 16l and 4c sites, as opposed to in \(\text{Mo}_5\text{SiB}_2\) and \(\text{Ti}_5\text{SiB}_2\). Indeed, compared to \(\text{Ti}_5\text{SiB}_2\), charge has been moved from the 16l, Si and B sites to the 4c sites in \(\text{Ti}_4\text{MoSiB}_2\), clearly reflecting the higher electronegativity of Mo. This is also reflected in the shift of electrons from the metal sites in \(\text{Mo}_5\text{SiB}_2\) to the metalloids in \(\text{Ti}_4\text{MoSiB}_2\) and \(\text{Ti}_5\text{SiB}_2\) due to the less electronegative Ti occupying the 16l sites. The presence of more electrons around the 4c site in \(\text{Ti}_4\text{MoSiB}_2\) also agrees with observations from figure 2, where it was argued that a relatively larger depletion of electrons could be interpreted from the DOS and total -pCOHPs for states related to the 16l–4c bond than for states related to the rest of the structure when substituting Mo for Ti at the 4c site. Further, for \(\text{Ti}_4\text{MoSiB}_2\) the partial DOS of the 16l and 4c sites at the 16l–4c peak are almost the same height, while for \(\text{Ti}_5\text{SiB}_2\) and \(\text{Mo}_5\text{SiB}_2\) the 16l sites clearly contributes more to the peak than the 4c sites, which also agrees with an accumulation of charge at the 4c site in \(\text{Ti}_4\text{MoSiB}_2\).

### 3.4. Force constant analysis

Finally, we present an analysis of the force constants for the 12 shortest bonds in the three structures, depicted in figure 1(b). The projections of each force constant matrix along the direction of the corresponding bond are shown in figure 4(b). The plotted value reflects the force on an atom $a$ upon moving another atom $b$ along the direction of the bond. For most bonds \(\text{Mo}_5\text{SiB}_2\) experiences the strongest interactions, while \(\text{Ti}_5\text{SiB}_2\) shows the weakest interactions. The most notable exception to this trend is the B–B bond shown in blue, for which the interaction is considerably weaker in \(\text{Mo}_5\text{SiB}_2\) than in \(\text{Ti}_4\text{MoSiB}_2\) and \(\text{Ti}_5\text{SiB}_2\), for which the interaction is similar.

The two 16l–B bonds (orange and green) and the 16l–4c bond (brown) are very similar between \(\text{Mo}_5\text{SiB}_2\) and \(\text{Ti}_4\text{MoSiB}_2\), while the bonds are similar and often somewhat shorter in \(\text{Ti}_5\text{SiB}_2\). However, the 4c sites are negatively charged, leading to an attractive electrostatic force between the 16l and 4c sites, as opposed to in \(\text{Mo}_5\text{SiB}_2\) and \(\text{Ti}_5\text{SiB}_2\). Indeed, compared to \(\text{Ti}_5\text{SiB}_2\), charge has been moved from the 16l, Si and B sites to the 4c sites in \(\text{Ti}_4\text{MoSiB}_2\), clearly reflecting the higher electronegativity of Mo. This is also reflected in the shift of electrons from the metal sites in \(\text{Mo}_5\text{SiB}_2\) to the metalloids in \(\text{Ti}_4\text{MoSiB}_2\) and \(\text{Ti}_5\text{SiB}_2\) due to the less electronegative Ti occupying the 16l sites. The presence of more electrons around the 4c site in \(\text{Ti}_4\text{MoSiB}_2\) also agrees with observations from figure 2, where it was argued that a relatively larger depletion of electrons could be interpreted from the DOS and total -pCOHPs for states related to the 16l–4c bond than for states related to the rest of the structure when substituting Mo for Ti at the 4c site. Further, for \(\text{Ti}_4\text{MoSiB}_2\) the partial DOS of the 16l and 4c sites at the 16l–4c peak are almost the same height, while for \(\text{Ti}_5\text{SiB}_2\) and \(\text{Mo}_5\text{SiB}_2\) the 16l sites clearly contributes more to the peak than the 4c sites, which also agrees with an accumulation of charge at the 4c site in \(\text{Ti}_4\text{MoSiB}_2\).

### Table 2. Elastic properties and ductile characteristics for the three different phases, including experimental results for \(\text{Mo}_5\text{SiB}_2\) [44] at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>(\text{Ti}_5\text{SiB}_2)</th>
<th>(\text{Ti}_4\text{MoSiB}_2)</th>
<th>(\text{Mo}_5\text{SiB}_2)</th>
<th>(\text{Mo}_5\text{SiB}_2) [44]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_{11}) (GPa)</td>
<td>280.9</td>
<td>361.4</td>
<td>480.3</td>
<td>480</td>
</tr>
<tr>
<td>(c_{33}) (GPa)</td>
<td>225.2</td>
<td>247.8</td>
<td>398.6</td>
<td>415</td>
</tr>
<tr>
<td>(c_{12}) (GPa)</td>
<td>102.9</td>
<td>101.0</td>
<td>170.6</td>
<td>166</td>
</tr>
<tr>
<td>(c_{13}) (GPa)</td>
<td>108.6</td>
<td>107.5</td>
<td>203.7</td>
<td>197</td>
</tr>
<tr>
<td>(c_{44}) (GPa)</td>
<td>63.1</td>
<td>91.5</td>
<td>162.7</td>
<td>174</td>
</tr>
<tr>
<td>(c_{66}) (GPa)</td>
<td>88.3</td>
<td>121.7</td>
<td>136.4</td>
<td>143</td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>157.9</td>
<td>175.7</td>
<td>279.1</td>
<td>277</td>
</tr>
<tr>
<td>(G) (GPa)</td>
<td>73.0</td>
<td>102.9</td>
<td>142.5</td>
<td>151</td>
</tr>
<tr>
<td>(E) (GPa)</td>
<td>189.8</td>
<td>258.2</td>
<td>365.3</td>
<td>383</td>
</tr>
<tr>
<td>(G/B)</td>
<td>0.463</td>
<td>0.585</td>
<td>0.511</td>
<td>0.545</td>
</tr>
<tr>
<td>(\nu)</td>
<td>0.300</td>
<td>0.255</td>
<td>0.282</td>
<td>0.270</td>
</tr>
<tr>
<td>(c_{13} - c_{44}) (GPa)</td>
<td>45.5</td>
<td>16.0</td>
<td>41.0</td>
<td>23.0</td>
</tr>
<tr>
<td>(c_{12} - c_{66}) (GPa)</td>
<td>14.6</td>
<td>-20.7</td>
<td>34.2</td>
<td>23.0</td>
</tr>
</tbody>
</table>

3.5. Mechanical properties

The calculated mechanical and elastic properties for \(\text{Ti}_5\text{SiB}_2\), \(\text{Ti}_4\text{MoSiB}_2\) and \(\text{Mo}_5\text{SiB}_2\) are presented in table 2, including the elastic constants \(c_{ij}\), bulk modulus \(B\), shear modulus
Figure 5. Calculated ductile characteristics for Ti$_5$SiB$_2$ (orange circle), Ti$_4$MoSiB$_2$ (dark blue cross) and Mo$_5$SiB$_2$ (light blue diamond), and for comparison the experimental results for Mo$_5$SiB$_2$ (turquoise diamond) at room temperature [44]. (a) The ductility of the tree phases according to the Pugh criteria for ductility on the y-axis: $G/B < 0.57$, and the Frantsevich criteria on the x-axis: $\nu > 0.26$. (b) The ductility according to the two Pettifor criteria, where negative values indicate brittle material properties.

4. Summary

Out of the three T2 phases considered herein, only two have been synthesized and predicted stable: Mo$_5$SiB$_2$ and Ti$_4$MoSiB$_2$. To understand why 80% of Mo can be substituted for Ti in Mo$_5$SiB$_2$ and still be stable whereas Ti$_5$SiB$_2$ is not stable (or at best metastable), we have investigated and compared their bonding characteristics using several approaches.

We find that the key component governing the large, but not complete, substitution of Mo for Ti can be related to the interaction between the metal sites 16l and 4c in the metal and metal–boron layers, respectively. This interaction is found to be optimized for Ti$_4$MoSiB$_2$ with bonding states being completely filled. In addition, Bader analysis indicates an attractive electrostatic force between the 16l and 4c sites in Ti$_4$MoSiB$_2$ which is repulsive in Ti$_5$SiB$_2$ and Mo$_5$SiB$_2$. The Bader analysis also shows a charge transfer from the metal sites 16l and 4c to the metalloids Si and B upon substitution of Mo for Ti, due to the lower electronegativity of Ti than Mo. This causes a depletion of electrons around the 16l and 4c sites which moves the bonding peak of 16l–4c bond closer to the Fermi level. Bandstructure calculations show metallic properties for all three structures.

From analysis of the elastic properties, we find that the new quaternary structure Ti$_4$MoSiB$_2$ is stiffer than the two ternary T2 phases Mo$_5$SiB$_2$ and Ti$_5$SiB$_2$.

Conflict of interest

There are no conflicts to declare.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
Acknowledgments

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