Multielemental single–atom-thick A layers in nanolaminated \(V_2(Sn, A)C\) (\(A = Fe, Co, Ni, Mn\)) for tailoring magnetic properties

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Edited by C. N. R. Rao, New Chemistry Unit, CSIR Centre of Excellence, International Centre for Materials Science and Sheikh Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, and approved November 27, 2019 (received for review September 18, 2019)

Tailoring of individual single–atom-thick layers in nanolaminated materials offers atomic-level control over material properties. Nonetheless, multielement alloying in individual atomic layers in nanolaminates is largely unexplored. Here, we report 15 inherently nanolaminated \(V_2(A,Sn)C\) (\(A = Fe, Co, Ni, Mn\), and combinations thereof, with \(n = 1/3\)) MAX phases synthesized by an alloy-guided reaction. The simultaneous occupancy of the 4 magnetic elements and 5n in the individual single–atom-thick A layers constitutes high-entropy MAX phase in which multielemental alloying exclusively occurs in the 2-dimensional (2D) A layers. \(V_2(A,Sn)C\) exhibit distinct ferromagnetic behavior that can be compositionally tailored from the multielement A-layer alloying. Density functional theory and phase diagram calculations are performed to understand the structure stability of these MAX phases. This 2D multielemental alloying approach provides a structural design route to discover nanolaminated materials and expand their chemical and physical properties. In fact, the magnetic behavior of these multielemental MAX phases shows strong dependency on the combination of various elements.

MAX phases | high-entropy ceramics | multielement alloys | magnetism

Tailoring individual single–atom-thick layers in nanolaminated materials offers atomic-level control over modifying a desired property of a material. For example, artificially nanolaminated magnetic materials are widely used in storage media and devices. Notably, the demonstration of the giant magnetoresistance (GMR) effect has enabled hard drives and other storage media (1). The GMR sensitivity is expected to be highest when only single-atom layers of ferromagnetic materials are sandwiched since alignment of magnetization vectors of neighboring ferromagnetic atoms has the lowest energy cost.

Conceptually, this type of structure with single–atom-thick layers can be correlated to \(M_{n+1}AX_n\) phases (or MAX phases), which are a family of inherently nanolaminated ternary compounds with hexagonal crystal structure (space group \(P_6\text{3}m\text{mc}\), \(\text{I}9\text{h}\)). Here, \(M\) is an early transition metal, \(A\) is mainly from \(A\) group elements, \(X\) is carbon and/or nitrogen, and \(n = 1\) to \(3\) (\(2, 3\)). Their crystal structure can be depicted by alternative stacking of \(M_{n+1}AX_n\) sublayer and a single atomic layer of \(A\), usually referred to as \(211, 312, 413\) phases, respectively, according to the value of \(n\). If alloying or replacement of ferromagnetic elements at specific crystal sites in MAX phases could be realized, their magnetic properties may also be tailored. The key notion here is that the \(A\) layer is just 1-atom thick. However, there are few reports on magnetic MAX phases in which \(M\) site contains Mn or Fe, such as \((\text{Cr}_0.75\text{Mn}_{0.25})_2\text{GeC}\) (4), \(\text{Mn}_{2}\text{GaC}\) (5), \((\text{V,Mn})_{2}\text{GaC}\) (6), and \((\text{Cr,Fe})_2\text{AlC}\) (7), etc.

Control of the occupancy of magnetic elements on the \(A\) rather than \(M\) sites would be crucial to tune magnetic properties. The finding of iron in the \(A\) site of \(\text{Mo}_2(\text{GaAuFe})\text{C}\) (8) is encouraging; however, the presence of secondary iron-containing impurity phases in the \(\text{Mo}_2(\text{GaAuFe})\text{C}\) films impedes the determination of magnetic properties on the \(A\) plane. Moreover, theoretical predictions suggest that Ni and Co should tend to occupy the \(M\) sites of the MAX phases (9), but this has not been demonstrated experimentally, likely due to the thermodynamically preferred formation of competing binary MA alloys or intermetallic phases. Generally, the late transition elements of \(\text{Fe, Co, Ni, and Mn have not been considered as possible A-site elements in the definition of MAX phases. It would be of great interest to introduce these magnetic elements at \(A\) sites since the overlap between electron clouds of \(M\) and \(A\) atoms is limited compared with that between \(M\) and \(X\) atoms, which should aid in preserving the magnetic properties. A possible approach to realize this is by alloying with other main group elements in such a way that the alloying transforms neither the atomic stacking in the crystal nor their bonding with the parent structure. \(Fe, Co,\) and \(Ni\) have been used as additives for the formation of \(M_n^+\text{SnC}_2\) (\(M^+ = \text{Ti, Zr, Hf}\)) MAX phases (10), while none of the Fe/Co/Ni...
were detected in the final target MAX phases. The $A_2Sn_3$ ($A = Fe$, Co, Ni, Mn, or their binary mixtures) phases belong to the same space group ($P6_3/mmc$ or 194) as MAX phases. This similarity in crystal structures facilitates the nucleation of MAX phases in saturated alloys by a reaction between a binary carbide and an intermediate state of $A_2Sn_3$ alloys. During such a reaction, these complex atoms in molten (or solid) alloys may thermodynamically and coherently arrange with $[M_6C]$ octahedral building blocks to form ternary-layer structure. Thus, it would be of great interest to obtain magnetic MAX phases by an alloy-guided reaction.

Here, we demonstrate this approach to $A$-site alloying of Sn with Fe/Co/Ni/Mn magnetic elements to synthesize a series of magnetic MAX phases of $V_2(A_2Sn_3)_xCO_y(C = Fe, Co, Ni, Mn, or their binary/ternary/quaternary combination). The regular $M_2AX$ crystal structure of $V_2SnC$ is retained, with a mixture of 2 to 5 elements (Sn plus 1 or more of Fe, Co, Ni, and Mn) randomly occupying the A sites. The magnetic properties of $V_2(A_2Sn_3)_xCO_y$ MAX phases exhibit distinct ferromagnetic behavior that can be tailored by their constitutive elements. These results have wide-ranging implications since they not only can be used for tailoring magnetic properties but most importantly, demonstrate the formation of multielement A layers as an analogy to high-entropy alloys (11, 12), 2-dimensional (2D) in the sense that alloying exclusively occurs in the single–atom-thick A layers, in layered transition metal carbides.

Results and Discussion

MAX Phases Containing 1 Magnetic Element. X-ray diffraction (XRD) pattern of V-Fe-Sn-C system is close to the characteristic crystal structure of $V_2AlC$ MAX phase (13), with characteristic peaks at 20 close to 13°, 20 close to 26°, and 20 close to 40°, indicating formation of a 211 MAX phase (shown in Fig. 1A) and also, with some by-products of Sn metal, intermetallic compounds (FeSn2), and nonstoichiometric vanadium carbide (VC) (SI Appendix, Fig. S1A). The micromorphology of observed particles with terraces is typical layered structure of MAX phases (Fig. 1B). The atomic force microscopy (AFM) measurement also shows the typical layer structure in nanoscale (SI Appendix, Fig. S2), and the height of terrace is about 3 nm, which is close to double length of unit cell of $M_2AX$ in c direction. In previously reported $M'_2SnC_2$ ($M' = Ti, Zr, Hf$) phases (10), Fe was absent in the final products. Here, however, the corresponding energy-dispersive X-ray spectroscopy (EDS) spectra of these particles showed the presence of Fe beside V, Sn, and C (Fig. 1C). The relative atomic ratio of $V_2(Fe + Sn)$ is close to 2:1, consistent with the stoichiometry of 211 MAX phases (SI Appendix, Table S1). The high content of Fe (9.4 at.%) and its uniform distribution in elemental mapping (SI Appendix, Fig. S3) further indicate that Fe is incorporated in the as synthesized MAX phase.

To determine the position of Fe, we performed high-resolution, high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and lattice-resolved EDS as shown in Fig. 1 D–G. STEM images acquired with the beam along the [1120] and [1100] zone axes are shown in Fig. 1D and E, respectively. One layer of brighter spots (the A atomic layers) is interleaved by 2 adjacent layers of darker spots (the M atomic layers). Carbon is typically not visible because of its low contrast compared with the heavier M and A atoms, and the characteristic zigzag stacking of the Mn+1Xn slabs viewed along the [1120] zone axes is seen (14–17). STEM-EDS mapping (Fig. 1F) and line scanning (Fig. 1G), which indicate that V is in the M sites following the zigzag stacking, and overlapped Fe (purple) and Sn (green) are proving that both are in the A sites of MAX phase. The compositions of the elements V, Sn, and Fe are 67, 22, and 11 at. % (atomic percentage), respectively (SI Appendix, Table S2). The molar ratio is in good agreement with the above EDS result. Thus, the chemical formula of the resultant MAX phase is close to $V_2(Sn_{2/3}Fe_{1/3})C$. To prove the generality of this methodology, we used Co, Ni, and Mn instead of Fe in the starting materials and followed the same chemical synthesis process. The comprehensive characterization of MAX phases whose A sites contain Co, Ni, and Mn elements are shown in SI Appendix, Figs. S4–S6 and section S1).

MAX Phases Containing 2 Magnetic Elements. If 2 magnetic elements can be simultaneously incorporated into the MAX structure, this would offer additional prospects for tuning magnetic properties since strong spin-electron coupling or interaction between different magnetic elements may enhance the magnetic properties as known from, for example, permalloy $Ni_{80}Fe_{20}$ with high magnetic permeability (18). For incorporation of Fe and Co, the XRD pattern (Fig. 2A) showed that the main product is a 211 MAX phase with small amounts of by-products (SI Appendix, Fig. S7). SEM demonstrated the typical terraced laminate microstructure (Fig. 2B). From the EDS results in SEM (Fig. 2C), V, Fe, Co, Sn, and C (5 elements) were detected; the molar ratio of $V, Fe + Co + Sn$ is very close to 2:1; and the Sn:(Co + Fe) ratio is 2:1 (SI Appendix, Table S3). Elemental mapping further provided evidence that Fe, Co, and Sn have the same distribution (SI Appendix, Fig. S8). The molar ratio of $V, Fe + Co + Sn$ is very close to 2:1, and the Sn:(Co + Fe) ratio is 2:1. Therefore, the obtained MAX phase has the formula of $V_2(Fe_{1/2}Co_{1/2})Sn_{2/3}C$. Furthermore, STEM images of the $V_2(Fe_{1/2}Co_{1/2})Sn_{2/3}C$ phase with the beam along the [1120] and [1100] zone axes are shown in Fig. 2D and E, respectively. Furthermore, atomically resolved EDS mapping analysis (Fig. 2F) and line scan analysis (Fig. 2G) in STEM mode provided direct evidence that Fe, Co, and Sn elements only occupy A sites.

Following the same synthesis methodology, we also synthesized several other MAX phases with 2 magnetic elements on the A site: that is, $V_2(Fe_{1/2}Ni_{1/2})Sn_{2/3}C$, $V_2(Fe_{1/2}Ni_{1/2})Sn_{2/3}C$, $V_2(Mn_{1/2}Co_{1/2})Sn_{2/3}C$, $V_2(Mn_{1/2}Fe_{1/2})Sn_{2/3}C$, and $V_2(Mn_{1/2}Ni_{1/2})Sn_{2/3}C$. Phase composition, micromorphology, and elemental distribution are provided in SI Appendix, Figs. S9–S13.
Multielement A-Site Phases. A multielemental feature in chemical composition of a single-phase homogeneous material can generally have drastic implications for physical and chemical properties as realized for so-called high-entropy alloys or multiprincipal element alloys (11, 12). In analogy with this materials design strategy, we posed the hypothesis that, since 1 or 2 magnetic elements from these 4 (Fe, Co, Ni, and Mn) can be alloyed with Sn at the A site, it would be logical that also 3 or even 4 magnetic elements could be simultaneously incorporated. We therefore performed the same synthesis for all combinations of 3 of these elements. The XRD and SEM-EDS results showed the formation of MAX phases of $V_2(A(Sn_{1-x})C$, where A is a combination of 3 elements from Fe, Co, Ni, and Mn and $x = 1/3$. The details are provided in SI Appendix, Figs. S14–S17.

Furthermore, we synthesized an MAX phase with all 4 magnetic elements as well as Sn simultaneously. The XRD pattern shows that the final product is composed of MAX phase and various tin alloys (Fig. 3A and SI Appendix, Fig. S18). The laminated morphology of the particles is similar to the above-mentioned MAX phases (such as in Figs. 1B and 2B) but with more rounded edges (Fig. 3B). EDS in SEM detected all constituent elements (V, Sn, Fe, Co, Ni, Mn, and C) along Sn, Fe, Co, Ni, Mn and C elements. (Scale bars: STEM images, 1 nm.) a.u., arbitrary unit; cps, counts per second.

Phase Diagrams. Fig. 4 shows the calculated isothermal sections at 1,100 °C of the phase diagrams of V-Sn-C, $V(Sn_{2/3}Fe_{1/3})C$, and V-Fe-C systems. These results indicate that $V_2SnC$ is the only thermodynamically stable ternary phase in the V-Sn-C system (Fig. 4A) at equilibrium with Sn metal and vanadium carbide. In the case of Fe addition (Fig. 4B), the $V_2(Fe_{1/3}Sn_{2/3})C$ phase can also be at equilibrium with $V_2C_2$ and FeSn2, consistent with the experimental results (Fig. L4). However, in the V-Fe-C phase diagram, the hypothetical ternary MAX phase $V_2FeC$ is not stable (Fig. 4C). Instead, vanadium carbides ($V_2C$ and $V_3C_2$) and an Fe-rich V-Fe intermetallic phase are the most competitive phases, corroborated by the experimental results. In fact, all of our attempts to synthesize $V_2AC$ ($A = Fe, Co, Ni, and Mn$; i.e., without Sn) phases failed (SI Appendix, Fig. S19).

The Gibbs free energy values of $V_2(Fe_{1/3}Sn_{2/3})C$ as well as intermediate phases during synthesis are shown in Fig. 4D. According to this, $V_2(Fe_{1/3}Sn_{2/3})C$ can appear at temperatures as low as 400 °C. Below this temperature, the $V_2C$ and FeSn3 phases are dominant. Above 750 °C, $V_2C$ and FeSn3 gradually disappear and transform into $V_2(Fe_{1/3}Sn_{2/3})C$ phase by a peritectic reaction: that is, solid $V_2C$ and an intermediate liquid Fe-Sn3 transform into $V_2(Fe_{1/3}Sn_{2/3})C$. Without the presence of Fe (or Co, Ni, and Mn), the formation of $V_2Sn3$ is instead thermodynamically favored. Fe has higher affinity to Sn and thus, a stronger tendency to form Fe-Sn alloys than V does. This should favor nucleation of $VC_{1-x}$ at low temperature and promote the peritectic reaction between $VC_{1-x}$ and liquid FeSn3 alloy to form the final $V_2(Fe_{1/3}Sn_{2/3})C$ phase.

In general, the stable $5_2(A(Sn_{1-x})C$ (A = Co, Ni, or Mn) MAX phases follow similar reaction paths as $V_2(Fe_{1/3}Sn_{2/3})C$ because of the reduced Gibbs free energy of the phase in the V-A-Sn-C system through the addition of A elements. The same is apparently true for multielement MAX phases $V_2(A(Sn_{1-x})C$ where A is 2, 3, or 4 of Fe, Co, Ni, and Mn. The mixing entropy at the A site must, therefore, account for most of the decrease in Gibbs free energy and the corresponding thermodynamic stability.

Density Functional Theory Calculations. Here, first-principles density functional theory calculations (19) were performed on the configurations $V_2C$ (A = Sn, Fe, Co, Ni, Mn) and $V_2(A(Sn_{1-x})C$ (A = Fe, Co, Ni, Mn). The corresponding total energies (SI Appendix, Table S5), lattice parameters and bond lengths (SI Appendix, Table S6), and atomic charges (SI Appendix, Table S7) are provided. Side-view images of $V_2SnC$ (Fig. S4), $V_2FeC$ (SI Appendix, Fig. S20A), and $V_2Sn_{2/3}Fe_{1/3}C$ (Fig. S5) are presented, and the corresponding charge density distributions in real space are also provided. Based on the total energies, the reaction energies for the possible chemical reactions numbered as Reactions S1 to S4 in SI Appendix, section S4 were also calculated. These results imply that A-site alloying in $V_2(A(Sn_{1-x})C$ (A = Fe, Co, Ni, Mn) is thermodynamically favored. Compared with $V_2AC$ (A = Fe, Co, Ni, Mn), $V_2SnC$ may show a higher stability due to the lower atomic charge and fewer valence electrons of Sn.
according to the findings of a previous report (20). In fact, the calculation results of phonon dispersion (SI Appendix, Fig. S21) show that V$_2$SnC is dynamically stable, while V$_2$FeC is not and thus, should not exist in the current space group.

The projected densities of states (PDOSs) of V$_2$SnC (Fig. 5 B), V$_2$FeC (SI Appendix, Fig. S20 B), and V$_2$(Fe$_{1/3}$Sn$_{2/3}$)C (Fig. 5 D) were also investigated. Sn showed a small contribution in the vicinity of Fermi level in the PDOS of V$_2$SnC, while Fe presented large density of states around the Fermi level of V$_2$FeC. This is also consistent with a lower stability of V$_2$FeC than V$_2$SnC due to the higher electron energy in the PDOS. Regarding the solid solution V$_2$(Fe$_{1/3}$Sn$_{2/3}$)C, Fe showed a lower PDOS in the vicinity of Fermi level compared with that of V$_2$FeC.

**Structure Stability.** In earlier work, Fe/Co/Ni have been shown to effectively promote the formation of M$_3$SnC$_2$ (M = Ti, Zr, Hf) MAX phases (10) without incorporation of Fe, Co, or Ni in the final MAX phases. In contrast, in these experiments, adding Fe/Co/Ni/Mn element into V/Sn/C raw materials did not promote the formation of V$_2$SnC but a series of V$_2$(A$_x$Sn$_{1-x}$)C (A = Fe, Co, Ni, Mn, or their combination) MAX phases. This also indicates that the M element (or the M$_{n+1}$X$_n$ layer) plays an important role in the incorporation of Fe, Co, Ni, and Mn elements into the A layer. As mentioned by Villars (21), at the microscopic level, it is well known that the structural stability is determined by 3 pertinent factors, namely 1) the difference in atomic radius, 2) the electronegativity difference, and 3) the electron per atom ratio (electron concentration).

Vanadium has 1 more outmost d electron but smaller atomic radius than titanium (also Zr and Hf). Thus, the corresponding M$_{n+1}$X$_n$ layer should become more compact. Therefore, the space available for Sn atoms in V$_2$SnC is less than that in M$_3$SnC$_2$ (M = Ti, Zr, Hf) MAX phases. Fe, Co, Ni, and Mn have smaller atomic radii than Sn. Thus, these elements can pack closely to Sn atoms and reduce the final molar volume in V$_2$(A$_x$Sn$_{1-x}$)C MAX phases, meaning that the mixture of A element and Sn would keep the structure stable in a constrained A layer. That is, the M$_{n+1}$X$_n$ layers provide less room for the A-element layers in V$_2$SnC when compared with M$_3$SnC$_2$ (M = Ti, Zr, Hf) MAX phases.

However, the criterion of atomic radius cannot be the only factor determining the structure stability; the electronegativity...
also accounts for the bonding structure and strength in alloys. The electronegativity (Allen scale) difference between the present A elements and Sn is also very small ($\chi_{\text{Fe}} = 1.75$, $\chi_{\text{Co}} = 1.8$, $\chi_{\text{Ni}} = 1.88$, and $\chi_{\text{Sn}} = 1.82$). Obviously, the compatibility of A atoms with Sn atoms will not modify the stacking mode of A element in between $\text{M}_n\text{A}_{1-x}\text{A}_x$ layers due to similarity in electron donor–acceptor capability.

Moreover, the electron concentration effect is crucial in complex materials, such as ternary MAX phases, because of complex electronic interactions among the constituent elements. As mentioned by Mizutani (22), the Hume–Rothery rules, which are guiding principles in the search of new alloys, use $e/a$ as its electron concentration rule to show a unique $e/a$-dependent phase stability (here, $e$ is total itinerant electron of all constituent elements in a primitive cell, and $a$ is the corresponding total atom numbers). Different phases can successively exist at a particular $e/a$ range. The itinerant electron of Fe, Co, Ni, and Mn is the same as that of Sn, which is 2. Therefore, the coexistence of these A elements with Sn at A site of MAX phases can stabilize the original crystal structure of $\text{V}_2\text{SnC}$.

**Magnetic Properties.** Temperature-dependent magnetization $M(T)$ curves under 0 field-cooled (SI Appendix, Fig. S22) and magnetic hysteresis loops (Fig. 6) of the as synthesized series of $\text{V}_2(\text{A}_{x}\text{Sn}_{1-x})_C$ ($\text{A} = \text{Fe, Co, Ni, Mn, or their combination}$) MAX phases were studied. For $\text{V}_2(\text{Fe}_{x}\text{Sn}_{1-x})_C$, except at 2 K, all of the magnetic hysteresis loops follow “S-shaped” character (Fig. 6d) with small coercive force and residual magnetization ($\text{SI Appendix}$, Table S8), suggesting that the $\text{V}_2(\text{Fe}_{x}\text{Sn}_{1-x})_C$ compound is a typical soft magnetic material (above 2 K) with saturation magnetization ($\chi$) gradually decreasing with increasing temperature. At 2 K, the coercive force ($H_c$), residual magnetization ($M_r$), and saturation magnetization ($M_s$) of $\text{V}_2(\text{Fe}_{x}\text{Sn}_{1-x})_C$ are 150.88 Oe, 0.00038 emu/g, and 0.0806 emu/g, respectively. In the case of $\text{V}_2(\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sn}_{0.5})_C$, the magnetic hysteresis loops were collected at 2, 50, 100, 200, 300, and 400 K (Fig. 6b and SI Appendix, Table S9). At 2 K, the coercive force ($H_c$), residual magnetization ($M_r$), and saturation magnetization ($M_s$) of $\text{V}_2(\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sn}_{0.5})_C$ are 481.85 Oe, 0.0262 emu/g, and 0.1378 emu/g, respectively.

Compared with Fe on A sites of $\text{V}_2(\text{Sn}_{1-x})_C$, the magnetization with 2 magnetic elements on A sites of $\text{V}_2(\text{Fe}_{x}\text{Co}_{x}\text{Sn}_{1-x-y})_C$ is stronger. Therefore, it can be concluded that the magnetic properties can be tuned by adjusting the quantity and type of magnetic elements on the A sites. For instance, for $\text{V}_2(\text{Fe}_{x}\text{Co}_{x}\text{Ni}_{1-x-y-z})_C$ (Fig. 6c), the residual magnetization ($M_r$) and saturation magnetization ($M_s$) at 2 K are 0.1499 and 0.7400 emu/g, respectively (SI Appendix, Table S10), much higher than for $\text{V}_2(\text{Fe}_{x}\text{Co}_{x}\text{Ni}_{1-x-y})_C$ and $\text{V}_2(\text{Fe}_{x}\text{Sn}_{1-x})_C$ MAX phase. In $\text{V}_2(\text{Mn}_{x}\text{Fe}_{x}\text{Co}_{x}\text{Ni}_{1-x-y-z})_C$ (Fig. 6d), which contains the antiferromagnetic element Mn at 2 K the coercive force ($H_c$), residual magnetization ($M_r$), and saturation magnetization ($M_s$) are 320.4 Oe, 0.0471 emu/g, and 0.5677 emu/g, respectively. Although the ferromagnetic properties of $\text{V}_2(\text{Fe}_{x}\text{Co}_{x}\text{Ni}_{1-x-y})_C$ in the range of 2 to 300 K, they are still much stronger than for the phases containing 1 or 2 magnetic elements. Thus, this approach provides a route for altering the magnetic properties of MAX phases by changing the chemical composition and component. The positions of magnetic elements (Fe, Co, Ni, Mn) in A layer are structurally identical but chemically disordered for their close atom masses and radii. If the distribution and proportion of magnetic elements in A layers can be controlled, the variation of magnetic properties of these MAX phases will be well understood. Moreover, one possible way to reduce the chemical disorder of magnetic elements is to take advantage of double-A layer in some MAX phases, such as Mo$_2$Ga$_2$C. Double-A layer in these MAX phases may provide additional out-of-plane coupling of spin electrons other than in-plane interaction, which would be promising to further enhance the magnetic properties.

**Concluding Remarks and Outlook**

We have demonstrated that the series of $\text{V}_2(\text{A}_{x}\text{Sn}_{1-x})_C$ phases ($\text{A} = \text{Fe, Co, Ni, Mn, or their binary/ternary/quaternary combinations}$) can be synthesized by A-site element alloying, providing a generally applicable route to introduce 1 or more magnetic elements in A sites and tune the resulting properties. A multielement phase $\text{V}_2(\text{A}_{x}\text{Sn}_{1-x})_C$ (where again $\text{A}$ is a combination of Fe, Co, Ni, and Mn and $x$ is close to 1/3) was realized. The fact that the magnetic properties are greatly enhanced for multielement A layers lends credence to this concept and offers a rich chemical space for discovering materials and properties using A-site multielement alloying strategy.

**Methods**

**Preparation of $\text{V}_2(\text{A}_{x}\text{Sn}_{1-x})_C$ ($\text{A} = \text{Fe, Co, Ni, Mn, and Combinations Thereof}$).** The starting powders were mixed in a stoichiometric ratio of V, Sn, C, A, NaCl, and KCl; the experimental details are shown in SI Appendix, section S6. After grinding for 10 min, the mixed powders were placed into an aluminum oxide boat. Then, the alumina boat was inserted into a tube furnace and heated to reaction temperature during 3 h with a heating rate of 10 °C/min under an argon atmosphere. After the end of reaction, residual chloride salts were washed out from MAX phases in deionized water. Some metal and alloys impurities were further dissolved in HCl acid in order to obtain pure MAX phase powders. The weight change during various steps of the process is provided in SI Appendix, Fig. S23 and Table S12.

**Computational Details.** All the first-principles calculations were performed using the VASP code (23, 24). Based on the projector-augmented wave pseudopotential (25) with a plane-wave cutoff energy of 500 eV, the generalized gradient approximation as implemented by Perdew–Burke–Ernzerhof (26) was used for describing the exchange-correlation functional. Regarding atomic charges, a Bader charge analysis (27) based on 180 Å × 180 Å × 180 grid was performed. Phonon dispersion was investigated with Phonopy software (28) and the VASP code based on the density functional perturbation theory (29). All of the structures were visualized in the VESTA3 code (30).

The Calculation of Phase Diagrams (CALPHAD) approach was applied to calculate the phase diagrams. Due to the lack of experimental data on the ternary V-Sn-C, V-Fe-C, and V-Sn-Fe-C compounds, first-principles calculations were conducted to support the CALPHAD work (31). The Gibbs free energy function of $\text{V}_2(\text{Sn,Fe})_C$ was then determined with the Neumann–Kopp rule and added in the CALPHAD-type dataset of the V-Sn-Fe-C system, which included the thermodynamic parameters of the binary V-Sn, V-Fe, V-C, Sn-C,
Sn-Fe, and Fe-C systems (32–36). All of the calculations were performed with the Thermo-Calc software.

Characterization. Phase composition of the samples was analyzed by XRD (DB Advance; Bruker AXS) with Cu Kα radiation. The microstructure and chemical character of the samples were observed by SEM (QUANTA 250 FEG; FEI) equipped with an energy-dispersive spectrometer. AFM analysis was performed by means of a Dimension 3100 V system (Veeco) under tapping mode. Scanning transmission electron microscopy (STEM) imaging and EDS analyzing were performed in a double-corrected FEI Titan 60 to 300 microscope. The magnetic properties were measured on a Quantum Design superconducting quantum interference device magnetometer.

Data Availability. The data presented in this article are available in SI Appendix. SI Appendix contains experimental conditions, XRD patterns, AFM topography, SEM images, SEM-EDS mapping, STEM images, and line scanning, density functional theory calculation, and magnetic characterization of V3(Al,Sr)10,C MAX phases.

ACKNOWLEDGMENTS. This study was supported financially by National Natural Science Foundation of China Grants 21671195, 21805295, and 21875271 and Chinese Academy of Sciences Grants 2019YFA0210000 and 174433KYSB20190019. We acknowledge support from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University through Faculty Grant SFO Mat-LIU 2009 00971. The Knut and Alice Wallenberg Foundation is acknowledged for support of the electron microscopy laboratory in Linköping through Grant KAW 2015.0043, a Scholar (J. Olof Roos), and an Academy Fellow grant (to P.E.). P.O.A.P. also acknowledges Swedish Foundation for Strategic Research Project Funding EM16-0004 and Research Infrastructure Fellow Rif 14-0074. We thank Cai Shen for the AFM characterization of MAX phases.

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