



Full length article

# Theoretical stability and materials synthesis of a chemically ordered MAX phase, $\text{Mo}_2\text{ScAlC}_2$ , and its two-dimensional derivate $\text{Mo}_2\text{ScC}_2$ MXene

Rahele Meshkian<sup>\*</sup>, Quanzheng Tao, Martin Dahlqvist, Jun Lu, Lars Hultman, Johanna Rosen

Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

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## ABSTRACT

We present theoretical prediction and experimental evidence of a new MAX phase alloy,  $\text{Mo}_2\text{ScAlC}_2$ , with out-of-plane chemical order. Evaluation of phase stability was performed by *ab initio* calculations based on Density Functional Theory, suggesting that chemical order in the alloy promotes a stable phase, with a formation enthalpy of  $-24$  meV/atom, as opposed to the predicted unstable  $\text{Mo}_3\text{AlC}_2$  and  $\text{Sc}_3\text{AlC}_2$ . Bulk synthesis of  $\text{Mo}_2\text{ScAlC}_2$  is achieved by mixing elemental powders of Mo, Sc, Al and graphite which are heated to  $1700$  °C. High resolution transmission electron microscopy reveals a chemically ordered structure consistent with theoretical predictions with one Sc layer sandwiched between two Mo–C layers. The two-dimensional derivative, the MXene, is produced by selective etching of the Al-layers in hydrofluoric acid, resulting in the corresponding chemically ordered  $\text{Mo}_2\text{ScC}_2$ , i.e. the first Sc-containing MXene. The here presented results expands the attainable range of MXene compositions and widens the prospects for property tuning.

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## 1. Introduction

It has been about six decades since Nowotny et al. discovered a family of laminated material called *H*-phases [1]. After their revival by Barsoum et al. some decades later [2], the family was expanded and given the nomenclature  $M_{n+1}AX_n$  (MAX) phases,  $n = 1-3$ , being composed of an early transition metal (*M*), an *A*-group element primarily from group 13 and 14 (*A*), and carbon and/or nitrogen (*X*). These compounds are inherently laminated, and exhibit a combination of metallic and ceramic properties which stem from strong metallic-covalent *M*-*X* bonds in combination with weaker bonding between *M*-*A* atoms. Consequently, MAX phases display high electrical and thermal conductivity, good resistance to oxidation and thermal shock, and are elastically stiff and easily machinable. To date, more than 70 MAX phases have been synthesized in both bulk and thin film form.

Substitution of a fraction of *M*, *A*, or *X* atoms can be beneficial for property tuning, e.g., for increasing the hardness [3], or for introducing magnetic properties [4,5]. MAX phase alloys to date are to a major extent solid solutions, and in particular alloys of  $211$  ( $n = 1$ )

stoichiometry have not shown any tendency to order in atomic layers composed of one element only, possibly due to a high configurational entropy within these systems and only one crystallographic site for each *M*, *A*, and *X* element [6]. This is opposed to quaternary MAX phases of  $312$  ( $n = 2$ ) or  $413$  ( $n = 3$ ) stoichiometry and with *M*-site alloying, which can display an out-of-plane chemical order. Such examples are the recently reported  $\text{Mo}_2\text{TiAlC}_2$  and  $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ , which were theoretically predicted and subsequently synthesized by Anasori et al. [7]. This is in addition to previously discovered  $\text{Cr}_2\text{TiAlC}_2$  and  $\text{V}_{1.5}\text{Cr}_{1.5}\text{AlC}_2$ , reported by Liu et al. [8] and Caspi et al. [9], respectively. Note that for  $\text{V}_{1.5}\text{Cr}_{1.5}\text{AlC}_2$ , a partially ordered structure has been observed. In an explanatory and predictive theoretical study by Dahlqvist et al. [6], the authors have investigated the stability of  $\text{TiMAiC}$ ,  $\text{TiM}_2\text{AlC}_2$ ,  $\text{MTi}_2\text{AlC}_2$ , and  $\text{Ti}_2\text{M}_2\text{AlC}_3$  where *M* is from group 4–6 in the Periodic table of elements, trying to identify the origin behind the chemical ordering. Extending beyond that study, exploring a combination of *M* elements that can neither be found in a pure  $312$  MAX phase nor energetically promote a stacking in which *M* is surrounded by *C* in a face-centered cubic (fcc) configuration, we have here investigated quaternary MAX phases in the Mo–Sc–Al–C system.

Interest in Al-containing MAX phases increased after evidence of their resistance to oxidation upon formation of protective oxide layers [10,11], also used in studies focused towards crack healing

\* Corresponding author.

E-mail address: [rahele.meshkian@liu.se](mailto:rahele.meshkian@liu.se) (R. Meshkian).

[12,13]. Moreover, selective etching of Al has been shown to produce MXenes, graphene analogous materials that are both electrically conducting and hydrophilic [14]. The quest for Mo-containing MXenes in particular was elevated after a number of theoretical studies, predicting these compounds as promising thermoelectric material [15], as catalyst [16] and also as efficient electrodes for Li-ion batteries [17]. The first Mo<sub>2</sub>C MXene was reported in 2015 [18,19], and has since been found to have high potential for, e.g., energy storage, in particular for electrode material in e.g. Li-ion batteries [20].

There is only one previous report stating synthesis of a Sc-based MAX phase; Sc<sub>2</sub>InC [1,21]. However, no information is presented on the specific synthesis conditions, and no experimental evidence of the resulting material or its properties. There is a theoretical report on the structural and elastic properties of a number of known and hypothetical M<sub>2</sub>InC phases with M = Sc, Ti, V, Nb, Zr, Hf and Ta. Beside the calculated crystal parameters, the authors have reported the theoretical Young's, shear, and bulk moduli, which for Sc<sub>2</sub>InC are well below the other phases investigated [22].

Consequently, exploring synthesis of a MAX phase based on Al, Mo and Sc is highly motivated from a fundamental as well as a property perspective. In the present study, we have theoretically predicted and experimentally verified the existence of Mo<sub>2</sub>ScAlC<sub>2</sub> as a new chemically ordered MAX phase. Structural and compositional characterization show separation of the elements into individual atomic layers. Furthermore, we present evidence of the corresponding MXene; Mo<sub>2</sub>ScC<sub>2</sub>.

## 2. Computational details

First-principles calculations were performed by means of density functional theory (DFT) and the projector augmented wave method [23,24] as implemented within the Vienna *ab-initio* simulation package (VASP) [25–27]. We adopted the non-spin polarized generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof (PBE) [28] for treating electron exchange and correlation effects. A plane-wave energy cut-off of 400 eV was used and for sampling of the Brillouin zone we used the Monkhorst–Pack scheme [29]. For each considered phase the calculated total energy is converged to within 0.5 meV/atom with respect to *k*-point sampling and structurally optimized in terms of unit-cell volumes, *c/a* ratios (when necessary), and internal parameters to minimize the total energy.

Chemically disordered structures denote a solid solution of Sc and Mo on the *M*-sites. These are modelled using the special quasi-random structure (SQS) method [30,31] on supercells of 4 × 4 × 1 M<sub>3</sub>AX<sub>2</sub> unit cells, with a total of 96 *M*-sites, respectively. Convergence tests with respect to total energy show that these sizes are appropriate to use, based on an energy of the 4 × 4 × 1 unit cells being within 2 meV/atom compared to larger supercells.

Evaluation of phase stability was performed by identifying the set of most competing phases at a given composition, using a linear optimization procedure [31,32] including all competing phases in the system. A phase is considered thermodynamically stable when its energy is lower than the set of most competing phases, and when there is no imaginary frequencies in phonon spectra, i.e. an indicated dynamic stability. The approach has been proven successful to confirm already experimentally known MAX phases as well as to predict the existence of new ones [7,33,34].

When the temperature *T* ≠ 0 K, Gibbs free energy of a disordered phase, Δ*G*<sub>cp</sub><sup>disorder</sup>, can be approximated using

$$\Delta G_{cp}^{\text{disorder}} = \Delta H_{cp}^{\text{disorder}} - T\Delta S, \quad (1)$$

where Δ*H*<sub>cp</sub><sup>disorder</sup> is the formation enthalpy and Δ*S* is the entropy per formula unit of an ideal solution of Sc and Mo atoms on the *M*-sites, expressed as

$$\Delta S = -yk_B[z \ln(z) + (1 - z) \ln(1 - z)], \quad (2)$$

where *y* is number of *M*-sites per formula unit, i.e., *y* = *n* + 1, and *z* = *Mo*/(*Sc* + *Mo*).

Moreover, when *T* ≠ 0 K, the configurational entropy Δ*S* will decrease the free energy, Δ*G*<sub>cp</sub><sup>disorder</sup>, for the solid solution. By using Eqs. (1) and (2), an order-disorder temperature *T*<sub>disorder</sub> can be calculated for which Δ*G*<sub>cp</sub><sup>disorder</sup>[*T*] = Δ*H*<sub>cp</sub><sup>order</sup>. This gives an estimate above which temperature the disordered structure is energetically favorable as compared to the ordered structure. The temperature can then be compared to the experimental conditions used, e.g., typical bulk synthesis temperatures of 1200–1600 °C (1473–1873 K).

## 3. Experimental details

Elemental powders of graphite (99.999%), Mo (99.99%), (Sigma-Aldrich), Sc (99.99%, Stanford Advanced Material), Al (99.8%, ALFA AESAR) with mesh sizes of 200, 400, 200 and 200, respectively, were used for the materials synthesis. These powders were mixed in an agate mortar and placed in a covered Al<sub>2</sub>O<sub>3</sub> crucible, which was inserted in a tube furnace. This was heated at a rate of 10 °C per minute up to 1700 °C, where it was kept for 30 min, with a resulting total duration of 4 h. After cooling down to room temperature in the furnace, the sintered sample was crushed and mixed, resulting in a fine Mo<sub>2</sub>ScAlC<sub>2</sub> powder.

Structural characterization was performed by X-ray diffraction (XRD) on a diffractometer (Rikagu Smartlab, Tokyo, Japan), with Cu-K<sub>α</sub> radiation (40 kV and 44 mA). *θ*-2*θ* scans were recorded between 3° and 120° and step scans of 0.02° with a step size of 7 s. The scan was analyzed by Rietveld refinement using FULLPROF code [35,36]. The fitting parameters used in the program were 5 backgrounds parameters, scale factor, *X* and *Y* profile parameter to limit the peak width to the major phase, lattice parameters, atomic positions and occupancies for all phases, and overall B-factor for the main phase. Both MAX and MXene samples were also characterized by using the Linköping double C<sub>s</sub> corrected FEI Titan3 60–300 operated at 300 kV, equipped with the Super-X EDX system to perform atomic structural analysis.

For MXene preparation, ~1 g of the fine powder was added to ~20 ml of 48% aqueous hydrofluoric acid (HF), and kept at 50 °C for a duration of ~16 h. The suspension was afterwards filtered and dispersed in water ~10 times in order to remove all the remaining acid and the reaction products. Subsequent intercalation of the MXene sheets were realized by adding ~0.1 g of the powder in ~1 ml of an organic base, tetrabutylammonium hydroxide (TBAOH), and shaking it manually for ~5 min. After centrifuging the solution for 5 min the remaining TBAOH can be washed away using water, a procedure repeated 2–3 times.

## 4. Results and discussion

For Mo<sub>2</sub>ScAlC<sub>2</sub> and Sc<sub>2</sub>MoAlC<sub>2</sub>, six different layer sequences were considered, see Anasori et al. [37] for layer stacking definitions. In addition, a solid solution of Sc and Mo on the *M*-sites was also taken into account, see Data in Brief Table 1.

Only Mo<sub>2</sub>ScAlC<sub>2</sub> of order A, i.e., with Sc at Wyckoff site 2a and Mo at site 4f, is predicted stable at 0 K with a calculated formation enthalpy of –24 meV/atom. A complete list of considered competing phases used for the phase stability evaluation can be

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