

Screening of the mechanical stability of M_2AX phases for nuclear applications

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Abstract

In the present work, we apply a high-throughput density functional theory (DFT) screening of interesting M_2AX phase compounds for nuclear applications by assessing their mechanical stability. Evaluation of mechanical stability allows to assess thermodynamically unstable phases and does not require the assessment of competing MX and intermetallic phases. We consider all possible combinations with $M=\{\text{Ti, Cr, Zr, Nb}\}$, $A=\{\text{Al, Si, Sn, Pb, Bi}\}$ and $X=\{\text{C}\}$, including “out-of-plane” ordering that is so far unexplored and unobserved in M_2AX phases. For all fifty possible combinations, we determine the elastic constants and verify their mechanical stability. In addition, for each combination, the free surface energy is computed and the fracture toughness, K_{IC} , is determined. The results are discussed in terms of combinations with high mechanical stability and high K_{IC} . Apart from suggestions of interesting new combinations, the results also form the basis for any plasticity or fracture mechanics model for these MAX phases.

1. Introduction

The synthesis and characterization of new ternary carbides and nitrides, so-called MAX phases, is a fast-evolving research area in recent years. Presently, over 150 different MAX phases have been synthesized and characterized [1, 2]; and the search for new MAX phases continues. In these phases with the $M_{n+1}AX_n$ general stoichiometry, M is an early transition element, A an element of the A-group or late transition element, X carbon or nitrogen, and $n = 1, 2$ or 3 . The MAX phases share many properties of MX carbides and nitrides, but with improved mechanical and thermal properties. Their specific layered structure allows for plastic deformation via basal

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dislocations and ripplocations, making them softer and more ductile than the corresponding MX phases. Hence, most MAX phases are readily machinable and quite damage tolerant [1-3].

Amongst others, this set of attractive properties have prompted the interest of the nuclear industry. The MAX phases are presently considered as candidate coating materials for fuel claddings (for example, so-called accident tolerant fuel claddings for Gen-II/III light water reactors) [4], as well as structural and functional materials in Gen-IV fission reactor concepts (for example, pump impellers for heavy liquid metal-cooled reactors) [4, 5]. In the interest of waste management, as well as neutron reaction cross-sections, the search of new MAX phases is mainly limited to the elements: $M=\{\text{Ti, Cr, Zr, Nb}\}$, $A=\{\text{Al, Si, Sn, Pb, Bi}\}$ and $X=\{\text{C}\}$ [6].

With the evolution of computational resources and advanced computational models, computational materials design plays an ever-important role in the synthesis of new materials. In particular, for the MAX phases, several efforts were made to predict the stability of new MAX phases based on density functional theory (DFT) calculations. Recent efforts explore different combinations [7, 8] or solid solutions [9, 10] of different elements. In all these cases, the thermodynamic stability of new MAX phase compounds is determined via their formation (free) energy. These methods, however, hinge on the fact that the competing MX phases must also be accounted for. Moreover, some phases may be thermodynamically unstable, yet metastable at room temperature (RT). For example, Poulou et al. [11] have demonstrated that Zr_2AlC is thermodynamically unstable at RT, while Lapauw et al. [12] have successfully synthesized it.

Clearly, thermodynamic stability of a compound at RT is not a necessity for its existence at RT, with diamond probably the most well-known example. Rather, stability against small deformations (i.e., mechanical stability) is essential for a phase to be (meta)stable. Therefore, we propose high-throughput DFT screening of new MAX phases (of nuclear interest) via the evaluation of their mechanical stability. Mechanical stability is satisfied if the elastic tensor of a phase is positive definite, i.e., all Eigen values of the elastic tensor are positive. This method allows the prediction of metastable phases and removes the complexity of studying all competing phases. Hence, it can be a powerful complement to thermodynamic computations and experimental synthesis by trial and error.

In the present work, we apply a high-throughput DFT screening of M_2AX phases of nuclear interest in the (Ti, Cr, Zr, Nb)-(Al, Si, Sn, Pb, Bi)-C system. Thereby, we consider all possible combinations with “out-of-plane” ordering that are so far unexplored and unobserved in the M_2AX phases [2]. For all possible combinations (fifty in total), we determine the elastic constants of these phases and verify their mechanical stability. In addition, for each

combination, the free surface energy is computed and the fracture toughness, K_{IC} , is determined. The results are discussed in terms of combinations with high mechanical stability and K_{IC} . Apart from suggesting interesting new combinations, the results also form the basis for any plasticity or fracture mechanics model for these MAX phases.

2. Methods

The elastic constants and free surface energy were obtained via density functional theory (DFT) calculations employing the Vienna ab initio simulation package (VASP) [13, 14]. Projector Augmented Waves (PAW) were used to describe the wave functions with the standard PAW potentials supplied with VASP [15, 16]. The code was applied using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional [17]. The Methfessel-Paxton method [18] with finite temperature smearing was applied, using a smearing width of 0.3 eV. The box size, minimization scheme, plane-wave cut-off energy and k-points set used to compute the different quantities are summarized in **Table 1**. The applied settings lead to a convergence error of less than 5%.

Table 1 – VASP computation parameters for elastic constants and free surface energy.

	Elastic constants	Surface energy
supercell size	8 atoms $1 \times 1 \times 1$	24 atoms $1 \times 1 \times 3$
k-points*	$15 \times 15 \times 5$	$15 \times 15 \times 1$
cut-off	450 eV	450 eV
minimization scheme	ionic relaxation variable volume & cell shape	ionic relaxation variable volume & cell shape

* Γ -point centered grid for hexagonal lattices following the Monkhorst-Pack scheme [19].

3. Results & Discussion

The elastic constants were calculated for all possible combinations of $(M_1, M_2)_2AC$ phases, as indicated in **Fig. 1**. For $M_1, M_2 = \{\text{Ti, Cr, Zr, Nb}\}$ and $A = \{\text{Al, Si, Sn, Pb, Bi}\}$, this leads to 50 unique combinations. It is noted that combinations with $M_1 \neq M_2$ were also included as limiting case for out-of-plane chemical ordering in (M_1, M_2) solid solutions, which was so far unobserved and unassessed. Up to now, out-of-plane chemical ordering was only observed in $M_{n+1}AX_n$ phases with $n > 2$ (see [2] and references therein).

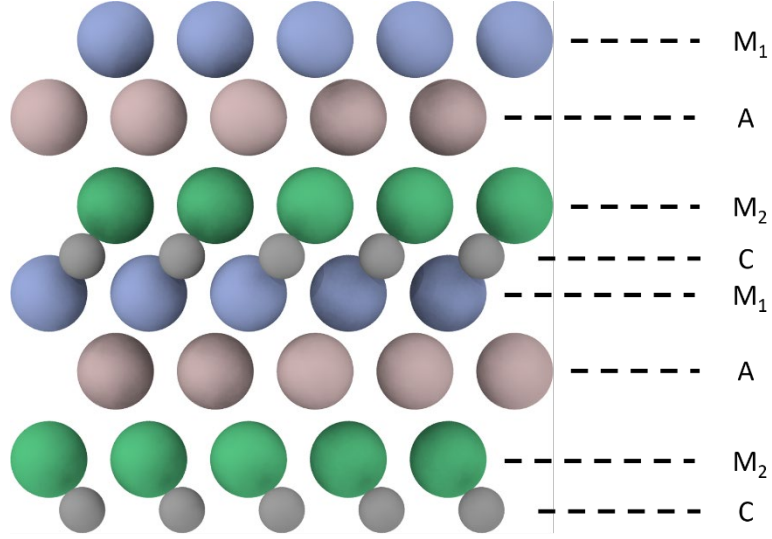


Fig. 1 – Schematic representation of the investigated $(M_1, M_2)_2AC$ phases.

A phase is “mechanically stable”, i.e., stable against small deformations, if the elastic tensor is positive definite. For hexagonal lattices, this translates into the conditions [20],

$$\begin{cases} E_1 = C_{11} - |C_{12}| > 0 \\ E_2^2 = C_{33}(C_{11} + C_{12}) - 2C_{13}^2 > 0 \\ E_3 = C_{44} > 0 \\ E_4 = C_{66} > 0 \end{cases} \quad (1)$$

In **Fig. 2**, $C_{\min} = \min\{E_1, E_2, E_3, E_4\}$ is plotted together with the Voigt average estimate for polycrystals of the shear modulus, G , bulk modulus, B , and Young’s modulus, Y , for all considered combinations. The latter moduli are related to the elastic constants via the relations,

$$\begin{cases} G = \frac{(2C_{11}+C_{33})-(C_{12}+2C_{13})+3(2C_{44}+C_{66})}{15} \\ B = \frac{(2C_{11}+C_{33})+2(C_{12}+2C_{13})}{9} \\ Y = \frac{9BG}{3B+G} \end{cases} \quad (2)$$

The constant, C_{\min} , provides a measure for the mechanical stability of the considered phase, i.e., larger values indicate more stable phases. In the figure, all investigated $(M_1, M_2)_2AC$ phases are ordered following descending C_{\min} .

With respect to mechanical stability, Cr_2AlC is significantly more stable than the other combinations ($C_{\min} = 140$ GPa). Interestingly, the Cr_2AlC MAX phase is also one of the most studied MAX phases. We observe that all combinations with $A=\{\text{Al}, \text{Si}\}$ are particularly stable,

especially in combination with $M=\{Cr,Ti\}$. Conversely, combinations with $A=\{Bi\}$ are particularly unstable, especially in combination with $M=\{Cr\}$. For combinations with $A=\{Pb,Sn\}$, the occupation of both M_1 and M_2 layers are essential for their mechanical stability.

Both the shear modulus and Young's modulus values follow the same trend as C_{min} . The bulk modulus, on the other hand, varies in the range 100-220 GPa but does not follow any trend. The latter lack of correlation is consistent with the fact that the bulk modulus describes the response of the crystal against equiaxial compression/expansion and thus does not contain a shear component.

Where available, the computed elastic moduli are compared to experimental values [3, 21]. As shown in **Fig. 2**, the calculated values are in good agreement with the experimental ones. This observation illustrates the reliability of the performed calculations.

The strength of the proposed method, i.e., screening of the mechanical stability is well illustrated in the example of the Zr_2AlC phase. DFT-based thermodynamic calculations performed by Poulou et al. [11] have shown that the Zr_2AlC phase is thermodynamically unstable at RT. While this MAX phase is predicted to be stable at higher temperatures, the experimental synthesis of the Zr_2AlC phase by Lapauw et al. [12] has clearly shown that it is at least metastable at RT. This (meta)stability at RT is well reflected by its rather high mechanical stability ($C_{min} = 93$ GPa) predicted in this work. Thus, while thermodynamic calculations are essential tools to design experimental synthesis conditions for the MAX phases, they are not necessarily good predictors of stability in screening tests.

Another example of the strength of the proposed screening method is reflected in the work by Horlait et al. [22]. In that work, the synthesis of Zr_2BiC was attempted, but could not be achieved. This negative result is consistent with our predictions of low mechanical stability for phases with $A=\{Bi\}$. In particular, with $C_{min} = 45$ GPa, Zr_2BiC is about half as stable as the metastable Zr_2AlC phase and only one third as stable as the most stable Cr_2AlC phase.

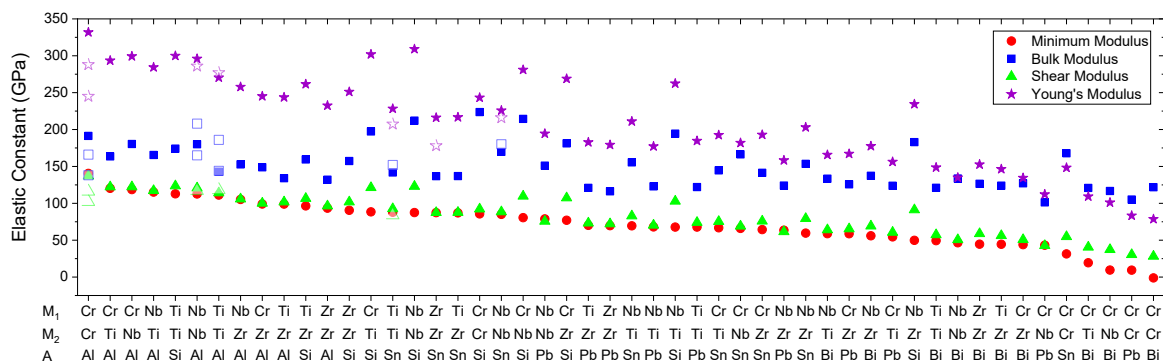


Fig. 2 – Elastic moduli of the investigated MAX phases ordered following descending C_{\min} . Available experimental values are represented by open symbols [3, 21].

Besides its (mechanical) stability, the resistance of any material to crack propagation is an important engineering property. This property is expressed by the fracture toughness, K_{IC} , which is defined as,

$$K_{IC} = \sqrt{2\gamma Y}, \quad (3)$$

with γ the free surface energy and Y the Young's modulus. In turn, γ is calculated following,

$$\gamma = \frac{E_{\text{slab}} - E_{\text{perf}}}{2A}, \quad (4)$$

with E_{slab} the total energy of the “slab” with appropriate free surface boundary conditions; E_{perf} the total energy of the fully periodic supercell; and A the area of the free surface.

For the specific case of the M_2AC phases considered in this work, four non-equivalent (0001) free surfaces can be constructed. These free surface configurations correspond to cleavage between M_1A , M_2A , M_1C and M_2C layers (see also **Fig. 1**).

In **Fig. 3**, K_{IC} is plotted using both the lowest (K_{IC}^{\min}) and highest (K_{IC}^{\max}) value for the free surface energy. For comparison, K_{IC} obtained via the correlation derived in Niu et al. [23] is also included in this figure. The correlation is given by,

$$K_{IC}^{\text{Niu}} = V_0^{1/6} G \sqrt{B/G}, \quad (5)$$

with V_0 the equilibrium volume per atom (in m^3). In **Fig. 3**, the computed combinations are ordered following descending K_{IC}^{\min} . Depending on the used value for the surface energy or the used correlation, K_{IC} can vary significantly. However, all estimations for K_{IC} follow the same trend as K_{IC}^{\min} . Here, the estimates based on Niu's regression form an upper bound for K_{IC} . We observe that the combinations leading to the highest mechanical stability also lead to large K_{IC} values, i.e., $A=\{\text{Al}, \text{Si}\}$ and $M=\{\text{Ti}, \text{Cr}\}$. Conversely, the combinations resulting in the lowest mechanical stability also lead to lowest K_{IC} values, i.e., $A=\{\text{Bi}\}$.

It should be noted that experimentally, the fracture toughness of the MAX phases is 3-6 times higher than the ones reported here. In particular, the experimentally determined $K_{IC} = 6.5 \text{ MPa} \cdot \sqrt{\text{m}}$ value for Ti_2AlC [3] is higher than the calculated K_{IC} values that are in the $1.0 - 2.0 \text{ MPa} \cdot \sqrt{\text{m}}$ range. The higher observed fracture toughness values are the result of plastic deformation that is not accounted for in our calculations. While MAX phases are ceramics, they can accommodate plastic deformation via dislocations and ripplocations (see [1] and references therein). Therefore, the values obtained in this work form a lower limit corresponding to the case of fully brittle fracture.

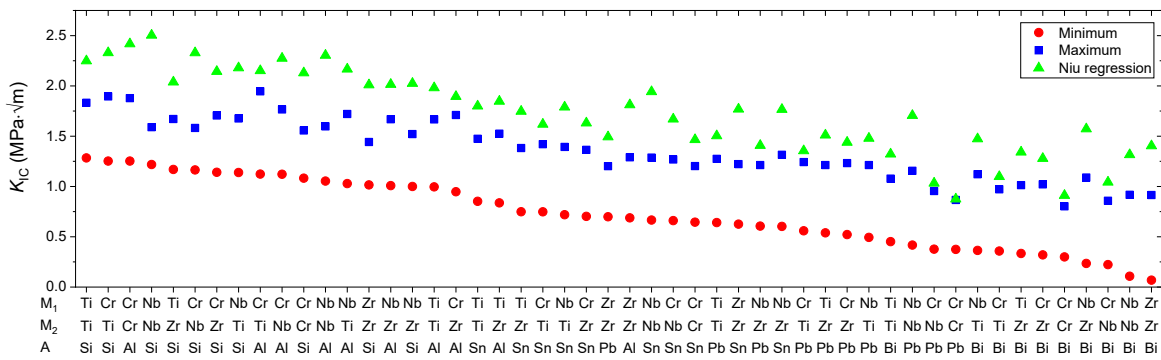


Fig. 3 – Fracture toughness, K_{IC} , obtained via equations (3) and (5) and ranked following descending K_{IC}^{\min} .

The free surface energy corresponding to cleavage through the four possible different layers is shown in **Fig. 4**. The free surface energy is ranked following descending K_{IC}^{\min} . Clearly, γ follows the same trend as K_{IC} . We observe that γ associated to MA cleavage is systematically lower than γ associated to MC cleavage. This suggests that cracks are likely to propagate by cleavage through MA layers, rather than through MC layers.

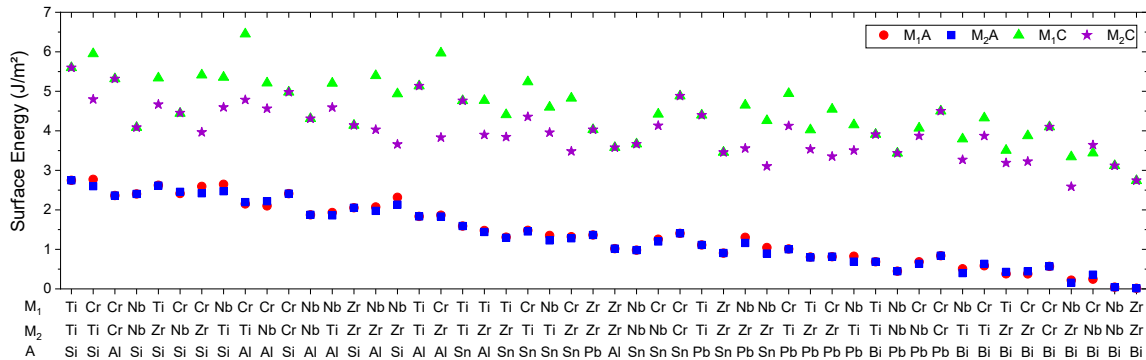


Fig. 4 – Free surface energy associated to MC and MA cleavage, ordered with descending K_{IC}^{\min} .

4. Conclusions

We have performed a high-throughput screening of the mechanical stability of different combinations of M_2AC phases of relevance for nuclear applications in the (Ti, Cr, Zr, Nb)-(Al, Si, Sn, Pb, Bi)-C system. We found that the highest mechanical stability regards combinations $M=\{\text{Ti,Cr}\}$ and $A=\{\text{Al,Si}\}$; and the lowest for any combination containing $A=\{\text{Bi}\}$. We found that phases with high mechanical stability also lead to high fracture toughness, K_{IC} , while the ones with low mechanical stability lead to low K_{IC} . Based on our analysis, the synthesis of some solid solution combinations, possibly leading to out-of-plane ordering, can be attempted. From the free surface energy, we conclude that crack propagation in M_2AC phase compounds occurs preferentially by means of MA cleavage rather than MC cleavage. The obtained data can serve as a basis for any plasticity or fracture mechanics model for these MAX phase compounds. The herein proposed high-throughput screening method allows the prediction of new, stable combinations of MAX phase compounds in a specific system. It does not require the thermal stability of competing (i.e., carbide and intermetallic) phases and, therefore, presents a low-cost complement to thermodynamic parameterizations and experimental synthesis by trial and error.

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Data Availability

All the data that support the findings of this study are available upon reasonable request.

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