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 MXn+1Xm 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 MXn+1Xm (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 has 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 M2AX3 structure, TiCr2AlC2, in which Ti is sandwiched between two Cr-C layers. This was soon followed by the discovery of TiMo2AlC2 (33, 34), V23Cr13AlC3 (35), Ti2Mo2AlC3 (33), and V23Cr18AlC3 (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 o-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 vacancy sites, Mo1.33C 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 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 C2/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.
RESULTS

Theoretical prediction and materials synthesis

We start with theoretical phase stability calculations of in-plane chemically ordered MAX phase (i-MAX) compositions \((V_{2/3}Zr_{1/3})_2AlC\), \((Zr_{2/3}V_{1/3})_2AlC\), \((Mo_{2/3}Y_{1/3})_2AlC\), and \((Y_{2/3}Mo_{1/3})_2AlC\). Out of these, two are found to be thermodynamically stable \([(V_{2/3}Zr_{1/3})_2AlC\text{ and } (Mo_{2/3}Y_{1/3})_2AlC\) (Table 1)] 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 compared 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 \((Zr_{2/3}V_{1/3})_2AlC\) and \((Y_{2/3}Mo_{1/3})_2AlC\) under the same conditions were not successful, consistent with the theory presented here.

Structural determination

X-ray diffraction (XRD) of \((V_{2/3}Zr_{1/3})_2AlC\) 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 \(Zr_3Al, V_5Al_8\) and \(Al_4C_3\) in Fig. 1A and \(Mo_2AlC, Mo_2C\) in Fig. 1C. Note that the 110 peak, corresponding to an interplanar distance of 0.45 and 0.47 nm for \((V_{2/3}Zr_{1/3})_2AlC\) 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 \(Mo_2AlC\) nor \(Y_2AlC\) exists. The lattice parameters for \((V_{2/3}Zr_{1/3})_2AlC\) are \(a = 9.204\ Å, b = 5.157\ Å, c = 13.549\ Å, and \(\beta = 103.445°\), 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 \(\beta = 103.359°\).

Figure 2 (A and B) shows overview scanning transmission electron microscopy (STEM) images of in-plane and out-of-plane chemical order for \((V_{2/3}Zr_{1/3})_2AlC\), 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 with \(Zr\) 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 HRSTEM–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 \((Zr_{2/3}V_{1/3})_2AlC\) and \((Mo_{2/3}Y_{1/3})_2AlC\) are given in Table 1.

We also notice some irregular atomic stacking going from one \(M\) layer to another when passing the carbon layer. This is found for both \((Zr_{2/3}V_{1/3})_2AlC\) 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 (\(Cc\), \(P2_1/c\), and \(C222_1\)) are shown in fig. S3. Corresponding detailed structural information (space group, lattice parameter, and Wyckoff position) is obtained from http://advances.sciencemag.org/ on December 24, 2017

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

<table>
<thead>
<tr>
<th>Targeted ordered phase</th>
<th>(\Delta H_{up}) (meV per atom)</th>
<th>Equilibrium simplex*</th>
<th>Experimental observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>((V_{2/3}Zr_{1/3})_2AlC)</td>
<td>−50</td>
<td>(V_2AlC, Zr_4Al_3C, Zr_2Al_3, V_3C)</td>
<td>Yes</td>
</tr>
<tr>
<td>((Zr_{2/3}V_{1/3})_2AlC)</td>
<td>+40</td>
<td>(Zr_4Al_3C, Zr_2Al_3, V_3C, V_2AlC)</td>
<td>No</td>
</tr>
<tr>
<td>((Mo_{2/3}Y_{1/3})_2AlC)</td>
<td>−101</td>
<td>(YMo_2C, Mo_3Al, YAl_2, YAl_3C_3)</td>
<td>Yes</td>
</tr>
<tr>
<td>((Y_{2/3}Mo_{1/3})_2AlC)</td>
<td>+13</td>
<td>(YAl_2, Mo_3Al, Y_4C_3, Y_2AlC)</td>
<td>No</td>
</tr>
</tbody>
</table>

*For each phase, we present the identified equilibrium simplex (set of most competing phases).

Comparison of i-MAX and MAX phase structures

The unique structure of the i-MAX phases (Zr_{2/3}V_{1/3})_2AlC and (Mo_{2/3}Y_{1/3})_2AlC discovered here, as well as that of the previously reported (Mo_{2/3}Sc_{1/3})_2AlC [42], in comparison to traditional 211 MAX phases, is depicted in Fig. 5 (A to E), showing a structural overview of MAX (top row) and i-MAX phase (middle row). For simplicity, (V_{2/3}Zr_{1/3})_2AlC composition configured in an i-MAX chemical order is used for both structures. For the MAX phase structure, the hexagonal pattern is present in all layers. For the i-MAX structure, the hexagonal pattern is present in the carbon layer only (Fig. 5C). From a top view, the M layer (M^1 + M^2) also seems to form a hexagonal pattern, (Fig. 5A); however, the side view in Fig. 5E shows that V and Zr do not reside in the same layer because Zr is moved closer to the Al layer. M^1 forms a honeycomb lattice with M^2 located in the center of each hexagon. Still, the major structural difference between the i-MAX and the MAX phase is found in the Al layer (Fig. 4B), being hexagonal for the MAX phase while closely resembling a Kagomé lattice for the i-MAX. Figure 5 (F and G) shows Al arranged in an ideal Kagomé pattern and our calculations for the three relaxed i-MAX phases. All exhibit small undulations or ripple in Al atom locations in a Kagomé-like lattice given in Fig. 5 (G and H). From the DFT calculations made here for the i-MAX phases, we find that the deviations from an ideal Kagomé lattice is largest for (Mo_{2/3}Sc_{1/3})_2AlC (6.6° and 0.06 to 0.10 Å offset) [42] and smallest for (Mo_{2/3}Y_{1/3})_2AlC (2.6° and 0.02 to 0.05 Å offset) with (V_{2/3}Zr_{1/3})_2AlC in between, at 5.2°/0.06 to 0.07 Å offset. Possible mechanisms for these relaxations may be related to the atomic size difference of M^1 and M^2 where the larger atom, M^2, is pushed out of the M^1 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.

Compared to the MAX phase structure, we observe two major differences that affect local coordination in i-MAX: (i) The M atoms, that is, V and Zr (Mo and Y), no longer form a single M layer. Instead, the Zr (Y) atom is moved closer to the Al layer. (ii) The Al layer is no longer hexagonally coordinated because the Al-Al coordination is reduced from six to four.

Order versus disorder

To date, three i-MAX phases have been discovered: (V_{2/3}Zr_{1/3})_2AlC, (Mo_{2/3}Y_{1/3})_2AlC, and the recently reported (Mo_{2/3}Sc_{1/3})_2AlC [42]. Characteristic of these phases is the fact that the minority metal M^2 has a larger atomic radius than the majority metal M^1. Another common feature is the smaller electronegativity of M^2 compared to the M^1 (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\(^\circ\)C to 1600\(^\circ\)C (1473 to 1873 K). Similar theoretical results have been reported for different structures of ordered hypothetical phases \( Cr_4H_2Al_3C_3 \) and \( (Ti_{1/3}Zr_{2/3})_2AlC \) (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 $C2/c$. 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$_2$AlC nor Y$_2$AlC 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

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**Table 2. Calculated crystallographic data for monoclinic $C2/c$ (V$_{2/3}$Zr$_{1/3}$)$_2$AlC and (Mo$_{2/3}$Y$_{1/3}$)$_2$AlC structures.** Structural relaxation performed using GGA-PBESol exchange-correlation functional.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameters (Å, degrees)</th>
<th>Atom</th>
<th>Wyckoff site</th>
<th>Atomic coordinates (fractional)</th>
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<tbody>
<tr>
<td>(V$<em>{2/3}$Zr$</em>{1/3}$)$_2$AlC</td>
<td>$a = 9.1720$, $b = 5.2808$, $c = 13.6416$</td>
<td>Zr1</td>
<td>8f</td>
<td>0.04244, 0.41965, 0.11240</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90.0000$, $\beta = 103.0708$, $\gamma = 90.0000$</td>
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<td>8f</td>
<td>0.27100, 0.42163, 0.07627</td>
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<td></td>
<td>V2</td>
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<td>4d</td>
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<td>C2</td>
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<td>0.41285, 0.26073, 0.00003</td>
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</table>

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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 $C2/c$. The unit cell dimensions are represented with black lines in the schematics. Scale bar, 4 nm (1 nm for enlarged parts).
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 $A = Al$.

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$_{2/3}$Y$_{1/3}$)$_2$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 $C_2/c$ 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.
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 (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 LDA and PBEsol energies, where the entropic contribution $\Delta S$, assuming an ideal solution of $M^1$ and $M^2$ on the $M$ sites, is given by

$$\Delta S = -2k_B[z \ln(z) + (1 - z) \ln(1 - z)]$$

where $z$ is the $M^2$ concentration. By using Eqs. 2 and 3, an order-disorder temperature $T_{\text{disorder}}$ can be calculated according to

$$T_{\text{disorder}} = \frac{\Delta H_{\text{disorder}} - \Delta H_{\text{order}}}{\Delta S}$$

for which $\Delta G_{\text{disorder}}[T] = \Delta H_{\text{order}}$ is fulfilled and hence give an estimate above which temperature disorder is expected.

**Materials synthesis**

Polycrystalline (V$_{2/3}$Zr$_{1/3}$)$_2$AlC and (Mo$_{2/3}$Y$_{1/3}$)$_2$AlC samples were synthesized by solid-state reaction from elemental powders: graphite (99.999%), Mo (99.99%), Y (99.5%), Zr (99%), and V (99.5%) from Sigma-Aldrich, and Al (99.8%) from Alfa Aesar. To obtain (V$_{2/3}$Zr$_{1/3}$)$_2$AlC, 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
obtain (Mo_{2/3}Y_{1/3})_2AlC, we mixed elemental Mo/Y/Al/C powders of a 2:4:3:3 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 (\( \lambda_{Cu} \approx 1.54 \text{ Å} \)). For these measurements, a graded Bragg-Brentano HD, with a 1/4° divergent and 1/2° anti-scattered slits, a continuous scan from 5° to 120° was performed on the sample using a Soller slit (with an opening radius of 0.04°), in the incident and the diffracted beam side, were used. A constant scan size 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 300–300 operated at 300 kV. SAED was performed on an FEI Tecnai T20 TEM operated at 200 kV. The samples 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

section 51. Dynamical stability

section 52. Elemental mapping

section 53. Candidate structures

section 54. Impact of atomic size

section 55. Cell size convergence for disordered structures

section 56. Competing phases used for stability calculations

fig. 51. Dynamical stability of ordered structures.

fig. 52. Elemental mapping of (Mo_{2/3}Y_{1/3})_2AlC.

fig. 53. Comparison of different in-plane chemically ordered candidate structures.

fig. 54. Calculated energy and structural changes upon metal displacement.

fig. 55. Structural changes upon metal displacement.

fig. 56. Ratio of two Al-Al distances upon metal displacement.

fig. 57. Energy change upon metal displacement.

fig. 58. Supercell convergence.

fig. table 51. Energy degeneracy of candidate structures.

table 52. Calculated crystallographic data for different candidate structures of (V_{2/3}Zr_{1/3})_2AlC.

table 53. Calculated crystallographic data for different candidate structures of (Mo_{2/3}Y_{1/3})_2AlC.

table 54. Calculated crystallographic data for different candidate structures of (V_{2/3}Zr_{1/3})_2AlC using the LDA exchange-correlation functional.

table 55. Calculated crystallographic data for different candidate structures of (Mo_{2/3}Y_{1/3})_2AlC using the LDA exchange-correlation functional.

table 56. Calculated crystallographic data for different candidate structures of (V_{2/3}Zr_{1/3})_2AlC using the GGA-PBEsol exchange-correlation functional.

table 57. Calculated crystallographic data for different candidate structures of (Mo_{2/3}Y_{1/3})_2AlC using the GGA-PBEsol exchange-correlation functional.

phases: Materials

table 58. Phases considered for the quaternary Ti-Al-N-C system.

phases: Materials

table 59. Phases considered for the quaternary V-Zr-N-C system.

REFERENCES AND NOTES


