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First-principles calculations of structural, electronic, elastic and thermal properties of phase M₂SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W)

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Abstract: The structural, electronic and elastic properties of the M₂SiC 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 serie. 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 M₂SiC was characterized by a profound anisotropy for the shear planes (1010) and compressibility in the direction is higher than that along the cone except for W₂SiC, 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, M₂AX or 211, M₃AX₂ or 312 and M₄AX₃ or 413. The physical properties of MAX phases vary from phase to another and depend on M, A and X elements. M₂SiC (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 M₂SiC (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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[18]. 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 $9 \times 9 \times 2$ 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

 M_2SiC (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 a_0 , c_0 and the internal structural parameter z_0 , 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, a_r , of the 211 MAX phases to describe the distortion as follows:

$$a_{\rm r} = \frac{\sqrt{3}}{2\sqrt{4z^2(\frac{c}{a})^2 + \frac{1}{12}}}$$
(1)



Fig. 1 Structural model for crystalline structure of M₂SiC phase

where z is the internal coordinate of the C atoms. As defined, a_r 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 a_r 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 W_2SiC . The variation of the lattice constants c and aas 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, c_0/a_0 ratio decreases when the number of valence electrons of M element is enhanced. The a_0 and c_0 values of the series of M₂SiC phases, where M belongs the same column, increase when they go downward the column: $\{a_0 \text{ and } c_0\}$ (Ti₂/V₂/Cr₂SiC) < $\{a_0 \text{ and } c_0\}$ (Zr₂/Nb₂/ Mo₂SiC) $\leq \{a_0 \text{ and } c_0\}$ (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 Ti₂AlN, Ti₂AlC, V₂AlC, Cr₂AlC, Nb₂AlC, Nb₂AlC and Zr₂InC, 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/a_0 and c/c_0) versus applied hydrostatic pressure (p). We clearly observe a quadratic

M ₂ SIC (M-11, V, C1, Z1, NO, MO, H1, 14 and W) phases at zero pressure									
Phase	a_0 /Å	c_0 /Å	c_0/a_0	B ₀ /GPa	B'	Z	a _r		
Ti ₂ SiC	3.2002	12.8160	4004	173.68	4.281	0.0910	1.409		
V ₂ SiC	2.9172	12.0549	4132	214.01	4.231	0.0922	1.304		
Cr ₂ SiC	2.8406	11.8612	4175	223.40	4.238	0.0893	1.354		
Zr ₂ SiC	3.2778	13.6240	4156	162.09	3.971	0.0945	1.236		
Nb ₂ SiC	3.1875	12.4175	3895	217.94	4.223	0.0962	1.342		
Mo ₂ SiC	3.0790	12.2099	3998	246.59	3.851	0.0931	1.377		
Hf ₂ SiC	3.2817	13.4067	4085	181.12	4.289	0.0967	1.223		
Ta ₂ SiC	3.2597	12.4195	3810	218.21	4.411	0.0991	1.325		
W ₂ SiC	3.1005	12.2470	3950	262.93	4.108	0.0939	1.366		

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 M₂SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases at zero pressure



Fig. 2 Lattice constants *a* and *c* and distorsion a_r in M₂SiC 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 $(a/a_0, c/c_0=1+\alpha p+\beta p^2)$. In contradiction to some other MAX phases [26-32], the compressibility of M₂SiC along the *a*-axis is greater than that along *c*-axis, except for Nb₂SiC, which are nearly identical and in W_2SiC , 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 Nb₂AsC 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 M₂AlC 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-Cand M—Al bonds have comparable strength in M₂AlC with M=Cr, Nb. EMMERLICH et al [31] reported for M₂AlC 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_2AIC [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 M₂SiC 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



Fig. 3 Relative changes of lattice constants a/a_0 and c/c_0 in M₂SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases as function of pressure

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 Hf₂SiC, Ta₂SiC and W₂SiC 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, M₂SiC 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 $E_{\rm F}$ of Hf₂SiC lies below the valence-band maximum near Γ point. In W₂SiC,

more valence electrons present in the unit cell, and the E_F lies about 2.5 eV which is higher than that in Hf₂SiC. This leads to some additional occupation of bonding states near the Fermi level. The initially unoccupied valence band near the Γ point shifts downward and is located below the Fermi level in W₂SiC. The substitution of Hf by Ta and then by W in M₂SiC introduces extra valence electrons per atom and correspondingly Fermi level moves to a higher energy.

The calculated total densities of states (TDOS) for Hf₂SiC, Ta₂SiC and W₂SiC 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 $(E_{\rm F})$ is 3.59, 3.01 and 2.12 eV/cell for W₂SiC, Hf₂SiC and Ta₂SiC. Therefore, we expect that the electrical conductivity decreases in the sequence of $W_2SiC \rightarrow Hf_2SiC \rightarrow Ta_2SiC$. The understanding of the chemical bonding in M₂SiC requires the calculating their partial density of states (PDOS). The PDOS spectrum for M₂SiC, 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





Fig. 4 Electronic band dispersion curves of Ta_2SiC (a), W_2SiC (b) and Hf_2SiC (c) along some high symmetry directions of Brillouin zone

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 M_2SiC 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 (1010) formed by the $\langle 0111\rangle$ and $\langle 0110\rangle$ directions, which is identical to the shear anisotropy factor for the shear plane (0110) formed by the $\langle 1011\rangle$ and $\langle 0001\rangle$ directions [40]:

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

The calculated shear anisotropic factor of M_2SiC 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_2SiC (b), W_2SiC (a) and Hf_2SiC (c)

measure of the degree of elastic anisotropy possessed by the crystal. According to this, M₂SiC 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]

$$k_c / k_a = (C_{11} + C_{12} - 2C_{13}) / (C_{33} - C_{13})$$
(3)

On can notice that k_c/k_a decreases with increasing VEC. The k_c/k_a values for all M₂SiC 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 V₂SiC

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

anisotropy fact	01 /1 01 W1251C	$(\mathbf{W} \mathbf{H}, \mathbf{V}, \mathbf{C})$	1, 21, 10, 100, 100, 100, 100, 100, 100,	III, Ia alla w) phases				
Phase	$\overline{C_{11}}/\mathrm{GPa}$	C ₃₃ /GPa	C ₄₄ /GPa	C_{12}/GPa	a C	C ₁₃ /GPa	C ₆₆ /GPa	k_c/k_a	B _V /GPa
Ti ₂ SiC	311	343	155	84		107	119	0.7669	173
V ₂ SiC	313	344	194	131		154	91	0.7157	205
Cr ₂ SiC	337	440	64	138		178	99	0.4542	133
Zr ₂ SiC	267	280	116	91		110	88	0.8117	159
Nb ₂ SiC	325	357	195	139		172	93	0.6486	219
Mo ₂ SiC	339	380	139	161		191	89	0.6243	238
Hf ₂ SiC	308	305	142	90		129	109	0.7954	179
Ta ₂ SiC	332	361	203	136		173	98	0.6489	221
W ₂ SiC	375	419	132	157		224	109	0.4307	264
Phase	B _R /GPa	<i>B</i> /GPa	G _V /GPa	G _R /GPa	G/GPa	E/GPa	σ	A	B/G
Ti ₂ SiC	172	172.5	130	127	128.5	309	0.20	1.4	1.34
V ₂ SiC	204	204.5	131	114	122.5	306	0.25	2.22	1.66
Cr ₂ SiC	226	179.5	87	82	84.5	225	0.33	0.6	2.12
Zr ₂ SiC	159	159	97	95	96	240	0.24	1.41	1.65
Nb ₂ SiC	217	218	132	113	122.5	309	0.26	2.30	1.77
Mo ₂ SiC	235	236.5	108	102	105	274	0.30	1.64	2.25
Hf ₂ SiC	179	179	117	112	114.5	283	0.23	1.6	1.56
Ta ₂ SiC	219	220	137	118	127.5	320	0.25	2.34	1.72
W ₂ SiC	258	261	112	108	110	289	0.31	1.52	2.37

Table 2 Calculated elastic constants C_{ij} , ratio k_c/k_a , bulk modulus *B* and shear modulus *G*, elastic modulus *E*, Poisson ratio *v* and anisotropy factor *A* of M₂SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases

these bounds for a hexagonal lattice can be found in Refs. [47,48]. We also calculated the elastic modulus (E) and Poisson ratio (v), 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]:

$$E = 9BG/(3B+G) \tag{4}$$

$$v = (3B - E)/(6B)$$
 (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 V₂SiC, 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 V₂SiC. 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 M₂SiC (M=Cr, Mo and W) is brittle, whereas M₂SiC (M=V, Nb and Ta) is between the two categories of materials. M₂SiC, 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 M₂SiC materials. The stability of these compounds can also be



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 M₂SiC phases as function of VEC

confirmed by providing the Poison 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 modules (*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_xN_{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 M2SiC 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 M₂SiC. Figure 7 illustrates the calculated elastic constant C₄₄ of M₂SiC (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 M₂AlC (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.



Fig. 7 Calculated elastic constant C_{44} of M₂SiC as function of VEC (Solid lines represent the second-order polynomial fit)

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_{min} can be calculated after replacing different atoms by an

equivalent atom with a mean relative atomic mass $M_{\rm m}$:

$$k_{\min} = k_{\rm B} v_{\rm m} (M_{\rm m}/\rho)^{-\frac{1}{3}}$$
 (6)

where $k_{\rm B}$ is the Boltzmann constant.

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

$$v_{\rm m} = \left[\frac{1}{3} \left(\frac{2}{v_{\rm t}^3} + \frac{1}{v_{\rm l}^3}\right)\right]^{-\frac{1}{3}}$$
(7)

where v_1 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]:

$$v_{1} = \left(\frac{3B+4G}{3\rho}\right)^{\frac{1}{2}}, \quad v_{t} = \left(\frac{G}{\rho}\right)^{\frac{1}{2}}$$
 (8)

One of the most important parameters that determine the thermal characteristics of materials is the Debye temperature (θ_D). The Debye temperature is closely related to many physical properties such as elastic constant, specific heat and melting temperature. A higher $\theta_{\rm D}$ 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 $k_{\rm B}T$ 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]:

$$\theta_{\rm D} = \frac{h}{k_{\rm B}} \left[\frac{3}{4\pi V_{\rm a}} \right]^{\frac{1}{3}} v_{\rm m} \tag{9}$$

The computed thermal properties of M₂SiC (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 M₂SiC decrease, except for the series M = Ti, Zr and Hf, where it is lower for Zr₂SiC. When the M element changes in the same line of the periodical table, the Debye temperature and the minimum thermal conductivity of M₂SiC 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 M2SiC 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 3 Calculated density ρ , longitudinal, transverse and average sound velocities $v_{\rm b}$ $v_{\rm t}$ and $v_{\rm m}$, Debye temperature $\theta_{\rm D}$ and minimum thermal conductivity $k_{\rm min}$ for M₂SiC (M=Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) phases

Phase	$\rho/(g \cdot cm^{-3})$	$v_l/(\mathbf{m}\cdot\mathbf{s}^{-1})$	$v_t/(m \cdot s^{-1})$	$v_{\rm m}/({\rm m}\cdot{\rm s}^{-1})$	$\theta_{\rm D}/{\rm K}$	k _{min}
Ti ₂ SiC	4.4581	8790	4648	5195	577	1.40
V_2SiC	5.3071	8326	4534	5058	595	1.43
Cr ₂ SiC	5.7731	7702	3763	4227	512	1.15
Zr ₂ SiC	5.8297	7025	4022	4468	543	0.96
Nb ₂ SiC	6.8665	7453	4534	5009	642	1.11
Mo ₂ SiC	7.6207	7032	4195	4643	617	1.05
Hf ₂ SiC	10.546	5609	4382	4671	691	0.8
Ta ₂ SiC	11.6815	5777	4626	4907	751	0.95
W ₂ SiC	13.2825	5542	4296	4586	733	0.75

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_0/a_0 as a function of valence electron concentration.

3) With the exception of V_2SiC , 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.

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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 值约为 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。M=Ti, V 和 Cr 系列 金属在 VEC 值为 8.5 时畸变最小(遵循抛物线变化),而其他金属的变形随着 VEC 值的增大和 k_c/k_a 因子的减小而 增大。M₂SiC 的主要特征是在 (1010) 剪切面具有强烈的各向异性。除 W₂SiC 外,沿该方向的可压缩性比沿锥面 方向的可压缩性高。

关键词: 三元碳化物; 从头计算法; 晶体结构; 电子结构

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