Systematization of MAX phases formability and exploration of their new phases for future MXenes

Yiming Zhang¹, Zeyu Mao¹ ², Qi Han¹, Youbing Li¹ ³, Mian Li¹, Shiyu Du¹, Zhifang Chai¹, Qing Huang¹*

1. Engineering Laboratory of Advanced Energy Materials, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China
2. School of Materials Science and Engineering (MSE), Xi’an Jiaotong University
3. University of Chinese Academy of Sciences, 19A Yuquan Rd, Shijingshan District, Beijing, 10049, China

Abstract

As a fast-growing family of 2D materials, MXenes are rising into the limelight due to their attractive properties that leading to applications in energy storage, catalysis, microwave attenuation, etc. As their precursors, MAX phases are a family of layered, hexagonal-structure ternary carbides and nitrides. The exploration of novel MAX phases would largely expand the candidates for future MXenes with various component elements and microstructures. Meanwhile, apart from their indispensable role in ‘Top-down’ synthesis of MXenes, MAX phase materials show remarkable combination of characteristics of metals and ceramics, endowing them great interest as both structural and functional materials. Up to now, there are more than 100 MAX compositions synthesized to date; and discoveries of new MAX phases (Ti₃AuC₂, Ti₃IrC₂, Ti₂ZnC, Nb₂CuC et al.) are continuously being reported by experimental scientists. To increase the efficiency in the successful search for novel MAX phases, a general guideline should be set up to direct experiments through an information-prediction system incorporating all MAX phases’ databases and high-quality regularities. In this work, we introduce structure mapping methodology, which has shown its viability of being an effective guideline in design of MAX phases; and also provide simple principles for experimental scientists in the search for novel MAX phases. In fact, above-mentioned new MAX phases have fallen into structure-stability regime that framed by this structure mapping methodology. These new MAX phases, whatever experimentally reported or theoretically predicted, will largely enrich the structure-modification and property-tuning of derived MXenes.

* Corresponding author. Tel/Fax: +86-(0)574-86686062, e-mail address: huangqing@nimte.ac.cn
Postal address: Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences. No. 1219 Zhongguan West Road, Zhenhai District, Ningbo, Zhejiang Province, P.R. China, 315201
1. Introduction

Two-dimensional (2D) materials have attracted great attention during the past decade for their high application potential due to their intrinsic fascinating physical and chemical properties. This merit has led to both a new wave of research on known 2D materials, as well as the discovery of many new 2D materials. Owning to their extraordinary properties and being considered for varieties of potential and different applications, the carbides and nitrides of transition metals (MXenes) are garnering tremendous interest.\textsuperscript{[1-4]}

The $\text{M}_{n+1}\text{AX}_n$ (or MAX phases), as the most common precursors for MXenes, are layered machinable ternary carbides and nitrides; where “M” is an early transition metal, “A” is an A group element (mostly from groups 13 and 14), “X” is C and/or N, and $n = 1$ to 3. During the past, this type of material have attracted considerable attention due to 1) their unique combination of both metallic and ceramic properties, 2) the ease by which one can tune their chemistry, while keeping their structures the same, and 3) the recent discovery of both in- and out-of-plane ordered phases, which opens the door to the discovery of many more, and 4) most noteworthy they are precursors of MXenes that have been found promising in varied functional applications.\textsuperscript{[5-10]} Currently, 14 $M$-elements and 20 $A$-elements have been introduced into various end-member MAX phases, resulting more than 100 MAX compositions synthesized to date (shown in Figure 1). The chemical diversity of these MAX phases holds the key to eventually optimizing properties for prospective applications, and also to the capability of exfoliation for varieties of MXenes. In order to explore novel MAX phases efficiently, \textit{ab initio} calculations have been carried either through calculating whether a compound is stable on an absolute scale, or showing that a given MAX phase is more stable than all other competing phases.\textsuperscript{[7, 11-14]} However, without time-consuming full DFT calculations, these analyses have all failed to reveal any correlations or systematic behavior.\textsuperscript{[7, 11]} As a result, alternative strategies have to be introduced in to develop general chemical design regularities with the hope that they can provide sufficient insight to help forecast, with some certainty, new MAX phases.
**Figure 1.** Elements introduced in various end-member MAX phases. M elements are in red, A elements are in blue, and X elements are in green. Iron element can both occupy M and A sites.

During the past, structure mapping, a well-constructed strategy to build classification schemes for homologous compounds from database of known structures, has played an important role as a useful *a priori* guide for finding stable phases and serving as a visualization tool for filling compositional and structural gaps in a bi-variate way.\(^\text{[15]}\)

There is a long and distinguished tradition of such maps, several examples including the figures developed by Hume-Rothery under Engel-Brewer theories,\(^\text{[16]}\) Mooser-Pearson plots,\(^\text{[17]}\) Philips and van Vechten diagrams,\(^\text{[18-19]}\) Zunger maps,\(^\text{[20]}\) Villars maps,\(^\text{[21-25]}\) Pettifor maps,\(^\text{[24-26]}\) ones developed by Xue *et al.*\(^\text{[27-28]}\) for ABO\(_3\)-type perovskite formability classification, and others.\(^\text{[29-38]}\)

In this work, we are aiming to construct one single 2D structure map to identify characteristic domain the M\(_{n+1}\)AX\(_n\) phases could form; so that all of the MAX phases structure data could be ordered and eventually understood within a microscopic theory. The chemical scales are proposed to provide guiding principles in the search for new MAX phases. The implication of structure mapping of MAX phases on synthesis of MXenes is also discussed.

2 **Exploration of the factors regulating MAX phases structure**

Historically, physical factors governing structural stability are carefully chosen to serve as the coordinates of structure maps; and from the current viewpoint of *material informatics*, structure mapping can be treated as a classification tool whereby through
the choice of appropriate coordinates, one can map clustering of crystal structure related data.

It is known that the structural stability is determined by different groups of factors, namely the 1) geometrical factor (size factor); 2) electron concentration factor, 3) electrochemical factor (electronegativity difference), and 4) angular character of the $s$, $p$, and $d$ valence orbitals.$[39-41]$ The majority of structure mapping constructions are based on taking coordinates that reflect the most important physical factors determining the structural stability of the particular class of compounds under consideration. For example, Mooser and Pearson$[17]$ chose the electronegativity difference $\Delta \chi$ as one coordinate and the average value of the principal quantum number $\bar{n}$ as the other in their study of valence compounds structures. Phillips and Van Vechten$[18]$ employed the physically motivated coordinates $E_h$ and $C$, which are the covalent and ionic contribution to the average spectroscopic energy gap respectively, to separate the structure types within $sp$-valent AB octet semiconductors and insulators successfully. Zunger$[20]$ adopted $R_{y}^{AB}$ and $R_{z}^{AB}$ for obtaining a reasonable structural separation of all the known AB compounds within three separate 2D maps, where the $R_{y}^{AB}$ is a measure of the size mismatch between the A and B atoms, and the $R_{z}^{AB}$ is a measure of the average propensity of the two atoms to form $sp$ hybrids. Xue et al.$[27-28]$ based on the ideal A-O and B-O bond distances derived from bond-valence model, to construct two-dimensional structure maps for predicting the formability of perovskites. By contrast, Villars$[21-23]$ introduced three-dimensional maps $(\Delta \chi, \Delta R, \bar{N})$ aiming to obtain a structural separation of all iso-stoichiometric binary compounds within a single framework, where the three coordinates reflect the importance of the electronegativity difference $\Delta \chi$, the atomic-size difference $\Delta R$, and the average number of valence electrons per atom $\bar{N}$ in the determination of the structural stability. In principle, the classifications of the structures of homologous compounds has to take all of these factors into account; however, it makes the perfectly ordering within a single two- or three- dimensional map challenge with the use of unique physical coordinates. This situation becomes more serious when faced with ternary compounds, such as MAX phases; and the mixture of metallic, covalent, and ionic bonding characteristics further complicate the cases.
Considering the fact of above four types of factors are not wholly independent of each other, and it is their interplay that determines the structural stability of compound phases.\cite{42} In this work, our goal is to identify two most important factors within these four groups for constructing a visualizable 2D structure map; in order to capture the dominant factors that control the formability of MAX phases, and then quantify key design variables for their experimental development.

2.1 Determining the types of factors
The electron concentration effect is crucial in complex materials such as MAX phases in this case, due to the intricate ways of electronic interactions among the constituent elements.\cite{43} As mentioned by Barsoum,\cite{7} it is not too bleak if the "To Be or Not to Be" problem of MAX phases could be looked from the viewpoint of valence electron density of given MAX phases, \( n_{\text{val}} \); which is further connected to average number of formal valence electrons. Taking this inspiration into consideration, the electron concentration factor is adopted as one coordinate in this work, the determination of the expressions and values of this factor will be stated in section 2.2.

It is known that the unit cell of MAX phase structures is composed of edge-sharing \( \text{M}_6\text{X} \) octahedra with A-site elements located at the center of trigonal prisms; and currently, A-site element replacement in traditional MAX phases by later transition-metals is becoming a buzzing field for opening a door to explore new types of MAX phases.\cite{44-49} It can be seen that the distortion of ideal trigonal prism induced by newly introduced A-site elements would strongly affect the viability of these novel MAX phases. A parameter \( p_r \), given by Hug et al.\cite{50}, has been used to measure this type of distortion; which is determined by inter-atomic distances between M-site and A-site elements, as well as between M-site elements. Based on above analysis, it is natural to choose size factor as the other coordinate. The determination of the expressions and values of this factor will be described in section 2.2.

2.2 Determining the expression and values of factors
Determining the values of electron concentration factor: There are two different parameters that can be used to define the electron concentration:\cite{43} one is an average number of itinerant electrons per atom, \( \text{ela} \); while the other is the average number of total electrons, including \( d \)-electrons accommodated in the valence band, which is
valence electrons (referred to as VEC). Both of e/a and VEC play crucial roles for the chemical bonding of a solid, and are closely related. The main difference is that the e/a had been introduced as a concept defined under the assumption that ‘free’ electrons are uniformly distributed over a crystal, whereas the valence electrons are locally defined for individual constituent elements in a real space.\textsuperscript{[51-52]} It is known that for M-X bonding, the $p$-$d$ interaction between M-site and X-site atoms are quite strong; and the hybridization between the M-site $d$ orbitals and the X-site $2p$ orbitals lead to strong covalent bonds. While for M-A bonding, the interactions between the $d$ electrons of the M atoms and $p$ electrons of the A atoms are weaker than those between the M and X atoms; and A-site $d$ electrons do not appear to play a role in bonding.\textsuperscript{[7]} Following above analysis, here we choose valence electron values of M-site and X-site elements; and choose itinerant electron values of A-site elements for calculating electron concentration. The values of valence electrons are collected from general inorganic chemistry textbook;\textsuperscript{[53]} and the itinerant electrons are taken from Mizutani and Sato.\textsuperscript{[54]} Table 1 listed the valence/itinerant electron values adopted for the elements used in this work.

**Determining the values of size factor:** In Hume-Rothery’s Rules, which distinguished the factors that influence compound formation and control alloying behavior over a span of nearly 90 years,\textsuperscript{[55-59]} the difference percentage of solvent and solute atomic radii is adopted as size factor to characterize the mismatch between solvent and solute atoms.\textsuperscript{[59-60]} Borrowing the ideas from Hume-Rothery’s Rules, the difference between the atomic radii of M-site elements and A-site elements divided by the radii of M-site elements is used as size factor in this work. Here the values of atomic radii, based on experimental evaluation and theoretical calculations,\textsuperscript{[61-62]} are taken from CRC Handbook.\textsuperscript{[63]} Table 2 listed the atomic radius values adopted for the elements used in this work.
### Table 1 The valence/itinerant electron values adopted in this work

| Elements | Valence Electrons | Elements | Itinerant Electrons | Elements | Valence Electrons |
|----------|-------------------|----------|---------------------|----------|-------------------|
| **M**    |                   | **A**    |                     | **X**    |                   |
| Sc       | 3                 | Al       | 3.01                | C        | 4                 |
| Ti       | 4                 | Si       | 4.00                | N        | 5                 |
| V        | 5                 | P        | 4.97                |          |                   |
| Cr       | 6                 | S"      | 6.00                |          |                   |
| Mn       | 7                 | Mn       | 1.05                |          |                   |
| Zr       | 4                 | Fe       | 1.05                |          |                   |
| Nb       | 5                 | Co       | 1.03                |          |                   |
| Mo       | 6                 | Ni       | 1.16                |          |                   |
| Lu"     | 3                 | Cu       | 1.00                |          |                   |
| Hf       | 4                 | Zn       | 2.04                |          |                   |
| Ta       | 5                 | Ga       | 3.00                |          |                   |
|          |                   | Ge       | 4.05                |          |                   |
|          |                   | As       | 4.92                |          |                   |
|          |                   | Pd       | 0.96                |          |                   |
|          |                   | Ag       | 1.01                |          |                   |
|          |                   | Cd       | 2.03                |          |                   |
|          |                   | In       | 3.03                |          |                   |
|          |                   | Sn       | 3.97                |          |                   |
|          |                   | Ir       | 1.60                |          |                   |
|          |                   | Pt       | 1.63                |          |                   |
|          |                   | Au       | 1.00                |          |                   |
|          |                   | Tl       | 3.03                |          |                   |
|          |                   | Pb       | 4.00                |          |                   |

* The value of 3 is used for Lu by considering to follow the periodic trend

** The work of Mizutani and Sato\[54\] does not record itinerant electrons for Sulfur, here the value of 6 is used for Sulfur.
Table 2 The atomic radius values adopted in this work (Unit: Å)

| Elements | Atomic Radius | Elements | Atomic Radius | Elements | Atomic Radius |
|----------|---------------|----------|---------------|----------|---------------|
| M        |               | A        |               | X        |               |
| Sc       | 1.59          | Al       | 1.24          | C        | 0.75          |
| Ti       | 1.48          | Si       | 1.14          | N        | 0.71          |
| V        | 1.44          | P        | 1.09          |          |               |
| Cr       | 1.30          | S        | 1.04          |          |               |
| Mn       | 1.29          | Mn       | 1.29          |          |               |
| Zr       | 1.64          | Fe       | 1.24          |          |               |
| Nb       | 1.56          | Co       | 1.18          |          |               |
| Mo       | 1.46          | Ni       | 1.17          |          |               |
| Lu       | 1.74          | Cu       | 1.22          |          |               |
| Hf       | 1.64          | Zn       | 1.20          |          |               |
| Ta       | 1.58          | Ga       | 1.23          |          |               |
|          |               | Ge       | 1.20          |          |               |
|          |               | As       | 1.20          |          |               |
|          |               | Pd       | 1.30          |          |               |
|          |               | Ag       | 1.36          |          |               |
|          |               | Cd       | 1.40          |          |               |
|          |               | In       | 1.42          |          |               |
|          |               | Sn       | 1.40          |          |               |
|          |               | Ir       | 1.32          |          |               |
|          |               | Pt       | 1.30          |          |               |
|          |               | Au       | 1.30          |          |               |
|          |               | Tl       | 1.44          |          |               |
|          |               | Pb       | 1.45          |          |               |
3 Results

In order to construct structure maps, the data of formable and non-formable MAX phases have to be collected. The formable MAX phases are experimental synthesized ones that are collected from Sokol et al.\textsuperscript{[10]} and new discoveries of our laboratory.\textsuperscript{[46-49]} the non-formable ones are recorded from Aryal et al.,\textsuperscript{[14]} which are screened based on elastic and thermodynamic stability by using ab initio calculations.

3.1 The structure map construction for MAX phases formability

Firstly, the structure maps plotted from the calculated electron concentration factor and size factor are constructed for traditional MAX phases (shown in Figure 2), where the M group elements include Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and Lu; the A elements include Al, Si, P, S, Ga, Ge, As, Cd, In, Sn, Tl, and Pb; and the X elements are either C and/or N.\textsuperscript{[7,64]} Most of the MAX phases are 211 phases, and so the developed structure mapping strategy is firstly applied to 211 phases (shown in Figure 2(a)). It is found that there exist two separable domains to which the formable/non-formable MAX phases are belonging. From Figure 2(a), it can be seen that the chosen scales and expressions of "electron concentration factor" and "size factor" in this work has achieved a highly successful formability/non-formability separation of 211-MAX phases, only with a few exceptions; and the details will be discussed later.

For the next trail, the structure map that has been plotted from 211-MAX phases is further applied to 312-MAX phases (shown in Figure 2(b)) and 413-MAX phases (shown in Figure 2(c)) for examining whether the constructed structure map is the one that could unify the formability/non-formability separation of traditional MAX phases. From Figure 2(b) and (c), it can be found that the same structure map has capability to locate formable/non-formable 312-MAX and 413-MAX phases into separated domains; which means one single structure map has the capability to classify the formability/non-formability for the whole family of traditional M\textsubscript{n+1}AX\textsubscript{n} (n = 1 to 3) phases.
Figure 2. The structure maps constructed from the calculated electron concentration factor and size factor for traditional MAX phases (pentagram symbols represent synthesized MAX phases; fork symbols represent unviable MAX phases): (a) Formable and non-formable separation for traditional 211-MAX phases; (b) Formable and non-formable separation for traditional 312-MAX phases; (c) Formable and non-formable separation for traditional 413-MAX phases.

3.2 The validation of the constructed structure map

The quest for generality raises the requirement of validating the developed structure map by using newly reported novel MAX phases, where the A-site elements have been extended to include Zn, Cu, Au, Ga; also, Mn is introduced in as M-site element \([44, 46, 49, 65-66]\). The validation results are shown in Figure 3. It is found that all of the newly reported novel MAX phases, except Mn$_2$GaC, are located within formable regions, which show the generality of the constructed structure map to whole family of M$_{n+1}$AX$_n$ phases.
Figure 3. The constructed structure map containing data of traditional MAX phases, as well as newly reported novel MAX phases (pentagram symbols represent synthesized MAX phases; fork symbols represent unviable MAX phases; circle symbols represent newly reported novel MAX phases): (a) Formable and non-formable separation for 211-MAX phases; (b) Formable and non-formable separation for 312-MAX phases
3.3 Employ the constructed structure map to explore potential MAX phases

In order to provide guidance for future experimental development of MAX-phases, the developed structure map is further employed to explore potential 211-MAX phases (shown in Figure 4). From the results shown in Figure 4, we propose several potential viable 211-MAX phases; including Ta<sub>2</sub>CoC, Ta<sub>2</sub>CoN, Ti<sub>2</sub>AgC, Ti<sub>2</sub>AgN, Ti<sub>2</sub>FeC, Ti<sub>2</sub>FeN, Ti<sub>2</sub>CoC, Ti<sub>2</sub>CoN, Ti<sub>2</sub>NiC, Ti<sub>2</sub>NiN, Ti<sub>2</sub>PtC, Ti<sub>2</sub>PtN, Ti<sub>2</sub>PdC, Ti<sub>2</sub>PdN, Ti<sub>2</sub>MnC, Ti<sub>2</sub>MnN, Ta<sub>2</sub>FeC, Ta<sub>2</sub>FeN, Nb<sub>2</sub>FeC, Nb<sub>2</sub>FeN, V<sub>2</sub>FeC, V<sub>2</sub>FeN.

![Figure 4](image-url)

**Figure 4.** The structure map of 211-MAX phases (pentagram symbols represent synthesized MAX phases; fork symbols represent unviable MAX phases; circle symbols represent newly reported novel MAX phases; asterisk symbols represent potential viable MAX phases).

4 Discussion

4.1 The validity of structure mapping approach

The crystallographic information is a prerequisite for any extensive materials modeling and analysis; making knowledge of crystal structures based on information about constituent elements is consequently a practically-pressing problem of crystal chemistry that continuing to be an area of ongoing research.\textsuperscript{[15,67]} Currently, there are three main approaches for determination of crystal structures:

1) **Experimental determination.** This kind of strategy was initiated in 1911 by von Laue et al.\textsuperscript{[68]} and Bragg,\textsuperscript{[69]} which has been a key tactic within the past several decades that has yielded many of important new materials we are studying and
using today. However, this approach is expensive despite the emergence of high throughput automation.\cite{70-73}

2) **Computational modeling.** The evolution of high-speed computers, the derivation of one-electron potentials that greatly simplify many-body interactions, as well as high-throughput computational infrastructure have made it possible to predict materials structures using quantum mechanics principles, as demonstrated by Curtarolo et al.,\cite{74-75} Lin,\cite{76} and Jain et al.\cite{77} These modeling efforts have made computational materials design a real possibility but difficulties still exist, as mentioned by Chelikowsky.\cite{39, 78} In addition, quantum mechanical calculations require some experiences and backgrounds that not every experimentalist have; and therefore artifacts can result from not properly chosen basis sets, \(k\)-mesh sizes, etc. that may lead to misinterpretations.

3) **Structure mapping.** The general compounding characteristics of different elements, as well as their reactivity towards specific compounds, are usually very complex; and cannot be easily explained and rationalized on the basis of a few physical concepts and data. However, the classical concepts of chemical bonding are still be useful for a qualitative interpretation and understanding of crystal structures.\cite{41} The structure mapping, which reveals inter-elemental reactivity trends in the Periodic Table, has been adopted as a successful non-experimental methods to build chemical design regularities by organizing and classifying homologous compounds from database of known structures. Here, the choice of factors for coordinates is critical. In order to achieve high predictive accuracy and provide clear formalism, descriptors that controlling the crystal structure in essence have to be selected. This point will be discussed in the section 4.2 and 4.3.

### 4.2 The validity of the size factor expression

In this work, we choose the difference between the atomic radii of M-site elements and A-site elements divided by the radii of M-site elements as size factor. However, atomic radii are not precisely defined.\cite{42, 60} Here, the recommended single-bond covalent radii are used; however, the 'radius' of an atom is probably affected by coordination number, oxidation state, or type of ligand.\cite{63} Allocating a single atomic diameter for each element, independent of its environment, and neighbor atoms is too
simplistic an approach. Further, in this work we only take the atomic size of M-site and A-site elements into consideration; but not the ones of X-site elements. The formation of M-X block also plays important role to the MAX phases formability. These factors contribute to the generalization and predictive accuracy of the constructed structure maps.

4.3 The validity of the factors choice
It has been mentioned that the structural stability is determined by four different groups. In this work, we have chosen electron concentration factor and size factor as controlling parameters to map associations of MAX phase structures to their compositions. Whereas the results show the feasibility of this choice, other factors can be introduced in to fully describe the MAX phases. For example, the electronegativity $\chi$, that is transferable to atoms in different atomic environments, can be seen as a measure to attract valence electrons from more electropositive atoms. As a result, the ones of the constituents of an compound could provide useful guidance for estimating the polarity of the chemical bonds between them; which would serve a key feature in the description of the electronic interactions pictured in terms of covalent bonding. Employing this parameter is proposed to enhance the description of covalent bonding characteristics within MAX phases.

4.4 The MAX phases with elements of high valence electron density
From the results demonstrated before, it can be found that the Cr- and Mn- containing MAX phases that have been synthesized locate within the non-formable zone. As mention by Barsoum,[7] above a certain valence electron density, $n_{val}$, the MAX phases are somehow destabilized; and referred Cr-containing MAX phases (e.g. Cr$_2$GeC, Cr$_2$AlC) as anomalous or borderline-stable compounds. In this work, the valence electron values of M-site elements (where for Cr is 6, and for Mn is 7) are taken into consideration for calculating the electron concentration factor; which have shown the consistence to the above statement.

However, it has to be pointed out that the size factor plays an important role in confronting the destabilizing effect of electron concentration factor. Taking Mo-containing MAX phases as examples. The valence electron values of Mo is 6, and all of Mo- containing MAX phases, but Mo$_2$GaC, are located within the non-formable region. The dragging of Mo$_2$GaC from non-formable region to formable region is
attributed to the size difference between Mo and Ga. This compounding effect of size factor and electron concentration factor could be further utilized to guide the novel MAX phases design, either through M-site and A-site replacement, or via solid solution.

5 Implication for future MXenes
The continuous breakthrough of MXenes and their promising application largely rely on their diversity of precursor: MAX phases. A element in MAX phase determines the etching chemistry. Up to now, near all MXenes are derived from Al-containing MAX phases (such as Ti$_3$AlC$_2$ in the first report) in hydrofluoric acid or its mixture solution.$^{[10]}$ Ti$_3$SiC$_2$ MAX phase was also successfully employed to synthesize MXenes in HF/H$_2$O$_2$ mixture.$^{[79]}$ Recently, our group developed an etching chemistry in molten salts whose redox potentials are higher than that of A elements in MAX phases.$^{[80]}$ Such Lewis-acid melts act similar to HF acid, and A elements can be effectively driven out from MAX phases to form chloride vapors. Due to strong Lewis acidity of melts (such as ZnCl$_2$ and CuCl$_2$), the range of MAX phase precursors for MXenes can potentially expand to nearly whole family members as long as A elements have low redox potentials. Thus, the exploration of new MAX phases to satisfy this A-site requirement would be of great importance in terms of finding of new MXenes. The above-mentioned structure-mapping methodology provide a simple but efficient way to predict some new MAX phases with various transition A elements (such as Mn, Fe, Co, Ni, Ag, Pt, Pd etc.) since their redox potentials are comparable with that of traditional main group A elements (such as Al, In, Ga, Si, Ge, Sn etc.).

These unexploited MAX phases would be potential precursors for future MXenes. Besides A element, the M element in final MXenes determine their physical properties (such as thermal, conductive, and mechanical behaviors) in addition to surface chemical reaction (such as functionalization with groups, absorption of ions, accommodation of active atoms for catalysis or energy storage). Early-transition metals and even some of rare earth metals (such as Sc, Y, and Lanthanide elements) could fall in candidate M elements in order to search possible MXenes. The structure mapping method will give a first sight on their structure stability before numerous trial-and-error experiments.

6 Conclusions
As one type of heterodesmic compounds, metallic, covalent and/or ionic interactions
are present to a differing extent within MAX phases. To get a full description of crystal structures for it, with regard to its chemical bonding and stability, the Schrödinger equations have to be solved. However, the fact of computational intensive characteristics limits the rate of potential new MAX phases investigation. In this work, we have employed structure mapping approach to develop classification schemes for MAX phases formability and non-formability. These maps are important not only for building the patterns to organize the formability of MAX phases, but also for exploring the new possible MXenes not yet studied.

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