Theoretical Prediction of Structural, Elastic and Electronic Properties of M_5Si_3 (M=Ti, Zr) Compounds

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Abstract Structural, elastic, electronic and mechanical properties of the M_5Si_3 (M=Ti, Zr) compounds with (Mn_5Si_3) 16H crystal structure have been studied with respect to pressure. Our computational method is based on a pseudo-potential plane-wave (PP-PW) method. The exchange correlation has been treated using the generalized gradient approximation (GGA) in order to work out the densities of states. Ground-state quantities, such as lattice parameter and bulk modulus, have been evaluated, as well as elastic constants and their pressure derivative. Elastic constants and their pressure dependence have been calculated. Also, bulk and shear moduli, Young's modulus and Poisson's ratio for ideal polycrystalline phases have been derived.

Keywords Ab-initio calculations · Band structures · Mechanical properties

1 Introduction

An intermetallic compound is a phase which crystallizes with a structure other than those of its components. Intermetallic compounds have been attractive candidates for high-temperature structural materials because of their desirable

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intrinsic properties. The great interest in transition metal silicide is related to their ultra-high temperature materials, good stability, high melting points, low densities, high oxidation resistance and excellent mechanical strength at elevated temperature [1–3].

The melting temperature of Ti (Zr) is 1841 K (2128 K), that of silicon is 1687 K, while the temperature of the compound Ti_5Si_3 (Zr_5Si_3) is higher which is of 2390 K (2520 K).

Ti_5Si_3 which contains 26.03 wt% (37.5 at.%) Si and crystallizes in a hexagonal $D8_8$ structure has the most suitable combination of high melting temperature (about 2130 °C), low density (4.32 g/cm^3), high strength and good oxidation resistance at high temperature [4]. Zr_5Si_3 and Ti_5Si_3 have the same crystal structure. Hong et al. [5] reported the first principles study for some physical properties of $D8_8$-Ti_5Si_3 phase, showing that the addition of low-rate metalloid atoms can stabilize this phase.

Williams et al. [6] analyzed the incorporation of carbon, nitrogen or oxygen atoms into the lattice of Ti_5Si_3 and concluded that the bonding changes that occurred on addition of carbon, nitrogen or oxygen acted to decrease the anisotropic thermal expansion measured.

On the other side, Celis et al. [7] studied the potentiality of the Mn_5Si_3 16H crystal structure for high-temperature structural applications choosing the Zr–Si system, produced the Zr_5Si_3, and concluded that this compound is a good candidate for high-temperature structural applications. However, and to the best of our knowledge, some properties such as elastic constants at high pressures are not well understood by experiments. This problem can be solved by ab-initio theoretical calculations.

As a potential high-pressure compound, our primary aim was therefore to present the results of a theoretical investigation of the structural, elastic, and electronic properties of Ti_5Si_3 and Zr_5Si_3.

However [8], Ti_5Si_3 and Zr_5Si_3 present a hexagonal crystal structure Mn_5Si_3-type with a space group $P6_3/mcm$, N° 193;

Pearson symbol is *hP16* as shown in Fig. 1. M_5Si_3 (M=Ti, Zr) contains two formula units per unit cell and has two species of atom that occupy three types of positions M_1 atoms are at x 0 1/4 and M_2 at 1/3 2/3 0, while Si atoms are at x' 0 1/4, where $x=0.2509$ and $x'=0.6072$ [6].

The paper is organized as follows. The computational method is described in Sect. 2. In Sect. 3, the results are presented and compared with available experimental and theoretical data. Conclusion is given in Sect. 4.

2 Computational Method

All the electronic structure calculations are implemented with the Cambridge Serial Total Energy Package (CASTEP) simulation programme [9] that solves the Schrödinger-like Kohn–Sham equations according to the formalism of the density functional theory (DFT) [10, 11]. We used the generalized gradient approximation (GGA), and a Perdew–Burke–Ernzerhof (PBE) scheme [12], for handling the electronic exchange correlation potential energy. Also, the pseudo-potentials were constructed using the ab-initio normconserving scheme to describe the valence electron interaction with the atomic core, in which the Ti ($3d^2 4s^2$), Zr ($4d^2$ $5s^2$) and Si($3p^2$ $3s^2$) orbitals are treated as valence electrons. The cutoff energy used for all structures is 450 eV. Brillouin zone (BZ) sampling is carried out using a 6× 6×5 Monkhorst–Pack mesh set [13]. Atomic positions are optimized within a density mixing scheme, based on a conjugate gradient (CG) method for eigenvalues minimization.

Actually, the equilibrium lattice parameter is determined from a structural optimization, using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique. This technique provides a fast way of finding the lowest energy structure, with the following thresholds for converged structures: (i) the potential energy difference between atomic iterations was less than 2×10^{-5}/atom, (ii) the forces on each atom were typically less than 0.005 eV/Å, (iii) atom displacement during geometry optimization less than 0.002 Å and (iv) maximum stress within 0.1 GPa.

3 Results and Discussion

3.1 Structural Properties

The unit cell is shown in Fig. 1. The considered M_5Si_3 (M=Ti, Zr) adopts the hexagonal structure with space group $P6_3/mcm$ (N°. 193). The results for lattice parameters a and c are reported in Table 1 and compared with experimental and previous theoretical calculations. Our calculated value for lattice parameters of M_5Si_3 (M=Ti, Zr) compounds are in excellent agreement with the experimental and previous theoretical data (Table 2).
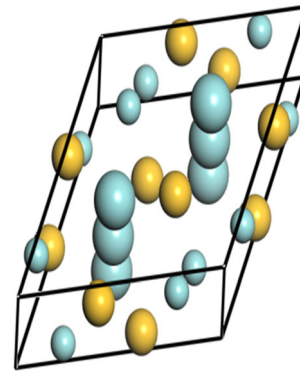

Fig. 1 Schematic representation of M_5Si_3 silicides with D8$_8$ structure

We are now interested in the pressure effect. We calculated the unit cell volume at values from 0 to 40 GPa of an applied hydrostatic pressure in order to construct an equation of state (EOS). The EOS was fitted to a third-order Birch–Murnaghan equation, as follows:

$$P = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \left[1 + \frac{3}{4} \left(4 - B' \right) \left\{ \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right\} \right], (1)$$

with V_0 corresponding to the value determined from the zero pressure data. We obtained the bulk modulus $B_0 = B_{EOS}$ and its pressure derivative B' at zero pressure ($B_0 = 139.65$ GPa, $B' = 3.88$) that is in good agreement with the values obtained via the elastic constants ($B = 138.71$).

The two ratios a/a_0 and c/c_0 of the lattice parameters have the same dependence on the pressure, which can be explained by the changes in bond lengths of Ti_5Si_3 and Zr_5Si_3, which have the same sensitivity to the pressure Fig. 2.

3.2 Elastic Constants

The calculated independent elastic constants C_{ij} for the two phases of M_5Si_3 (M=Ti, Zr) compounds are listed in Table 1. One condition for mechanical stability of a structure is that its strain energy must be positive against any homogeneous elastic deformation.

For a hexagonal crystal, let us recall that the generalized elastic stability criteria [17] are as follows:

$$C_{11} > 0, C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0, C_{11} - C_{12}$$

$$> 0, C_{11} + C_{33} + C_{12} > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2$$

$$> 0. \qquad (2)$$

The fact that our calculated elastic constants of the two considered phases satisfy all the above criteria indicates that these two considered phases of M_5Si_3 (M=Ti, Zr) (Fig. 3) are mechanically stable up to 40 GPa.

The C_{11} and C_{33} elastic constants, which correspond to the resistance to linear compression along the x and z

Table 1 Calculated lattice parameters (a and c, in Å, and V_0, in Å^3) of one unit formula; bulk modulus $^*B_0$ for a single crystal and its pressure derivative B'; elastic constants; shear modulus; Young's modulus; B/G ratio; longitudinal, transverse and average sound velocities in (m/s) and Debye temperature (Θ in Kelvin) calculated from the mean sound velocities for Ti$_5$Si$_3$ and Zr$_5$Si$_3$ in comparison with reported experimental and theoretical data

Property	Ti$_5$Si$_3$			Zr$_5$Si$_3$		
	Present	Expt.	Others	Present	Expt.	Others
a	7.4683	7.450 [6]		7.9962	7.886	7.893 [14]
c	5.1323	5.152 [6]		5.5673	5.558	5.504 [14]
V_0	248			308	152 [7]	
$^*B_0$	139.65			129.55		
$^*B'$	3.888			3.691		
C_{11}	293.20			263.56		
C_{33}	274.09			242.01		
C_{44}	96.07			78.07		
C_{12}	103.55			91.58		
C_{13}	48.83			52.83		
C_{66}	94.82			86		
$^{**}B_0$	138.71			128.00		133 [14]
$^{**}B'$	–			–		
G_v	101.34			86.55		
G_R	99.98			85.42		
G	100.66			85.98		88.5 [14]
E	251.75			216.49		217 [14]
B/G	1.378			1.488		
V_l	10,777			8677		
V_T	7618			6098		
V_M	8261			6618		
Θ_D	910			804		

crystallographic axes, are significantly larger than other elastic constants, resulting in a pronounced elastic anisotropy in our compounds.

However, C_{11} elastic constant always remains much larger than C_{33}, indicating that c-axis is more compressible than a-axis. In addition, the bulk and shear moduli (B and G) are two important mechanical quantities for technological and engineering applications. The latter (G), which is related to bond bending, depends on the nature of the bond and decreases according to the iconicity. To evaluate the elastic anisotropy of these compounds, we used the shear anisotropic factor which provides a measure of the degree of anisotropy in the connection between the carbon atoms in different planes. For M$_5$Si$_3$ (M=Ti, Zr) with the hexagonal structure, shear anisotropy factor $A(C_{ij})$, defined as $A=4C_{44}/(C_{11}+C_{33}-2C_{13})$ for the {100} planes of shear between the <011> and <010> directions [18]. For crystals with isotropic elastic properties $A=1$, while values smaller or greater than unity measure the degree of elastic anisotropy, as well as the ratio between linear compressibility coefficients for hexagonal crystals, i.e. $k_c/k_a=(C_{11}+C_{12}-2C_{13})/(C_{33}-C_{13})$ [19]. The computed shear anisotropic factors are listed in Table 3.

Table 2 Calculated atomic coordinates of M$_5$Si$_3$ (M=Ti, Zr) in comparison with reported data

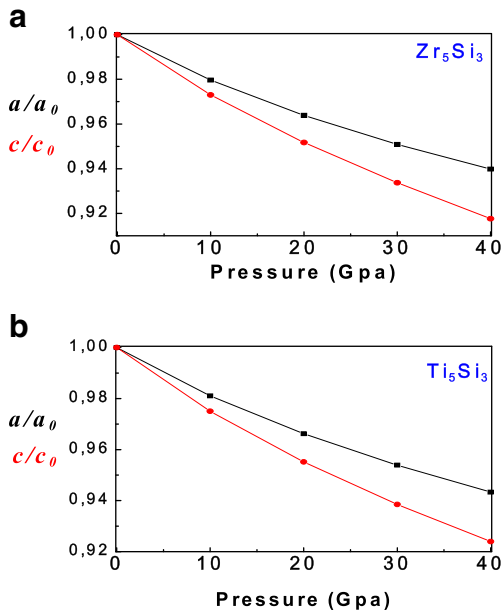| Atom	Site	Ti$_5$Si$_3$			Zr$_5$Si$_3$		
		x/a	y/b	z/c	x/a	y/b	z/c
M1	4d	1/3	2/3	0	1/3	2/3	0
					1/3 [15]	2/3 [15]	0 [15]
M2	6g	0.25	0	1/4	0.25	0	1/4
		0.240 [16]	0 [16]	1/4 [16]	0.254 [15]	0 [15]	1/4 [15]
		0.2473 [5]	0 [5]	1/4 [5]			
Si	6g	0.6080	0	1/4	0.6104	0	1/4
		0.615 [16]	0 [16]	1/4 [16]	0.6106 [15]	0 [15]	1/4 [15]
		0.6063 [5]	0 [5]	1/4 [5]			

Fig. 2 The two ratios a/a_0 and c/c_0 of the lattice parameters versus pressures for M_5Si_3

The polycrystalline Poisson's ratio (ν) Young's modulus (E) and Lamè constants (λ) are often used for polycrystalline materials when investigating their hardness. These quantities are calculated from the following formula:

Fig. 3 Elastic constants under pressures of M_5Si_3 (M=Ti, Zr)

Table 3 The ratio between linear compressibility coefficients, k_c/k_a, of hexagonal M_5Si_3 (M=Ti, Zr). The shear anisotropy factor A, $C_{11}–C_{12}$, B/G and Poisson's ratio ν were obtained. All constants are dimensionless

	k_c/k_a	A	$C_{11}–C_{12}$	B/G	ν
Ti_5Si_3	1.327	0.810	190	1.378	0.250
Zr_5Si_3	1.318	0.780	172	1.488	0.258
					0.227 [15]

$$E = \frac{9BG}{3B+G}, \quad \nu = \frac{3B-E}{6B}, \quad \lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}. \tag{3}$$

Pugh [20] proposed the B/G ratio to represent a measure of a "machinable behaviour". A high B/G value is then associated with ductility and a low value with brittleness. The critical value which separates ductile and brittle behaviours is at about 1.75. For instance, diamond has a B/G of 0.80 [21], while aluminium, cobalt, rhodium and iridium present B/G ratios of 2.74, 2.43, 1.77, and 1.74, respectively [20].

In Table 3, we have calculated the B/G Pugh ratio for M_5Si_3 (M=Ti, Zr) compounds under study. It can be seen that our calculations show that M_5Si_3 (M=Ti, Zr) compounds are of brittle character.

Besides B/G, it is well known that $C_{11}–C_{12}$ is also very significant characteristic for mechanical properties of materials [22].

Pointing out that Zr_5Si_3 has lower values of both $C_{11}–C_{12}$ (172 GPa) and Young's modulus (E=216 GPa) than Ti_5Si_3 ($C_{11}–C_{12}$=190 GPa and Young's modulus E=251 GPa), we may conclude for a better plasticity as far as Zr_5Si_3 is concerned. On the contrary, Ti_5Si_3 most probably presents the much poorest plasticity. To be complete, the five single-crystal elastic constants of Ti_5Si_3 and Zr_5Si_3 are listed in Table 3.

The Debye temperature may be estimated from the average sound velocity V_m [23].

$$\Theta = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{\frac{1}{3}} V_m, \tag{4}$$

where h is Planck's constants, k is Boltzman's constant, N_A is Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, ρ is the density and V_m is obtained from

$$V_m = \left[\frac{1}{3}\left(\frac{2}{V_s^3} + \frac{1}{V_l^3}\right)\right]^{-\frac{1}{3}}, \tag{5}$$

where V_s and V_l are the shear and longitudinal sound velocities, respectively. The arithmetic average of the Voigt and the Reuss bounds is called the Voigt–Reuss–Hill (VRH) average and is commonly used to estimate elastic moduli of
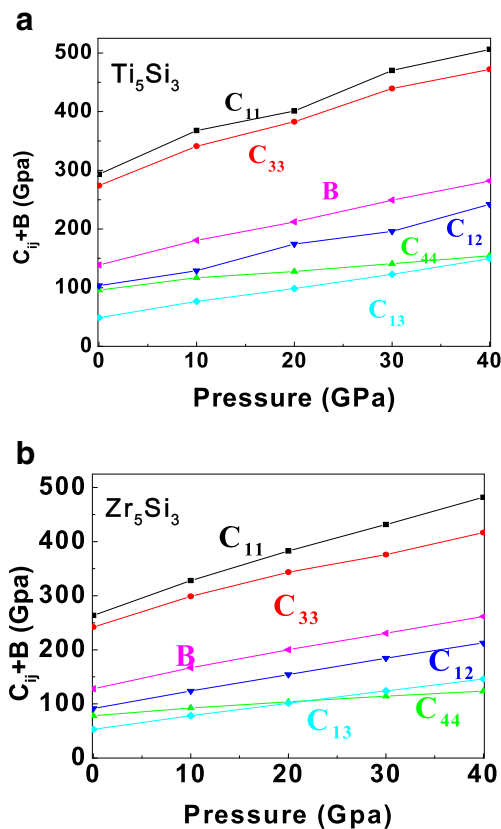
polycrystals. The polycrystalline moduli are the arithmetic of the values of the Voigt and Reuss moduli [24]:

$$G_H = \frac{1}{2}(G_R + G_V), \quad B_H = \frac{1}{2}(B_R + B_V). \tag{6}$$

Therefore, the probable values of the average shear and longitudinal sound velocities can be calculated from Navier's equation [14]:

$$V_S = \sqrt{\frac{G_H}{\rho}}, \quad V_l = \sqrt{\frac{\left(B_H + \frac{4}{3}G_H\right)}{\rho}}. \tag{7}$$

The longitudinal, transverse and average sound velocities and Debye temperature of M_5Si_3 (M=Ti, Zr) have been calculated and listed in Table 1. The obtained values of the polycrystalline Debye temperature calculated with Eq. (4) is 909 K and 804 K for Ti_5Si_3 and Zr_5Si_3, respectively, at ambient pressure. The pressure dependence of the Θ is shown in Fig. 4. Θ represents the temperature at which nearly all modes of vibrations in a solid are excited; this increase of Θ implies an increase in the rigidity of these compounds with the pressure.

3.3 Electronic Structures

The band structures of M_5Si_3 (M=Ti, Zr) along the various symmetry lines within the GGA scheme are given in Fig. 5. It can be seen that all these materials are metallic.

The electronic DOS of M_5Si_3 (M=Ti, Zr) compounds are shown in Fig. 6. The upper curve presents the total density of states per formula unit, and the lower curves give the contribution from Ti, Zr and Si atoms to the total DOS. We observe that there are four distinct structures. The states which are approximately located between −10 and −6 eV below the Fermi level originate from the bonding of Si-s and Ti(Zr)-d states with a small Ti(Zr)-p contribution.

Between −6 eV and the top of the valence bands reflects the bonding of Si-p and Ti(Zr)-d states. The two total density of states (TDOS) have some similarities; however in Fig. 6, and
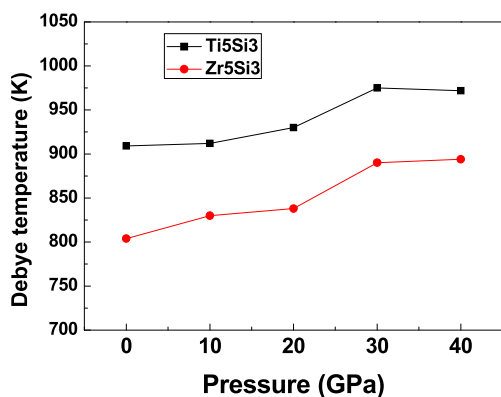
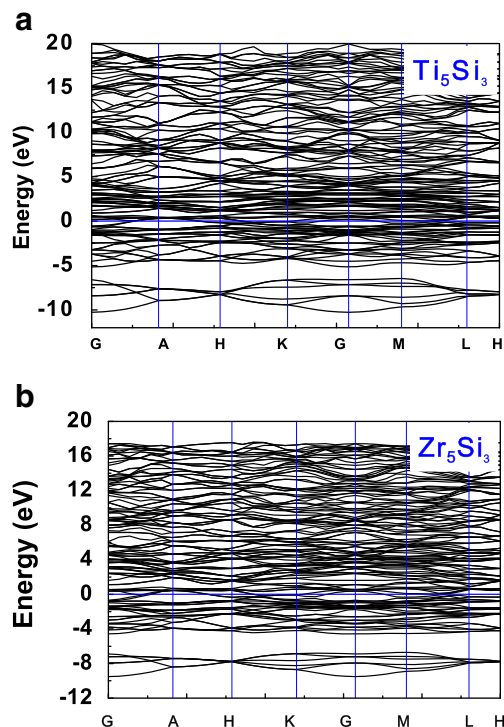**Fig. 4** Debye temperature under pressures of M_5Si_3 (M=Ti, Zr)

Fig. 5 M_5Si_3 band structure along high-symmetry directions in reciprocal space

in Zr_5Si_3 compound, the TDOS at the Fermi level has the smallest $n(E_f)$ with 8.6 states/eV/atom; the Ti_5Si_3 phase has
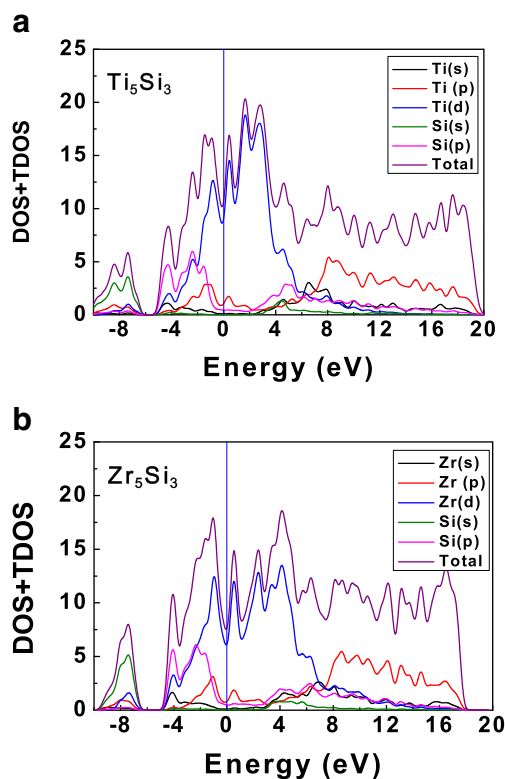
Fig. 6 Total and partial state densities of s-Si, p-Si, s-M, p-M and d-M in M_5Si_3 (M=Ti, Zr)

the largest $n(E_f)$ with 12.5 states/eV/atom. The electronic states between 0 and 6 eV are dominated mainly by Ti(Zr)-d states. In the rest of the conduction band, the electronic states are dominated by Ti(Zr)-p with the mixed character of Ti(Zr)-d, Ti(Zr)-s, Si-s and a small contribution of Si-p character.

4 Conclusion

Structural properties, elastic and electronic structure of M_5Si_3 (M=Ti, Zr) compounds are studied by DFT calculations. The calculated lattice constants are found to be in very good agreement with experimental results. As a result, the two ratios a/a_0 and c/c_0 of the lattice parameters have the same dependence on the pressure, which can be explained by the changes in bond lengths of Ti_5Si_3 and Zr_5Si_3 which have the same sensitivity to the pressure. Elastic and mechanical properties are obtained, which show that our compounds are mechanically stable. The aggregate elastic modulus B, G, E, Debye temperature Θ and elastic anisotropies were evaluated. Unfortunately, there is no experimental data for comparison. The results will stimulate further experimental and theoretical work in the future.

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