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Xinxin Qi  
Harbin Institute of Technology

Weilong Yin  
Harbin Institute of Technology

Sen Jin  
Henan Polytechnic University

Aiguo Zhou  
Henan Polytechnic University

Xiaodong He  
Harbin Institute of Technology

Guangping Song  
Harbin Institute of Technology

Yongting Zheng  
Harbin Institute of Technology

Yuelei Bai (baiyl@hit.edu.cn)  
Harbin Institute of Technology  
https://orcid.org/0000-0003-1738-3274

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DFT predictions and experimental confirmation of mechanical behaviour and thermal properties of the Ga-bilayer Mo$_2$Ga$_2$C

Xinxin Qi$^1$, Weilong Yin$^1$, Sen Jin$^2$, Aiguo Zhou$^2$, Xiaodong He$^1$, Guangping Song$^1$, Yongting Zheng$^1$, Yuelei Bai$^1$,*

1. National Key Laboratory of Science and Technology on Advanced Composites in Special Environments and Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, P. R. China
2. School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan 454003, P. R. China

Abstract. Mo$_2$Ga$_2$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, mechanical and thermodynamic properties of Mo$_2$Ga$_2$C were investigated by first principles. Using the "bond stiffness" model, the strongest covalent bonding (1162 GPa) were formed between Mo and C atoms in Mo$_2$Ga$_2$C, while the weakest Ga-Ga (389 GPa) bonding were formed between two Ga-atomic layers, different from other typical MAX phases. Of interest, 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 Mo$_2$Ga$_2$C, which was confirmed by indentation without any cracks. The high-temperature heat capacity and thermal expansion of Mo$_2$Ga$_2$C were calculated in the framework of quasi-harmonic approximation from 0 K to 2000 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; Stability; Heat capacity; Thermal expansion

*Corresponding author: Tel: +86-45186403956; Fax: +86-45186403956; Email: baiyl@hit.edu.cn, baiyl.hit@gmail.com.
1. Introduction

Over the past two decades, a class of ternary transition metal carbides or nitrides known as $M_nAX_{n+1}$ phases (where $M$ is an early transition metal, $A$ is a group IIIA or IVA element, $X$ is C and/or N, and $n = 1-3$), formed by inserting A-group atoms into the corresponding binary carbides or nitrides, have attracted growing attention due to their unique combination of metallic and ceramic properties [1]. Having this layered structure, the MAX phases exhibit a combination of the beneficial properties of both ceramic and metallic compounds, e.g. low density [2], low thermal expansion coefficient, high modulus, high strength [3], high temperature oxidation resistance [4], good thermal conductivity [5], electrical conductivity, easy processing [6], plastic and thermal impact resistance [5].

The $M_2AX$ (211) phases including solid solutions with $M = Ti, V, Cr, Nb, Ta, Zr, Hf, A = Al, S, Sn, As, In, Ga, and X = N, C$, have been studied extensively both experimentally and theoretically [7-13]. Among them, $Mo_2GaC$ [14] is an important MAX phase showing superconducting characteristics with $T_c \sim 4.0$ K. $Mo_2GaC$ is one of few having Mo as the sole occupant of the M-site [15] and was predicted to have a high bulk and low shear moduli [16]. Recent studies on the MAB phase had shown that $MoAlB$ with Al bilayer had better damage tolerance and antioxidant properties [17, 18]. Interestingly, the discovered $Mo_2Ga_2C$ in 2015 [19] also has a Ga bilayer, which provides us a chance to examined the effect of the A-group bilayer on the properties of the MAX phases.

$Mo_2Ga_2C$ had been mainly used to produce MXenes materials since it was discovered by Hu et al in 2015 [20-22]. At present, the research on $Mo_2Ga_2C$ mainly focused on its mechanical properties, Hadi et al [23] calculated elastic properties including Debye temperature and theoretical Vickers hardness and Wang et al [24]
predicted the stability of another structure of Mo$_2$Ga$_2$C under pressure. However, there was little research on Mo$_2$Ga$_2$C in the field of high temperature. He et al [25] found Mo$_2$Ga$_2$C will decompose when the temperature is higher than 700°C and new study of Jin et al found that Mo$_2$Ga$_2$C’s thermal conductivity and electrical resistivity were lower than those of most MAX phases probably due to the extra Ga layer [26].

For structural applications, the mechanical properties are critical, especially the damage tolerance and fracture toughness [27]. 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 [28, 29]. 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 [30]. 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 [28, 31], and thermal properties by quasi harmonic approximation (QHA) [32], with some significant advantages, such as low cost and high efficiency [33].

The present work is to investigate the mechanical and thermal properties as well as phase stability of Mo$_2$Ga$_2$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 details

2.1 Density functional theory settings

All first principles calculations were performed within the framework of density
functional theory (DFT) as implemented in VASP (the Vienna Ab initio Simulation Package) [34]. A selection of exchange-correlation functional was used, including those within generalized gradient approximation (GGA) [35], comprising PBE, RPBE [36] and PW91 [37], and also a local density approximation (LDA) functional [38]. The projector-augmented wave (PAW) method was used, with 4p⁶4d⁵5s¹, 4s²4p¹ and 2s²2p² electrons included as valence states for Mo, Ga and C respectively, with the cut-off energy of 350 eV and k-points sampled using Monkhorst-Pack meshes of 12×12×2 for the geometry optimization and the elastic constant determination, and 36×36×6 when calculating the electronic density of states, resulting in that total energies were converged to within ±1 meV/atom, with atomic forces less than 1 meV/Å. The relaxation of atomic geometries was achieved using the conjugate-gradient method.

The supercell approach and the force-constant method were used for the phonon dispersion and density of states. The real space force constants of the supercells were calculated using density functional perturbation theory (DFPT), and the phonon modes were calculated based on force constants using the PHONOPY package [39]. A 2×2×1 supercell with an energy cut-off of 350 eV and a k-points mesh of 6×6×2 was constructed for the resulting forces on the perturbed atoms [40], with the phonon dispersion along the four high-symmetry points (Γ(0 0 0), F(0 0.5 0), Q (0 0.5 0.5), Z (0 0 0.5)) spanning the whole Brillouin zone. The convergence condition for the calculation is that the change in total energy is less than 10⁻⁸ eV/atom.

2.2 Thermodynamic analysis on phase stability

To assess the phase stability of a particular MAX phase it is essential to account for the stability of all other competing compounds. The phase stability of Mo₂Ga₂C was examined by “linear optimization procedure” developed by Dahlqvist et al [41] for
MAX phases, to determine the most stable combination of competing phases for a given chemical composition $b^M$, $b^A$ and $b^X$. The optimization problem can be expressed by the following equation:

$$\min E_{\text{comp}}(b^M, b^A, b^X) = \sum_{i=1}^{n} x_i E_i$$  \hspace{1cm} (1)$$

where $x_i$ and $E_i$ are the amount and energy of competing compound $i$, respectively. Notably, the minimization has to be subjected to the constraints

$$x_i \geq 0, b^M = \sum_{i=1}^{n} x_i^M, b^A = \sum_{i=1}^{n} x_i^A, b^X = \sum_{i=1}^{n} x_i^X$$  \hspace{1cm} (2)$$

For Mo$_2$Ga$_2$C, $b^M = 2$, $b^A = 2$, $b^X = 1$. It follows that the formation enthalpy $\Delta H_{\text{comp}}$ with respect to the identified most stable combination of competing phases is thus calculated according to

$$\Delta H_{\text{comp}} = E - \min E_{\text{comp}}(b^M, b^A, b^X)$$  \hspace{1cm} (3)$$

where $E$ is the total energy of Mo$_2$Ga$_2$C.

**2.3 Model of bond stiffness**

In the previous work on the MAX phases, Bai et al proposed a theoretical model to quantificationally calculate the bond stiffness from the DFT-simulated results for characterizing the bond strength [28, 31], and based on the calculated bond stiffness further established a criteria 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 [28]. This model assumed that a second-order polynomial relation exists between the applied hydrostatic pressure ($P$) and 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 lengths $d/d_0$ ($d_0$ 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 [31].

\[
d / d_0 = C_0 + C_1 P + C_2 P^2
\]  

\[
k = \left| \frac{\text{d}(d / d_0)}{\text{d} P} \right|^{-1} = \left| C_1 + 2C_2 P \right|^{-1}
\]

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

2.4 Heat capacity and thermal expansion

Here, 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 derived us in

\[
\frac{\partial F(V, T)}{\partial V}_{V_{eq}(T)} = 0, \quad C_P = -T \frac{\partial^2 F(V, T)}{\partial T^2}_{V_{eq}(T)}
\]

In the present work, $F(V, T)$ is calculated from first principles within the framework of DFT and QHA [32], where phonon frequencies are volume-dependent, but at a fixed volume they are independent of temperature. In practice, the free energy is expressed as the sum of the following separate parts:

\[
F(V, T) = E_{tot}(V) + F_{el}(V, T) + F_{qha}(V, T)
\]

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.
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

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

(8)

where \( \hbar \) is the reduced Planck constant and \( k_B \) is the Boltzmann constant. Furthermore, \( C_v(T) \) can be estimated from the calculated \( F(V, T) \) using the standard thermodynamic relation. The electronic free energy \( F_{\text{el}}(V, T) \) is usually divided into the energy \( E_{\text{el}}(V, T) \) due to electronic excitations and a remaining part as [42]

\[
F_{\text{el}}(V, T) = E_{\text{el}}(V, T) - TS_{\text{el}}(V, T)
\]

(9)

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

\[
S_{\text{el}}(V, T) = -g k_B \sum_i \left[ f_i(V, T) \ln f_i(V, T) + [1 - f_i(V, T)] \ln [1 - f_i(V, T)] \right]
\]

(10)

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

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

(11)

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

\[
E_{\text{el}}(V, T) = g \sum_i f_i(V, T) \epsilon_i(V)
\]

(12)

3. Experimental details

The fabrication details of Mo2Ga2C were described elsewhere [25, 26]. In brief, Mo2C powders (Sigma Aldrich Co., USA, 99.5 wt.%, 325 mesh) and Ga (Beijing Xingrongyuan Co., China, 99.99 wt.%) 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 Mo$_2$Ga$_2$C samples were prepared by hot pressing at 750 °C for 8 h [43]. The Vickers’ hardness of bulk Mo$_2$Ga$_2$C was tested on the polished surface of sintered sample.

4. Results and Discussions

4.1 Crystal structures

The previous work [18, 29] indicates 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-RPBA and GGA-PW91) were used for the equilibrium lattice constant of Mo$_2$Ga$_2$C (Table 1). The LDA results over-bind as are often the case with this approximation, and are the least accurate of the considered functional [44]. In contrast, GGA functional often overestimate 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.

Two crystal structures of Mo$_2$Ga$_2$C are considered (Figure 1), where the atomic coordinates are Mo (1/3, 2/3, $z_{Mo}$), Ga1 (1/3, 2/3, $z_{Ga1}$) and C (0, 0, $z_{C}$) for Mo$_2$Ga$_2$C-1 and Mo (1/3, 2/3, $z_{Mo}$), Ga1 (1/3, 2/3, $z_{Ga1}$), Ga2 (2/3, 1/3, $z_{Ga2}$) and C (0, 0, $z_{C}$) for Mo$_2$Ga$_2$C-2. Table 1 lists the energy of the two structures, showing the one with Ga atoms on the same side (Mo$_2$Ga$_2$C-1) has lower energy (-7.45eV/atom). This means that Mo$_2$Ga$_2$C-1 is thermodynamically stable. It follows that the structure of Mo$_2$Ga$_2$C-1 is
used in the subsequent research. As shown in Figure 1, Mo-C layer is separated by single Ga layer along the c-axis direction in Mo$_2$GaC, and Mo$_2$Ga$_2$C is formed by the insertion of carbon borides into double Ga layers along the c-axis. Mo$_2$Ga$_2$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 is staggered. Comparing Ga-bilayer Mo$_2$Ga$_2$C and Ga-monolayer Mo$_2$GaC, the insertion of an additional Ga layer has a negligible effect on the lattice constants a and b (3.066 Å and 3.085 Å), but the lattice constants c increases significantly from 13.12 Å to 18.10 Å.

The bond lengths between adjacent atoms (marked in Figure 1) of Mo$_2$Ga$_2$C are given in Table 2, including the corresponding data of Mo$_2$GaC and Mo$_2$AlC for comparison. The Mo-C bond lengths in Mo$_2$Ga$_2$C (2.1225 Å) and Mo$_2$GaC (2.1224 Å) show that addition of a Ga layer has little effect on the Mo-C layer. However, inserting Ga layers results in slightly decreasing Mo-Ga bond length from 2.7697 Å in Mo$_2$Ga$_2$C to 2.7545 Å in Mo$_2$GaC.

4.2 Intrinsic and thermodynamic phase stability

The intrinsic stability of Mo$_2$Ga$_2$C is investigated by examining its lattice dynamics (phonon). The phonon dispersion and density of state of Mo$_2$Ga$_2$C are showed in Figure 2. Of importance, no imaginary frequencies in the phonon spectrum mean the intrinsic stability of Mo$_2$Ga$_2$C that the Gibbs free energy is near a minimum for small deformation. Notably, the high-frequency phonon states above 15 THz are mainly caused by the vibration of C atoms because of its strong bonding with Mo atoms by Mo-C bonds and low atomic mass. And the low-frequency lattice vibration should be attributed to the Mo and Ga atoms, due to the high mass of Mo atoms (despite their
strong bonding), and weak bonding of Ga atoms (despite their low mass) by Mo-Ga bonds, as similar to the calculated results of other MAX phases [45].

After analysing the intrinsic stability of Mo$_2$Ga$_2$C, the thermodynamic stability of Mo$_2$Ga$_2$C is evaluated by the linear optimization procedure [41] (Section 2.2), where all the competing phases are included in Mo-Ga-C system (Table 3). Obviously, the negative $\Delta H_{\text{comp}}$ (Table 1) shows their thermodynamic stability of Mo$_2$Ga$_2$C (-0.025 eV·atom$^{-1}$) as well as Mo$_2$GaC (-0.004 eV·atom$^{-1}$). It is worth noting that the $\Delta H_{\text{comp}}$ of Mo$_2$Ga$_2$C is smaller than that of Mo$_2$GaC, indicating the higher thermodynamic stability of the former. Here, it can be concluded that Mo$_2$Ga$_2$C is intrinsically and thermodynamically stable, consistent with experiments [19].

4.3 Electronic structure and bond stiffness

Total and partial density of states of Mo$_2$Ga$_2$C are showed in Figure 3, including Mo$_2$GaC for comparison. In Mo$_2$Ga$_2$C, C-s and Mo-d states fall into the energy range from -13 eV to -8 eV. With increasing energy range from -8 eV 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 eV and 0 eV, there is an overlapping region between Mo-d and Ga-p states, which means a weak chemical bond between Mo and Ga. Notably, the present electronic structure and chemical bonding of Ga-bilayer Mo$_2$Ga$_2$C are similar with Ga-monolayer Mo$_2$GaC and other typical MAX phases [46-51].

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 use of the model of “bond stiffness” (section 2.3). Table 2 lists the calculated bond stiffness of Mo$_2$Ga$_2$C at 0 GPa,
also including Mo$_2$GaC and MoC for comparison. Of much interest, the Ga-Ga bond has the lowest stiffness (389 GPa) in Mo$_2$Ga$_2$C, instead of M-A bonds in Mo$_2$Ga$_2$C and other typical MAX phases [31]. 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 [25]. However, Mo-C bonds are still the strongest ones with the bond stiffness of 1162 GPa, similar with the typical MAX phases [31], which indicates that 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 Mo$_2$Ga$_2$C and typical MAX-phase Mo$_2$GaC. Also, it is not surprising that Mo$_2$Ga$_2$C has similar Mo-C and Mo-Ga bond stiffness (1162 GPa and 571 GPa) with Mo$_2$GaC (1188 GPa and 563 GPa). On the other hand, the Mo-Ga bond stiffness is similar between Mo$_2$Ga$_2$C (571GPa) and Mo$_2$GaC (563GPa). It can be concluded that the addition of a layer into Mo$_2$GaC 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 [18].

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, micro-scale plastic deformation and so on [52, 53]. The previous work indicates that the ratio $k_{\text{min}}/k_{\text{max}}$ 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 [18, 28, 29]. When $k_{\text{min}}/k_{\text{max}}$ is more than 1/2, this class of ceramics exhibit low damage tolerance and fracture properties of typical brittle ceramics with indentation cracks, such as Ti$_2$SC [54], (MC)$_n$Al$_3$C$_2$ and (MC)$_n$Al$_4$C$_3$ [55]. 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 [44]. The present $k_{\text{min}}/k_{\text{max}}$ (0.33) of Ga-bilayer Mo$_2$Ga$_2$C
is lower than 0.43 of Al-bilayer MoAlB and 0.47 of Ga-monolayer Mo2Ga2C, which indicates the high damage tolerance and fracture toughness of both Mo2Ga2C and Mo2GaC. Of much interest, this prediction is well consistent with the present indentation on Mo2Ga2C under 21.66 N, indeed without cracks (Figure 5). Furthermore, it shows the model of “bond stiffness” is reliable.

4.4 Thermodynamic properties

The isobaric heat capacities $C_P$ of Mo2Ga2C as well as Mo2GaC and experimental value of MoC [56] against increasing the temperature are illustrated in Figure 6a, with effect of electronic excitation. Of much interest, 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 Mo2Ga2C as well as Mo2GaC. In fact, 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. This is consistent with the electron density at the Fermi level shown in the electronic DOS plots (Figure 3). Notably, the $C_P$ of Mo2Ga2C at 300 K is around 0.6-108 J·mol$^{-1}$·K$^{-1}$. Moreover, their capacities of Mo2Ga2C from 300 K to 2000 K can be expressed using the following equation:

$$C_{P,Mo_2Ga_2C}^{\text{PBE-qha}} = 115.97 + 1.59 \times 10^2 T - 1.14 \times 10^6 T^{-2} \quad (21)$$

Interestingly, the $C_P$ of Mo2Ga2C is 1.26-1.29 times of that of Mo2GaC 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]:
\[ C_p(M_{n+1}AX_n) = (n+1) \times C_p(MX) \]  

In fact, the \( C_p \) of MAX phases is determined approximately by their constituent elements, which is applicable for the present Mo2Ga2C. However, due to the double Ga layer, the \( C_p \) of Mo2Ga2C is 2.3 times of that of MoC.

The thermal expansion of Mo2Ga2C and Mo2GaC in the temperature range of 300K-2000 K are shown in Figure 6b. Notably, the average linear thermal expansion coefficient (TEC) with electronic excitations for Mo2Ga2C from 300 K to 2000 K is 24.6\( \times 10^{-6} \) K\(^{-1} \), where the electronic excitations act to decrease the thermal expansion as a function of temperature. As the temperature rises above 1000 K, the slope of thermal expansion increasing speed is more and more slow, 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 Mo2Ga2C is larger than that of Mo2GaC, 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 \( \approx 5-15\times 10^{-6} \) K\(^{-1} \) [5], which means the present TEC of Mo2Ga2C is higher than other MAX phases. In general, TECs are intimately related to the interatomic bond strengths. Compared with typical MAX phases Ti2AlC, Mo2Ga2C has the weaker Ga-Ga bond (Table 2), resulting the higher TEC than Ti2AlC (8.8\( \times 10^{-6} \) K\(^{-1} \)) [57]. This means the more serious deformation of Mo2Ga2C at high temperature.
5. Conclusion

(1) The structure of Mo$_2$Ga$_2$C could be described as a layered structure similar to MAX phase: the strong binding Mo-C atomic layer and the Mo-Ga layer with weak Al-Al 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 phase stability of Mo$_2$Ga$_2$C is studied by lattice dynamics theory and linear optimization method based on the first principle respectively, which shows the intrinsic and thermodynamic stability of Mo$_2$Ga$_2$C.

(3) The bond in Mo$_2$Ga$_2$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), indicating the high damage tolerance and fracture toughness of Mo$_2$Ga$_2$C similar with other typical MAX phases. Intestinally, this prediction has been confirmed by the present indentation of Mo$_2$Ga$_2$C.

(4) By including contributions from phonons and electrons, the heat capacity and thermal expansion of Mo$_2$Ga$_2$C are predicted, both higher than that of Mo$_2$GaC, which would provide some support for the application scenarios of the former.

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Figure captions

Figure 1 Crystal structure of Mo$_2$Ga$_2$C-1 (a), Mo$_2$Ga$_2$C-2 (b), Mo$_2$GaC (c) and MoC (d). The purple, green and brown spheres correspond to the Mo, Ga and C atoms, respectively.

Figure 2 Phonon dispersions (a) and density of state (b) of Mo$_2$Ga$_2$C along the high symmetry directions

Figure 3 Total and partial density of states of Mo$_2$Ga$_2$C (a) and Mo$_2$GaC (b)

Figure 4 Pressure dependence of the normalized cell volume $V/V_0$ as well as the normalized lattice parameters $a/a_0$, $b/b_0$ and $c/c_0$ of Mo$_2$Ga$_2$C (a) and the normalized bond length $d/d_0$ in Mo$_2$Ga$_2$C (b)

Figure 5 (a) Vickers’ hardness of Mo$_2$Ga$_2$C vs indentation depth where the hardness at the depth of 0.02 nm/s; (b) the Vickers’ indentation conducted on Mo$_2$Ga$_2$C with the load at 21.66 N.

Figure 6 Heat capacity (a) and thermal expansion (b) of Mo$_2$Ga$_2$C, while “exp” means the data from ref. [56].
|                | Mo$_2$Ga$_2$C-1 | Mo$_2$Ga$_2$C-2 | Mo$_2$GaC   | MoC         |
|----------------|-----------------|-----------------|-------------|-------------|
|                | LDA  | GGA  | PBE  | RPBE | PW91 | GGA   | Exp. [19] | GGA  | GGA  | PBE  | PBE  |
| Lattice parameters |     |      |      |      |      |       |           |      |      |      |      |
| a (Å) | 3.000 | 3.066 | 3.086 | 3.073 | 3.085 | 3.03396 | 3.080 | 3.083 |
| c (Å) | 17.95 | 18.10 | 18.19 | 18.08 | 18.29 | 18.0814 | 13.12 | 15.250 |
| V (Å$^3$) | 139.9 | 147.33 | 150.00 | 147.91 | 150.84 | 144.1393 | 107.87 | 125.58 |
| Internal coordinates | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| z$_{Mo}$ | 0.066 | 0.0647 | 0.0642 | 0.0647 | 0.0681 | 0.0681 | 0.0681 | 0.0681 |
| z$_{Ga1}$ | 0.682 | 0.6813 | 0.6812 | 0.6813 | 0.6831 | 0.6831 | 0.6831 | 0.6831 |
| z$_{Ga2}$ | 0.3015 | 0.3015 | 0.3015 | 0.3015 | 0.3015 | 0.3015 | 0.3015 | 0.3015 |
| z$_C$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Density (g·cm$^{-3}$) | 7.74 | 7.74 | 7.74 | 7.74 | 7.74 | 7.74 | 7.74 | 7.74 |
| Energy (eV·atom$^{-1}$) | -7.45 | -7.45 | -7.45 | -7.45 | -7.45 | -7.45 | -7.45 | -7.45 |
| $\Delta H_{\text{comp}}$ (eV·atom$^{-1}$) | **-0.025** | 1.34 | 1.34 | 1.34 | 1.34 | **-0.004** | **-0.004** | **-0.004** |
| DOS at $E_f$ (States·eV$^{-1}$·Unit cell$^{-1}$) | 3.753 | 4.863 | 4.863 | 4.863 | 4.863 | 4.863 | 4.863 | 4.863 |
| Bulk modulus (GPa) | 141.46 | 244.29 | 244.29 | 244.29 | 244.29 | 244.29 | 244.29 | 244.29 |
| Pressure derivative | 4.73 | 4.19 | 4.19 | 4.19 | 4.19 | 4.19 | 4.19 | 4.19 |
Table 2 Bond length ($d$, Å) and bond stiffness ($k$, GPa) in Mo$_2$Ga$_2$C and Mo$_2$GaC

| Phase  | Mo1-C/B | Mo2-C/B | Mo-Ga/Al | Ga-Ga/Al-Al | B-B | Al-B |
|--------|---------|---------|----------|--------------|-----|------|
| Mo$_2$Ga$_2$C | $d$ | 2.1225 | | 2.7545 | 2.4866 | | |
| | $k$ | 1162 | | 571 | 389 | | |
| Mo$_2$GaC | $d$ | 2.1224 | | 2.7697 | | | |
| | $k$ | 1188 | | 563 | | | |
| MoC | $d$ | 2.1895 | 2.2526 | | | | |
| | $k$ | 1163 | 889 | | | | |
| MoAlB [18] | $d$ | 2.3735 | 2.3541 | 2.7117 | 2.6669 | 1.8085 | 2.3209 |
| | $k$ | 764 | 1135 | 731 | 526 | 1205 | 717 |
| Mo$_2$AlC [31] | $d$ | 2.1170 | | 2.7903 | | | |
| | $k$ | 1111 | | 515 | | | |
| Ti$_2$AlC [31] | $k$ | 741 | 680 | 366 | | | |
Table 3 Unit cell volume, lattice parameters, and total energies, per formula unit, for competing phases considered in the ternary Mo–Ga–C system.

| Phase     | Space group | \( V_0 \) (Å\(^3\)) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( E_0 \) (eV) | Most competing phases |
|-----------|-------------|------------------------|-------------|-------------|-------------|----------------|-----------------------|
| C         | P6/mmc      | 22.76                  | 2.509       | 2.509       | 4.172       | -35.97         | 3/28                  |
| Ga        | I4/mmm      | 38.00                  | 2.926       | 2.926       | 4.437       | -5.75          | 0                     |
| Mo        | IM3-M       | 31.81                  | 3.168       | 3.168       | 3.168       | -21.59         | 0                     |
| Mo\(_2\)Ga | PM3-N       | 123.30                 | 4.977       | 4.977       | 4.977       | -71.85         | 0                     |
| Mo\(_3\)Ga\(_3\) | P-1 | 1318.95              | 9.558       | 9.592       | 9.5927      | -319.59        | 1/28                  |
| MoC-1     | P63/mmc     | 125.58                 | 3.083       | 3.083       | 15.250      | -117.63        | 0                     |
| MoC-2     | Fm3-m       | 84.05                  | 4.380       | 4.380       | 4.380       | -78.00         | 0                     |
| Mo\(_2\)C-1 | P6-m2       | 39.47                  | 2.895       | 2.895       | 5.435       | -29.11         | 0                     |
| Mo\(_2\)C-2 | PBCN        | 151.27                 | 4.759       | 6.067       | 5.238       | -124.30        | 0                     |
| Mo\(_2\)GaC | P6/mmc     | 107.87                 | 3.080       | 3.080       | 13.124      | -68.21         | 25/28                |
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