Prediction and synthesis of a family of atomic laminate phases with Kagomé-like and in-plane chemical ordering

Martin Dahlqvist,* Jun Lu, Rahele Meshkian, Quanzheng Tao, Lars Hultman, Johanna Rosen*

The enigma of MAX phases and their hybrids prevails. We probe transition metal (M) alloying in MAX phases for metal size, electronegativity, and electron configuration, and discover ordering in these MAX hybrids, namely, (V2/3Zr1/3)2AlC and (Mo2/3Y1/3)2AlC. Predictive theory and verifying materials synthesis, including a judicious choice of alloying M from groups III to VI and periods 4 and 5, indicate a potentially large family of thermodynamically stable phases, with Kagomé-like and in-plane chemical ordering, and with incorporation of elements previously not known for MAX phases, including the common Y. We propose the structure to be monoclinic 22/c. As an extension of the work, we suggest a matching set of novel MXenes, from selective etching of the A-element. The demonstrated structural design on simultaneous two-dimensional (2D) and 3D atomic levels expands the property tuning potential of functional materials.

INTRODUCTION

Atomically layered materials, with controlled structure and composition, allow for materials with promise for next-generation memory devices (1), thermoelectrics (2), and energy storage (3–7). Moreover, opportunities for high chemical diversity and structural complexity bring new and unique properties. A material family that holds such promise is the group of the MAX phases—ceramic-metallic hybrids that consist of MXn1 sheets (for example, TiC) sandwiched in between one-atom-thick A-layers (Si, Al, Ga, etc.) (8, 9)—and their two-dimensional (2D) derivatives, MXenes (3, 4, 10, 11).

MAX phases are a group of thermodynamically stable, atomically laminated compounds composed of a transition metal M, an A-group element A, and carbon and/or nitrogen X, of the general formula Mx+1AXn (n = 1 to 3) (8, 9). MAX phases have attracted large interest due to their combination of metallic and ceramic attributes, being electrically and thermally conductive, exceptionally damage tolerant, lightweight, and able to maintain strength at high temperatures (8, 10). Some phases also show self-healing characteristics (12, 13) and reversible deformation (14), and recently, magnetism was added to the long list of obtainable properties (15–18). The family of MAX phases is large (>70 phases and counting).

The possibility of forming solid solutions on the M, A, or X sites have attracted considerable attention (16, 19–24) for effects, such as material strengthening (25), or in general, for the possibility of tuning or altering properties (26, 27). Furthermore, alloying may also allow addition of elements beyond those traditionally used in MAX phases (28–30). However, attaining an exact a priori defined composition for a solid solution is challenging. This is in contrast to chemically ordered systems, where the composition may be governed by the underlying crystal symmetry/lattice.

Recently, Liu et al. (31, 32) synthesized a chemically ordered alloy with a M2AX2 structure, TiCr2AlC2, in which Ti is sandwiched between two Cr-C layers. This was soon followed by the discovery of TiMo2AlC2 (33, 34), V1.5Cr1.5AlC2 (35), Ti2Mo2AlC3 (33), and V2.2Cr1.8AlC3 (35), the latter two with a M2AX3 structure. Most recently, the ordered Mo2ScAlC2 was also reported (36). The stability of these materials is suggested to stem from the following: (i) by multiple M sites that ensure breaking of an energetically unfavorable stacking of M and C, where M is surrounded by C in a face-centered cubic configuration and also (ii) by M having a larger electronegativity than Al, resulting in fewer electrons available for populating antibonding Al-Al orbitals (37). This example of a class of layered MAX phases, displaying out-of-plane chemical ordering, is one for which we introduce the notation α-MAX here.

Notably, chemically ordered MAX phase structures have been reported for 312 (n = 2) and 413 (n = 3) phase structures only, having multiple M sites, each with different symmetry. In addition, ordered carbon vacancies have been reported for 413 (n = 3) phases Nb2AlC3 and V4AlC3, having multiple C sites (38–40). However, for the most common MAX phase structure, that is, 211 (n = 1), only chemically disordered alloys with M site solid solution (15–17, 20, 41) have until recently been realized. In a very recent report, we presented the first material synthesis and verified the calculated stability of the 211 phase (Mo2/3Sc1/3)2AlC, for which the M sublattice is populated by Mo and Sc in a 2:1 ratio (42) and for which there is an in-plane chemical order. This novel 211 MAX phase with in-plane chemical order was referred to as i-MAX. Furthermore, selective etching of Al and Sc realized a novel 2D material with ordered di-vacancies, Mo1.13C MXene, which displayed superior volumetric capacitance compared to other 2D materials investigated to date (42).

Inspired by the above results, we probe with M elements of different size, electronegativity, and electron configuration, and seek ordering in MAX phase hybrids. Through predictive phase stability theory and verifying materials synthesis involving selected transition metal elements from groups III to VI and periods 4 and 5, we identify thermodynamically stable in-plane chemically ordered MAX phases (i-MAX). The common feature is that each M plane is composed of two different metals, M1 and M2, with M1 arranged in a honeycomb lattice and M2 positioned in the center of the hexagon, resulting in a 2:1 ratio of M1 and M2. Two new i-MAX phases, (V2/3Zr1/3)2AlC and (Mo2/3Y1/3)2AlC, are presented, both displaying the characteristics of Kagomé-like Al lattice and in-plane chemical ordering. Together with our recent discovery of (Mo2/3Sc1/3)2AlC (42), we thus propose a new family of chemically ordered laminated materials, i-MAX, with a monoclinic 22/c structure. This discovery will allow property tuning through novel chemistries and ordering as well as selective etching for synthesis of the novel 2D counterpart, that is, MXenes (4, 42, 43).

Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden.
*Corresponding author. Email: martin.dahlqvist@liu.se (M.D.); johanna.rosen@liu.se (J.R.)
RESULTS
Theoretical prediction and materials synthesis

We start with theoretical phase stability calculations of in-plane chemically ordered MAX phase (i-MAX) compositions \((\frac{2}{3}Zr_{1/3})_2AlC\), \((\frac{2}{3}V_{1/3})_2AlC\), \((Mo_{2/3}Y_{1/3})_2AlC\), and \((Y_{2/3}Mo_{1/3})_2AlC\). Out of these, two are found to be thermodynamically stable \([(\frac{2}{3}Zr_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\)] and dynamically stable as seen by the calculated phonon dispersion (fig. S1). Note that these two ordered phases have a formation enthalpy of \(-50\) and \(-101\) meV per atom, respectively, which correspond to known ternary MAX phases indicate highly stable compounds (44, 45), a finding reported here for the first time. Subsequent materials synthesis was focused on the compounds of theoretical predictions were experimentally verified upon optimized synthesis conditions. Attempts to synthesize \((\frac{2}{3}Zr_{1/3})_2AlC\) and \((\frac{2}{3}Y_{1/3})_2AlC\) under the same conditions were not successful, consistent with the theory presented here.

Structural determination

X-ray diffraction (XRD) of \((\frac{2}{3}Zr_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\) samples are shown in Fig. 1 (A and C) with a corresponding simulated pattern in Fig. 1 (B and D) based on structures with monoclinic \(C2/c\) symmetry being relaxed with generalized gradient approximation–Perdew-Burke-Ernzerhof as improved for solids (GGA-PBEsol). Structures relaxed with PBE [local density approximation (LDA)] give peaks that are significantly off, at too low (high) 20 angles, compared to the measured spectra. There is an overall match between measured and simulated i-MAX patterns, as indicated by the stars. Unmarked peaks correspond to impurity phases \(Zr_4AlC_3\), \(V_5Al_8\) and \(Al_4C_3\) in Fig. 1A and \(Mo_4AlC_3\), \(Mo_2Al_3\), \(V_2C\) in Fig. 1C. Note that the 110 peak, corresponding to an interplanar distance of 0.45 and 0.47 nm for \((\frac{2}{3}Zr_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\), appears in the XRD pattern around 19.7° and 18.8°, respectively. This peak does not exist in traditional ternary 211 MAX phases, and it is solely due to \(V/Zr\) and Mo/Sc chemical ordering. This observation is potentially very useful for the identification of other i-MAX phases. Moreover, for \((Mo_{2/3}Y_{1/3})_2AlC\), the peak around 13° is solely from the i-MAX phase because neither Mo2AlC nor Y2AlC exists. The lattice parameters for \((\frac{2}{3}Zr_{1/3})_2AlC\) are \(a = 9.204\) Å, \(b = 5.157\) Å, \(c = 13.549\) Å, and \(\beta = 103.445^\circ\), and for \((Mo_{2/3}Y_{1/3})_2AlC\), the parameters are \(a = 9.679\) Å, \(b = 5.285\) Å, \(c = 14.076\) Å, and \(\beta = 103.359^\circ\).

Figure 2 (A and B) shows overview scanning transmission electron microscopy (STEM) images of in-plane and out-of-plane chemical order for \((\frac{2}{3}Zr_{1/3})_2AlC\), along with schematic illustrations, showing a characteristic laminated structure resembling a MAX phase. However, Fig. 2A shows a “buckled” \(M\) layer consisting of a chemically ordered configuration of \(Zr\) and \(V\). This is shown in more detail in Fig. 2 (C to E) for three different in-plane crystallographic directions, where the brighter spots correspond to \(Zr\), whereas the less bright ones correspond to \(V\), and \(Zr\) extending toward the Al layer. The schematic illustration and high-resolution STEM (HRSTEM) images reveal that in-plane chemical order is only evident from the [010] and [110] direction, as expressed in monoclinic coordinates (Fig. 2, C and D). These two crystallographic directions differ by a 60° rotation with respect to the out-of-plane axis. The third crystallographic direction [100] (Fig. 2E) is obtained by ±30° rotation with respect to a perpendicular out-of-plane axis from Fig. 2 (C and D) and shows a mixed contribution of both \(Zr\) and \(V\) atoms. This orientation looks identical to a traditional MAX phase when viewed along the [1120] zone axis, expressed in the conventional hexagonal coordinates. From analysis of selected-area electron diffraction (SAED) in Fig. 2 (C to E), along with simulated SAED patterns, we suggest the crystal structure to be monoclinic with \(C2/c\) symmetry. Compositional analysis from HR STEM–energy-dispersive x-ray (EDX) shows a 2:1 \(V/Zr\) ratio.

In addition, \((Mo_{2/3}Y_{1/3})_2AlC\) displays the same structure and chemical order with buckled \(M\) layers, as seen from HRSTEM images and SAED patterns in Fig. 3. However, Mo and Y have similar Z contrast and are not easily distinguishable. To resolve these metals, we performed atomic-resolution STEM-EDX mapping of Mo, Y, and Al within the sample (fig. S2), where Y atoms occupy sites closer to the Al layer. Compositional analysis shows that Mo/Y and (Mo+Y)/Al ratios are close to 2:1. This confirms the formation of a characteristic in-plane chemically ordered i-MAX structure.

From Figs. 2 and 3, it is clear that the \(Zr\) (Y) atoms are closer to the Al layer as compared to the V (Mo) atoms. Moreover, throughout all HRSTEM images, the Al layer also forms a mirror plane for the nearest \(Zr\) (Y) and V (Mo) layers. A schematic representation of the suggested monoclinic structure with \(C2/c\) symmetry from four crystallographic directions is depicted in fig. S3A. Detailed structural data (space group, lattice parameter, and Wyckoff position) for \((\frac{2}{3}Zr_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\) are given in Table 2.

We also notice some irregular atomic stacking going from one \(M\) layer to another when passing the carbon layer. This is found for both \((\frac{2}{3}Zr_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\) in Figs. 2A and 3A, respectively. This has been modeled by constructing additional structures resembling \(C2/c\) but with different atomic stacking going from one \(M\) layer to another when passing the carbon layer. Schematic representations of \(C2/c\) and the three additional stackings (\(Cmcm\), \(P2_1/c\), and \(C22_1\)) are shown in fig. S3. Corresponding detailed structural information (space group, lattice parameter, and Wyckoff position) for each phase, we present the identified equilibrium simplex (set of most competing phases).

Table 1. Predicted and verified compounds. Calculated stability and experimental observations for \((\frac{2}{3}Zr_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\) as well as the hypothetical \((\frac{2}{3}V_{1/3})_2AlC\) and \((\frac{2}{3}Mo_{1/3})_2AlC\).

| Targeted ordered phase | \(\Delta H_{\text{ep}}\) (meV per atom) | Equilibrium simplex* | Experimental observation |
|------------------------|---------------------------------|----------------------|-------------------------|
| \((\frac{2}{3}Zr_{1/3})_2AlC\) | −50 | \(V_2AlC, Zr_4AlC_3, Zr_2AlB, V_6C\) | Yes |
| \((\frac{2}{3}V_{1/3})_2AlC\) | +40 | \(Zr_2AlC_B, Zr_4AlB, V_6C, V_6C\) | No |
| \((Mo_{2/3}Y_{1/3})_2AlC\) | −101 | \(YMoC_2, Mo_4Al, YAl_2, YAl_2C_3\) | Yes |
| \((\frac{2}{3}Mo_{1/3})_2AlC\) | +13 | \(YAl_2, Mo_4Al, Y_4C_3, Y_4AlC\) | No |

*For each phase, we present the identified equilibrium simplex (set of most competing phases).
for the respective stacking of (Zr2/3V1/3)2AlC and (Mo2/3Y1/3)2AlC are given in tables S3 and S4. The energy of all four atomic stackings are within 1 meV per atom (table S2), that is, effectively degenerate. For comparison, we also used GGA-PBE and LDA exchange-correlation functionals. For all three functionals, we found the energy for both i-MAX phases to be within 1 meV per atom (that is, effectively degenerate) (table S1). Again, the smallest lattice parameters are obtained with LDA, whereas GGA-PBE results are the largest (tables S2 to S5).

To date, three i-MAX phases have been discovered: (V2/3Zr1/3)2AlC, (Mo2/3Y1/3)2AlC, and the recently reported (Mo2/3Sc1/3)2AlC (42). Characteristic of these phases is the fact that the minority metal M2 has a larger atomic radius than the majority metal M1. Another common feature is the smaller electronegativity of M1 compared to the M2 at lower coordination numbers. From a top view, the hexagonal pattern is present in the carbon layer only (Fig. 5A); however, the side view in Fig. 5E shows that V and Zr (Mo and Y), no longer form a single layer toward the Al layer, as discussed below. A preliminary comparison with plan-view HRSTEM (ongoing work), such as in Fig. 2B, reveals undulations in Al position of the same order as the DFT results.

Ordered versus disorder

To date, three i-MAX phases have been discovered: (V2/3Zr1/3)2AlC, (Mo2/3Y1/3)2AlC, and the recently reported (Mo2/3Sc1/3)2AlC (42). Characteristic of these phases is the fact that the minority metal M2 has a larger atomic radius than the majority metal M1. Another common feature is the smaller electronegativity of M2 compared to the M1 (Table 2). However, the redistribution of the Al layer into a Kagomé-like lattice indicates that size matters, and hence, the influence of difference in electronegativity is believed to be of less importance.
In section S4, we shed light on the impact that different atomic (metal) sizes may have on structure and stability. We choose \( M_1 \) and \( M_2 \) in such a way that they should either be similar or have a significant difference. \( M_1 \) is kept constant as V (Mo) while changing \( M_2 \) to Zr, Ti, or V (Y, V, Ti, or Mo). Using different relaxation schemes, we find that displacement of \( M_2 \) away from the \( M_1 \) layer and toward the Al layer is only favored when the size of \( M_2 \) is significantly larger than \( M_1 \). We also find that a significant gain in energy is achieved by redistributing the Al atoms into a Kagomé-like lattice.

Summarizing the results so far, a requirement for formation of i-MAX phases is a large difference in atomic size between \( M_1 \) and \( M_2 \) with a corresponding 2:1 ratio, because it allows for formation of an \( M_1 \) honeycomb pattern with \( M_2 \) in its center. To minimize stress in-plane, \( M_2 \) is displaced toward the Al-layer, which redistribute into a Kagomé-like lattice. Possible mechanisms for this redistribution are the rather weak bonding between \( M \) and Al as compared to \( M \) and C.

We now compare the energy between in-plane chemical order (i-MAX) and a disordered distribution on the \( M \) lattice (MAX phase). This energy difference \( \Delta E \) for \((V_{2/3}Zr_{1/3})_2AlC\), \((Mo_{2/3}Y_{1/3})_2AlC\), and \((Mo_{2/3}Sc_{1/3})_2AlC\) is much larger as compared to the hypothetical \((V_{2/3}Ti_{1/3})_2AlC\) (Table 3). Using Eq. 4, we transform \( \Delta E \) into an order-disorder temperature \( T_{\text{disorder}} \), that is, above which temperature the disordered structure is energetically favorable due to configurational entropy, ideally well above the typical bulk synthesis temperatures of 1200\(^\circ\) to 1600\(^\circ\)C (1473 to 1873 K). Similar theoretical results have been reported for different structures of ordered hypothetical phases Cr\(_4\)Hf\(_2\)Al\(_3\)C\(_3\) and (Ti\(_{1/3}\)Zr\(_{2/3}\))\(_2\)AlC (23, 46). Here, we note that \( T_{\text{disorder}} \) scales almost linear with the differences in metallic radius of \( M_1 \) and \( M_2 \). This is not the case...
for differences in electronegativity (Table 3). These results can be compared with formation of o-MAX phases, where a difference in electronegativity is suggested to be a key component (37) and where there is a stability enhancement of the solid solution when mixing \( M^1 \) and \( M^2 \) of similar electronegativity or valence (24). We also note that the disorder on the \( M \) lattice for the compositions investigated here does result in displacement of \( M^2 \) toward the Al layer, although not as much as for i-MAX phases and a retained hexagonal structure of the Al layer (for example, disorder suppress formation of a Kagomé-like lattice).

On the basis of the information presented here together with the phase reported by Tao et al. (42), the i-MAX phases are a new family of MAX phase–related materials with an in-plane chemical order. Furthermore, all theoretical and experimental work performed is consistent with a structure described by space group \( C2/\text{c} \). The three i-MAX phases discovered to date [(\( V_{2/3}Zr_{1/3} \))\(_2\)AlC, (\( Mo_{2/3}Y_{1/3} \))\(_2\)AlC, and (\( Mo_{2/3}Sc_{1/3} \))\(_2\)AlC] (42) all share the common feature of having a larger atomic radius of the minority metal \( M^2 \) (Zr, Y, Sc) compared to the majority metal \( M^1 \) (V, Mo). Thus, a large difference in atomic radius, which in turn induces a change in the out-of-plane coordinates for the minority metal and also induces a change in the Al layer to form a Kagomé-like lattice, seems to be a rule of thumb for the formation of an i-MAX phase. Note that the calculated stability of i-MAX phases is high compared to conventional MAX phases, in particular when considering that neither \( Mo_2AlC \) nor \( Y_2AlC \) MAX phase exists. The latter two are predicted not to be stable with a formation enthalpy of +32 and +185 meV per atom, respectively. Consequently, i-MAX is

![Fig. 3. In-plane chemically ordered structure of (Mo\(_{2/3}Y_{1/3}\))\(_2\)AlC. Overview and enlarged HRSTEM, SAED, and schematic representation along (A) [110] and (B) [100] zone axis, respectively, based on a monoclinic structure of space group \( C2/\text{c} \). The unit cell dimensions are represented with black lines in the schematics. Scale bar, 4 nm (1 nm for enlarged parts).](http://advances.sciencemag.org/)

### Table 2. Calculated crystallographic data for monoclinic \( C2/\text{c} \) (\( V_{2/3}Zr_{1/3}\))\(_2\)AlC and (\( Mo_{2/3}Y_{1/3}\))\(_2\)AlC structures.

| Compound                  | Lattice parameters (Å, degrees) | Atom     | Wyckoff site | Atomic coordinates (fractional) |
|---------------------------|---------------------------------|----------|--------------|---------------------------------|
| (\( V_{2/3}Zr_{1/3}\))\(_2\)AlC | \( a = 9.1720 \) \( b = 5.2808 \) \( c = 13.6416 \) | Zr1      | 8f           | \(-0.04224 \) 0.41965 0.11240   |
|                           | \( \alpha = 90.0000 \) \( \beta = 103.0708 \) \( \gamma = 90.0000 \) | V1       | 8f           | 0.27100 0.42163 0.07627          |
|                           |                                 | V2       | 8f           | 0.60922 0.40678 0.07628          |
|                           |                                 | Al1      | 4e           | 0.00000 0.07157 0.25000          |
|                           |                                 | Al2      | 8f           | 0.74432 0.15903 0.25156          |
|                           |                                 | C1       | 4d           | 0.25000 0.25000 0.50000          |
|                           |                                 | C2       | 8f           | 0.41401 0.25792 0.00009          |
| (\( Mo_{2/3}Y_{1/3}\))\(_2\)AlC | \( a = 9.5764 \) \( b = 5.5433 \) \( c = 14.1582 \) | Mo1      | 8f           | 0.27064 0.42356 0.07656          |
|                           | \( \alpha = 90.0000 \) \( \beta = 103.6620 \) \( \gamma = 90.0000 \) | Mo2      | 8f           | 0.60998 0.40389 0.07660          |
|                           |                                 | Al1      | 4e           | 0.00000 0.08027 0.25000          |
|                           |                                 | Al2      | 8f           | 0.74818 0.16062 0.25156          |
|                           |                                 | C1       | 4d           | 0.25000 0.25000 0.50000          |
|                           |                                 | C2       | 8f           | 0.41285 0.26073 0.00003          |
evidently formed, although included elements do not constitute corresponding ternary MAX phases. This implies that i-MAX will widen the range of attainable chemistries for these atomically laminated materials. One such example is that the work presented here includes an element never used in MAX phases before, Y, as exemplified in (Mo$_{2/3}$Y$_{1/3}$)$_2$AlC.

Close to all MXenes (the 2D derivative of selected MAX phases) to date originate from selectively etching the Al layer from a MAX phase (3, 4, 43, 47). This concept was recently expanded by selective etching of Al and Sc in (Mo$_{2/3}$Sc$_{1/3}$)$_2$AlC i-MAX, which resulted in a novel 2D material with ordered divacancies, Mo$_{1.33}$C MXene, which displayed superior volumetric capacitance compared to all other 2D materials investigated to date (42). All materials presented here are based on $A = Al$.

This implies that the family of i-MAX is likely a parent material for a large number of novel MXenes with vacancy ordering or possible chemical ordering. Therefore, the present finding is of utmost importance for property tuning potential for MAX phases and their 2D derivatives, MXenes, because it allows for control of both composition and structure when specific metal combinations are chosen. Investigations on i-MXenes are ongoing in our laboratory.

CONCLUSIONS

We have used a combination of DFT calculations, materials synthesis, and atomic-resolution STEM and XRD analysis to predict and verify in-plane chemical order in the laminated novel phases (V$_{2/3}$Zr$_{1/3}$)$_2$AlC and (Mo$_{2/3}$Sc$_{1/3}$)$_2$AlC. Together with the recently synthesized (Mo$_{2/3}$Sc$_{1/3}$)$_2$AlC, we propose a new family of in-plane chemically ordered phases, i-MAX, including, but likely not being limited to, transition metals from groups III to VI and periods 4 and 5. We propose the i-MAX structure to be of monoclinic $C2/c$ symmetry, although with identified related structures close to degenerate in energy. Our results demonstrate that the in-plane chemical order from a 2:1 ratio of the two metals is important because it enables formation of a honeycomb pattern of the majority metal (V and Mo), whereas the minority metal of a larger atomic radius is displaced toward the Al layer, leading to a significant lowering in energy and a redistribution of the Al layer to form a Kagomé-like lattice. The discovery of this family of chemically ordered quaternary laminates widens the attainable chemistries of MAX phase–related materials,

![Fig. 4. Local atomic coordination in i-MAX phases.](image)

![Fig. 5. Overview of atomic structure in MAX versus i-MAX and comparison of ideal Kagomé and Kagomé-like lattices.](image)
which will undoubtedly open up for altered and new properties. Chemical ordering, and in particular Kagomé-like ordering, in a material sits at the crossroad of fascinating straits of condensed matter physics, giving rise to phenomena, such as the anomalous Hall effect and multiferroicity (48, 49). Furthermore, we expect a wealth of related novel 2D materials, MXenes, with either in-plane chemical order or vacancy ordering induced by choice of etching procedure.

**MATERIALS AND METHODS**

**Computational details**

All first-principles calculations based on DFT were performed with the Vienna ab initio simulation package (50–52) using the projector augmented wave method (53, 54) with non-spin-polarized GGA as parameterized by PBE (55) for treating electron exchange and correlation effects. For in-plane chemically ordered phases, we also considered the LDA and PBEsol (56) functionals, the latter for potential improvement of equilibrium properties, such as bond length and lattice parameters. We used plane waves up to an energy cutoff of 400 eV, and for the evaluation of equilibrium properties, such as bond length and lattice parameters. For in-plane chemically ordered phases, we also considered parameterized by PBE (55) and the hypothetical (V2/3Ti1/3)2AlC. The corresponding temperature, disorder required for decreasing the free energy of the disordered phase to below 10⁻⁴ eV Å⁻¹ used for calculations of the force constants. The thermodynamic stability was evaluated using a linear optimization procedure based on the simplex method, which compares the energy of the compound of interest to all possible linear combinations of other competing phases under the constraint of a fixed stoichiometry (45, 60). Temperature-dependent effects, such as lattice vibrations, were not considered because this contribution from a phase, significant or not, tends to be cancelled out in the calculated stability (61). This approach has been proven to work exceptionally well for MAX phases (45, 62, 63), where experimental synthesis conditions also allow migration of elements to equilibrium positions. The linear combination of competing phases resulting in the lowest energy is called equilibrium simplex or set of most competing phases. A compound’s stability can be quantified in terms of formation enthalpy ΔHₚₛ by comparing its energy to the energy of the equilibrium simplex

\[
\Delta H_{cp} = E[\text{compound}] - E[\text{equilibrium simplex}] \tag{1}
\]

If ΔHₚₛ < 0, then the compound is considered stable, whereas for ΔHₚₛ > 0, it is considered to be unstable or at best metastable. For a compound found not to be stable, the equilibrium simplex indicated which other phases were more stable. Competing phases included in the evaluation of phase stability are those experimentally known and hypothetical phases that exist in similar and/or with neighboring elements in the periodic table. Considered competing phases for the Mo-Y-Al-C and V-Zr-Al-C systems were based on experimental phase diagrams and what was present in similar systems (section S6).

Chemically disordered candidate structures (for example, solid-solution alloys of M¹ and M² on the M sublattice) were modeled using the special quasi-random structures method (64). Energy convergence with respect to the size of the super cell was performed, showing that a cell size of 6 × 3 × 1 M₂AX unit cells or larger display an energy within 2 meV per atom, whereas lattice parameters a and c are within 0.3%. See section S5 for further information of super cell convergence in terms of calculated energies and lattice parameters.

When T ≠ 0 K, the Gibbs free energy ΔGₚₛ for a disordered phase was approximated using

\[
\Delta G_{\text{disorder}} = \Delta H_{\text{disorder}} - T \Delta S \tag{2}
\]

where the entropic contribution ΔS, assuming an ideal solution of M¹ and M² on the M sites, is given by

\[
\Delta S = -2k_B \ln(z) + (1 - z) \ln(1 - z) \tag{3}
\]

where z is the M² concentration. By using Eqs. 2 and 3, an order-disorder temperature Tₚₛ can be calculated according to

\[
T_{\text{disorder}} = \frac{\Delta H_{\text{disorder}} - \Delta H_{\text{cp}}}{\Delta S} \tag{4}
\]

for which ΔGₚₛ(T) = ΔHₚₛ(T) is fulfilled and hence give an estimate above which temperature disorder is expected.

**Materials synthesis**

Polycrystalline (V2/3Zr1/3)₂AlC and (Mo2/3Y1/3)₂AlC samples were synthesized by solid-state reaction from elemental powders: graphite (99.99%), Mo (99.9%), Zr (99%), and V (99.5%) from Sigma-Aldrich, and Al (99.8%) from Alfa Aesar. To obtain (V2/3Zr1/3)₂AlC, we mechanically mixed elemental V/Zr/Al/C powders of a 2:4:3:3 stoichiometry in an agate mortar, heated them at 10°C/min up to 1500°C in an alumina crucible under five standard cubic centimeter per minute (scm) Ar flow, and finally held them at 1500°C for 2 hours. To

| M¹ | M² | ΔE (meV per atom) | Tₚₛ (K) | Difference between M² and M¹ | Atomic radius* (Å) | Electronegativity* |
|----|----|------------------|--------|-----------------------------|-------------------|------------------|
| V  | Zr | −136             | 4951   | 0.25                        | −0.30             |                  |
| Mo | Y  | −197             | 7192   | 0.41                        | −0.94             |                  |
| Mo | Sc | −82              | 2999   | 0.23                        | −0.80             |                  |
| V  | Ti | −12              | 438    | 0.18                        | −0.09             |                  |

*1.35 Å for V, 1.60 Å for Zr, 1.39 Å for Mo, 1.80 Å for Y, 1.62 Å for Sc, and 1.47 Å for Ti. **1.63 Å for V, 1.33 Å for Zr, 2.16 Å for Mo, 1.22 Å for Y, 1.36 Å for Sc, and 1.54 Å for Ti.
obtain (Mo0.5Y0.5)2AlC, we mixed elemental Mo/Y/Al/C powders of a 2:4:3 stoichiometry in an agate mortar, then heated them at 10°C/min up to 1600°C in an alumina crucible under five SCCM Ar flow, and finally held them at 1600°C for 10 hours. The samples were cooled down to room temperature in the furnace, and the obtained powder was crushed and sieved through a 450-mesh sieve.

Materials characterization
XRD was performed on a PANalytical X’Pert powder diffractometer, with Cu source (dKCu ≈ 1.54 Å). For these measurements, a graded Bragg-Brentano HD, with a 1/4° divergent and 1/2° anti-scattered slits, and a 5-mm anti-scatter slit together with a Soller slit (with an opening radius of 0.04°), in the incident and the diffracted beam side, were used. A continuous scan from 5° to 120° was performed on the sample using a step size of 0.008° with a 40-s time per step. STEM combined with high-angle annular dark-field imaging and EDX analysis with a Super-X EDX detector was performed in the double-corrected Linköping FEI Titan® 60-300 operated at 300 kV. SAED was performed on an FEI Tecnai T20 TEM operated at 200 kV. The specimens were prepared by embedding the ground-mixed powder in a Cu grid with C film.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/7/e1700642/DC1

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Prediction and synthesis of a family of atomic laminate phases with Kagomé-like and in-plane chemical ordering

Martin Dahlqvist, Jun Lu, Rahele Meshkian, Quanzheng Tao, Lars Hultman and Johanna Rosen

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