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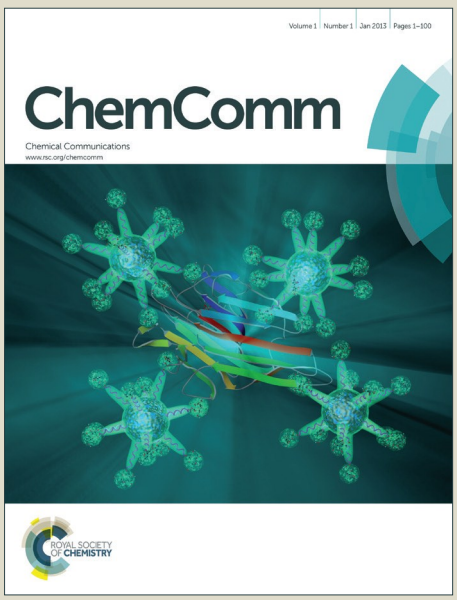

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Mo_2Ga_2C: A New Ternary Nanolaminated Carbide

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We report the discovery of a new hexagonal Mo_2Ga_2C phase, wherein two Ga layers – instead of one - are stacked in a simple hexagonal arrangement in between Mo_2C layers. It is reasonable to assume this compound is the first of a larger family.

The ternary $M_{n+1}AX_n$, or MAX, phases (where M is an early transition metal, A is an A group element mostly groups 13 and 14, X is C and/or N, and n = 1 to 3), phases are a large family, 70+, of nanolayered, machinable solids.[1,2,3]There are approximately 50 M_2AX, or 211, phases, five M_3AX_2, or 312, phases and a growing number of M_4AX_3, of 413, phases since that structure was first established in Ti_3AlN_4. In all cases, the $M_{n+1}AX_n$ unit cells are hexagonal – space group $P6_3/mmc$ – with two formula units per unit cell. In these compounds, near close-packed M atoms are interleaved with a single layer of pure A-element; the X atoms occupy the octahedral sites in between the M atoms. In the 211's, every third layer is an A-group element, in the 312's every fourth layer, and in the 413's every fifth. Recently, these solids have attracted much attention due to their unusual and sometimes unique combination of properties.

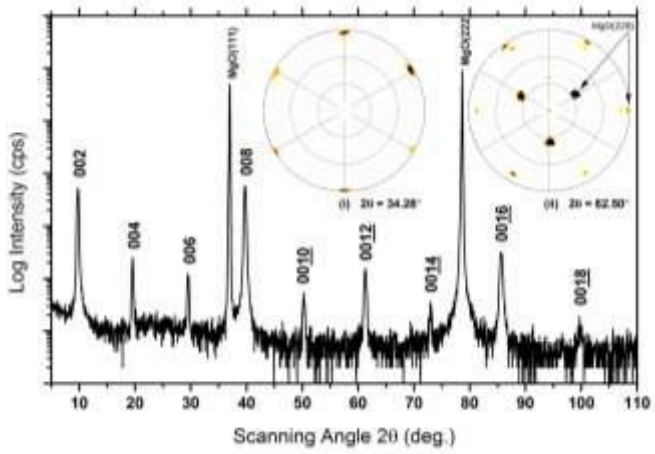
Of special interest to this work is the first, and sole, Mo-containing MAX phase, Mo_2GaC, first synthesized in 1967 by reacting Mo and C powders with liquid Ga for four weeks at 850 °C in an evacuated quartz capsule.[4] Superconducting behavior below 7 K has been reported.[4,5] More recently a theoretical paper was published predicting some of its properties.[6] Compared to Nb_2GaC and V_2GaC, Mo_2GaC was predicted to have the highest bulk and lowest shear modulus.

In efforts to synthesize Mo_2GaC, an XRD peak around 9° 2θ, suggested the possible existence of Mo_3GaC_2. However, since the latter is predicted to be highly unstable,[5] further work described herein, led us to the discovery of a new phase: Mo_2Ga_2C, wherein two Ga layers - instead of one in Mo_2GaC and all other MAX phases - are stacked in a simple hexagonal arrangement in between Mo_2C layers.

The processing details can be found in ESI. In short, the new phase was produced in two forms: thin film and bulk. The thin films were grown by direct current magnetron sputtering of elemental targets on MgO (111) substrates. Bulk Mo_2Ga_2C samples were synthesized by, first heating a 2:1 molar ratio of Mo:C powders in flowing Ar at 1000 °C for 12 h. The resulting, lightly sintered, Mo_2C compact was crushed into a powder and mixed with Ga in 1:8 molar ratio. First, the Ga was heated to 45 °C to melt it and the Mo_2C powder was homogeneously mixed into the melt in a mortar and pestle, before the mixture was allowed to solidify. The mixture was then placed in a quartz tube that was evacuated using a mechanical pump and sealed. Then quartz tube was placed in an alumina furnace and heated at a rate of 10 °C/min to 850 °C, and held at that temperature for 48 h. After furnace cooling, the powder was immersed in a 37 wt% HCl for 3 days to dissolve any residual Ga and Ga_2O_3 if present. A predominantly single phase powder, with 18 wt.% Mo_2C, was obtained after separating the solution and cleaned for several times using deionized water and dried in air.

The morphologies of all phases resulting from the bulk form were imaged in a scanning electron microscope (SEM) (Supra 50VP, Carl Zeiss AG, Germany) equipped with an energy dispersive spectroscope (EDS). X-ray diffraction, XRD, of the resulting powders were carried using a diffractometer (see Supp. Materials for details). High resolution scanning electron microscopy (HRSTEM) and X-ray energy dispersive spectroscopy (EDX) were performed with a double C_s corrected FEI Titan3 60–300 operated at 300 kV, equipped with the Super-X EDX system. Selected area electron diffraction (SAED) characterization was carried out using a FEI Tecnai G2 TF20 UT instrument operated at 200 kV with a point resolution of 0.19 nm.

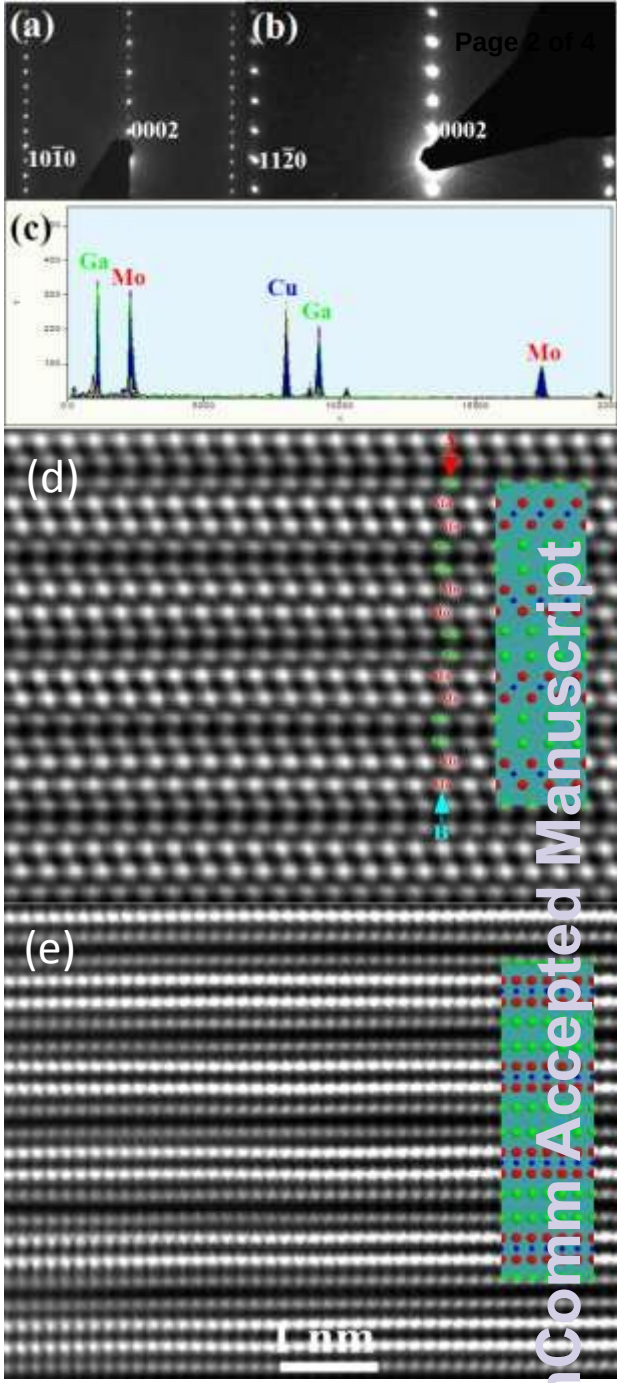
Figure 1 shows a θ-2θ XRD pattern of a thin film sample, where the two peaks with highest intensities at 2θ = 36.97° and 78.64° can be assigned (111) and (222) diffractions, respectively, of the MgO substrate. The other nine peaks originate from phases in the thin film with a d spacing with a least common multiple of ~ 9.04 Å. The insets in Fig. 1, shows two XRD pole figures of the thin film sample acquired respectively at constant 2θ = 34.26° (inset (i) in Fig. 1b) and 62.50° (inset (ii) in Fig. 1. At 2θ = 34.26°, six poles can be seen at Ψ = 87-90° with 60° separations in between, which shows a sixfold symmetry in the in-plane directions with respect to the sample surface. This symmetry can be assigned to a phase from the film with an in-plane d spacing of ~ 2.62 Å. At 2θ = 62.50°, three poles can be seen at Ψ = 33-39° with 120° separations in between, while two groups of six poles with 60° separations in between are observed at Ψ = 81° and Ψ = 87-90°, respectively. The poles at Ψ = 33-39° and 87-90° are assigned to MgO{220} from the MgO(111) substrate, which has a threefold rotational axis along MgO[111]. The sixfold symmetric poles at Ψ = 81° can be assigned to a phase oriented in accordance with the in-plane orientation of the substrate,



i.e. it is epitaxially grown on the MgO substrate.

Fig. 1 XRD pattern of Mo_2Ga_2C thin film sample. The two peaks with highest intensities at 2θ=36.97° and 78.64° are those of the MgO substrate. The other 9 peaks come from the thin film and represent a series of interplanar spacing d with a least common multiple of ~9.04 Å. The pole figure labelled (i) was acquired at a constant 2θ = 34.26° - and one labelled (ii) was acquired at 2θ = 62.50°.

Figures 2a, and b are SAED patterns from the new compound. The phase has a hexagonal structure with a and c lattice parameters of 3.05 Å and 18.19 Å, respectively. The possibility that those patterns originate from a 312 MAX structure (i.e., the hypothetical Mo_3GaC_2 which is not stable [5]) can be excluded for the following reasons. As noted above, the chemical composition analysis shown in Fig. 2c exhibits a different Mo/Ga ratio from that of Mo_3GaC_2 phase. The structure is also not that of Ta_2S_2C and Nb_2S_2C phases, which have the same[7, 8], or at least similar "221" stoichiometries, since they belong to the space group R-3m. Furthermore the stacking observed in HRSTEM (below), is inconsistent with either of these sulphides or a 312 MAX phase.



To reveal the detailed structure, Z contrast image was carried out by HRSTEM. Figures 2c and 2d show HRSTEM images with the beam aligned along the $[11\bar{2}0]$ and $[10\bar{1}0]$ zone axes, respectively. The Z contrast images show a double-layer structural feature. The bright and dark spots should correspond to the Mo and Ga atoms, respectively.

Fig. 2 (a) Selected area electron diffraction of Mo_2Ga_2C thin films in $[11\bar{2}0]$ and, (b) $[10\bar{1}0]$ zone axes, (c) EDS spectrum; d) HAADF images in the (d) $[11\bar{2}0]$ and, (e) $[10\bar{1}0]$ zone axes. Insets are corresponding atomic structure models of indicating corresponding positions of Ga and Mo atoms in the stacking sequence.

The corresponding EDX maps shown in Figs. 3(a-f) confirm the Mo-Mo-Ga-Ga-Mo-Mo layering. The simplest description of the structure is the following: Start with a 211 MAX phase structure and simply insert one extra Ga layer on top of the existing Ga. Surprisingly, the two Ga layer lie exactly on top of each other (i.e. not close-packed), an unusual arrangement indeed.

Based on the Z-contrast images, the distance between adjacent Mo layers was estimated to be 2.27 Å. The separation width between the Mo and Ga layers is shortest: 2.09Å. The same stacking position of the two adjacent Ga layers leads a large separation width. The separation width between the adjacent Ga layers is about 2.64 Å. Based on the measured data, initial atomic positions of Mo and Ga are found and used as input data to the Rietveld refinement below.

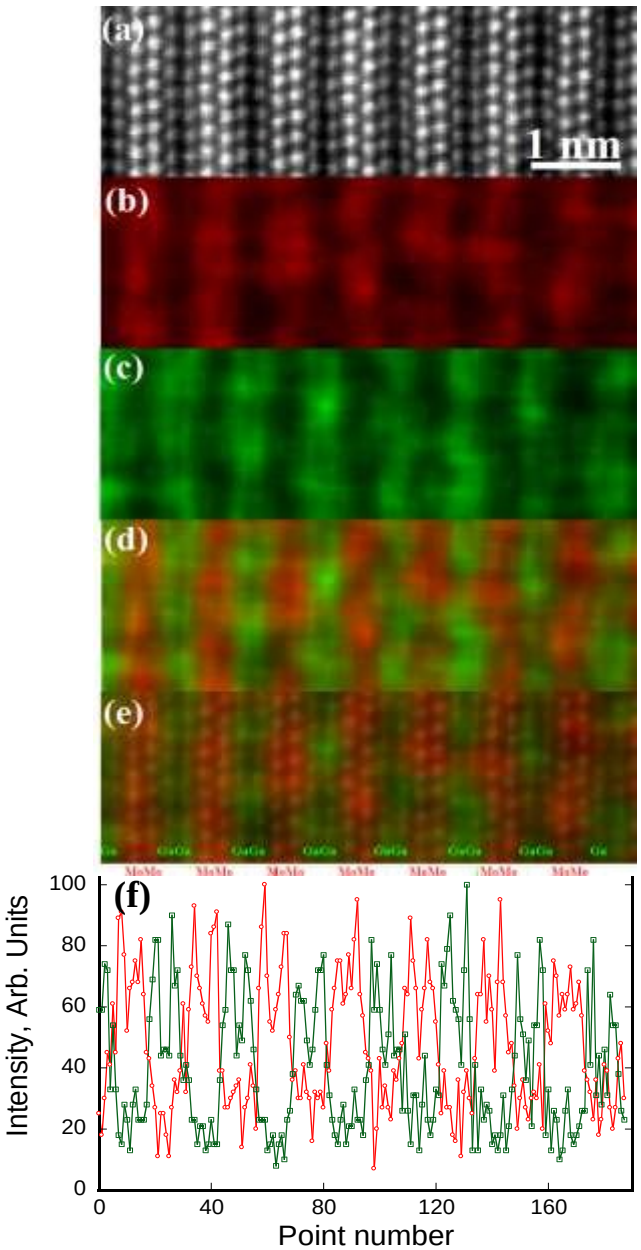


Fig. 3 (a) HAADF image and corresponding, b) Mo, c) Ga, and, d) Mo and Ga maps, (e) HAADF image superimposed with Mo and Ga maps, (f) line scan along [0001] direction a Mo_2Ga_2C film.

Figure **4** shows a typical XRD pattern of the phase obtained after dissolving the unreacted Ga from the bulk sample. When this new phase was imaged in a HRSTEM (see above) its structure was found to be unlike any other MAX phase known in that there were two Ga layers separating the Mo_2C blocks. Making use of this insight, the XRD pattern was analysed assuming the unit cell shown in inset of Fig. 4.

To determine the composition of this new phase elastic recoil detection analysis (ERDA) was carried out on a close to phase pure thin film sample containing traces of Mo-C intermetallic phases, and the Mo, Ga and C contents, in at. %, were found to be, respectively, 38.9%, 42.5%, 18.3%, with a trace amount of oxygen. (0.34 at. %). The composition is consistent with 2:2:1 within the error margins of the technique.

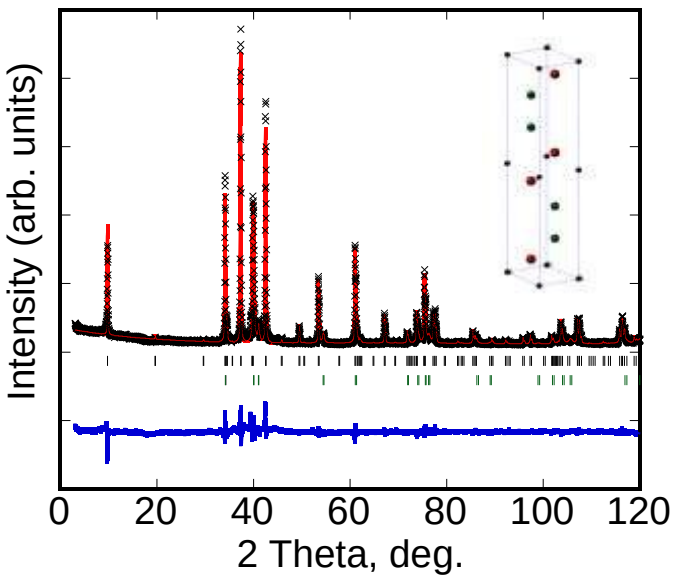


Fig. 4 Powder XRD patterns indexed to Mo_2Ga_2C showing observed pattern (black crosses), Rietveld generated pattern (red line) and difference between the two (blue line). The black and green ticks below the pattern represent the peak positions of Mo_2Ga_2C phase, and Mo_2C phase, respectively. The χ^2 value was 4.93. Inset shows schematic of unit cell where Ga atoms are green, Mo are red and carbon are black.

The results of Rietveld analysis are summarized in Table 1. The space group assumed was that of the MAX phases: P63/mmc The a and c-lattice parameters were calculated to be 3.03396(4) Å and 18.0814(3) Å, respectively. The overall temperature factor was calculated to be 0.22(3) $Å^2$ with 6.5(6) % of the sample is preferably oriented in the direction of (00l). The presence of 19.8(4) wt% of Mo_2C was also found. When this phase was taken into account the χ^2 value was 4.93. The occupancies for all atoms were fixed to be 100%.

A list of the hkl indices of the various peaks – theoretical and experimentally observed - and their intensities and d spacings are listed in Table S1, which shows generally good agreement between theory and experiment. It should be noted here that since the simple

hexagonal arrangement of the Ga atoms is somewhat unusual, other arrangements were tested, where the Ga layers were sheared with respect to each other. The χ^2 values in those cases were significantly higher than for the unit cell shown in inset of Fig. 1a

Table 1: Atomic positions in Mo_2Ga_2C determined from Rietveld analysis of XRD pattern shown in Fig. 1. The space group was P63/mmc. The a and c-lattice parameters were calculated to be 3.03396(4) Å and 18.0814(3) Å, respectively.

Element	x	y	z	Wykcoff positions
Mo	1/3	2/3	0.06571(11)	4f
Ga	1/3	2/3	0.68247(13)	4f
C	0	0	0	2a

The importance of this work lies beyond the discovery of a totally new phase, as exciting as that may be. After Kudielka and Rohde, [9] discovered the first MAX phase – then referred to as a H phase – in 1960, Nowotny and co-workers discovered over 50 such phases including the 312 phases.[10] In 1999 Ti_4AlN_3 - the first 413 phase – was discovered; [11] since then over five 413 phases have been discovered, *not* including solid solutions. Based on this track record it is quite reasonable to assume that Mo_2Ga_2C is the first of distinct family of MAX-related phases.

Notes and references

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