

This is the accepted manuscript made available via CHORUS. The article has been published as:

Materials synthesis, neutron powder diffraction, and first-principles calculations of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ i-MAX phase used as parent material for MXene derivation

A. Mockute, Q. Tao, M. Dahlqvist, J. Lu, S. Calder, E. N. Caspi, L. Hultman, and J. Rosen

Phys. Rev. Materials **3**, 113607 — Published 27 November 2019

DOI: [10.1103/PhysRevMaterials.3.113607](https://doi.org/10.1103/PhysRevMaterials.3.113607)

Materials synthesis, neutron powder diffraction, and first principles calculations of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ *i*-MAX phase used as parent material for MXene derivation

A. Mockute,^{1,2} Q. Tao,¹ M. Dahlqvist,¹ J. Lu,¹ S. Calder,² E. N. Caspi,³ L. Hultman,¹ J. Rosen¹

¹*Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*

²*Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA*

³*Physics Department, Nuclear Research Centre - Negev, P.O. Box 9001, Beer Sheva 84190, Israel*

Abstract

The research on low-dimensional materials has increased drastically in the last decade, with the discovery of 2D transition metal carbides and nitrides (MXenes) produced by atom-selective chemical etching of laminated parent $M_{n+1}AX_n$ (MAX) phases. Here, we apply density functional theory and subsequent materials synthesis and analysis to explore the phase stability and Mo/Sc intermixing on the *M*-site in the chemically ordered quaternary *i*-MAX phase $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$. Transmission electron microscopy confirms the theoretical predictions of preferential in-plane ordering of Mo and Sc, with the highest crystal quality obtained for the ideal Mo:Sc ratio of 2:1 (predicted as the most stable), as well as a retained *i*-MAX structure even for an increased relative Sc content, with Sc partially occupying Mo sites. The results are supported by refined neutron diffraction data, which show space group $C2/c$ (#15), and a C occupancy of 1. Subsequent chemical etching produces MXene for $x = 0.66$, while for $x = 0.33$ and 0.5 no MXene is observed. These results demonstrate that a precise control of the *i*-MAX composition is crucial for derivation of MXene, with a MXene quality optimized for a Mo:Sc ratio of 2:1 with minimal intermixing between Mo and Sc.

Introduction

Inherent atomic laminates with the general formula $M_{n+1}AX_n$ (M – early transition metal, A – A-group element, X – C or N, and $n = 1-3$) constitute a family of ~155 members of isostructural carbides and nitrides [1]. Commonly being referred to as MAX phases, they combine both metallic and ceramic properties with extreme damage tolerance, and are promising candidates for applications such as high temperature components, sliding electrical contacts, and contacts for 2D electronic circuits [2, 3]. This group of materials offers exceptional prospects for property tuning through simultaneous control of structure and composition as well as a large number of MAX phase forming elements, and is thus a vast playground for synthesis of multicomponent alloys [4-6]. Further manipulation of the composition and structure can be achieved through variation of the layer stacking sequence, resulting in MAX phase-like structures such as M_2A_2X [7-9] and $M_3A_2X_2$ [9], and selective removal of the *A* layer through chemical etching, a more recent pathway for obtaining novel two-dimensional (2D) MAX phase derivatives termed MXenes [10, 11]. Compared to other well-known 2D materials, such as graphene and transition metal dichalcogenides (TMD), MXenes stand out with extreme chemical versatility further complemented with surface functionalization. They are, unlike most other 2D materials, combining being conductive and hydrophilic [11] which allows formation of stable water-based colloidal solutions.

One of the most recent achievements in MAX-phase research is synthesis of chemically-ordered quaternaries, where *M*-site alloying realizes both out-of-plane and in-plane elemental

order, referred to as *o*-MAX and *i*-MAX phases, respectively. Preferential arrangement of *M* element into distinct layers (*o*-MAX) has so far been observed in $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ [12], $(\text{Cr}_{1/2}\text{V}_{1/2})_{n+1}\text{AlC}_n$ for $n = 2$ and 3 [13], $(\text{Mo}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ [14, 15], $(\text{Mo}_{1/2}\text{Ti}_{1/2})_4\text{AlC}_3$ [15] and $(\text{Mo}_{2/3}\text{Sc}_{1/3})_3\text{AlC}_2$ [16]. In Ti-containing *o*-MAX phases ordering is suggested to originate from *M* elements surrounded by C in a face-centered cubic configuration being energetically unfavorable for one of the *M* elements, thus forcing preferential bonding to the *A* element (Al) and therefore separating the different type of *M* elements into distinct layers [17]. In-plane chemical order (in *i*-MAX), on the other hand, originates at least in part from a difference in atomic size of the two *M* elements [18, 19]. The first reported example was $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ [20], soon thereafter followed by $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ [21], $(\text{Cr}_{2/3}\text{Y}_{1/3})_2\text{AlC}$ [21], $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ [22], $(\text{V}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ [19], $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlC}$ [19], $(\text{W}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ [23], $(\text{W}_{2/3}\text{Y}_{1/3})_2\text{AlC}$ [23], $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$ [18], $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{GaC}$ [18], and $(\text{Mo}_{2/3}\text{RE}_{1/3})_2\text{AlC}$, where RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu [24]. It is interesting to note that all discovered *o*-MAX phases crystallize in $n = 2$ and 3 stoichiometries, while *i*-MAX phases have so far been observed solely for $n = 1$. The stoichiometry seems to be the determining factor for the type of ordering, exemplified from the quaternary Mo-Sc-Al-C system with Mo:Sc ratios of 2:1 and formation of *o*-MAX $(\text{Mo}_{2/3}\text{Sc}_{1/3})_3\text{AlC}_2$ vs. *i*-MAX $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$. An important feature of *i*-MAX phases such as $(\text{Mo}_{2/3}M_{1/3})_2\text{AlC}$ and $(\text{W}_{2/3}M_{1/3})_2\text{AlC}$ where $M = \text{Sc}$ and Y , is that chemical etching extracts not only the *A* element Al, but also the *M* element Sc and Y, resulting in $\text{Mo}_{1.33}\text{C}$ and $\text{W}_{1.33}\text{C}$ MXenes with ordered vacancies. These MXenes have demonstrated superior volumetric capacitance and promising catalytic properties [23, 25, 26].

The formation of quaternary *i*-MAX phases is a recent discovery, where the atomic structure and space group determination has been identified from X-ray diffraction combined with electron microscopy. However, a more detailed analysis of both structure and composition is required, not only for fundamental understanding of the origin of the *i*-MAX formation, but also for controlled realization of corresponding MXene. How sensitive the latter is to diverging structure and composition from the ideal *i*-MAX phase is also important information for potentially controlling the vacancy formation in the 2D counterpart. In the present study we have therefore investigated the theoretical stability of the first *i*-MAX phase discovered, $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$, upon a Mo:Sc ratio diverging from the ideal 2:1 ratio. Furthermore, corresponding experimental synthesis shows evidence for a retained *i*-MAX structure even for an increased relative Sc content, verified from structure and occupancy analysis through neutron powder diffraction. In addition, we accurately determined the position of C by neutron powder diffraction. Subsequent MXene derivation is, moreover, found to be sensitive to the *i*-MAX composition.

Computational details

We have used a theoretical approach based on the MIT *ab initio* phase stability (MAPS) [27] code as implemented in the alloy theoretic automated toolkit (ATAT) [28], within a high-throughput density functional theory (DFT) framework to investigate alloying trends within the *M*-sublattice of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$. Furthermore, to simulate disordered solid solutions of Mo and Sc we used the special quasirandom structures (SQS) method [29]. To ensure convergence of SQS generated supercells with respect to energy and structural parameters, we generate supercells with different number of atoms for each composition. For supercells with more than 144 atoms, the energy difference was within 5 meV/atom, and the lattice parameters were within 0.5 %.

Electronic structure calculations were carried out using DFT and the projector augmented wave method [30, 31] with the Perdew-Burke-Ernzerhof (PBE) [32] generalized gradient approximation (GGA) exchange-correlation potential as implemented within the Vienna *ab initio* simulation package (VASP) [33-35]. The electronic wave functions were expanded in a plane-wave basis set with a cutoff energy of 400 eV, and for sampling of the Brillouin zone we used Monkhorst-Pack [36] with 5000 k -points per reciprocal atom. All calculations were performed at zero pressure and at 0 K.

We also investigated the stability of the $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ system for x diverging from the ideal *i*-MAX composition of $x = 2/3$. For a given $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ composition, a linear optimization procedure [6, 37] was used to identify a set of most competing phases, typically denoted the equilibrium simplex. The stability is evaluated in terms of the formation enthalpy ΔH_{cp} by comparing the energy of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ to the identified equilibrium simplex according to

$$\Delta H_{\text{cp}} = E[(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}] - E[\text{equilibrium simplex}], \quad (1)$$

where $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ is considered stable for $\Delta H_{\text{cp}} < 0$, and not stable or at best metastable for $\Delta H_{\text{cp}} > 0$. All considered phases within the quaternary Mo-Sc-Al-C system along with the structural information and calculated total energies are presented in **Table S1** [38].

At finite temperature, $T > 0$ K, the Gibbs free energy $\Delta G_{\text{cp}}^{\text{disorder}}[T]$ for a disordered distribution of Mo and Sc is approximated using

$$\Delta G_{\text{cp}}^{\text{disorder}}[T] = \Delta H_{\text{cp}}^{\text{disorder}}[0 \text{ K}] - TS, \quad (2)$$

where T is the temperature and S is the configurational entropy per formula unit for an alloy with random distribution of Mo and Sc on the M sublattice. S is approximated using

$$S = \alpha \{-k_B [x \ln x + (1 - x) \ln(1 - x)]\}, \quad (3)$$

where k_B is the Boltzmann's constant, x is the concentration of Mo on the M sublattice, and the prefactor α is 1/2 when we consider disorder on the entire M sublattice. For partially disordered intermixing of Sc on the Mo-sites in an ideal *i*-MAX structure, see **Figure 1**, α is 1/3 since Mo and Sc occupy different M -sublattices. The in-plane ordering for an ideal *i*-MAX structure can be described as a characteristic alternating two Mo and one Sc atom arrangement within M -layers, revealed in [010] and [110] orientations, with Sc atoms slightly extending out towards Al-layers (see **Figure 1**).

To determine the dynamical stability of the studied ordered structure, we performed phonon calculations using density functional perturbation theory along with Phonopy [39].

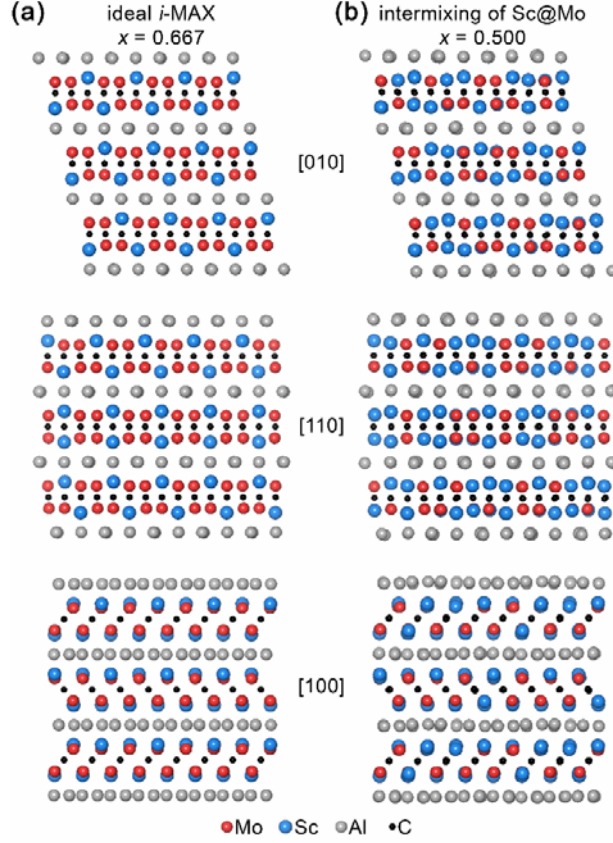


Figure 1 Schematic illustration of (a) an ideal *i*-MAX structure, with $x = 2/3$ in $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$, compared to (b) an *i*-MAX structure with 25 % intermixing of Sc on the Mo-sites in (a), $x = 0.500$, along [010], [110], and [100] zone axis. Molybdenum, scandium, aluminum, and carbon are in red, blue, grey, and black, respectively.

Experimental details

Elemental powders of Mo (99.99 %, Sigma-Aldrich), Sc (99.99 %, Stanford Advanced Material), Al (99.8 %, Alfa Aesar), and graphite (99.999 %, Sigma Aldrich) were mixed in nominal $(\text{Mo}_{1/3}\text{Sc}_{2/3}\text{Al})_2\text{C}$, $(\text{Mo}_{1/2}\text{Sc}_{1/2}\text{Al})_2\text{C}$, and $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ ratios and placed in a capped Al_2O_3 crucible. The powder mixtures were heated in a tube furnace at a rate of 8 °C/min up to 1500 °C where it was held for 10 h under flowing of Ar. After cooling down to room temperature (RT) in the furnace, the pellet was crushed into fine powder.

The etching of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ has been reported previously [24]. In short, 1 g of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ was etched in 20 ml 48% HF for 24 h at room temperature. The etching of $(\text{Mo}_{1/3}\text{Sc}_{2/3})_2\text{AlC}$ and $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ was attempted by adding 1 g of each into 20 ml 20% HF at room temperature for 1h.

X-ray diffraction (XRD) was carried out on a PANalytical X'Pert powder diffractometer, with a line focus Cu source ($\lambda_{\text{Cu}} = 1.54 \text{ \AA}$). Scanning transmission electron microscopy combined with high angle annular dark field imaging (STEM-HAADF) was performed in the double-corrected Linköping FEI Titan³, operated at 300 kV. Selected area electron diffraction (SAED) was performed on a FEI Tecnai T20 TEM operated at 200 kV. Energy dispersive X-ray spectroscopy (EDX, Oxford Instruments X-Max detector) was performed inside a scanning electron microscope (SEM, LEO 1550). Neutron powder diffraction (NPD) analysis

of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ and $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ has been carried out using the HB-2A high-flux powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory (ORNL, USA). 5 g of powder sample was loaded in a vanadium cylindrical sample holder. Measurements were performed with $\lambda = 1.54 \text{ \AA}$ neutron wavelength produced by (115) reflections from a vertically focusing Ge monochromator. The data was collected by a 44 ^3He detector bank covering 2θ range of 7° – 150° in steps of 0.05° at room temperature.

Results and Discussion

Figure 2a shows the calculated formation enthalpies ΔH_{cp} (per atom) derived from different chemically-ordered configurations within the M sublattice in $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$. The identified set of the most competing phases used to calculate ΔH_{cp} at given x is found in **Table S2**. In total, 1500 structures (fully relaxed), with a unit cell size up to 32 atoms, have been included. In addition, we included chemical disorder through use of SQS supercells assuming the initial MAX phase space group symmetry $P6_3/mmc$ (#194). These cells are found to have energies well above the ordered structures of lowest energy, even when an entropy contribution at 1773 K is considered. This is a clear indication of preference for chemical order, which is most notable at $x = 2/3$, where two low-energy structures, close to degenerate in energy (within 2 meV/atom), are identified with space group symmetry $C2/c$ (#15) and $Cmcm$ (#63). Schematics of these are found in **Figure 3a**, where structure #1404 corresponds to space group symmetry $Cmcm$ (#63), and #546 to space group symmetry $C2/c$ (#15). Both symmetries are previously reported for i -MAX structures [18, 19, 25]. A discussion related to the almost degenerate energies of the two polymorphs, $C2/c$ (#15) and $Cmcm$ (#63), has previously been conducted (see Supporting Information in Ref. [24]). These results support that a 2:1 ratio of the two metals is a specific ratio which induce a strong preference for chemical order. Moreover, both identified structures are dynamically stable, i.e., stable to lattice vibrations with no imaginary phonon frequencies as shown in **Figure S1**.

As x decreases from $2/3$, i.e., with an increasing Sc content, the formation enthalpy of the low-energy structures is increased (stability reduced), see **Figure 2b**, though still stable. A closer examination of several low-energy structures at $x = 1/2$ shows that all bear close resemblance to the ideal i -MAX structure of space group symmetry $C2/c$ (#15), but with intermixing of Sc on the Mo sites, see **Figure 3b** with four such examples. This motivates a more detailed investigation of intermixing of Sc on the Mo sites. We therefore set initial symmetries of both space group 15 and 63 and extend the unit cell up to 192 and 96 atoms, respectively, to model disordered intermixing of Sc on the Mo sites. Corresponding formation enthalpy ΔH_{cp} for the intermixing is shown in **Figure 2b** at 0 K and with entropic contribution to the Gibbs free energy ΔG_{cp} at 1773 K. At 0 K, there is a steady increase in ΔH_{cp} (reduced stability) with increasing Sc intermixing on the Mo sites for both symmetries. However, when considering contribution from configurational entropy at 1773 K, a decrease in ΔG_{cp} (increased stability) is found for intermixing up to ~ 20 at.% Sc on the Mo sites. With an additional degree of intermixing, ΔG_{cp} is increased, but is still stable and well below the curve for complete disorder on the M -lattice (black dashed curve in **Figure 2b**). This indicates that a deviation from the ideal i -MAX ratio of $x = 2/3$ while still retaining the i -MAX structure is possible due to intermixing of Sc on Mo sites, as the Sc site is populated by Sc only, which is, in turn, correlated to the formation of a Kagomé-like structure in the Al layer. This formation has been shown to have a large effect on the resulting low energy and high stability of the i -MAX phases [18, 19]. Structures with $x > 2/3$ in **Figure 2a** (green crosses) are at best equal to the dG line, but most are above. Hence, there is no strong preference for having Mo on Sc-sites.

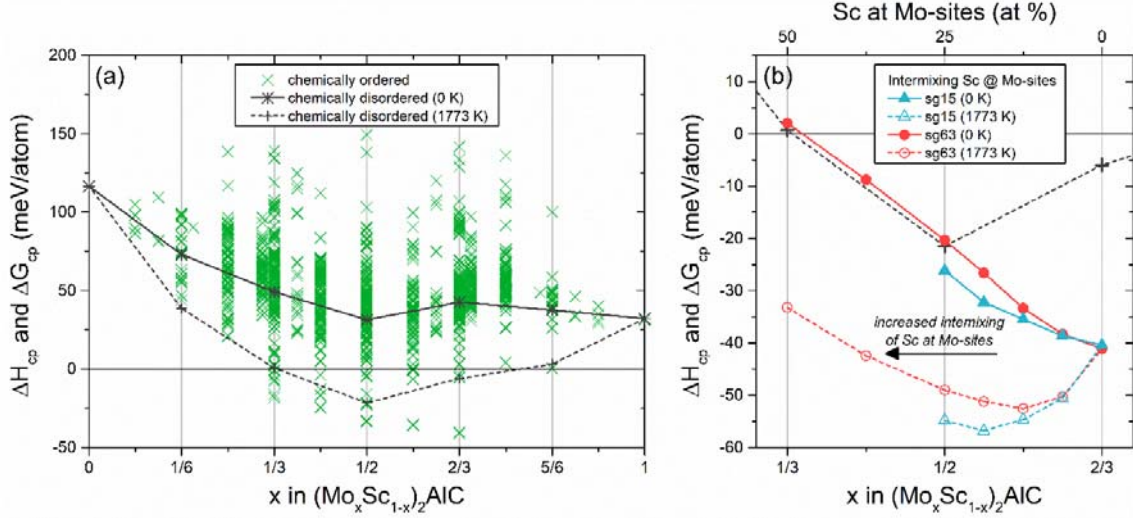


Figure 2 (a) Calculated formation enthalpy for $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ as a function of Mo concentration x for different configurations of chemical order (green cross) and for chemical disorder (black star, solid line) of Mo and Sc. For chemical disorder, the entropy contribution to Gibbs free energy at 1773 K has also been approximated (black plus, dashed line). (b) Calculated formation enthalpy and Gibbs free energy for partial intermixing of Sc on Mo sites in the in-plane ordered $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ *i*-MAX structure considering space group 15 (blue triangles) and space group 63 (red circles) at 0 K (filled symbols) and with entropic contribution to the free energy at 1773 K (open symbols). Here black pluses with solid line are the same as in (a).

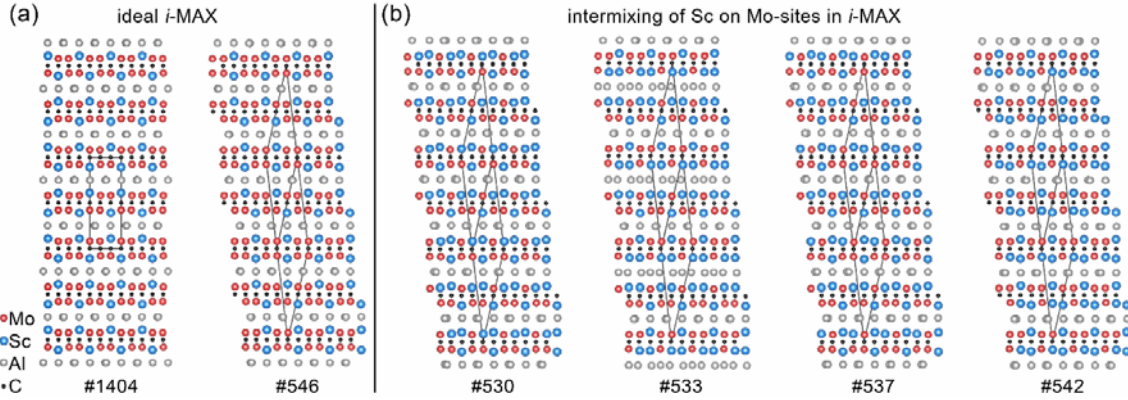


Figure 3 Schematic illustration of low-energy chemically ordered structures identified for $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ with (a) $x = 0.667$ and (b) $x = 0.5$.

Figure S2 shows the calculated structural information of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ with $x = [0.500 - 0.667]$ for initial symmetries of space group 15. $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ is of particular interest in this study, with the following lattice parameters: $a = 9.367 \text{ \AA}$, $b = 5.427 \text{ \AA}$, $c = 13.961 \text{ \AA}$, $\alpha = 90.000^\circ$, $\beta = 103.597^\circ$, and $\gamma = 90.000^\circ$.

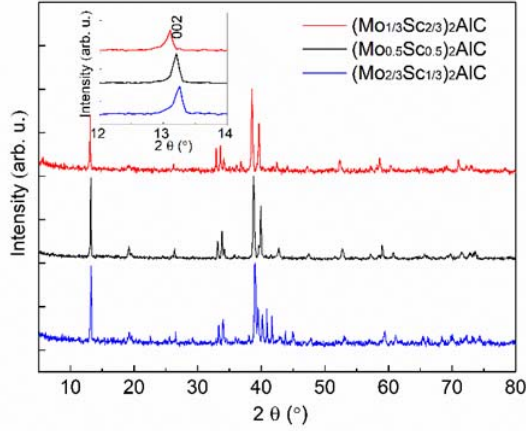


Figure 4 XRD of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ with nominal $x = 0.33, 0.5$, and 0.66 . Inset shows an enlarged view of the (002) peak.

Figure 4 shows XRD patterns of synthesized $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ with nominal $x = 0.33, 0.5$, and 0.66 . The (002) peak shifts towards lower 2θ angles with increasing amount of Sc indicating expansion of the lattice constant c , in agreement with theoretical calculations. Main impurity phases are identified as $\text{Mo}_3\text{Al}_2\text{C}$ together with some ScAl_3C_3 , and Sc_2OC for $x = 0.66$; Sc_2OC and $\text{Sc}_2\text{Al}_2\text{C}_3$ for $x = 0.33$ and $x=0.5$. The MAX phase competing with $\text{Sc}_2\text{OC}/\text{Sc}_2\text{Al}_2\text{C}_3$ in Sc-rich ($x \leq 0.5$) starting powder mixtures results in a deviation from the targeted Mo:Sc ratios. SEM-EDX spectra have been acquired on individual particles of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ (**Figure S3**), where Mo:Sc ratios have been determined as 1.32 and 0.88 for $x = 0.5$ and $x = 0.33$, respectively, i.e. Sc-deficient compared to the corresponding nominal ratios of 1 and 0.5. For Mo-rich starting powder composition ($x = 0.66$), on the other hand, the resulting Mo:Sc ratio of 1.96 is very close to the ideal i -MAX value of 2.

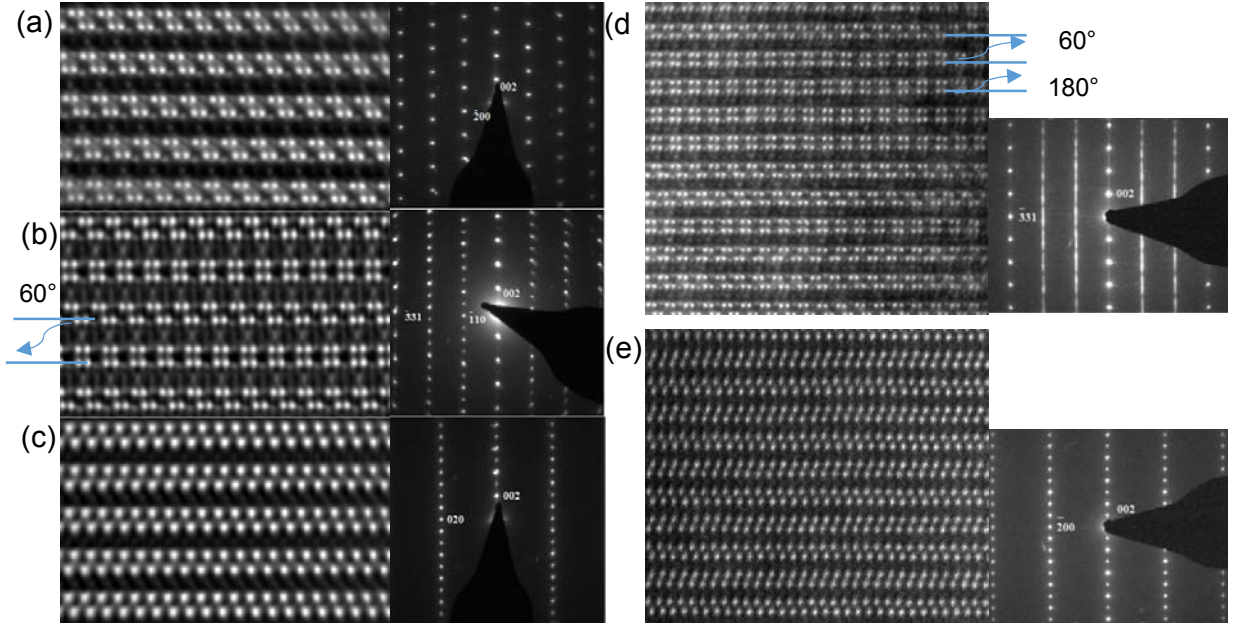


Figure 5 STEM images and corresponding SAED patterns of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ along (a) $[010]$, (b) $[110]$, and (c) $[010]$ zone axes as well as $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ along (d) $[110]$ and (e) $[010]$ zone axes. The arrows indicate two kinds of stacking: 60° rotation or 180° of two adjacent carbide layers.

Figure 5 shows STEM images of two samples, $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ (**Figure 5a-c**) and $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ (**Figure 5d-e**). The crystal structure of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ investigated by STEM has previously been reported by Tao *et al.* [25], and is shown here for comparison. Briefly, $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ crystallizes in the monoclinic $C2/c$ (15) lattice. Mo and Sc atoms form an ordered structure in the transition metal carbide $[(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{C}]$ layers. This in-plane ordered structure stands out as alternating two bright spots and one dark spot in the STEM images, corresponding to two columns of Mo atoms and one column of Sc atoms. The layers are stacked in an $A-B-A-B$ sequence and are rotated by 60° with respect to each other. The readers are referred to Ref. [24] for a detailed description of the stacking sequence. The crystal quality of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{C}$ is higher than that of $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$, where stacking faults were identified as the main defect in the latter sample. **Figure 5d** shows the STEM image of $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ along $[110]$ zone axis. The structure of a single transition metal carbide layer is identical to that of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$. Two bright spots and one dark spot pattern is still present, corresponding to two columns of Mo atoms (or Mo-rich atomic layers) and one column of Sc atoms (or a Sc-rich atomic layer). However, the stacking of ordered $(\text{Mo}_{2/3}\text{Sc}_{1/3})$ layers along c axis can be rotated by 60° or 180° with respect to each other, resulting in a random stacking sequence. For example, arrows and lines in **Figure 5d** indicate two trilayers with two different stacking sequences. In addition, $(-11\bar{1})$ in SAED along $[110]$ axis smears out and becomes a line, instead of well-defined spots found in $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$. An even higher Sc content ($x = 0.33$) further reduces the crystal quality, however, the i -MAX structure is still retained with Sc partially occupying Mo sites (not shown here).

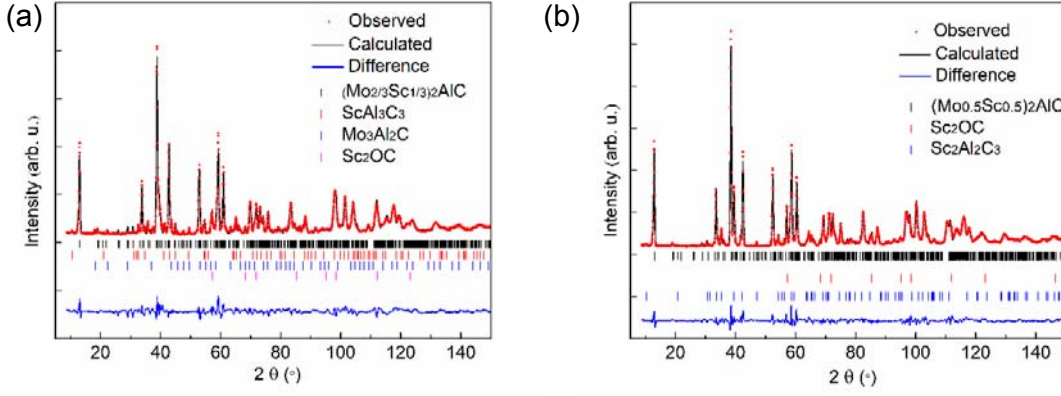


Figure 6 Rietveld analysis of neutron powder diffraction data of (a) $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ and (b) $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$. The observed counts and the refined model are represented by black dots and solid red line, respectively. The difference curve between the data and the model is plotted at the bottom of the figure by a solid blue line. The positions of calculated reflections are marked by short vertical lines.

Figure 6 shows the Rietveld analysis (using the FullProf Suite [40]) of neutron powder diffraction of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ and $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$. Both patterns agree well with that of a model based on the $C2/c$ crystal structure proposed in our previous report [25]. The refined cell parameters and atom coordinates are summarized in **Table 1**. Compared to $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$, the lattice parameters of $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ are larger for all three axes, which is expected considering the larger atomic size of Sc compared to Mo and in agreement with theoretical predictions. The experimentally determined lattice parameters are in excellent correspondence with the calculated values. The phases and their relative amounts included in Rietveld refinement are listed in **Table 2**. It is worth noting that the sample with equal amounts of Mo and Sc has the highest phase purity.

We also consider the effect of intermixing of Mo/Sc on the diffraction pattern for all three metal sites in the $C2/c$ structure. We find that the Sc site is fully occupied by Sc in both compounds, while the Mo sites can be partially occupied by Sc. For the $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$, by adding intermixing on the Sc site, the overall χ^2 remains around 20. However, partially substituting Sc with Mo would quickly suppress the intensity of (110) peak. Thus, we conclude that the Sc site is fully ordered, and keep this fixed in the subsequent refinement. We also refined the occupancy of the Mo sites. By adding Sc on the Mo site, the refinement improves a lot and converges at an occupancy value of 0.707(13) Mo/0.293(13) Sc. Compared to the composition obtained from EDX, the amount of Sc determined from the refinement of the occupancy is slightly higher. For the $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$, we initially constrain the Mo/Sc ratio based on the composition from EDX, and then investigate the distribution of Mo/Sc on the metal sites. Similar to $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$, intermixing on Sc site does not influence much on the overall χ^2 , but quickly suppresses the intensity of (110) peak. We make the conclusion that within the sensitivity of the current diffraction experiment, $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ is fully ordered on both sites. We also note that the refinement suggests a full occupancy of C in both samples.

Table 1 Cell parameters and atom coordinates of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ and $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ obtained from Rietveld refinement of neutron powder diffraction data. Occ. is atomic occupancies. Numbers in parentheses are standard deviations of the last significant digit, representing the statistical uncertainty component.

Sample	$(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$	$(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$
Space group	15 ($C2/c$)	15 ($C2/c$)
χ^2	27.0	22.9
R_{wp}	8.94 %	7.74 %
a (Å)	9.34354(69)	9.41512 (39)
b (Å)	5.39631(37)	5.44870 (20)
c (Å)	13.87249(56)	13.99971 (41)
α (deg)	90	90
β (deg)	103.28733(336)	103.26508(248)
γ (deg)	90	90
Sc	8f (0.95279, 0.42114, 0.10163) Occ. 1	8f (0.95061, 0.41761, 0.10472) Occ. Sc 1
Mo	8f (0.27678, 0.41606, 0.08261) Occ. 1	8f (0.27749, 0.41709, 0.08405) Occ. Mo 0.707(13) Sc 0.293(13)
	8f (0.61569, 0.41319, 0.09051) Occ. 1	8f (0.27749, 0.41709, 0.08405) Occ. Mo 0.707(13) Sc 0.293(13)
Al	8f (0.73088, 0.16544, 0.25073) Occ. Al 1	8f (0.73185, 0.17542, 0.25520) Occ. Al 1
	4e (0.00000, 0.91965, 0.25000) Occ. Al 1	4e (0.00000, 0.92522, 0.25000) Occ. Al 1
C	8f (0.41720, 0.23938, 0.00000) Occ. C 1	8f (0.41534, 0.24111, 0.00000) Occ. C 1
	4d (0.25000, 0.25000, 0.50000) Occ. C 1	4d (0.25000, 0.25000, 0.50000) Occ. C 1

Table 2 Phase composition of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ and $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ samples from Rietveld refinement of neutron diffraction data.

	Sample	
Fract. (%)	$(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$	$(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$
<i>i</i> -MAX phase	77.78 ± 1.17	92.94 ± 1.35
$\text{Mo}_3\text{Al}_2\text{C}$	17.30 ± 0.82	-
ScAl_3C_3	3.07 ± 0.13	-
Sc_2OC	1.85 ± 0.06	3.86 ± 0.11

$\text{Sc}_2\text{Al}_2\text{C}_3$	-	3.20 ± 0.16
------------------------------------	---	-----------------

In our previous work we have shown that selective etching of Sc and Al from $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ leads to formation of $\text{Mo}_{1.33}\text{C}$ MXene with ordered vacancies [25]. A similar etching procedure was also applied to other *i*-MAX phases, $(\text{W}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ and $(\text{W}_{2/3}\text{Y}_{1/3})_2\text{AlC}$, to obtain vacancy-ordered $\text{W}_{1.33}\text{C}$ [23]. Here, we attempted to produce MXene also from $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ with $x = 0.5$ and $x = 0.33$. $(\text{Mo}_{1/3}\text{Sc}_{2/3}\text{Al})_2\text{C}$ reacts readily with HF, while $(\text{Mo}_{1/2}\text{Sc}_{1/2})_2\text{AlC}$ is somewhat slower, however, the reaction in both cases resulted in formation of an unidentified fluoride, and no MXene could be observed (**Figure 7**). This can be explained by the stability of the resulting Mo_xC after removal of Al and Sc atoms. In $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$, Mo and Sc are well ordered with only minor intermixing between respective site, and the remaining $\text{Mo}_{1.33}\text{C}$ slabs after etching (including surface terminations) are relatively stable. On the contrary, for $x < 0.66$, the degree of intermixing is higher with Sc partially occupying the Mo-sites. After Sc removal by HF etching, the remaining Mo_xC becomes unstable and reacts with HF to form a fluoride. These results demonstrate that precise composition control is extremely important in conversion of the MAX phase into MXene. It also suggests that the MXene quality is optimized for a Mo:Sc ratio of 2:1 with minimal intermixing between Mo and Sc. Presumably, the same optimal *M* element ratio is valid for $(\text{W}_x\text{Sc}_{1-x})_2\text{AlC}$, $(\text{W}_x\text{Y}_{1-x})_2\text{AlC}$, and other *i*-MAX phases shown to form MXenes.

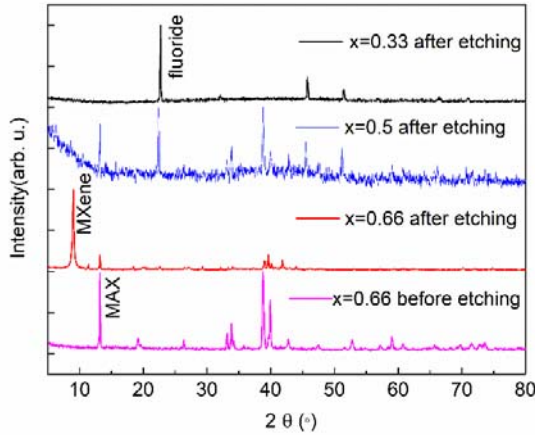


Figure 7 XRD of $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ with nominal $x = 0.33$, 0.5 , and 0.66 after etching in HF. MXene is only produced for composition with $x = 0.66$.

Conclusions

The $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlC}$ *i*-MAX structure of space group 15 is stable for $x = [0.33; 0.66]$ with a strong tendency for in-plane ordering on the *M*-sublattice and with an optimal Mo:Sc ratio of 2:1. Higher Sc content affects the crystal quality, however, the *i*-MAX structure is still retained with Sc partially occupying Mo-sites. Subsequent chemical etching removes both Al and Sc and yields MXene for $x = 0.66$, consistent with previous reports, while for $x < 0.66$ no MXene has been observed, likely due to instability of the remaining Mo_xC slabs. The results show that even though the *i*-MAX phase is stable over a range of relative *M* element compositions, control thereof is crucial for use of the *i*-MAX as a parent material to derive MXene.

Acknowledgements

J.R. acknowledges support from the Swedish Foundation for Strategic Research (SSF) for Project Funding (EM16-0004) and from the Knut and Alice Wallenberg (KAW) Foundation for a Fellowship Grant and Project funding (KAW 2015.0043). All authors also acknowledge support to the Linköping Electron Microscopy Laboratory (KAW), and from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No 2009 00971). The Swedish Research council is also gratefully acknowledged through Project 642-2013-8020 and the VR International Postdoc grant 2015-00607. The calculations were carried out using supercomputer resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC), High Performance Computing Center North (HPC2N) and the PDC Center for High Performance Computing. The project used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

References

- [1] M. Sokol, V. Natu, S. Kota, M.W. Barsoum, On the Chemical Diversity of the MAX Phases, *Trends in Chemistry*, 1 (2019) 210-223.
- [2] M.W. Barsoum, T. El-Raghy, Synthesis and Characterization of a Remarkable Ceramic: Ti_3SiC_2 *Journal of the American Ceramic Society*, 79 (1996) 1953-1956.
- [3] M.W. Barsoum, MAX phases: Properties of machinable ternary carbides and nitrides, Wiley-VCH2013.
- [4] T. Lapauw, B. Tunca, D. Potashnikov, A. Pesach, O. Ozeri, J. Vleugels, K. Lambrinou, The double solid solution $(\text{Zr}, \text{Nb})_2(\text{Al}, \text{Sn})\text{C}$ MAX phase: a steric stability approach, *Sci. Rep.*, 8 (2018) 12801.
- [5] B. Manoun, S.K. Saxena, G. Hug, A. Ganguly, E.N. Hoffman, M.W. Barsoum, Synthesis and compressibility of $\text{Ti}_3(\text{Al}, \text{Sn}_{0.2})\text{C}_2$ and $\text{Ti}_3\text{Al}(\text{Co}_{0.5}, \text{Ni}_{0.5})_2$, *J. Appl. Phys.*, 101 (2007) 113523.
- [6] M. Dahlqvist, B. Alling, J. Rosén, Stability trends of MAX phases from first principles, *Phys. Rev. B*, 81 (2010) 220102.
- [7] C.-C. Lai, R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund, O. Rivin, E.N. Caspi, O. Ozeri, L. Hultman, P. Eklund, M.W. Barsoum, J. Rosen, Structural and chemical determination of the new nanolaminated carbide $\text{Mo}_2\text{Ga}_2\text{C}$ from first principles and materials analysis, *Acta Mater.*, 99 (2015) 157-164.
- [8] C. Hu, C.-C. Lai, Q. Tao, J. Lu, J. Halim, L. Sun, J. Zhang, J. Yang, B. Anasori, J. Wang, Y. Sakka, L. Hultman, P. Eklund, J. Rosen, M.W. Barsoum, $\text{Mo}_2\text{Ga}_2\text{C}$: a new ternary nanolaminated carbide, *Chemical Communications*, 51 (2015) 6560-6563
- [9] H. Fashandi, C.-C. Lai, M. Dahlqvist, J. Lu, J. Rosen, L. Hultman, G. Greczynski, M. Andersson, A. Lloyd Spetz, P. Eklund, $\text{Ti}_2\text{Au}_2\text{C}$ and $\text{Ti}_3\text{Au}_2\text{C}_2$ formed by solid state reaction of gold with Ti_2AlC and Ti_3AlC_2 , *Chemical Communications*, 53 (2017) 9554-9557.
- [10] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, Two - dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 , *Advanced Materials*, 23 (2011) 4248-4253.
- [11] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M.W. Barsoum, Two-dimensional transition metal carbides, *ACS Nano*, 6 (2012) 1322-1331.
- [12] Z. Liu, E. Wu, J. Wang, Y. Qian, H. Xiang, X. Li, Q. Jin, G. Sun, X. Chen, J. Wang, M. Li, Crystal structure and formation mechanism of $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ MAX phase, *Acta Mater.*, 73 (2014) 186-193.
- [13] E.N. Caspi, P. Chartier, F. Porcher, F. Damay, T. Cabioc'h, Ordering of (Cr,V) layers in nanolamellar $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$ compounds, *Mater. Res. Lett.*, 3 (2015) 100-106.
- [14] B. Anasori, J. Halim, J. Lu, C.A. Voigt, L. Hultman, M.W. Barsoum, $\text{Mo}_2\text{TiAlC}_2$: A new ordered layered ternary carbide, *Scr. Mater.*, 101 (2015) 5-7.

- [15] B. Anasori, M. Dahlqvist, J. Halim, E.J. Moon, J. Lu, B.C. Hosler, E.N. Caspi, S.J. May, L. Hultman, P. Eklund, J. Rosen, M.W. Barsoum, Experimental and theoretical characterization of ordered MAX phases $\text{Mo}_2\text{TiAlC}_2$ and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$, *J. Appl. Phys.*, 118 (2015) 094304.
- [16] R. Meshkian, Q. Tao, M. Dahlqvist, J. Lu, L. Hultman, J. Rosen, Theoretical stability and materials synthesis of a chemically ordered MAX phase, $\text{Mo}_2\text{ScAlC}_2$, and its two-dimensional derivate Mo_2ScC_2 MXene, *Acta Mater.*, 125 (2017) 476-480.
- [17] M. Dahlqvist, J. Rosen, Order and disorder in quaternary atomic laminates from first-principles calculations, *Physical Chemistry Chemical Physics*, 17 (2015) 31810-31821.
- [18] M. Dahlqvist, A. Petruhins, J. Lu, L. Hultman, J. Rosen, Origin of Chemically Ordered Atomic Laminates (iMAX): Expanding the Elemental Space by a Theoretical/Experimental Approach *ACS Nano*, 12 (2018) 7761-7770.
- [19] M. Dahlqvist, J. Lu, R. Meshkian, Q. Tao, L. Hultman, J. Rosen, Prediction and synthesis of a family of atomic laminate phases with Kagomé-like and in-plane chemical ordering, *Science Advances*, 3 (2017) 1700642.
- [20] R. Meshkian, Q.Z. Tao, M. Dahlqvist, J. Lu, L. Hultman, J. Rosen, Theoretical stability and materials synthesis of a chemically ordered MAX phase, $\text{Mo}_2\text{ScAlC}_2$, and its two-dimensional derivate Mo_2ScC_2 MXene, *Acta Mater.*, 125 (2017) 476-480.
- [21] J. Lu, A. Thore, R. Meshkian, Q. Tao, L. Hultman, J. Rosén, Theoretical and experimental exploration of a novel in-plane chemically ordered $(\text{Cr}_{2/3}\text{M}_{1/3})_2\text{AlC}$ i-MAX phase with $\text{M} = \text{Sc}$ and Y , *Crystal Growth and Design*, 17 (2017) 5704-5711.
- [22] L. Chen, M. Dahlqvist, T. Lapauw, B. Tunca, F. Wang, J. Lu, R. Meshkian, K. Lambrinou, B. Blanpain, J. Vleugels, J. Rosen, Theoretical prediction and synthesis of $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ i-MAX phase, *Inorganic Chemistry*, 57 (2018) 6237-6244.
- [23] R. Meshkian, M. Dahlqvist, J. Lu, B. Wickman, J. Halim, J. Thörnberg, Q. Tao, S. Li, S. Intikhab, J. Snyder, M.W. Barsoum, M. Yildizhan, J. Palisaitis, L. Hultman, P.O.Å. Persson, J. Rosen, W-Based Atomic Laminates and Their 2D Derivative $\text{W}_{1.33}\text{C}$ MXene with Vacancy Ordering, *Adv. Mater.*, 30 (2018) 1706409.
- [24] Q. Tao, J. Lu, M. Dahlqvist, A. Mockute, S. Calder, A. Petruhins, R. Meshkian, O. Rivin, D. Potashnikov, E.N. Caspi, H. Shaked, A. Hoser, C. Opagiste, R.-M. Galera, R. Salikhov, U. Wiedwald, C. Ritter, A.R. Wildes, B. Johansson, L. Hultman, M. Farle, M.W. Barsoum, J. Rosen, Atomically Layered and Ordered Rare-Earth iMAX Phases: A New Class of Magnetic Quaternary Compounds, *Chemistry of Materials*, 31 (2019) 2476-2485.
- [25] Q.Z. Tao, M. Dahlqvist, J. Lu, S. Kota, R. Meshkian, J. Halim, J. Palisaitis, L. Hultman, M.W. Barsoum, P.O.Å. Persson, J. Rosen, Two-dimensional $\text{Mo}_{1.33}\text{C}$ MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering, *Nature Communications*, 8 (2017) 14949.
- [26] I. Persson, A. el Ghazaly, Q. Tao, J. Halim, S. Kota, V. Darakchieva, J. Palisaitis, M.W. Barsoum, J. Rosen, P.O.Å. Persson, Tailoring Structure, Composition, and Energy Storage Properties of MXenes from Selective Etching of In-Plane, Chemically Ordered MAX Phases, *Small*, 14 (2018) 1703676.
- [27] A. van de Walle, G. Ceder, Automating first-principles phase diagram calculations, *Journal of Phase Equilibria*, 23 (2002) 348.
- [28] A. van de Walle, M. Asta, G. Ceder, The alloy theoretic automated toolkit: A user guide, *Calphad*, 26 (2002) 539-553.
- [29] A. Zunger, S.H. Wei, L.G. Ferreira, J.E. Bernard, Special quasirandom structures, *Phys. Rev. Lett.*, 65 (1990) 353-356.
- [30] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B*, 50 (1994) 17953-17979.
- [31] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, 59 (1999) 1758.
- [32] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.*, 77 (1996) 3865-3868.
- [33] G. Kresse, J. Hafner, Ab initio molecular dynamics for open-shell transition metals, *Phys. Rev. B*, 48 (1993) 13115-13118.

- [34] G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science*, 6 (1996) 15-50.
- [35] G. Kresse, J. Furthmuller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B*, 54 (1996) 11169.
- [36] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B*, 13 (1976) 5188-5192.
- [37] M. Dahlqvist, B. Alling, I.A. Abrikosov, J. Rosén, Phase stability of Ti_2AlC upon oxygen incorporation: A first-principles investigation, *Phys. Rev. B*, 81 (2010) 024111.
- [38] See Supplemental Material at [will be inserted by publisher] for more information., DOI.
- [39] A. Togo, F. Oba, I. Tanaka, First-principles calculations of the ferroelastic transition between rutile-type and CaCl_2 -type SiO_2 at high pressures, *Phys. Rev. B*, 78 (2008) 134106.
- [40] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B: Condensed Matter*, 192 (1993) 55-69.