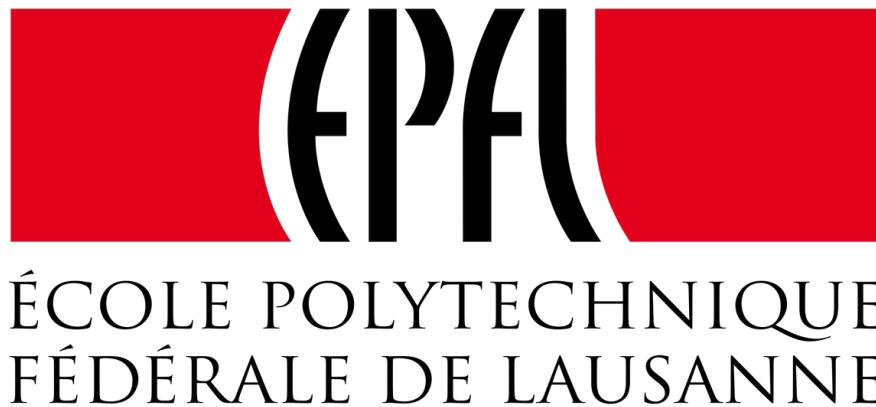


Semester Project
A New Algorithm of MAX Phase Materials
Finder



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1 Introduction

1.1 MAX Phase Materials

MAX phase materials are a group of solid materials composed of layered transition metal carbides or nitrides with hexagonal lattice. The name ‘MAX’ comes from their chemical formula $M_{n+1}AX_n$, with n ranging from 1 to 4. There are some exceptions, which are included in Figure 1. M stands for early transition metal such as Titanium, Vanadium, Zirconium, A means 3A-6A (main group) elements such as Sulfur, Aluminum, Gallium, and finally X represents either carbon or nitrogen. The structure of MAX phase materials consists of near closed pack M layers, interleaved pure A layers and X elements filling the octahedral sites between.[1] Therefore, they possess a fashion of alternating metallic bonding layer and covalent bonding layer.

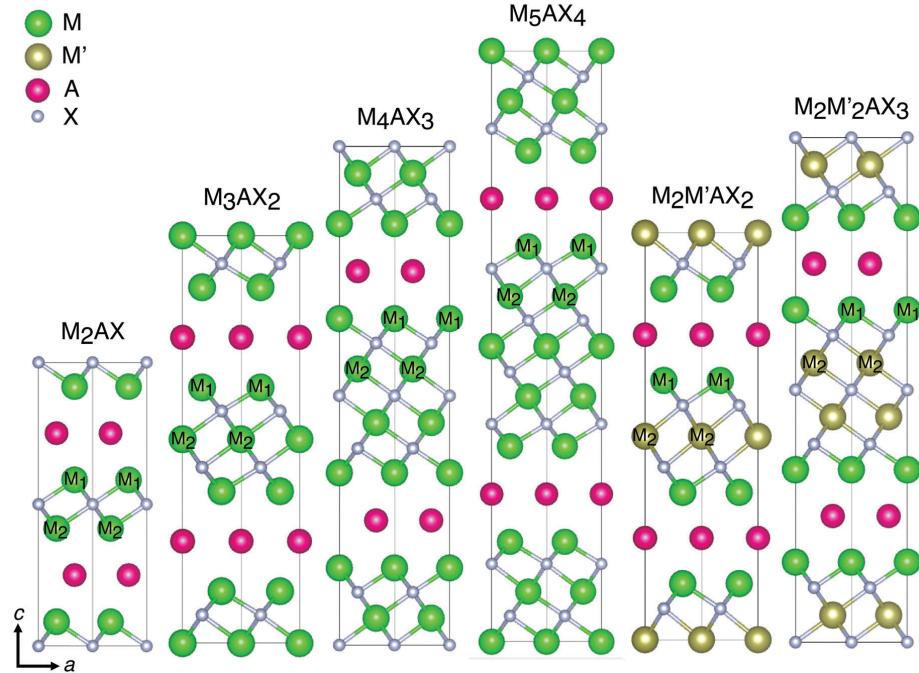


Figure 1: Overview of known MAX phase structures
source: [2]

[2]Usually MAX phase materials are considered as ceramics because they are produced at elevated temperature and they are made of metal and non-metal elements. However, MAX phases materials are metallic, because there

are partially occupied d-orbitals near their Fermi level. Therefore, they are electrically conductive in planes or across the planes because of these metallic bonding between each transition metal elements. Due to their structure and bonding type, MAX phase materials have good mechanical and thermal stability and they have been implemented in the usage under harsh environment. For example, Titanium silicon carbide (Ti_3SiC_2) was found to be stable at the temperature as high as 1800C under an argon atmosphere.

Recently, the application of MAX phases is gradually shift from solely on their interesting mechanical properties to the possibilities of exfoliation from themselves into MXenes. It has found that by using the combination of acid treatment and sonication (or exfoliation in general), some of the bonds between M-A can be broken while the bonds between M-X remain virtually intact. After washing the broken A element out of the MAX phase materials, the remaining structure can be a single or multilayers. A typical acid exfoliation process is shown as Figure 2.

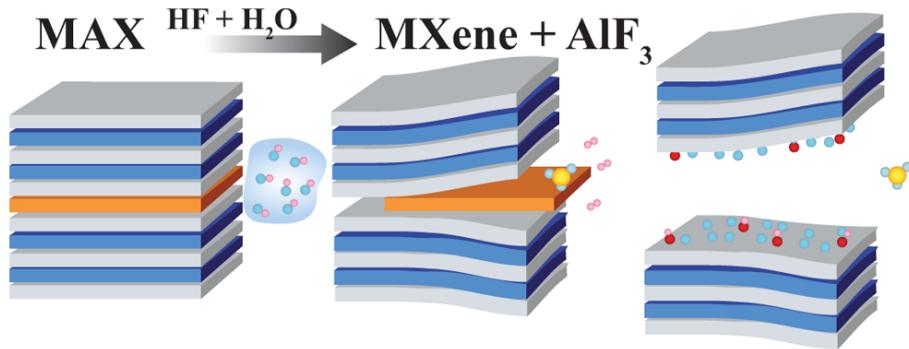


Figure 2: Example of acid exfoliation from MAX to MXenes
source: [3]

1.2 MXenes

[4]As mentioned in the end of last part, these experimentally derived two-dimensional structures (single or multilayers) products such as Nb_2C , Ti_3C_2 are called MXenes. Again, the name ‘MXenes’ originates from the MAX phase materials but without the A element to indicate they are derivatives of MAX phase materials and use the suffix ‘ene’ to emphasize the analogous to graphene. The overview of MXenes structures are indicated as Figure 3.

MXenes materials are chemically stable compared with MAX phase materials, because the A elements are relatively weakly bonded, they (-A bonds) are therefore relatively reactive. Still, in contrast to the limit application of MAX phase materials, MXenes already have many (some are theoretical) applications like for the optical, thermoelectric and magnetic use. For instance, it is theoretically shown that after a certain surface functionalization, some of the MXenes can turn into semiconductors.

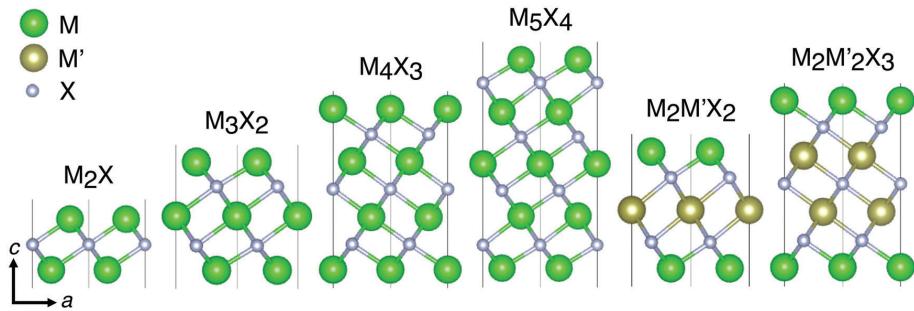


Figure 3: Overview of known MXenes structures
source: [2]

2 Motivation

Considering the variety of MAX phase materials, many MXenes with different properties should therefore be expected. As mentioned before, it is known MAX phase materials is the source to produce MXenes. It has been theoretically analyzed that MAX phase materials are promising candidates for a successful exfoliation into MXenes. Moreover, it is shown that, based on density functional theory, among 82 known crystalline MAX phase materials except for the MAX phase materials with the A elements of S or P, many of them exhibit higher possibility for exfoliation into MXenes.

Given the above mentioned, because there are only 82 experimentally known MAX phase materials now, accelerating the searching of MAX phase materials will hence speed up the discovering of MXenes. In this report, from the theoretical view point, my advisor and I aim to device an algorithm to test whether an arbitrary structure is MAX-phase-materials-like or not. That is, they are layered structure and have an alternating bonding type for planes.

3 Methodology

3.1 Automatic Program structure

As mentioned from the last chapter, the goal is to create an automatic program to test if any input structure is two-dimensional or not. Based on the reference paper[5], the method to extract the two-dimensional sub-structures (if any) from arbitrary input structures are indicated as follow.

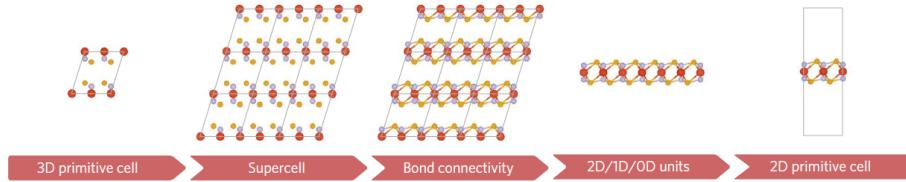


Figure 4: Illustration of automatic program steps

source: [5]

1. First is to create a super cell ($3 \times 3 \times 3$) using the input structure and evaluate all the interatomic distances inside the supercell.
2. If the interatomic distance satisfies the defined criteria for bonding, both atoms are therefore considered to be ‘connected’. Once the bonds are identified, the connected groups (manifold) then can be constructed.
3. After the identification, the dimensionality of manifold is evaluated. With a small allowance (or without), if the ranking of manifold under periodic environment equals 2, the manifold is assumed to be two-dimensional.
4. Finally, the primitive cell of the two-dimensional manifold is constructed and sent as output.

The overall structure of method is already shown. Now the point is to choose a suitable criterion to identify if the pair is connected and to translate such concept into the algorithm of code. Two algorithms are introduced as follow.

3.2 The original algorithm

For crystal packing and supramolecular interaction analysis, van der Waal radii play an important role in searching for a better understanding of the physical properties. Van der Waal radii are first proposed by Diderik van der Waal to recognize that atoms are not simply a point and are ascribed as ‘personalities’ to each type of elements even in different situations in which its number of

valence electrons may be quite different. The volume enclosed by these radii are called van der Waal volume. The van der Waal volume is therefore the volume ‘occupied’ by an individual atom (or molecule) and the chemical bond can be thought as forming when there is an overlap over van der Waal volume.

The original algorithm is based on the van der Waal radii mentioned above to recognize whether a pair of atoms are chemically connected. Given a set of vdw radii, after the evaluation of interatomic distance ($d_{i,j}$), the chemical bond is identified if:

$$d_{i,j} < r_i^{vdW} + r_j^{vdW}$$

From the statistical analysis over 5 million interatomic distances, covalent bonds are likely to form when the distance between atoms is shorter than the sum of the vdw radii by more than a quantity Δ , on average equal to 1.3 Å.

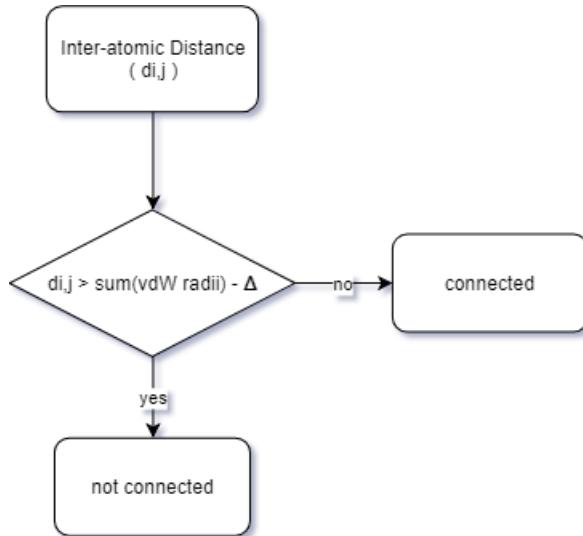


Figure 5: Schematic flowchart of original algorithm

3.3 The new algorithm

The new algorithm is based solely on the geometry and the central concept is simply to find out the maximum first neighbor distance as a threshold.

$$r_{threshold} \equiv MAX(MIN(r_{neighbor}))$$

If the interatomic distance ($d_{i,j}$) is smaller than the threshold, the pair of atoms is recognized to be connected:

$$d_{i,j} < r_{threshold}$$

For example, as shown in the graph below, the first step is to find the minimum neighbor distances for each atom (A: AC, B: BD, C: CA, D: BD), and then is to find the maximum among them. Therefore, first nearest neighbor distance is BD, which is as the expectation to be maximum first neighbor distance.

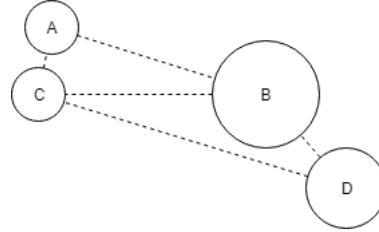


Figure 6: Example structure
(BD is the Max first neighbor distance)

However, normally the first neighbor distances can be a distribution (a slightly different in number) instead of the same value for all. Therefore, if the algorithm is simply to extract the maximum from all the smallest neighbor distances of every atoms, the bigger threshold may be omitted. To spot the right threshold, I modified the algorithm by implementing the radial distribution function.

Radial distribution function (or pair correlation function $g(r)$) describes how the number density varies as a function of distance from a reference particle. As shown by the graph, the first and second peaks correspond to the average first and second nearest neighbor distance respectively.

The concept of radial distribution function is borrowed. After finding the maximum nearest neighbor distances, for each pair of atoms (say, A-B) with atomic distance equal to this maximum nearest neighbor distance, the radial distribution is calculated with respect to the other atom element type in the pair (say, RDF of atom A with respect to element type B). The distances corresponding to first peak is denoted. Then, among each radial distribution function, the threshold is defined as the maximum of distance within first peak distance plus an arbitrarily defined allowance $\Delta \equiv 0.1\text{\AA}$:

$$r_{threshold} \equiv MAX(r_{RDF} \leq r_{firstpeak} + \Delta)$$

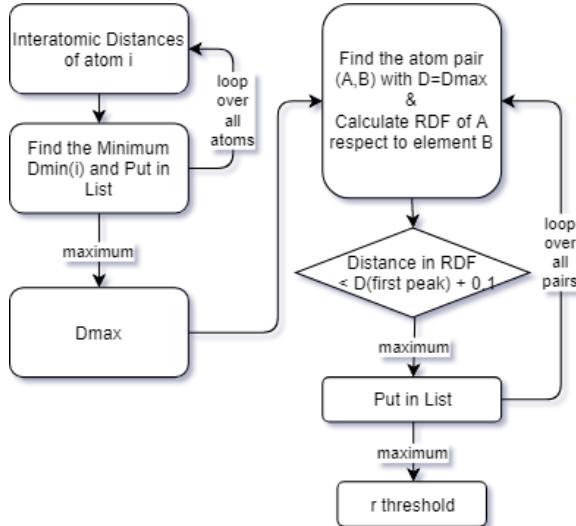


Figure 7: Schematic flow chart of finding threshold distance

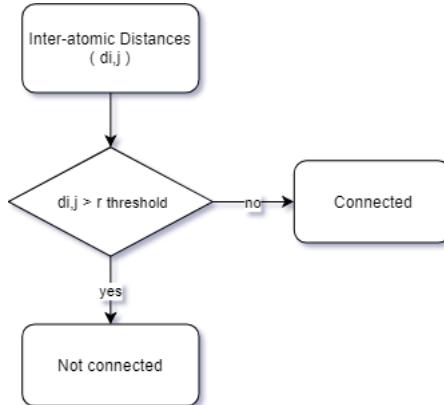


Figure 8: Schematic flow chart of new algorithm

3.4 Testing

In order to check the feasibility of new algorithm, with original algorithm as comparison, two different structure data bases are tested by two algorithms respectively. One contains structures which are all identified as van der Waal (vdW) layered materials, that is, with covalent bonds in the plane and van der Waal bonds out of plane; the other contains some known MAX phase materials plus other structures.

4 Result and Discussion

4.1 van der Waal bonded materials

In this section, the data base containing 88 kinds of vdW bonded layer structures is tested by both algorithm. The result is shown as Table 1. All the structures in the first database are those already successfully checked to be layered structure by the original algorithm and therefore, here the result from the original algorithm is only for the comparison. From a simple observation, it's easy to notice that the new algorithm works very bad to successfully identify the vdW layer compared to the original algorithm.

Material Formula	New Algorithm	Original Algorithm
B4Ca2H20O18	not layered	layered
Mg4O16S4	layered	layered
C16H40Cl8Cu2N4O8	not layered	layered
C48H32Co4N8O16	not layered	layered
Hg6Se8Tl4	not layered	layered
C32H28K4O8Se4	layered	layered
O2Se2U2	layered	layered
Cl4K4O12	not layered	layered
Hg8I4O4	not layered	layered
C8H16Cu4N8O8S8	not layered	layered
C12H12Cu3N8	not layered	layered
Ba4H32O20	not layered	layered
H16O8	not layered	layered
C48H92Na4O52	not layered	layered
Ag3Bi3S6	layered	layered
C128H88La8O72	not layered	layered
Cu4O14P4	not layered	layered
F24Ge10	not layered	layered
As3H5O10	not layered	layered
Cl4O12Pb4V4	not layered	layered
C4H4Br2Cu2N2	not layered	layered
Fe2H2O4	not layered	layered
C128H192O80Pb16	layered	layered
C14H28I2Na2O12	not layered	layered
I6In2O18	not layered	layered
AgBiSe2	layered	layered
Cu2K2Pd2Se10	layered	layered
C144H224I40N16Pb12	not layered	layered
As5Cu3Gd3	not layered	layered
O42S12Sb4	not layered	layered

Table 1. vdW bonded materials

Material Formula	New Algorithm	Original Algorithm
O10S2V2	not layered	layered
C64H32O32Pb8	not layered	layered
C76H52Mn4N12O20	not layered	layered
H8Mg6O18Si4	layered	layered
B6S20Tl6	not layered	layered
Cu2S4W	not layered	layered
Au2K2Se2	not layered	layered
H32K8O64P16Zn4	not layered	layered
Ba8Se20Sn4	not layered	layered
CrHO2	not layered	layered
H4O18P4Sr2	not layered	layered
O32Te8Tl8U4	not layered	layered
C16H24Co2N44	not layered	layered
C32H36N8Na4O12S4	not layered	layered
K8La4P8S28	not layered	layered
C24H16Mn2N16	layered	layered
C32H40Gd4N4O40	not layered	layered
C4H8Er4O22P2S2	not layered	layered
H64Mo16O80	not layered	layered
C28H32N4Na4O28S4	layered	layered
C14H18N2Ni2O14	layered	layered
C48B2O28P8	not layered	layered
C56H52Na4O12	not layered	layered
Ba2BrCuO2	layered	layered
KLaS2	layered	layered
P8Pd8Se8	not layered	layered
C32H72Ce4Cu2O68	not layered	layered
C28H28N16Ni2O8	layered	layered
C64H76K4O20S4	not layered	layered
C40H36Cu2N8O12	not layered	layered
Na2O18Ti6	layered	layered
Cl6Tc2	not layered	layered
Ga16Pb8Se32	not layered	layered
C8H20Cu3N2O14P4	layered	layered
Al2F8Tl2	not layered	layered
C68H104O68Sr8	not layered	layered
Na28O228W36	not layered	layered
C64H88Cs4O24	not layered	layered
C40H84Co10O60	not layered	layered
C24H16N16O12Zn4	not layered	layered
C20H28Ba2O26	not layered	layered
C20H72Cd4O40	not layered	layered
C20H24Ag4N20O20	not layered	layered
C24H28O32Sm4	layered	layered
C84H52Cd4N20O20	not layered	layered

Table 1. vdW bonded materials

Material Formula	New Algorithm	Original Algorithm
C72H44Cu4N12O24	not layered	layered
Cu2Na3O3	not layered	layered
H6NaO14S2V3	not layered	layered
K4O20Te4V4	not layered	layered
C16H8N6Ni2O2S4	not layered	layered
K2Mn2Sb2	layered	layered
Cs2F20O12Re6	not layered	layered
C48H64Ag4F24N16P4	layered	layered
P20Tl4	layered	layered
C34H22La2O22	not layered	layered
Eu4K8Se20Si4	layered	layered
C28H28Mn2N20	not layered	layered
C48H44Cd4Cl4N8O16	not layered	layered

At first, the result is quite different from our expectation since the new algorithm is supposed to have a much general definition on two-dimensional materials due to its purely geometric concept. However, as the result reveals, it does not seem like to be a general concept. After a closer view on structures, for those tested to be layered by new algorithm, they normally have a relatively denser structure; for those not, on the contrary, they normally have a sparse structure (or like a molecular structure) shown as below.

Examples of Sparse Structure

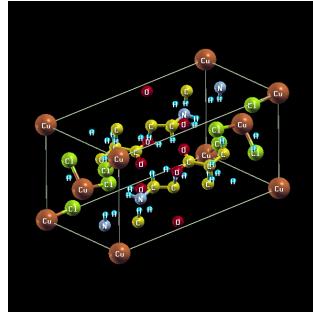


Figure 9: Ex1.C16H40Cl8Cu2N4O8

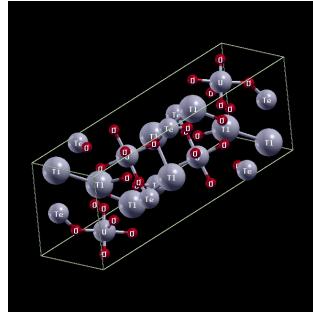


Figure 10: Ex2.C48H92Na4O52

For the original algorithm, each type of element has their own ‘personality’, that is, their own, unchangeable vdW radii. Therefore, during the examination, for some atom pairs, although they could be far apart, they could still be considered as ‘bonded’ due to their (or one of their) relatively longer vdW radii. This phenomenon becomes more significant when the structure becomes more and more sparse. On the other hand, focusing on denser structure, the effect of

vdW radii is less. This explains why the new algorithm fails to identify most of the vdW bonded materials. Because new algorithm only relies on the threshold of maximum nearest neighbor distance, for some far apart pair distances, they may be bigger than the threshold and not to be considered as bonded while been bonded from the view of original algorithm.

4.2 MAX phase materials with other structures

Both algorithms are implemented respectively on the same database containing overall 96 different species including 35 known MAX phase materials (based on the definition from section 1.1) and 61 kinds of other structures. Result is shown as Table 2. Again, from a simple observation, a huge difference could easily be noticed. That is, an almost opposite result is shown compared to section 4.1. The original algorithm only detected 2 kinds of materials to be two-dimensional with 0 accuracy while the new algorithm identified 58 kinds of materials with accuracy up to 0.603.

Table 2. MAX phase materials with other structures

Material Formula	New Algorithm	Original Algorithm
C ₂ Al ₂ Cr ₄	layered	not layered
CS ₂ Ta ₂	layered	layered
In ₃ Ti ₃	not layered	not layered
C ₄ Al ₂ Ta ₆	layered	not layered
C ₂ S ₂ Ti ₄	layered	not layered
Ga ₂ N ₂ V ₆	layered	not layered
C ₂ Ge ₂ Ti ₄	layered	not layered
Al ₆ Hf ₁₀ N ₂	not layered	not layered
CInSc ₃	not layered	not layered
C ₂ Ga ₂ Ti ₄	layered	not layered
N ₂ P ₂ V ₆	layered	not layered
C ₂ S ₂ Zr ₄	layered	not layered
C ₂ Cr ₆ Ge ₂	not layered	not layered
C ₄ Al ₂ Ti ₆	layered	not layered
Al ₂ N ₆ Ti ₈	layered	not layered
C ₁₂ Al ₆ Zr ₈	layered	not layered
C ₁₀ Al ₆ Zr ₆	layered	not layered
C ₂ Pb ₂ Zr ₄	layered	not layered
C ₄ Al ₈ Mo ₁₂	not layered	not layered
C ₄ Al ₈ Ta ₁₂	not layered	not layered
CA ₁ Ti ₃	not layered	not layered
C ₂ Hf ₄ Tl ₂	layered	not layered
CInTi ₃	not layered	not layered
NTi ₃ Tl ₁	not layered	not layered
CNb ₂ S ₂	layered	layered
Cr ₃ NSn	not layered	not layered
C ₁₀ Al ₆ Zr ₄	layered	not layered

Table 2. MAX phase materials with other structures

Material Formula	New Algorithm	Original Algorithm
C2Cr6P2	layered	not layered
C6Al2Ta8	layered	not layered
Al2N2Ti4	layered	not layered
Hf2N2S	layered	not layered
C2Ge2V4	layered	not layered
C2Al2V4	layered	not layered
Cr6N2P2	layered	not layered
C4Al8Nb12	not layered	not layered
Ca1Sc3	not layered	not layered
C9Al6Ti15	layered	not layered
C2P2V6	not layered	not layered
C8Al6Zr4	layered	not layered
Al2Hf6N2	not layered	not layered
C2Ga2Ta4	layered	not layered
C6Al4Zr3	layered	not layered
Hf2N2S	layered	not layered
Al8N4Nb12	not layered	not layered
C2Al2Nb4	layered	not layered
InNSc3	not layered	not layered
C3P6V12	not layered	not layered
C2Hf4Pb2	layered	not layered
C2Cr10Si6	not layered	not layered
C2Ge2V6	layered	not layered
C2Cd2Ti4	layered	not layered
C4Si2Ti6	layered	not layered
C2Ge6Mo10	not layered	not layered
Cr6Ge2N2	not layered	not layered
C2Ti4Tl2	layered	not layered
C2Al6Zr10	not layered	not layered
Ga2N2Ti4	layered	not layered
C5Al4Hf2	layered	not layered
C5Al4Zr2	layered	not layered
C18Mo6S44	not layered	not layered
CSc3Tl	not layered	not layered
C6Al4Hf3	layered	not layered
Cr4Ga2N2	layered	not layered
N2Sn6Zr10	not layered	not layered
C10Al6Hf6	layered	not layered
C2As2Nb4	layered	not layered
Cr3GaN	not layered	not layered
Al2N2Zr6	not layered	not layered
Ga8N4V12	not layered	not layered
C6Al2Ta8	layered	not layered

Table 2. MAX phase materials with other structures

Material Formula	New Algorithm	Original Algorithm
N4S2Zr4	layered	not layered
C2Tl2Zr4	layered	not layered
AlNTi3	not layered	not layered
C2As2V4	layered	not layered
N2SZr2	layered	not layered
Mo4N8S16	not layered	not layered
As2N2V6	not layered	not layered
C6Al6Sc2	layered	not layered
C10Al6Zr6	layered	not layered
Ge2N2V6	layered	not layered
C10Al6Hf4	layered	not layered
C2Nb4S2	layered	not layered
C2Al2Ta4	layered	not layered
C2Pb2Ti4	layered	not layered
C2As6V10	not layered	not layered
CPbSc3	not layered	not layered
In2N2Zr4	layered	not layered
C8Al6Hf4	layered	not layered
N2P6V10	not layered	not layered
C2Cr4Ga2	layered	not layered
CSc3Sn	not layered	not layered
C2As2V6	not layered	not layered
In2N2Ti4	layered	not layered
As2Cr6N2	not layered	not layered
C4Ge2Ti6	layered	not layered
C2Ga2Mo4	layered	not layered
CGaSc3	not layered	not layered
C2As2Cr6	not layered	not layered
C2Nb4P2	layered	not layered

Compared with the vdW bonded materials, MAX phase materials are normally much denser due their alternatively covalent and metallic bonding nature. From the previous section, it is known that the original code is only suitable on detecting two-dimensional material when a sparse or loose structure is under consideration. Take a dense structure as example, there won't be any two-dimensional material identified since all (or most of) the interatomic distances within such structure are smaller than the sum of their own (atom pair) vdW radii and therefore, the structure is always considered to be fully connected, that is, a three-dimensional structure. That's the reason why the original algorithm fails in this section on detecting MAX phase materials.

On the other hand, the reason why the new algorithm works well lies in its purely geometric concept. Again, for a dense structure (such as MAX phase materials), because the nearest neighbor distances now are normally smaller than the sum of vdW radii, they are all already chemically bonded. However, whether they are bonded or not doesn't matter but which type of bonding they are is of our concern. Since they are now all chemically bonded, their interatomic distance becomes proportional to their interatomic force, such as force in a metallic or covalent bond. By choosing the maximum nearest neighbor distance as threshold, it represents the smallest atomic force contributing from its neighbor; atom pairs with smaller interatomic distance are therefore ‘much connected’ due to a stronger interatomic force. Because MAX phase materials have a structural fashion of alternating bonding types, that is, a layer of metallic bond, a layer of covalent bond, a layer of metallic bond . . . and so there should have an alternating bonding length, the new algorithm thus can extract all the MAX phase materials in the database solely by this geometric concept.

As mentioned before, the new algorithm identified 58 kinds of materials to be layered materials and among these 58 kinds materials, the only two materials identified by the original algorithm are also identified by the new algorithm. The left 38 materials are basically interconnected three dimensional materials after the checking of their structures, which are shown as below.

Examples of dense (3-D) structure

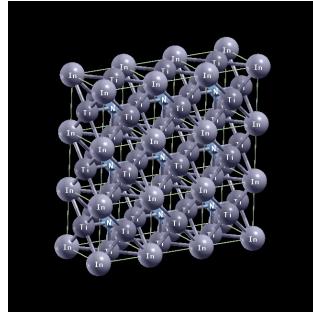


Figure 11: Ex1.InNTi3

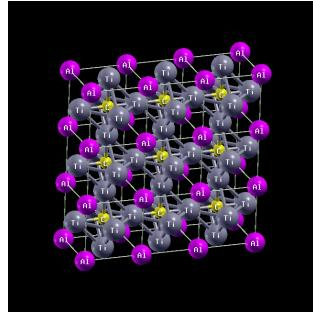


Figure 12: Ex2.CaAlTi3

For all the 35 known MAX phase materials in the database, the new algorithm is successful to identify all of them to be layered and two examples are shown as Figure 13-16. In addition, the results are listed as Table 3. Among these structures, most of them are in the form of M₂AX and their extracted structures are as our expectation to be in the form of MXenes, Mn+1Xn due to the weaker M-A bonds and corresponding longer interatomic distances.

Table 3 Identified Known MAX phase Materials

C2Al2Cr4	C4Al2Ta6	C2S2Ti4	C2Ge2Ti4
C2Ga2Ti4	C2S2Zr4	C4Al2Ti6	Al2N6Ti8
C2Pb2Zr4	C2Hf4Tl2	C6Al2Ta8	Al2N2Ti4
C2Ge2V4	C2Al2V4	C2Ga2Ta4	C2Al2Nb4
C2Hf4Pb2	C2Cd2Ti4	C4Si2Ti6	C2Ti4Tl2
Ga2N2Ti4	Cr4Ga2N2	C2As2Nb4	C6Al2Ta8
C2Tl2Zr4	C2As2V4	C2Nb4S2	C2Al2Ta4
C2Pb2Ti4	In2N2Zr4	C2Cr4Ga2	In2N2Ti4
C4Ge2Ti6	C2Ga2Mo4	C2Nb4P2	

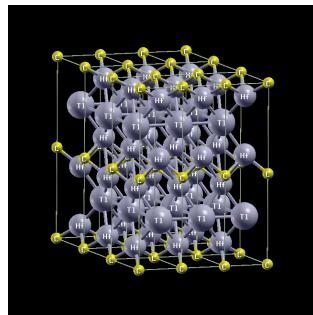


Figure 13: C2Hf4Tl2

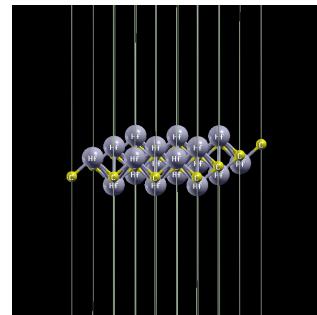


Figure 14: C2Hf4Tl2 derived MXene

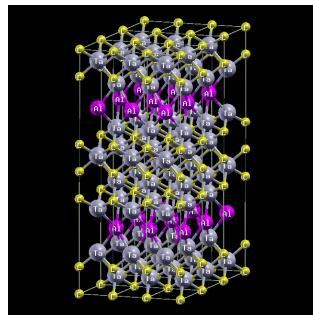


Figure 15: C6Al2Ta8

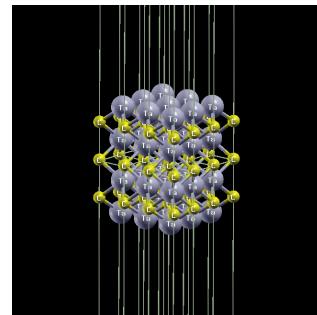


Figure 16: C6Al2Ta8 derived MXene

There are only 35 known MAX phase materials and so it means there are other 23 kinds of materials which are layered while they do not belong to known MAX phase materials. Therefore, in order to have an understanding of these materials, a closer view of their structures and formulas is performed. It is found that:

1. These materials have the same structural fashion as MAX phase materials, that is, an alternating bonding type plane.

2. Except for the difference of number, these materials have the same chemical compositions available for the definition of MAX phase materials.

Examples of potential MAX phase materials

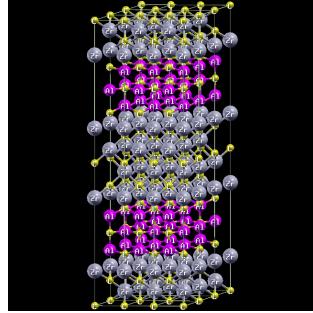


Figure 17: Ex1.C12Al6Zr8

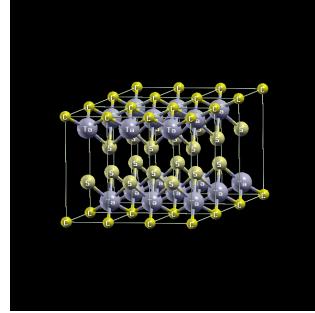


Figure 18: Ex2.CS2Ta2

Combining the two points from above, it is logical to say these materials may be the new types of MAX phase materials and they are listed as Table 4.

Table 4 Proposed new MAX phase materials

CS2Ta2	Ga2N2V6	N2P2V6	C12Al6Zr8	N2Szr2
C10Al6Zr6	CNb2S2	C10Al6Zr4	C2Cr6P2	C6Al6Sc2
Hf2N2S	Cr6N2P2	C9Al6Ti15	C8Al6Zr4	Ge2N2V6
C2Ge2V6	C5Al4Hf2	C5Al4Zr2	C6Al4Hf3	C10Al6Hf4
C10Al6Hf6	N4S2Zr4	C8Al6Hf4		

5 Conclusion

After the testing, a new algorithm is able to recognize all the known MAX phase materials where the original algorithm fails. Furthermore, some new MAX phase materials are proposed with the help of new algorithm but whether they really belong to MAX phase materials is still not sure.

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