First-principles calculations of structural, electronic, elastic and thermal properties of phase M$_2$SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W)

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Received 30 April 2014; accepted 4 September 2014

Abstract: The structural, electronic and elastic properties of the M$_2$SiC phases were studied, where M are 3d, 4d, and 5d early transition metals. The valence electron concentration (VEC) effect of Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W on these properties was examined. The $C_{44}$ saturates for a VEC value in surrounding of 8.5 for each series. Hf-s, Ta-s and W-s electrons mainly contribute to the density of states at the Fermi level, and should be involved in the conduction properties. The distortion increases with increasing VEC and decreasing $k_c/k_a$ factor except for the series M=Ti, V and Cr, where it is lower at the VEC value of 8.5 (it follows a parabolic variation). The M$_2$SiC was characterized by a profound anisotropy for the shear planes (10T0) and compressibility in the direction is higher than that along the cone except for W$_2$SiC, where it is lower.

Key words: ternary carbides; ab initio calculation; crystal structural; electronic structure

1 Introduction

The MAX phases with chemical formula M$_{n+1}$AX$_n$, where M is a transition metal, A is an A-group element, and X is C or N and $n$ varies from 1 to 3, discovered by NOWOTNY [1], have recently attracted the interest of both material scientists and physicists due to their astonishing combination of properties. These materials combine some of the best attributes of metals and ceramics. They behave as metals in terms of their machinability, electrical and thermal conductivities. They behave as ceramics in terms of their specific stiffness and high temperature oxidation resistances [2–14]. This unique combination of characteristics makes them potential materials for many applications, such as rotating electrical contacts and bearings, heating elements, nozzles, heat exchangers, tools for die pressing [10]. Many of these applications are currently field-tested and are at various stages of development. Based on the $n$ value, this class of materials form three groups, M$_2$AX or 211, M$_3$AX$_2$ or 312 and M$_4$AX$_3$ or 413.

The physical properties of MAX phases vary from phase to another and depend on M, A and X elements. M$_2$SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases are members of this fascinating family of materials. In the present work, we report the first-principles study of the structural, electronic and elastic properties of M$_2$SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases as a function of valence electron concentration (VEC) (average number of valence electrons per atom), by using the state of the pseudo-potential plane-wave method (PP-PW) in the framework of the density functional theory (DFT) in conjunction with the generalized gradient approximation (GGA).

2 Computational method

The first-principles calculations were performed by employing the PP-PW approach based on the DFT [15,16] and implemented in the Cambridge Serial Total Energy Package [17]. The exchange-correlation potential was treated within the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof.

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DOI: 10.1016/S1003-6326(15)63680-9
In order to reduce the required number of plane waves, chemically inactive core electrons are effectively replaced with an ultra-soft pseudo-potential [19]. Two parameters that affect the accuracy of calculations are the kinetic energy cut-off which determines the number of plane waves in the expansion and the number of special k-points used for the Brillouin zone (BZ) integration. We performed convergence with respect to Brillouin zone sampling and the size of the basis set. Converged results were achieved with a 9×9×2 special k-points mesh [20]. The size of the basis set was given by cut-off energy equal to 350 eV. Careful convergence tests show that with these parameters, relative energy converged to better than 5×10⁻⁶ eV/atom. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique [21], which provides a fast way of finding the lowest energy structure, was used in the geometry optimization. The tolerances for the geometry optimization were the difference in total energy within 5×10⁻⁶ eV/atom, the maximum ionic Hellmann–Feynman force within 0.01 eV/Å, the maximum ionic displacement within 5×10⁻⁴ Å and the maximum stress within 0.02 eV/Å³. The elastic coefficients were determined from the first-principles calculations by applying a set of given homogeneous deformations with a finite value and calculating the resulting stress with respect to optimizing the internal degrees of freedoms, as implemented by MILMAN et al [22].

3 Results and discussion

3.1 Structural properties
M₂SiC (M = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) compounds crystallize in the Cr₂AlC crystal structure, with space group P63/mmc (#194). The atomic positions in the elementary cell are: C (0, 0, 0), Si (1/3, 2/3, 3/4) and M (1/3, 2/3, z). Two lattice constants a and c and the internal structural parameter z define the structure. Figure 1 shows a structural model for the crystalline structure of M₂SiC phase. The optimized equilibrium lattice parameters a₀, c₀ and the internal structural parameter z₀, for all M₂SiC series as determined from geometry within GGA are given in Table 1. There is a good agreement between our calculated lattice constants and internal parameter of Nb₂SiC and those previously reported by COVER et al [23] and GHEBOULI et al. [24]. The compounds with M elements belonging to the same line of the periodic table are grouped together. HUG [25] defined for a parameter, a₉, of the 211 MAX phases to describe the distortion as follows:

\[ a_9 = \sqrt{\frac{3}{2}} \left[ \frac{z^2}{a^2} \right]^{1/2} \left[ \left( \frac{c}{a} \right)^2 + \frac{1}{12} \right] \]  

where z is the internal coordinate of the C atoms. As defined, a₉ is the ratio of the distances between two opposite faces contained in the basal planes and two faces not in the basal planes. This factor equals unity for the cubic octahedron. The calculated a₉ values for the studied M₂SiC phases are listed in Table 1 and plotted in Fig. 2. The distortion increases with increasing VEC except for the series M=Ti, V and Cr, where it has a lower value in V₂SiC (it follows a parabolic variation). The distortion is clearly the highest in Ti₂SiC, Mo₂SiC and W₂SiC. The variation of the lattice constants c and a as a function of the VEC for the three series is shown in Fig. 2. These parameters show a decrease with increasing VEC for all series. From Table 1, for the same VEC, c₀/a₀ ratio decreases when the number of valence electrons of M element is enhanced. The a₀ and c₀ values of the series of M₂SiC phases, where M belongs the same column, increase when they go downward the column: \{(a₀ and c₀) (Ti₂/V₂/Cr₂SiC)<{a₀ and c₀} (Zr₂/Nb₂/Mo₂SiC)<{a₀ and c₀} (Hf₂/Ta₂/W₂SiC). As Si and C atoms are the same in the three compounds, this result can be easily explained by considering the atomic radii of M atoms. The larger size of M atoms forces the system to have larger lattice constants.

The computed equilibrium geometry of M₂SiC unit cell at applied hydrostatic pressure in the range of 0–20 GPa with the step of 5 GPa is performed to investigate the structural parameters under pressure effect. It is assumed that no phase transformation occurred in these systems. Also, it was reported that no phase transformation was observed in the MAX phases Ti₃AlN, Ti₃AlC, V₃AlC, Cr₃AlC, Nb₃AlC, Nb₂AlC and Zr₃InC, which were investigated under pressure of 50 GPa by using a synchrotron radiation and a diamond-anvil cell to measure the pressure dependencies of the lattice parameters [26,27]. Figure 3 plots the relative changes of the lattice parameters (a/a₀ and c/c₀) versus applied hydrostatic pressure (p). We clearly observe a quadratic
Table 1 Lattice constants $a_0$ and $c_0$, $c_0/a_0$ ratio, bulk modulus $B_0$ and its pressure derivative $B'$, internal parameter $z$ and distortion of M$_2$SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases at zero pressure

<table>
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<tr>
<th>Phase</th>
<th>$a_0$/Å</th>
<th>$c_0$/Å</th>
<th>$c_0/a_0$</th>
<th>$B_0$/GPa</th>
<th>$B'$</th>
<th>$z$</th>
<th>$a_r$</th>
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<td>3.2002</td>
<td>12.8160</td>
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<td>173.68</td>
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<td>12.0549</td>
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<td>4.231</td>
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<td>11.8612</td>
<td>4.175</td>
<td>223.40</td>
<td>4.238</td>
<td>0.0893</td>
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<td>13.6240</td>
<td>4.156</td>
<td>162.09</td>
<td>3.971</td>
<td>0.0945</td>
<td>1.236</td>
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<tr>
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<td>12.4175</td>
<td>3.895</td>
<td>217.94</td>
<td>4.223</td>
<td>0.0962</td>
<td>1.342</td>
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<td>12.2099</td>
<td>3.998</td>
<td>246.59</td>
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<td>13.4067</td>
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<td>181.12</td>
<td>4.289</td>
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<tr>
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<td>12.4195</td>
<td>3.810</td>
<td>218.21</td>
<td>4.411</td>
<td>0.0991</td>
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<tr>
<td>W$_2$SiC</td>
<td>3.1005</td>
<td>12.2470</td>
<td>3.950</td>
<td>262.93</td>
<td>4.108</td>
<td>0.0939</td>
<td>1.366</td>
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</table>

Fig. 2 Lattice constants $a$ and $c$ and distorsion $a_r$ in M$_2$SiC phases as function of VEC

dependence in all curves of the studied compounds in the considered range of pressure. The solid curve is the quadratic least-squares fit $(a/a_0, c/c_0=1+ap+bp^2)$. In contradiction to some other MAX phases [26–32], the compressibility of M$_2$SiC along the $a$-axis is greater than that along $c$-axis, except for Nb$_2$SiC, which are nearly identical and in W$_2$SiC, it is greater along the $c$-axis. The same behaviour has been observed in other MAX phases [27,31–33]. Different reasons have been reported to explain this behaviour. With subjecting Nb$_2$AsC to hydrostatic pressure up to 41 GPa, KUMAR et al [33] found that the pressure contraction along the $a$-direction was greater than that along the $c$-axis, and concluded that Nb−As bond must be quite resistant to compression along the $c$-axis. Experiments on M$_2$AlC phases (M=Ti, V, Cr, Zr, Nb and Ta) [27] revealed that the compressibility in the $c$-axis was lower than that along $a$-axis for $M$ = Cr and Nb. It was suggested that $M$−C and $M$−Al bonds have comparable strength in M$_2$AlC with $M$=Cr, Nb. EMMERLICH et al [31] reported for M$_2$AlC phases (M= Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) that for the $M$ element with a VEC of 4, the compressibility in $c$-axis is larger than that along the $a$-axis. As the VEC increases and reaches 5, it decreases and becomes comparable to that along the $a$-axis, whereas at VEC=6, the compressibility in the $a$-axis is larger than that along the $c$-axis. The geometric alteration of the bonding configuration in combination with the increase in $M$−C bond stiffness is responsible in this compressibility change. A similar observation in compressibility along both $a$ and $c$ axes for Ta$_3$AlC [32] has been attributed to an increase in Ta−Al and Ta−Ta bonding strength as well as the interaction between TaC−TaC layers. Our results show that the compressibility along the $a$-axis is higher than that along the $c$-axis for all studied M$_2$SiC compounds and has VEC of 8.0, 8.5 and 9.0, except for $M$=Nb and W. These results conclude that the compressibility of the lattice parameters depend on the nature of $M$, $A$ and $X$ atoms. The calculated unit cell...
volumes at fixed values of applied hydrostatic pressure in the range of 0–20 GPa with the step of 5 GPa were used to construct the equation of state (EOS), which was fitted to the third-order Birch–Murnaghan equation [34]. We obtained, by least-squares fitting, the bulk modulus at zero pressure $B_0$ and its pressure derivative $B'$. These are listed in Table 1. Table 1 illustrates that the bulk modulus increases with increasing the number of valence electrons of the transition metal in the same row.

3.2 Electronic properties

The calculated energy band structures for Hf$_2$SiC, Ta$_2$SiC and W$_2$SiC at equilibrium lattice parameters, along the high symmetry directions in the Brillouin zone, where the transition metal element belongs to the sixth period, are shown in Fig. 4. We considered them as a prototype since the band profiles of the other compounds, where the transition metal element belongs to the other periods, are quite similar. The valence and conduction bands overlap considerably and there is no band gap at the Fermi level. As a result, M$_2$SiC will exhibit metallic properties. The noble metal carbides, such as PdC, AgC, PtC and NbC in zinc blende phase are metallic in nature [35–38]. The $E_F$ of Hf$_2$SiC lies below the valence-band maximum near $\Gamma$ point. In W$_2$SiC, more valence electrons present in the unit cell, and the $E_F$ lies about 2.5 eV which is higher than that in Hf$_2$SiC. This leads to some additional occupation of bonding states near the Fermi level. The initially unoccupied valence band near the $\Gamma$ point shifts downward and is located below the Fermi level in W$_2$SiC. The substitution of Hf by Ta and then by W in M$_2$SiC introduces extra valence electrons per atom and correspondingly Fermi level moves to a higher energy.

The calculated total densities of states (TDOS) for Hf$_2$SiC, Ta$_2$SiC and W$_2$SiC are presented in Fig. 5. The details of the peak structures and the relative heights of the peaks in their TDOS are rather similar, indicating similarity in chemical bonding. The computed number ($N$) of states at the Fermi level ($E_F$) is 3.59, 3.01 and 2.12 eV/cell for W$_2$SiC, Hf$_2$SiC and Ta$_2$SiC. Therefore, we expect that the electrical conductivity decreases in the sequence of W$_2$SiC $\rightarrow$ Hf$_2$SiC $\rightarrow$ Ta$_2$SiC. The understanding of the chemical bonding in M$_2$SiC requires the calculating their partial density of states (PDOS). The PDOS spectrum for M$_2$SiC, where M belongs to the fourth period, is shown in Fig. 5. Carbon does not contribute to the TDOS at the Fermi level and therefore is not involved in the conduction properties. M-s electrons mainly contribute to the TDOS at the
Fermi level, and should be involved in the conduction properties. Si electrons do not contribute significantly at the Fermi level. It is apparent that a covalent interaction occurs between the constituting elements. C-s and M-s as well as Si-s and M-s states are hybridized. The PDOS shows that the hybridization peak in energy of M-s and C-s is lower than that of M-s and Si-s. This suggests that the M-s—(Ti-s, V-s and Cr-s)—C-s bonds are stiffer than the (M-s)—(Si-s) bonds. The Fermi level moves from a lower to a higher energy with the substitution of the transition metals of Ti by V and Cr, which indicates that the increased extra valence electrons fill in the M-s—C-s and M-s—Si-s hybridized bonding states. The states located between −0.9 and −5.5 eV below the Fermi level in Hf2SiC are originated from the hybridization of (Hf-6s)—(C-2s) orbitals. These states shift downward and extend from −1.9 to −5.68 eV below Fermi level in Ta2SiC. This indicates that the stiffness of the M—Si and M—C bonds increases with increasing valence electron concentration.

### 3.3 Elastic properties

Table 2 lists our computed elastic constants of M2SiC phases (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W). To date, no direct experimental elastic constants are available to be compared with our results. Future experimental measurements will test our calculated predictions. The elastic constant \( C_{11} \), which provides a measure of rigidity against unidirectional deformation along \( a \)-axis is slightly lower than the elastic constant \( C_{33} \), which provides an estimation of the elastic response of the material to a unidirectional pressure along \( c \)-direction. This is in accordance with the response of \( a \)- and \( c \)-axis under hydrostatic pressure (Fig. 3).

The elastic anisotropy of crystals has an important implication in engineering since it is highly correlated with the possibility to induce microcracks in the materials [39]. Essentially, all known crystals are elastically anisotropic, and a description of such anisotropic behaviour has an important implication in engineering science as well as in crystal physics. To quantify the elastic anisotropy of M2SiC, we calculated the shear anisotropic factor (\( A \)) for the shear plane (10T0) formed by the (01T1) and (01T0) directions, which is identical to the shear anisotropy factor for the shear plane (01T0) formed by the (10T1) and (0001) directions [40]:

\[
A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \tag{2}
\]

The calculated shear anisotropic factor of M2SiC is given in Table 2. For an isotropic crystal, \( A \) is equal to 1, while any value smaller or larger than 1 indicates anisotropy. The magnitude of the deviation from 1 is a
Fig. 5 Total and partial densities of states of Ta$_2$SiC (b), W$_2$SiC (a) and Hf$_2$SiC (c)

measure of the degree of elastic anisotropy possessed by the crystal. According to this, M$_2$SiC is characterized by a profound anisotropy for the shear planes described above.

We use the ratio between the linear compressibility coefficients along the c- and a-axis, i.e., $k_c/k_a$, to characterize their elastic anisotropy (Table 2 and Fig. 6). For a hexagonal crystal, $k_c/k_a$ can be expressed as [41,42]

$$k_c / k_a = (C_{11} + C_{12} - 2C_{13}) / (C_{13} - C_{11})$$

On can notice that $k_c/k_a$ decreases with increasing VEC. The $k_c/k_a$ values for all M$_2$SiC phases are less than 1, which suggests that the compressibility along a-axis is higher than that along c-direction. It is observed that the distortion increases with decreasing $k_c/k_a$ except for the series M=Ti, V and Cr, where it is lower for V$_2$SiC compound.

Once the elastic constants are determined, we would like to compare our results with experiments, or predict what experiment would yield for the elastic constants. A problem arises when single-crystal samples cannot be obtained. Then, it is not possible to measure the individual elastic constants $C_{ij}$. Instead, the isotropic bulk modulus $B$ and the shear modulus $G$ are determined [43]. These data cannot in general be calculated directly from $C_{ij}$, but we can use our values to place bounds on the isotropic modulus. REUSS and ANGEW [44] found lower bounds for all lattices, while VOIGT [45] discovered upper bounds. HILL [46] showed that the Voigt and Reuss averages are limited and suggested that the actual effective modulus could be approximated by the arithmetic mean of the two bounds. The formulas for
Table 2 Calculated elastic constants $C_{ij}$, ratio $k_c/k_a$, bulk modulus $B$ and shear modulus $G$, elastic modulus $E$, Poisson ratio $\nu$ and anisotropy factor $A$ of $M_2SiC$ (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>$C_{11}$/GPa</th>
<th>$C_{12}$/GPa</th>
<th>$C_{44}$/GPa</th>
<th>$C_{12}$/GPa</th>
<th>$C_{13}$/GPa</th>
<th>$C_{66}$/GPa</th>
<th>$k_c/k_a$</th>
<th>$B}$/GPa</th>
<th>$G}$/GPa</th>
<th>$E}$/GPa</th>
<th>$\sigma$</th>
<th>$A$</th>
<th>$B/G$</th>
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<td>Ti$_2$SiC</td>
<td>311</td>
<td>343</td>
<td>155</td>
<td>84</td>
<td>157</td>
<td>119</td>
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<td>154</td>
<td>91</td>
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These bounds for a hexagonal lattice can be found in Refs. [47,48]. We also calculated the elastic modulus ($E$) and Poisson ratio ($\nu$), which are frequently measured for polycrystalline materials when investigating their hardness. These data are related to the bulk modulus $B$ and the shear modulus $G$ by the following equations [49]:

$$E = \frac{9BG}{(3B+G)}$$  \hspace{1cm} (4)

$$\nu = \frac{(3B-E)}{(6B)}$$  \hspace{1cm} (5)

The calculated bulk modulus, shear modulus, elastic modulus and Poisson ratio of $M_2SiC$ (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) are given in Table 2. The bulk modulus values calculated from the elastic constants have nearly the same ones as those obtained from the EOS fitting. This might be an estimate of the reliability and accuracy of our calculated elastic constants. We illustrate the VEC effect on elastic and shear moduli as shown in Fig. 6. With the exception of V$_2$SiC, which is anomalously soft, $E$ is the maximum at VEC of 8.5. The trends in $G$ are identical, with the $G$ values also peaking at VEC of 8.5, again with the exception of V$_2$SiC. The Poisson ratio falls in the range 0.2–0.33.

One can estimate the brittle and ductile behaviours of polycrystalline materials by considering $B$ and $G$ as the resistance to fracture and to plastic deformation. A low (high) $B/G$ ratio is therefore associated to brittleness (ductility) of materials. The consequence of brittleness is the sensitivity for thermal shocks, as the material cannot efficiently dissipate thermal stress via plastic deformations. Thus, a brittle solid can only be subjected to limited thermal shocks before its strength drops dramatically. The ductile materials are resistant to thermal shocks; their mechanical properties decrease slowly with increasing temperature. PUGH [50] proposed a critical value which separates ductile and brittle materials. It was fixed at about 1.75, i.e., if $B/G>1.75$, the material behaves in a ductile manner, otherwise, the material behaves in a brittle manner. From the computed $B/G$ ratios of Table 2 and referred to Pugh’s criterion, we can conclude that $M_2SiC$ (M=Cr, Mo and W) is brittle, whereas $M_2SiC$ (M=V, Nb and Ta) is between the two categories of materials. $M_2SiC$, with M=Ti, Zr and Hf is ductile.

The key criterion for mechanical stability of a crystal is that the strain energy must be positive [51]. For an hexagonal crystal, its five independent elastic constants should satisfy the well-known Born stability criteria [52], i.e., $C_{11} - |C_{12}| > 0$, $(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$ and $C_{44} > 0$. Our results reveal that the stability criteria are verified, implying the mechanical stability of $M_2SiC$ materials. The stability of these compounds can also be
confirmed by providing the Poisson ratio, whose value is usually between −1 and 0.5, corresponding to the lower and upper limit where the materials do not change their shapes.

Elastic deformation can be reduced to volume and shape changes [53]. The bulk modulus provides an estimation of the elastic response of the material to isotropic hydrostatic pressure. The shear moduli (\(G\) and \(C_{44}\)) provide a measure of rigidity against the shape deformation. WANG and ZHOU [53] and JHI et al [54] found that in transition-metal carbonitrides TiC\(_x\)N\(_{1-x}\), the hardness and shear module \(C_{44}\) reached an anomalous maximum for one valence electron number value in the unit cell, while the bulk and shear moduli did not show the maximum. \(C_{44}\) was demonstrated to be a better hardness predictor for this class of materials [53–55]. Because of the fact that M\(_2\)SiC phase has a close relationship with the transition-metal carbides both in crystal structure and atomic bonding characteristics, one could expect direct information on predicting the hardness by examining the correlation between \(C_{44}\) and VEC for M\(_2\)SiC. Figure 7 illustrates the calculated elastic constant \(C_{44}\) of M\(_2\)SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) as a function of the valence electron concentration (average number of valence electrons per atom). This variation is parabolic and similar in each series. In the same series, as the VEC is increased from 8.0 to 8.5, \(C_{44}\) increases and then decreases when the VEC reaches 9. We remark that \(C_{44}\) may saturate its maximum when the VEC is equal to 8.41, 8.56 and 8.48 for the compounds having M element from the fourth, the fifth and the sixth period, respectively. This trend is consistent with the literature on M\(_2\)AlC (M=Ti, V, Nb, Cr) [56,57]. This implies that the maximal hardness might be achieved when the VEC is in the range of 8.40–8.42, 8.55–8.57 and 8.47–8.49 for the compounds having M element from the fourth, the fifth and the sixth period, respectively.

3.4 Thermal properties

The thermal conductivity is the property of a material that indicates its ability to conduct heat. So, in order to know if material is a potential candidate for thermal barrier coating application, its thermal conductivity needs to be investigated. Based on the Debye model, CLARKE [58] suggested that the theoretical minimum thermal conductivity \(k_{\text{min}}\) can be calculated after replacing different atoms by an

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**Fig. 6** Ratio between linear compressibility coefficients \(k_c/k_a\) along c- and a-axis (a), shear modulus (b) and elastic modulus (c) in M\(_2\)SiC phases as function of VEC

**Fig. 7** Calculated elastic constant \(C_{44}\) of M\(_2\)SiC as function of VEC (Solid lines represent the second-order polynomial fit)
equivalent atom with a mean relative atomic mass $M_n$:

$$k_{min} = k_B \sqrt{\frac{M_m}{\rho}} \left(\frac{2}{3}\right)$$  \hspace{1cm} (6)

where $k_B$ is the Boltzmann constant.

The average sound velocity $v_m$ in the polycrystalline material is given by [59]

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{\frac{1}{3}}$$  \hspace{1cm} (7)

where $v_l$ and $v_t$ are the longitudinal and transverse sound velocities obtained by the shear modulus $G$ and the bulk modulus $B$ from the Navier’s equation [59]:

$$v_l = \left( \frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}}, \quad v_t = \left( \frac{G}{\rho} \right)^{\frac{1}{2}}$$  \hspace{1cm} (8)

One of the most important parameters that determine the thermal characteristics of materials is the Debye temperature ($\theta_D$). The Debye temperature is closely related to many physical properties such as elastic constant, specific heat and melting temperature. A higher $\theta_D$ implies a higher thermal conductivity. It is used to distinguish high and low temperature regions for a solid. All modes are expected to have energy $\theta_D$ if $T > \theta_D$, and if $T < \theta_D$ one can expect high-frequency modes to be frozen [60]. At low temperature, the vibrational excitation arises solely from acoustic modes. Hence, at low temperature, the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. The Debye temperature can be defined in terms of the mean sound velocity as follows [59]:

$$\theta_D = \frac{h}{k_B} \left[ \frac{3}{4\pi \rho v_a} \right]^{\frac{1}{3}} v_m$$  \hspace{1cm} (9)

The computed thermal properties of $M_2SiC$ (M= Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases, including the sound velocity, minimum thermal conductivity and Debye temperature as well as the density are summarized in Table 3. When the M element changes downward the column of periodical table, the Debye temperature and minimum thermal conductivity of $M_2SiC$ decrease, except for the series M = Ti, Zr and Hf, where it is lower for Zr$_2$SiC. When the M element changes in the same line of the periodical table, the Debye temperature and the minimum thermal conductivity of $M_2SiC$ saturate their maximum for a VEC value about 8.5. In this formulation, the Debye temperature is directly related to the elastic constants via average elastic wave velocity, so the variations of the Debye temperature and the minimum thermal conductivity of $M_2SiC$ depending on the chemical nature of the M elements have the same trend with the average elastic wave velocities. Unfortunately, as far as we know, there are no data available related to these properties in the literature for $M_2SiC$. Therefore, our calculated values can be considered prediction of these properties. Future experimental work will provide a comparison for our calculated results.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
<th>$v_l$ (m·s$^{-1}$)</th>
<th>$v_t$ (m·s$^{-1}$)</th>
<th>$\theta_D$ (K)</th>
<th>$k_{min}$</th>
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<td>Ti$_2$SiC</td>
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<td>577</td>
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<tr>
<td>Cr$_2$SiC</td>
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<td>7702</td>
<td>3763</td>
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<td>4022</td>
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<td>4534</td>
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<tr>
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<td>4626</td>
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<td>4586</td>
<td>733</td>
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</table>

4 Conclusions

1) The lattice constants decrease with increase in VEC of the M element in the same period.

2) A numerical first-principles calculation of the elastic constants was used to calculate $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$ and $C_{66}$. It is found that a quadratic dependence of the ratio $c/v_0$ as a function of valence electron concentration.

3) With the exception of V$_2$SiC, both the elastic and shear moduli peaks are at a VEC value of 8.5.

4) The distortion and bulk modulus increase with increasing VEC.

5) The Debye temperature and the minimum thermal conductivity of $M_2SiC$ saturate their maximum at a VEC value about 8.5.

6) Like all MAX phases, the compounds studied are electrical conductors and the conductivity is assured by the s electrons of the transition metals.

7) The analysis of the partial density of states shows a strong hybridization Si-s—M-s and C-s—M-s.

References


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M₂SiC(MAX)相(M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W)结构、电子特性、弹性和热性能的第一性原理计算

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摘要：研究M₂SiC相的结构、电子特性、弹性和热性能(M为3 d, 4 d和5 d前过渡金属)。分析Ti, V, Cr, Zr, Nb, Mo, Hf, Ta和W价电子浓度(VEC)对这些性能的影响。每个系列金属在VEC值为8.5时弹性常数C₄₄达到饱和。Hf-s, Ta-s和W-s电子主要在费米能级对态密度有贡献，可用于传导性能计算。

关键词：三元碳化物；从头计算法；晶体结构；电子结构

(Edited by Xiang-qun LI)