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Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:
http://dx.doi.org/10.1016/j.actamat.2015.07.063
Copyright: Elsevier
http://www.elsevier.com/

Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-122193
Structural and chemical determination of the new nanolaminated carbide Mo$_2$Ga$_2$C from first principles and materials analysis

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Abstract

Following our recent discovery of a new nanolaminated carbide, Mo$_2$Ga$_2$C, we herein present a detailed structural and chemical analysis of this phase based on ab initio calculations, X-ray photoelectron spectroscopy, high resolution scanning transmission electron microscopy, and neutron powder diffraction. Calculations suggest an energetically and dynamically stable structure for C in the octahedral sites between the Mo layers, with Ga bilayers – stacked in a simple hexagonal arrangement – between the Mo$_2$C layers. The predicted elastic properties are below those of the related nanolaminate Mo$_2$GaC. The predicted structure, including lattice parameters and atomic positions, is experimentally confirmed.

1. Introduction

The $M_{n+1}AX_n$ (MAX) phases, with $n = 1–3$, are inherently nanolaminated materials, where $M$ is an early transition metal, $A$ is an A-group element (mainly group 13 or 14), and $X$ is C or N [1–4]. Structurally, the MAX phases can be described as $M_{n+1}X_n$ layers interleaved by monolayers of pure $A$ element, for which two adjacent $M_{n+1}X_n$ layers are twinned across it. So far, more than 70 MAX phases have been synthesized. Before the late 2000s most predictions were carried out in an ad hoc fashion due to a lack of a comprehensive understanding of the respective material systems [5–8]. It is not until the last few years that the theoretical methods have been more systematic, which in turn provides better guidance for experimentalists to look for new MAX phases, see e.g. references [9–12].

Recently, we reported on a new ternary carbide, Mo$_2$Ga$_2$C, both in thin film and bulk form [13]. Similar to its MAX phase counterpart, Mo$_2$GaC, Mo$_2$Ga$_2$C is laminated, but instead of Ga monolayers interleaving the Mo$_2$C blocks, there is a Ga double-layer (bilayer) between the carbide layers. The resulting phase is of great interest because of its structural similarity with
Mo$_2$GaC, which is the only Mo-containing MAX phase synthesized so far. Other conceivable MAX phases within the Mo–Ga–C system are predicted to be not stable, i.e. positive formation enthalpy, with respect to their competing phases [14].

In our previous report, structural and compositional analysis of Mo$_2$Ga$_2$C was performed by X-ray diffraction (XRD), transmission electron microscopy (TEM), and elastic recoil detection analysis (ERDA). However, even though we argued that the most plausible position of C in the structure was in the octahedral sites between the Mo layers, direct evidence was lacking. Quite surprisingly, the Ga layers were stacked in a simple hexagonal arrangement, one that is quite rare in metals.

The purpose of this work is to explore the structure and chemistry of Mo$_2$Ga$_2$C. We have therefore investigated the phase stability of Mo$_2$Ga$_2$C from first principles, with respect to possible competing phases in the Mo–Ga–C system, and in different structural and chemical order. We also calculated its elastic constants and electronic structure. Thermal neutron powder diffraction (NPD) was used to supplement the experimental investigation due to the sensitivity to C and Ga positions within the unit cell, in the presence of Mo atoms. Based on our theoretical modeling, combined with X-ray photoelectron spectra (XPS) and NPD, we have definitively determined the structure of this compound.

2. Computational details

First-principles calculations were carried out using the projector augmented wave (PAW) method [15] as implemented within the Vienna *ab initio* simulation package (VASP) [16–18]. We adopted the generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof (PBE) [19] for treating electron exchange and correlation effects. Wave functions are expanded in a plane-wave basis set with an energy cutoff of 400 eV and for
sampling of the Brillouin zone we used the Monkhorst–Pack scheme [20]. The calculated total energy for all phases is converged to within 0.1 meV/atom in terms of $k$-point sampling. Structural optimizations were performed in terms of unit-cell volumes, $c/a$ ratios (when necessary), and internal parameters to minimize the total energy.

3. Experimental details

Mo$_2$Ga$_2$C thin films were deposited by direct current magnetron sputtering (DCMS) with 3 elemental targets: Mo ($\varnothing \approx 7.6$ cm, 99.95% purity, SCOTECH Ltd.), Ga ($\varnothing \approx 5.1$ cm, 99.99999% purity, 5N Plus UK Ltd.) and C ($\varnothing \approx 7.6$ cm, 99.99% purity, SCOTECH Ltd.), in ~0.5 Pa Ar with a base pressure in the range of $10^{-7}$ Pa. The Ga target was placed in a horizontal position, facing upwards, along the substrate normal, while the Mo and C targets were tilted $35^\circ$ away from the substrate normal, co-focused on the substrate. Details about sputtering from a liquid Ga target as well as the deposition system are described elsewhere [21]. The MgO(111) substrates were cleaned sequentially in acetone, ethanol and isopropanol ultrasonic bath for 10 min each. During depositions, the substrates were kept at 560 °C and rotated at 30 rpm in order to obtain more chemically homogeneous films.

The NPD experiment was carried out at the KARL double-axis diffractometer, mounted on the Israeli Research Reactor No. 1 (IRR-1) at the Nuclear Research Center, Soreq, Israel (Israel’s Atomic Energy Commission) [22]. The measurement was carried out at room temperature, with an incident neutron wavelength of 0.982(1) Å. This low incident wavelength, combined with an angular step of 0.05° and a ~0.25° monochromating single crystal’s mosaicity, generated sufficient angular range and angular resolution for this crystallographic study. The preparation of Mo$_2$Ga$_2$C powder samples for the NPD experiment is described in our previous work [13]. A ~10 g powder sample was loaded into a vanadium cylindrical sample holder, which was used
to significantly reduce coherent scattering from the holder. The results obtained were analyzed using the Rietveld refinement method, applied using the FullProf software package [23].

To acquire cross-sectional images and compositional maps on thin film samples, high resolution scanning transmission electron microscopy (HR-STEM) and X-ray energy dispersive spectroscopy (EDX) were performed within the Linköping double C₃ corrected FEI Titan³ 60–300 microscope equipped with the Super-X EDX system and operated at 300 kV.

XPS on phase pure thin films was performed using an AXIS UltraDLD system from Kratos and monochromatic Al Kα radiation. To avoid charging, caused by electron depletion while recording the XPS spectra, the samples were exposed to an electron flood gun. The binding energy scale of all XPS spectra presented here was calibrated against the Fermi edge (EF), which was set to a binding energy of 0 eV. The overall energy resolution obtained was better than 0.5 eV. Normalization of all spectra was performed at the background on the low binding energy side of the main peak/peaks. Prior to the acquisition of the spectra, the samples were exposed to an Ar⁺ bombardment corresponding to 500 eV beam energy for 60 s. The Ar⁺ bombardment was performed at an angle of 25° relative the surface, which efficiently removes most oxide overlays and most of the carbon containing contamination.

4. Results and discussion

The position of carbon in the crystal structure of Mo₂Ga₃C is challenging to obtain from STEM. However, STEM images revealed a relatively large atomic spacing between two adjacent Mo layers and two adjacent Ga layers. The more likely location for the C atoms – and the one we assumed in our first report [13] – is the octahedral sites created by the Mo layers (Fig. 1(a)). Other possibilities include structures with C atoms in between the Ga layers (Fig. 1(b)) or with the C between the Mo layers, but in a ‘zig-zag’ arrangement of Ga layers (Fig. 1(c)).
For a phase with a given composition and structure to be thermodynamically stable, its energy needs to be lower than the energy of any stoichiometric linear combination of all other competing phases in the system, that is

$$\Delta H_{cp} = E(\text{Mo}_2\text{Ga}_2\text{C}) - E(\text{competing phases}) < 0 \quad (1)$$

In order to identify the set of most competing phases at the Mo$_2$Ga$_2$C composition we make use of a linear optimization procedure [24,25] which has proven successful in confirming already experimentally known MAX phases, as well as predicting the existence of new ones [25–27]. Table 1 lists all competing phases together with their respective calculated volume, lattice parameters, and total energies.

In Table 2, the calculated equilibrium energies and lattice parameters show that Mo$_2$Ga$_2$C, with C atoms between the Mo-layers (Fig. 1(a)) is the most likely structure with a calculated negative $\Delta H_{cp}$ of $-9$ meV/atom. The energies for the structures with either C atoms between the Ga layers (Fig. 1(b)) or C atoms between the Mo layer plus a zigzag stacking of the Ga atoms (Fig. 1(c)), are significantly higher, $+786$ and $+124$ meV/atom, respectively. The latter two structures would also have $c$ parameters well below 18 Å, which is inconsistent with previous experimental results [13].

To further explore the various possible Mo$_2$Ga$_2$C structures we calculated their phonon spectra using the Phonopy code in combination with density functional perturbation theory in VASP using $4 \times 4 \times 1$ supercells. Fig. 2(a)–(c) shows the results for the structures shown in Fig. 1(a)–(c), respectively, from which we can conclude that the structure shown in Fig. 1(a) is dynamically stable, i.e. stable relative to lattice vibrations as evidenced by the fact that no imaginary phonon frequencies exist in the phonon spectrum. When the C atoms are placed between the Ga-layers (Fig. 1(b)), the phonon spectrum (Fig. 2(b)) is negative along some
directions, confirming that this structure is dynamically unstable. The same result applies for
the zig-zag stacking of Ga (Figs. 1(c) and 2(c)).

In Table 3, the calculated $a$ and $c$ lattice parameters and the structural model of the most stable
structure (Fig. 1(a)) are summarized, together with previous results from XRD Rietveld analysis
[13]. The Ga and Mo atomic arrangements are thus consistent with our previous suggestion
based on STEM images acquired along the [100] and [210] zone axes of the Mo$_2$Ga$_2$C phase as
well as Rietveld analysis of the XRD patterns. Furthermore, the calculated $a$ and $c$ lattice
parameters are in good agreement with the ones obtained from XRD. The Mo double-layers,
with C atoms occupying the octahedral interstitial sites, is identical to that found for the $M$–$C$
layers in other $M_2AX$ phases. In fact, the only structural difference between the $M_2A_2X$ and
$M_2AX$ is the insertion of an extra $A$ layer. We conclude that in Mo$_2$Ga$_2$C the C atoms reside
between the Mo layers and that the Ga atoms are stacked in a simple hexagonal arrangement
(Fig. 1(a)).

The NPD results were analyzed assuming the $P6_3/mmc$ space group, with the Mo and Ga atoms
occupying the ‘4f’ site and the C atoms occupying the ‘2a’ site (Fig. 1(a)). The C occupancy
was assumed to be incomplete within the refinement process, Mo$_2$Ga$_2$C$_{1-x}$, with $x$ representing
the deviation from complete occupation of the ‘2a’ site. In addition to $x$, the refinement process
yields the unit cell size parameters, the Mo and Ga layers position, $z_{Mo}$ and $z_{Ga}$, within the unit
cell, respectively, and their mean-square displacement (assumed to be isotropic) from
equilibrium position, $\langle u^2 \rangle$, due to temperature driven vibrations, see Table 3. The refined profile
agrees well with the observed results, see Fig. 3 (top), as shown by their difference, normalized
by the statistical uncertainty in the observed neutron count, Stat. SD, as shown in Fig. 3 (bottom),
which is randomly distributed around zero with reasonable deviations from it. The possibility
of preferred orientation within the powder grains, the effect of the average powder grains size,
and the possibility that the Ga atoms occupy the ‘4e’ crystallographic site, were considered and
found inconsistent with the observed results. In addition, the observed low-angle count is considerably high, (see inset in Fig. 3). As this count includes the 002 reflection, it was empirically taken into account within the analysis process. We speculate that this additional count may originate from a significant variance in $z_{\text{Mo}}$ and $z_{\text{Ga}}$, within each powder grain, from their mean respective values, which requires additional research.

The result from NPD Rietveld refinement, as summarized in Table 3, is in good agreement with the calculated structure as well as the XRD Rietveld analysis [13]. Apart from Table 3, the mean-square displacement $\langle u^2 \rangle$ of Mo, Ga, and C were determined to be <0.01 Å$^2$, ~0.03(1) Å$^2$, and <0.01 Å$^2$, respectively. Moreover, the NPD analysis shows a C occupancy deviation $|x| < 0.03$, i.e. suggesting fully occupied octahedral sites, within the NPD precision, with C atoms between the Mo layers. This further validates our previously reported analysis and the present theoretical work, which were based on a fixed 100% C occupancy on the octahedral sites.

Fig. 4 shows the electronic band structure and density of states (DOS) for Mo$_2$Ga$_2$C. Non-bonding core states of C 2s and Ga 2s are located at −11.4 to −12.9 eV and −4 to −10 eV, respectively. Between −4.3 and −7.3 eV the Mo 4d and C 2p states form a hybridized bond. The peak around −2.5 eV shows partial hybridization of Mo 4d and Ga 4p states. Between −2.5 eV and the Fermi level ($E_f$) there are several peaks arising from both Mo 4d and Ga 4p states, where none show any clear hybridization between each other. The peak located just below $E_f$ can mainly be attributed to Mo 4d states. $E_f$ is located near a local minimum.

To obtain the elastic properties of Mo$_2$Ga$_2$C, we used the method described by Fast et al. [28], where five different strains are applied to the hexagonal unit cell in order to obtain the five independent elastic constants $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, and $C_{44}$. The strain values used to calculate the elastic constants were ±0.01 and ±0.02. From the elastic constants $C_{ij}$ it is possible to estimate the Voigt bulk ($B_V$) and shear ($G_V$) moduli given by
\[ B'_V = \frac{2}{9} (C_{11} + C_{12} + 2C_{13} + C_{33}/2) \quad (2) \]

and

\[ G'_V = 115(2C_{11} + C_{33} - C_{12} - 2C_{13}) + 15(2C_{44} + 12(C_{11} - C_{12})) \quad (3) \]

In addition the Young’s modulus \((E)\), Poisson’s ratio \((\nu)\), and shear anisotropy factor \((A)\) is given by

\[ E = \frac{9B'_V G'_V}{3B'_V + G'_V} \quad (4) \]

\[ \nu = \frac{3B'_V - 2G'_V}{2(3B'_V + G'_V)} \quad (5) \]

\[ A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (6) \]

In Table 4, the calculated elastic properties for Mo2Ga2C are listed and compared to those of Mo2GaC. It is evident that the additional Ga layer in Mo2Ga2C results in a significant reduction of most of the elastic constants, Poisson’s ratio, and the anisotropy factor, \(A\).

Fig. 5(a) is a STEM image acquired along the [210] zone axis of Mo2Ga2C from a thin film sample. Fig. 5(b) and (c) show Mo + Ga EDX maps (center) and superimposed STEM images with Mo + Ga EDX maps (bottom) from the same acquisition regions. In Fig. 5(a), the contrasts show a layered structure constructed by Mo layers (white) and Ga layers (light gray), which is further indicated by green ‘Ga’ labels. These results confirm those previously obtained [13]. What is additional here is the clear evidence for a stacking fault, where the double Ga layers of Mo2Ga2C merge into a single Ga layer characteristic of Mo2GaC denoted by vertical green line in Fig. 5(a). The transition region is imaged at a higher magnification in Fig. 5(c), from which it is obvious that two Ga layers on the right merge into one on the left. In other areas (Fig. 5(b)),
single and double Ga layers are interleaved. In all cases, however, the Ga layers are separated by two Mo layers. The formation of such stacking faults most probably reflects local compositional Ga inhomogeneities. These micrographs suggest that one way to synthesize Mo$_2$Ga$_2$C is to anneal Mo$_2$GaC in a Ga-rich environment.

A comparison between the XPS results for Mo$_2$Ga$_2$C and Mo$_2$GaC is shown in Fig. 6, which presents the O 1s, C 1s, Mo 3d, and Ga 3p spectra for Mo$_2$GaC (a) and Mo$_2$Ga$_2$C (b). The O 1s and C 1s spectra show that, despite the Ar$^+$ bombardment, the samples still exhibit oxide and graphite components as revealed through the O 1s feature at 530.8 and 531.5 eV and the C 1s feature at 284.7 and 285.4 eV for the Mo$_2$GaC and Mo$_2$Ga$_2$C samples, respectively. More important, though, is the sharp carbide peaks at 283.3 and 283.7 eV for Mo$_2$GaC and Mo$_2$Ga$_2$C, respectively. The Mo 3d XPS spectra feature the primary spin–orbit components 3d$_{5/2}$ and 3d$_{3/2}$ at binding energies of 227.9 and 231.1 eV, respectively, for Mo$_2$GaC and at binding energies of 228.1 and 231.3 eV, respectively, for Mo$_2$Ga$_2$C. The Ga 3p$_{3/2}$ and 3p$_{1/2}$ components have the main features at binding energies of 104.0 and 107.1 eV, respectively, for Mo$_2$GaC and binding energies of 104.1 and 107.3 eV, respectively, for Mo$_2$Ga$_2$C.

To be able to interpret the XPS spectra presented in Fig. 6, it is necessary to compare them with the 3p XPS component of a metallic Ga reference. The Ga 3p XPS spectra of the reference sample are presented in Fig. 7. Prior to the Ar$^+$ bombardment (Fig. 7(a)) the Ga reference sample has a native oxide, Ga$_2$O$_3$, surface layer, which is also indicated by the shoulder on the high binding energy side of the Ga 3p$_{1/2}$ peak. The corresponding Ga 3p$_{3/2}$ peak for the Ga$_2$O$_3$ phase is located between the primary spin–orbit components of the metallic Ga. After Ar$^+$ bombardment of the Ga reference sample (Fig. 7(d)) the dominating features are the metallic Ga 3p$_{3/2}$ and 3p$_{1/2}$ peaks at 104.1 and 107.5 eV, respectively. Note that the peak locations for Ga in metallic Ga and in both MAX phases are almost identical.
Included in Fig. 7 are also the corresponding spectra for the Mo$_2$GaC and Mo$_2$Ga$_2$C MAX-phases shown in Fig. 7(b) and (c), respectively. The comparison shows that the Ga in the MAX-phases is partly oxidized and that the Mo$_2$GaC sample is significantly more oxidized as compared to the Mo$_2$Ga$_2$C sample. Elemental quantification using the XPS spectra presented in Fig. 6 indicates that both samples consists of 20 at.% of oxygen and with a O:Ga ratio of 1.4 and 0.32 for the Mo$_2$GaC and Mo$_2$Ga$_2$C samples, respectively. However, the oxidation process is limited to the near surface region, which is probed by XPS, while the rest of the material is intact as evidenced by the only 0.34 at.% O determined through using ERDA [13]. Since the samples are extensively exposed to the atmosphere, it is not unreasonable to assume that oxygen penetrates into the near surface region along grain boundaries and possibly further into the Ga-layers. The more oxidized Ga single-layer will have a different work function compared to the less oxidized Ga double-layer, which will cause an upward band bending and thus a depletion of electrons from the non-oxidized components in the sample [29]. This charge transfer is observed in Fig. 6, as all Mo$_2$GaC spectra are shifted toward lower binding energies compared to those in the Mo$_2$Ga$_2$C phase.

This interpretation explains why the main features of the O 1s, C 1s, Mo 3d, and Ga 3p spectra for the Mo$_2$GaC and the Mo$_2$Ga$_2$C in Fig. 6 do not line up. The broader appearance of the Mo 3d$_{5/2}$ for Mo$_2$GaC and the shoulder on the low binding energy side of the main 3d$_{5/2}$ peak in Mo$_2$Ga$_2$C suggest that there is some double-layered Ga in Mo$_2$GaC and some single-layered Ga in Mo$_2$Ga$_2$C, consistent with the defects observed in Fig. 5. The additional intensity around 229.2 eV in the Mo 3d spectrum for the Mo$_2$Ga$_2$C sample reveals the presence of MoO$_2$ [30]. However, the most important observation is the similarity between the Mo 3d and the C 1s peaks of Mo$_2$GaC, Mo$_2$Ga$_2$C, and Mo$_2$C [31], see Fig. 8, which implies that both Mo$_2$GaC and Mo$_2$Ga$_2$C consist of Mo$_2$C-layers. In fact, the XPS study confirms that there are no structural differences in the Mo$_2$C-layers between Mo$_2$GaC and Mo$_2$Ga$_2$C.
5. Conclusions

We have performed first principles calculations in combination with experimental work including NPD Rietveld refinement, HR-STEM, and XPS, to explore the structure and chemistry of Mo$_2$Ga$_2$C. The theoretical, as well as the experimental, results support the existence of a stoichiometric phase with a Ga bilayer – stacked in a simple hexagonal arrangement – between a pair of twinned Mo$_2$C layers. It follows that the only structural difference between Mo$_2$Ga$_2$C and the well-known Mo$_2$GaC MAX phase is the insertion of an additional Ga layer. Based on their similar structures and the track record of MAX phase discoveries, it is quite reasonable to assume that Mo$_2$Ga$_2$C is the first phase in a distinct family of MAX-related phases.

Acknowledgments

We acknowledge support from the Swedish Research Council (Project Grants #621-2011-4420, 642-2013-8020, and 621-2014-4890), the Swedish Foundation for Strategic Research through the Synergy Grant FUNCASE Functional Carbides for Advanced Surface Engineering (C.-C.L., J.R., P.E., M.W.B.), the Future Research Leaders 5 Program (P.E., J.L.), and the ERC Grant agreement [No. 258509] (J.R.). The Knut and Alice Wallenberg Foundation is acknowledged for a Wallenberg Academy Fellowship (J.R.) and for supporting the Electron Microscopy Laboratory at Linköping University operated by the Thin Film Physics Division. Calculations were performed utilizing supercomputer resources supplied by the Swedish National Infrastructure for Computing (SNIC) at the High Performance Computing Center North (HPC2N) and National Supercomputer Centre (NSC).
References


Table 1. Calculated unit cell volume, lattice parameters, and total energies, per formula unit, for competing phases considered in the ternary Mo–Ga–C system. The values for Mo$_2$Ga$_2$C phases are listed in Table 2.

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<th>Prototype structure</th>
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<th>$V_0$ (Å$^3$/uc)</th>
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<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
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<td>hR147</td>
<td>$P\bar{3}$ (148)</td>
<td>2625.14</td>
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<td>-217.436</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Cr$_2$Ga$_4$</td>
<td>c110</td>
<td>Im$\bar{3}$m (229)</td>
<td>102.47</td>
<td>5.106</td>
<td></td>
<td></td>
<td>-23.818</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Ti$_2$Al$_3$</td>
<td>tI8</td>
<td>$I4/mmm$ (139)</td>
<td>72.10</td>
<td>5.189</td>
<td></td>
<td>5.428</td>
<td>-18.485</td>
</tr>
<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Cd$_2$I$_3$</td>
<td>hP3</td>
<td>$P\bar{3}m$1 (164)</td>
<td>48.84</td>
<td>2.904</td>
<td></td>
<td>6.689</td>
<td>-16.658</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Ti$_2$Ga$_3$</td>
<td>tP10</td>
<td>$P4/m$ (83)</td>
<td>155.67</td>
<td>6.515</td>
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<td>3.667</td>
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<td>Mo$_2$Ga$_3$</td>
<td>FeSi</td>
<td>cP8</td>
<td>$P2_1,3$ (198)</td>
<td>126.05</td>
<td>5.014</td>
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<td>-13.760</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Ti$_2$Ga$_4$</td>
<td>hP18</td>
<td>$P6_3/mcc$ (193)</td>
<td>276.95</td>
<td>7.817</td>
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<td>5.234</td>
<td>-66.314</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>U$_2$Si$_2$</td>
<td>tP10</td>
<td>$P4/mmm$ (127)</td>
<td>154.78</td>
<td>6.784</td>
<td></td>
<td>3.363</td>
<td>-38.294</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Cr$_2$As$_3$</td>
<td>oP32</td>
<td>$Pnma$ (62)</td>
<td>510.53</td>
<td>9.839</td>
<td>7.807</td>
<td>6.639</td>
<td>-62.659</td>
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<td>Mo$_2$Ga$_3$</td>
<td>Cu$_2$Sb</td>
<td>tP6</td>
<td>$P4/mmm$ (129)</td>
<td>95.73</td>
<td>3.682</td>
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<td>7.062</td>
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<td>Mo$_2$Ga$_3$</td>
<td>Fe$_2$P</td>
<td>hP9</td>
<td>$P\bar{6}2m$ (189)</td>
<td>140.12</td>
<td>7.192</td>
<td></td>
<td>3.127</td>
<td>-24.527</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Mn$_2$Ge$_2$</td>
<td>hP42</td>
<td>$P3c$1 (158)</td>
<td>670.89</td>
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<td>-59.508</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Cr$_2$Si</td>
<td>cP8</td>
<td>$Pm\bar{3}n$ (223)</td>
<td>123.39</td>
<td>4.979</td>
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<td>-36.200</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Ca$_2$TiO$_3$</td>
<td>cP5</td>
<td>$Pm\bar{3}m$ (221)</td>
<td>71.57</td>
<td>4.152</td>
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<td>-44.274</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Cr$_2$AlC</td>
<td>hP8</td>
<td>$P6_3/mmc$ (194)</td>
<td>108.20</td>
<td>3.068</td>
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<td>13.272</td>
<td>-34.413</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Ti$_2$SiC$_2$</td>
<td>hP12</td>
<td>$P6_3/mmc$ (194)</td>
<td>151.38</td>
<td>3.086</td>
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<td>18.358</td>
<td>-54.040</td>
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<tr>
<td>Mo$_2$Ga$_3$</td>
<td>Ti$_2$AlN$_3$</td>
<td>hP16</td>
<td>$P6_3/mmc$ (194)</td>
<td>196.55</td>
<td>3.133</td>
<td></td>
<td>23.116</td>
<td>-73.789</td>
</tr>
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</table>
Table 2 Structural and stability related information for the three crystal structures with Mo$_2$Ga$_2$C composition presented in Fig. 1. The negative values for $\Delta H_{cp}$ indicate stability relative to the set of most competing phases.

<table>
<thead>
<tr>
<th></th>
<th>$V_0$ (Å$^3$/uc)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$E_0$ (eV/uc)</th>
<th>$\Delta E_{single}$ (meV/atom)</th>
<th>$\Delta H_{cp}$ (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C between Mo-layers (Figure 1(a))†</td>
<td>147.59</td>
<td>3.064</td>
<td>18.153</td>
<td>-75.384</td>
<td>-142</td>
<td>-9</td>
</tr>
<tr>
<td>C between Ga-layers (Figure 1(b))</td>
<td>143.41</td>
<td>3.068</td>
<td>17.596</td>
<td>-67.438</td>
<td>+653</td>
<td>+786</td>
</tr>
<tr>
<td>C between Mo-layers and zig-zag stacking of Ga (Figure 1(c))‡</td>
<td>146.47</td>
<td>3.091</td>
<td>17.705</td>
<td>-74.057</td>
<td>-9</td>
<td>+124</td>
</tr>
</tbody>
</table>

† Identified set of most competing phases at Mo$_2$Ga$_2$C composition are Mo$_3$Ga, MoC, and MoGa$_4$.
‡ Note that the space group considered for the zig-zag stacked Mo$_2$Ga$_2$C is $P\overline{3}m1$ (164).

Table 3 $a$ and $c$ lattice parameters and structural models of Mo$_2$Ga$_2$C obtained from the calculation (only the most stable structure, Fig. 1(a)) and from Rietveld analysis of XRD and NPD patterns.

<table>
<thead>
<tr>
<th></th>
<th>Calculation (Fig. 1(a))</th>
<th>XRD (from [13])</th>
<th>NPD†</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.06396</td>
<td>3.03396(4)</td>
<td>3.03(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>18.1532</td>
<td>18.0814(3)</td>
<td>18.1(1)</td>
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</tbody>
</table>

Space Group

<table>
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<tr>
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<th>$P\overline{6}_3/mmc$</th>
<th>$P\overline{6}_3/mmc$</th>
<th>$P\overline{6}_3/mmc$</th>
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<tbody>
<tr>
<td>Wyckoff Notation</td>
<td>$x$</td>
<td>$y$</td>
<td>$z$</td>
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<tr>
<td>Mo</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
</tr>
<tr>
<td>Ga</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
</tr>
<tr>
<td>C</td>
<td>2a</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4: Calculated elastic constants $C_{ij}$, bulk moduli $B_V$, shear moduli $G_V$, Young's moduli $E$, Poisson's ratio $\nu$, and the anisotropy factor $A$ for Mo$_2$Ga$_2$C (Fig. 1(a)) and Mo$_2$GaC.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{13}$ (GPa)</th>
<th>$C_{33}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$B_V$ (GPa)</th>
<th>$G_V$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$Ga$_2$C</td>
<td>244</td>
<td>62</td>
<td>108</td>
<td>341</td>
<td>78</td>
<td>154</td>
<td>86</td>
<td>218</td>
<td>0.26</td>
<td>0.85</td>
</tr>
<tr>
<td>Mo$_2$GaC</td>
<td>294</td>
<td>96</td>
<td>161</td>
<td>289</td>
<td>126</td>
<td>190</td>
<td>101</td>
<td>257</td>
<td>0.28</td>
<td>1.93</td>
</tr>
</tbody>
</table>
Fig. 1. Crystal structures of Mo$_2$Ga$_2$C composition with (a) C atoms between the Mo-layers, (b) C atoms between Ga-layers, and (c) C atoms between Mo-layer but a zig-zag stacking of the Ga atoms, where the Mo atoms are in red, Ga in blue and C in black. All illustrations are scaled accordingly to their actual structure sizes.
Fig. 2. Dynamical stability of Mo$_2$Ga$_2$C composition with (a) C atoms between the Mo-layers, (b) C atoms between Ga-layers, and (c) C atoms between Mo-layer but a zig-zag stacking of the Ga atoms.
**Fig. 3.** NPD of Mo$_2$Ga$_2$C, observed at room temperature (crosses) as a function of scattering angle, $2\theta$. The Rietveld refined NPD profile (top) is shown to fit the observed count, determined by the difference between the observed and refined profiles (bottom), normalized by the statistical uncertainty in the observed count (see text). The inset at the top-right corner presents the low-angle count. Selected reflections are denoted using their Miller indices.

**Fig. 4.** Calculated electronic band structure (left) and density of states (right) for Mo$_2$Ga$_2$C for the structure shown in Fig. 1(a). The Fermi level is indicated by the horizontal dashed line.
Fig. 5. (a) STEM image of $\text{Mo}_2\text{Ga}_2\text{C}$ phase acquired along its [210] zone axis, where the Ga layers are highlighted with green ‘Ga’ labels and lines. (b and c) STEM images (top), Mo + Ga EDX mappings (center), and superimposed STEM images and Mo + Ga EDX mappings (bottom) of $\text{Mo}_2\text{Ga}_2\text{C}$ phase acquired along the [210] zone axis.
Fig. 6. XPS spectra for (a) Mo$_2$GaC and (b) Mo$_2$Ga$_2$C. Panels (A)–(D) show the O 1s, C 1s, Mo 3d, and Ga 3p regions, respectively.
**Fig. 7.** Ga 3p XPS spectra for (a) metallic Ga with native Ga$_2$O$_3$ surface layer, (b) Mo$_2$GaC, (c) Mo$_2$Ga$_2$C, and (d) metallic Ga after 500 eV Ar$^+$ bombardment.
Fig. 8. XPS spectra for (a) Mo$_2$GaC, (b) Mo$_2$Ga$_2$C, and (c) β-Mo$_2$C obtained from Ref. [31]. Panels (A) and (B) show the Mo 3d and C 1s regions, respectively.