Density-functional-theory predictions of mechanical behaviour and thermal properties as well as experimental hardness of the Ga-bilayer $\text{Mo}_2\text{Ga}_2\text{C}$

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Abstract: $\text{Mo}_2\text{Ga}_2\text{C}$ is a new MAX phase with a stacking Ga-bilayer as well as possible unusual properties. To understand this unique MAX phase structure and promote possible future applications, the structure, chemical bonding, and mechanical and thermodynamic properties of $\text{Mo}_2\text{Ga}_2\text{C}$ were investigated by first-principles. Using the “bond stiffness” model, the strongest covalent bonding (1162 GPa) was formed between Mo and C atoms in $\text{Mo}_2\text{Ga}_2\text{C}$, while the weakest Ga–Ga (389 GPa) bonding was formed between two Ga-atomic layers, different from other typical MAX phases. The ratio of the bond stiffness of the weakest bond to the strongest bond (0.33) was lower than 1/2, indicating the high damage tolerance and fracture toughness of $\text{Mo}_2\text{Ga}_2\text{C}$, which was confirmed by indentation without any cracks. The high-temperature heat capacity and thermal expansion of $\text{Mo}_2\text{Ga}_2\text{C}$ were calculated in the framework of quasi-harmonic approximation from 0 to 1300 K. Because of the metal-like electronic structure, the electronic excitation contribution became more significant with increasing temperature above 300 K.

Keywords: MAX phase; first-principles; damage tolerance; heat capacity; thermal expansion

1 Introduction

Over the past two decades, a class of ternary transition metal carbides or nitrides known as $\text{M}_n\text{AX}_{n+1}$ phases (where M is an early transition metal, A is an A-group element, X is C and/or N, and $n = 1-3$), are formed by inserting A-group atoms into the corresponding binary carbides or nitrides, and have attracted growing

attention due to their unique combination of metallic and ceramic properties [1–3]. The recent work indicates that the MAX phase borides were also observed in experiments [4–7]. Having this layered structure, the MAX phases exhibit a combination of the beneficial properties of both ceramic and metallic compounds, e.g., low density [8], low thermal expansion coefficient, high modulus, high strength [9], high temperature oxidation resistance [10], good thermal conductivity [11], electrical conductivity, easy processing [12], and plastic and thermal impact resistance [11].

The M_2AX (211) phases including solid solutions

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with $M = \text{Ti, V, Cr, Nb, Ta, Zr, Hf, Mo, ...}$, $A = \text{Al, S, Sn, As, In, Ga, ...}$, and $X = \text{N, C, B}$, have been studied extensively both experimentally and theoretically [13–22]. Among them, Mo_2GaC [22] is an important MAX phase showing superconducting characteristics with $T_C \approx 4.0$ K. Mo_2GaC is one of few having Mo as the sole occupant of the M-site [23] and was predicted to have high bulk and low shear moduli [24]. Recent studies on the MAB phase have shown that MoAlB with Al-bilayer had better damage tolerance and antioxidant properties [4–7]. Interestingly, the discovered $\text{Mo}_2\text{Ga}_2\text{C}$ in 2015 [25] also has a Ga-bilayer, which provides us a chance to examine the effect of the A-group bilayer on the properties of the MAX phases.

$\text{Mo}_2\text{Ga}_2\text{C}$ has been mainly used to produce MXene materials since it was discovered by Meshkian *et al.* [26]. At present, the research on $\text{Mo}_2\text{Ga}_2\text{C}$ mainly focuses on its mechanical properties, Hadi [27] calculated elastic properties including Debye temperature and theoretical Vickers hardness, and Wang *et al.* [28] predicted the stability of another plausible metastable structure with close-packed Ga-layers of $\text{Mo}_2\text{Ga}_2\text{C}$ under a pressure higher than 24.3 GPa. However, there was little research on $\text{Mo}_2\text{Ga}_2\text{C}$ in the field of high temperatures higher than 500 °C. He *et al.* [29] found that $\text{Mo}_2\text{Ga}_2\text{C}$ would decompose when the temperature was higher than 700 °C, and Jin *et al.* [30] found that $\text{Mo}_2\text{Ga}_2\text{C}$'s thermal conductivity and electrical resistivity were lower than those of most MAX phases probably due to the extra Ga-layer.

For structural applications, the mechanical properties, especially the damage tolerance and fracture toughness are critical [31]. The density-functional-theory (DFT) was employed in 2002 by Wang and Zhou [32] for the compressibility of Ti_3SiC_2 , which was the earliest investigated MAX compound. Theoretical calculations on the pressure dependency of the MAX phases generally agreed with the experimental observations, and clarified some important problems [33,34]. As is well known, the crystal structure has an important influence on the macroscopic mechanical properties of materials. For example, it is generally believed that the high damage tolerance and high fracture toughness in MAX phase come from its layered structure and weak chemical bonding [35,36]. Bai *et al.* [35,37] proposed a theoretical model called “bond stiffness” to quantitatively study the strength of chemical bonds. The brittle fracture behaviour of MAX phase compound Ti_2SC is similar with traditional ceramics, where the main grain propagation

occurs at the diagonal of Vickers indentation [38]. The calculation results of bond stiffness show that the weakest Ti–S bond is still weaker than Ti–C bond, but the stiffness ratio of the weakest and strengthening bond is 0.78. For most of the MAX phases except Ti_2SC , the ratio is between 1/3 and 1/2 [39], where weak bonding among the sublayers of grains can cause typical delamination and crack deflection to avoid catastrophic crack propagating when a crack encounters this weak bonding, with consuming a lot of external energy. Notably, this “weak bonding” among M and A atoms of the MAX phases is relative to that among other atoms. Therefore, the ratio can be used as a theoretical judgment for the macromechanical behaviour of ternary layered ceramics. This finding shows that the MAX phases have extraordinary mechanical properties, which require that the M–A bond is not only weaker than the M–C bond, but is also “weak enough”. Moreover, as a candidate for high-temperature materials, it is important to understand the thermal properties, including their heat capacities and thermal expansion coefficients among others [40]. In addition to experiments, the recent progress in computational methods reminds that first-principles can be used to accurately predict the mechanical behaviour by the “bond stiffness” theoretical model [35,37] and thermal properties by quasi harmonic approximation (QHA) [41], with some significant advantages, such as low cost and high efficiency [42].

The present work is to investigate the mechanical and thermal properties as well as phase stability of $\text{Mo}_2\text{Ga}_2\text{C}$ with the Ga-bilayer by first-principles, which would provide a theoretical guidance for further understanding the influence of crystal structure on macro behaviour of MAX phases, and inspire future experimental research.

2 Theoretical

2.1 Density-functional-theory settings

All first-principles calculations were performed within the framework of density-functional-theory (DFT) as implemented within the Vienna *Ab initio* Simulation Package (VASP) [43]. A selection of exchange-correlation functional was used, including those within generalized gradient approximation (GGA) [44], comprising PBE, RPBE [45], and PW91 [46], and a local density approximation (LDA) functional [47]. The projector-augmented

wave (PAW) method was used, with $4p^6 4d^5 5s^1$, $4s^2 4p^1$, and $2s^2 2p^2$ electrons included as valence states for Mo, Ga, and C, respectively. The cut-off energy of 350 eV and k -points sampled using Monkhorst-pack meshes of $12 \times 12 \times 2$ were used to ensure total energy convergence to within $\pm 1.5 \times 10^{-4}$ eV/atom and a $36 \times 36 \times 6$ special k -point was used when calculating the electronic density of states. Tolerances were set to ensure the convergence of the total energy within $\pm 10^{-7}$ eV/atom, and the atomic forces were less than 10^{-3} eV/Å. The relaxation of atomic geometries was achieved using the conjugate-gradient method.

2.2 Model of bond stiffness

In the previous work on the MAX phases, Bai *et al.* [35,37] proposed a theoretical model to quantitatively calculate the bond stiffness from the DFT-simulated results for characterizing the bond strength. Based on the calculated bond stiffness, a criterion was further established to assess the damage tolerance and fracture toughness. High damage tolerance and fracture toughness without indentation cracks are observed when the ratio is lower than 1/2, but above this value, cracks are present in the Vickers indentation [35]. This model assumed that a second-order polynomial relation exists between the applied hydrostatic pressure (P) and the deformation of chemical bonds in a solid. In practice, the interatomic distance (bond length, d) as a function of P can be estimated from the lattice parameters and internal coordinates. Because the bond strength varies with increasing d , the relative bond length d/d_0 (d_0 is the bond length at 0 GPa) as a function of P should be then fitted by a quadratic curve, whose slope is defined as $1/k$, where k is the bond stiffness [37]:

$$d/d_0 = C_0 + C_1 P + C_2 P^2 \quad (1)$$

$$k = \left| \frac{d(d/d_0)}{dP} \right|^{-1} = |C_1 + 2C_2 P|^{-1} \quad (2)$$

where C_i ($i = 0, 1, 2$) are the quadratic fitting coefficients.

2.3 Heat capacity and thermal expansion

The critical issue in estimating thermodynamic properties including heat capacity and thermal expansion is how to calculate the Helmholtz free-energy $F(V, T)$ accurately as a function of V and T , where V and T represent volume and temperature, respectively. From this calculated $F(V, T)$ for the relevant range of V and T , the

temperature dependence of $V_{eq}(T)$ and the heat capacity $C_p(T)$ can be

$$\left. \frac{\partial F(V, T)}{\partial V} \right|_{V_{eq}(T)} = 0, \quad C_p = -T \left. \frac{\partial^2 F(V, T)}{\partial T^2} \right|_{V_{eq}(T)} \quad (3)$$

In the present work, $F(V, T)$ is calculated from first-principles within the framework of DFT and QHA [41], where phonon frequencies are volume-dependent, but at a fixed volume they are temperature-independent. In practice, $F(V, T)$ is expressed as the sum of the following:

$$F(V, T) = E_{tot}(V) + F_{el}(V, T) + F_{qha}(V, T) \quad (4)$$

where $E_{tot}(V)$ is the total energy at $T = 0$ K, $F_{el}(V, T)$ is the finite temperature electronic free energy as a result of electronic excitation, and $F_{qha}(V, T)$ is the free energy due to atomic vibrations (phonon), computed within QHA with the help of PHONOPY package [48]. The volume at each temperature must be calculated by minimization of the free energy at constant temperature. This removes the explicit temperature dependence in the frequencies: $\omega_i = \omega_i(V)$. The phonon contribution to free energy is given by

$$F_{qha}(V, T) = \sum_i \left[\frac{1}{2} \hbar \omega_i + k_B T \ln \left(1 - e^{-\frac{\hbar \omega_i}{k_B T}} \right) \right] \quad (5)$$

where $\hbar$ is the reduced Planck constant and k_B is the Boltzmann constant. Furthermore, $C_p(T)$ can be estimated from the calculated $F(V, T)$ using the standard thermodynamic relation. The electronic free energy $F_{el}(V, T)$ is usually divided into the energy $E_{el}(V, T)$ due to electronic excitations and a remaining part as [49]

$$F_{el}(V, T) = E_{el}(V, T) - TS_{el}(V, T) \quad (6)$$

where $S_{el}(V, T)$ is the electronic entropy, given by ideal mixing as

$$S_{el}(V, T) = -gk_B \sum_i [f_i(V, T) \ln f_i(V, T) + (1 - f_i(V, T)) \ln(1 - f_i(V, T))] \quad (7)$$

where g is 1 or 2 for collinear spin polarized and non-spin polarized systems, and $f_i(V, T)$ is the sum which runs over all electronic states with Fermi–Dirac occupation weights:

$$f_i(V, T) = \left[1 + \exp \left(\frac{\varepsilon_i(V) - \mu(V)}{T} \right) \right]^{-1} \quad (8)$$

where $\varepsilon_i(V)$ is obtained by integrating the density of states and $E_{\text{el}}(V, T)$ is given by

$$E_{\text{el}}(V, T) = g \sum_i f_i(V, T) \varepsilon_i(V) \quad (9)$$

3 Experimental

The fabrication details of $\text{Mo}_2\text{Ga}_2\text{C}$ were described in Refs. [29,30]. In brief, Mo_2C powders (99.5 wt%, 325 mesh; Sigma Aldrich Co., USA) and Ga (99.99 wt%; Beijing Xingrongyuan Co., China) were mixed with the molar ratio of 1:5, vacuum sealed in a glass tube, and annealed at 650 °C for 60 h. Thereafter, the samples were immersed in HCl for 48 h to remove extra Ga, followed by centrifugal washing and drying in vacuum.

The bulk $\text{Mo}_2\text{Ga}_2\text{C}$ samples were prepared by hot pressing at 750 °C for 8 h, and X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images were shown in Ref. [50]. Nano-indentation measurements were carried out using a Hysitron TI Premier instrumented quasi-static nano-mechanical tester with a 100 nm diamond Berkovich tip. Each indentation test consisted of a 5 s loading cycle to a peak load of 5 mN, followed by a 2 s-long hold segment, and then a 10 s unloading cycle. The maximum load was 1000 mN. The nano-indentation of bulk $\text{Mo}_2\text{Ga}_2\text{C}$ was tested on the polished surface of the sintered sample.

4 Results and discussion

4.1 Crystal structures

The previous Refs. [5,36] indicate that the exchange-correlation functional usually has a significant influence on the accuracy of DFT-calculated results. In the present work, four exchange-correlation functionals (LDA, GGA-PBE, GGA-RPBE, and GGA-PW91) were used for the equilibrium lattice constant of $\text{Mo}_2\text{Ga}_2\text{C}$ (Table 1). Experimental (Exp) values of lattice constant of $\text{Mo}_2\text{Ga}_2\text{C}$ [25] also were listed in Table 1. The LDA results are over-bound as often the case with this approximation, and are the least accurate of the considered functional [51]. In contrast, GGA functional often overestimates the lattice constants with all of the considered GGA functional providing high accuracy, with a relative error of 2.21%–4.07% in the present work. Overall, PBE exhibits the best performance, especially for the volume of the unit cell, and therefore is used in all subsequent calculations.

Crystal structures of $\text{Mo}_2\text{Ga}_2\text{C}$ are considered (Fig. 1), where the atomic coordinates are Mo_1 (1/3, 2/3, z_{Mo_1}), Ga (1/3, 2/3, z_{Ga}), and C (0, 0, z_{C}) for $\text{Mo}_2\text{Ga}_2\text{C}$, and the space group are $P6_3/mmc$. The previous work indicates its intrinsic and thermodynamic stability by lattice dynamics theory and linear optimization method based on the first-principles, respectively, by Lai *et al.* [52]. As shown in Fig. 1, Mo–C layer is separated by single Ga-layer along the c -axis direction in Mo_2GaC , and $\text{Mo}_2\text{Ga}_2\text{C}$ is formed by the insertion of carbide into

Table 1 Lattice parameters and equilibrium properties of $\text{Mo}_2\text{Ga}_2\text{C}$ and Mo_2GaC

		$\text{Mo}_2\text{Ga}_2\text{C}$				Exp *	Mo_2GaC	MoC
		LDA	GGA-PBE	GGA-RPBE	GGA-PW91		GGA-PBE	GGA-PBE
Lattice parameter	a (Å)	3.000	3.066	3.086	3.073	3.03396	3.080	3.083
	c (Å)	17.95	18.10	18.19	18.08	18.0814	13.12	15.250
	V (Å ³)	139.90	147.33	150.00	147.91	144.1393	107.87	125.58
Internal coordinate	z_{Mo}	0.0664	0.0647	0.0642	0.0647	—	0.088	—
	z_{Ga}	0.6820	0.6813	0.6810	0.6813	—	0.75	—
	z_{C}	0.0	0.0	0.0	0.0	—	0.0	—
Density (g·cm ⁻³)		—	7.74	—	—	—	8.42	—
Energy (eV·atom ⁻¹)		—	-7.45	—	—	—	-8.52	—
Densities of states at Fermi energy (states·eV ⁻¹ ·unit cell ⁻¹)		—	3.753	—	—	—	4.863	—
Bulk modulus (GPa)		—	141.46	—	—	—	244.29	—
Pressure derivative		—	4.73	—	—	—	4.19	—

* Exp means the data from Ref. [25].

Fig. 1 Crystal structures of (a) $\text{Mo}_2\text{Ga}_2\text{C}$, (b) Mo_2GaC , and (c) MoC . The purple, green, and brown spheres correspond to the Mo, Ga, and C atoms, respectively.

double Ga-layers along the c -axis. $\text{Mo}_2\text{Ga}_2\text{C}$ can also be described as a layered structure similar to the typical MAX phases: The Mo–C layer with strong binding force and the Mo–Ga layer with weak covalent

bond are staggered. Comparing Ga-bilayer $\text{Mo}_2\text{Ga}_2\text{C}$ and Ga-monolayer Mo_2GaC , the insertion of an additional Ga-layer has a negligible effect on the lattice constants a and b (3.066 and 3.085 Å), but the lattice constant c increases significantly from 13.12 to 18.10 Å.

The bond lengths between adjacent atoms (marked in Fig. 1) of $\text{Mo}_2\text{Ga}_2\text{C}$ are given in Table 2, including the corresponding data of Mo_2GaC and Mo_2AlC for comparison. The Mo_1 –C bond lengths in $\text{Mo}_2\text{Ga}_2\text{C}$ (2.1225 Å) and Mo_2GaC (2.1224 Å) show that the addition of a Ga-layer has little effect on the Mo–C layer. However, inserting extra Ga-layers results in slightly increasing Mo_1 –Ga bond length from 2.7545 to 2.7697 Å in $\text{Mo}_2\text{Ga}_2\text{C}$.

4.2 Electronic structure and bond stiffness

Total and partial densities of states of $\text{Mo}_2\text{Ga}_2\text{C}$ are shown in Fig. 2, including Mo_2GaC for comparison. In

Table 2 Bond length (d) and bond stiffness (k) in $\text{Mo}_2\text{Ga}_2\text{C}$, Mo_2GaC , MoC , and typical MAX phases

Phase		Mo_1 –C/B	Mo_2 –C/B	Mo_1 –Ga/Al	Ga–Ga/Al–Al	B–B	Al–B
$\text{Mo}_2\text{Ga}_2\text{C}$	d (Å)	2.1225	—	2.7545	2.4866	—	—
	k (GPa)	1162	—	571	389	—	—
Mo_2GaC	d (Å)	2.1224	—	2.7697	—	—	—
	k (GPa)	1188	—	563	—	—	—
MoC	d (Å)	2.1895	2.2526	—	—	—	—
	k (GPa)	1163	889	—	—	—	—
MoAlB [5]	d (Å)	2.3735	2.3541	2.7117	2.6669	1.8085	2.3209
	k (GPa)	764	1135	731	526	1205	717
Mo_2AlC [37]	d (Å)	2.1170	—	2.7903	—	—	—
	k (GPa)	1111	—	515	—	—	—
Ti_2AlC [37]	k (GPa)	741	680	366	—	—	—

Fig. 2 Total and partial densities of states of (a) $\text{Mo}_2\text{Ga}_2\text{C}$ and (b) Mo_2GaC .

Mo₂Ga₂C, there is a region of overlap between C-s and Mo-d states between −13 to −10 eV. With increasing energy range from −10 to −4 eV, the hybridization states of C-p and Mo-d electrons indicate a strong covalent bonding between C and Mo atoms, considering the wide energy range and high density of states. Between −3.5 and 0 eV, there is an overlapping region between Mo-d and Ga-p states, which means that weak chemical bonds exist between Mo and Ga atoms. Notably, the present electronic structure and chemical bonding of Ga-bilayer Mo₂Ga₂C are similar with Ga-monolayer Mo₂GaC and other typical MAX phases [53–56].

As stated above, the electronic structure by density of state can only provide some qualitative information about chemical bonding. The further quantitative characterization for bond strength should be conducted by using of the model of “bond stiffness” (Section 2.2). Table 2 lists the calculated bond stiffness of Mo₂Ga₂C at 0 GPa, also including Mo₂GaC and MoC for comparison. The Ga–Ga bond has the lowest stiffness (389 GPa) in Mo₂Ga₂C, instead of M–A bonds in Mo₂Ga₂C and other typical MAX phases [37]. It follows that the weakest bonding lies between two Ga atomic planes, which should contribute to the experimentally observed low-temperature decomposition at 700 °C by He *et al.* [29]. However, Mo–C bonds are still the strongest ones with the bond stiffness of 1162 GPa, similar with the typical MAX phases [37], which indicates that the addition of Ga-layer has a weak effect on the M–C slabs. This is attributed to the same structure of Mo–C layers between Mo₂Ga₂C and typical MAX phase Mo₂GaC. Also, it is not surprising that Mo₂Ga₂C has similar Mo–C and Mo–Ga bond stiffness (1162 and 571 GPa) with Mo₂GaC (1188 and

563 GPa). On the other hand, the Mo–Ga bond stiffness is similar between Mo₂Ga₂C (571 GPa) and Mo₂GaC (563 GPa). It can be concluded that the addition of a layer into Mo₂GaC lattice only results in the weakest Ga–Ga bond instead of Mo–Ga bond, which is also observed in the recent interest MAB phase MoAlB with Al-bilayer [5].

It is well established that weak M–A bond plays a key role in its unique mechanical properties of the MAX phases, such as high fracture toughness and damage tolerance, low hardness, microscale plastic deformation [31,57]. The previous work indicates that the ratio $k_{\min}/k_{\max}$ of the lowest bond stiffness to the highest bond stiffness determines the macroscopic mechanical properties of the ternary layered ceramics including MAX and MAB phases [5,35,36]. When $k_{\min}/k_{\max}$ is more than 1/2, this class of ceramics exhibits low damage tolerance and fracture properties of typical brittle ceramics with indentation cracks, such as Ti₂SC [58], (MC)_nAl₃C₂, and (MC)_nAl₄C₃ [59]. When the ratio is less than 1/2, these ceramics show high damage tolerance and high fracture toughness without indentation cracks, such as MoAlB and typical MAX phase ceramics [51]. The present $k_{\min}/k_{\max}$ (0.33) of Ga-bilayer Mo₂Ga₂C is lower than 0.43 of Al-bilayer MoAlB and 0.47 of Ga-monolayer Mo₂GaC, which indicates the high damage tolerance and fracture toughness of both Mo₂Ga₂C and Mo₂GaC. This prediction is well consistent with the present indentation on Mo₂Ga₂C under 1000 mN, indeed without cracks (Fig. 4). Furthermore, it shows that the model of “bond stiffness” is reliable.

4.3 Thermodynamic properties

The isobaric heat capacities C_p of Mo₂Ga₂C as well as

Fig. 3 Pressure dependence of (a) the normalized cell volume V/V_0 as well as normalized lattice parameters a/a_0 , b/b_0 , and c/c_0 of Mo₂Ga₂C and (b) normalized bond length d/d_0 in Mo₂Ga₂C.

Fig. 4 (a) Vickers hardness of $\text{Mo}_2\text{Ga}_2\text{C}$ vs. indentation depth where the hardness at the depth of 0.02 nm/s and (b) Vickers indentation conducted on $\text{Mo}_2\text{Ga}_2\text{C}$ with the load at 1000 mN.

Mo_2GaC and experimental values of MoC [60] variation with the temperature are illustrated in Fig. 5(a), with the effect of electronic excitation. A good agreement between calculated and experimental C_p of MoC indicates the high accuracy of the present prediction in the framework of QHA, including the electronic contribution. In the low-temperature range below 300 K, the electronic excitation has a negligible effect on C_p of $\text{Mo}_2\text{Ga}_2\text{C}$ as well as Mo_2GaC . In fact, electronic contributions in these systems seem to be much less than those resulting from lattice thermal expansion, and increase gradually with the increase of temperature. This is consistent with the electron density at the Fermi level shown in the electronic DOS plots (Fig. 2). Notably, the C_p of $\text{Mo}_2\text{Ga}_2\text{C}$ at 300 K is around $0.6\text{--}108 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Moreover, their capacities of $\text{Mo}_2\text{Ga}_2\text{C}$ from 300 to 1300 K can be expressed using Eq. (10):

$$C_{p,\text{Mo}_2\text{Ga}_2\text{C}}^{\text{PBE-qha}} = 115.97 + 1.59 \times 10^{-2}T - 1.14 \times 10^6 T^{-2} \quad (10)$$

Interestingly, the C_p of $\text{Mo}_2\text{Ga}_2\text{C}$ is 1.26–1.29 times of that of Mo_2GaC in the high-temperature range above 300 K, which is also observed in the previous studies that there is a certain relationship between the heat capacity of MAX phases and the corresponding binaries [1]:

$$C_p(\text{M}_{n+1}\text{AX}_n) = (n+1) \times C_p(\text{MX}) \quad (11)$$

In fact, the C_p of MAX phases is determined approximately by their constituent elements, which is applicable for the present $\text{Mo}_2\text{Ga}_2\text{C}$. However, due to the double Ga-layer, the C_p of $\text{Mo}_2\text{Ga}_2\text{C}$ is 2.3 times of that of MoC .

The thermal expansion of $\text{Mo}_2\text{Ga}_2\text{C}$ and Mo_2GaC in the temperature range of 300–1300 K is shown in

Fig. 5 (a) Heat capacity and (b) thermal expansion of $\text{Mo}_2\text{Ga}_2\text{C}$, while “Exp” means the data from Ref. [59].

Fig. 5(b). Notably, the average linear thermal expansion coefficient (TEC) with electronic excitations for $\text{Mo}_2\text{Ga}_2\text{C}$ from 300 to 1300 K is $24.6 \times 10^{-6} \text{ K}^{-1}$, where the electronic excitations act to decrease the thermal expansion as a function of temperature. As the temperature rises above 1300 K, the slope of thermal expansion increasing speed is slower, close to its high temperature limit. The thermal expansion of these two ternary carbides increases gradually due to the successively excitation of vibration modes.

In addition, in the whole temperature range, the coefficient of thermal expansion of $\text{Mo}_2\text{Ga}_2\text{C}$ is larger than that of Mo_2GaC , which is mainly due to the weaker Ga–Ga bond of the former and the downward shift of its phonon mode. To improve the prediction, and given the metal-like electronic structure, electronic excitations were included in addition to the standard phonon contribution. The average TECs of the MAX phases fall into the range of 5×10^{-6} – $15 \times 10^{-6} \text{ K}^{-1}$ [11], which means the present TEC of $\text{Mo}_2\text{Ga}_2\text{C}$ is higher than that of other MAX phases. In general, TECs are intimately related to the interatomic bond strengths. Compared with typical MAX phase Ti_2AlC , $\text{Mo}_2\text{Ga}_2\text{C}$ has a weaker Ga–Ga bond (Table 2), resulting in the higher TEC than that of Ti_2AlC ($8.8 \times 10^{-6} \text{ K}^{-1}$) [61]. This means the more serious deformation of $\text{Mo}_2\text{Ga}_2\text{C}$ at high temperatures.

The MAX phases have much potential for application as bond coat of the thermal barrier coatings (TBCs) due to high damage tolerance and oxidation resistance, but its TEC is much lower than that of the superalloys. The present finding that an additional A layer can increase the TEC of the MAX phases provides some insights to design new MAX compounds with proper TEC to satisfy the requirements of bond coat in TBCs.

5 Conclusions

1) DFT predicts the lattice parameters of $\text{Mo}_2\text{Ga}_2\text{C}$ with high accuracy, with the difference between experimental and theoretical values peaking at 4.07% for the LDA and 2.21% for the PBE. The structure of $\text{Mo}_2\text{Ga}_2\text{C}$ could be described as a layered structure similar to MAX phase: The strong bonding Mo–C atomic layer and the Mo–Ga layer with weak Ga–Ga bonds were staggered. The structure of Ga atoms on the same side had lower energy. Inserting Ga-layers

only increased the direction of *c*-axis, but did not change the bond length significantly.

2) The bond in $\text{Mo}_2\text{Ga}_2\text{C}$ with the lowest rigidity (Ga–Ga bonds, 389 GPa) is 0.36 times of the bond with the strongest rigidity (Mo–C bonds, 1002 GPa). The present $k_{\min}/k_{\max}$ (0.33) of Ga-bilayer $\text{Mo}_2\text{Ga}_2\text{C}$ is lower than 0.43 of Al-bilayer MoAlB and 0.47 of Ga-monolayer Mo_2GaC , which indicates the high damage tolerance and fracture toughness of both $\text{Mo}_2\text{Ga}_2\text{C}$ and $\text{Mo}_2\text{Ga}_2\text{C}$. This prediction has been confirmed by the present indentation of $\text{Mo}_2\text{Ga}_2\text{C}$.

3) By including contributions from phonons and electrons, the heat capacity and thermal expansion of $\text{Mo}_2\text{Ga}_2\text{C}$ are predicted. Electronic contributions in these systems seem to be much less than those resulting from lattice thermal expansion, and electronic contributions increase gradually with the increase of temperature. The coefficient of thermal expansion of $\text{Mo}_2\text{Ga}_2\text{C}$ is larger than that of Mo_2GaC , which is mainly due to the weaker Ga–Ga bond of the former and the downward shift of its phonon mode, which would provide some support for the application scenarios of the former.

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