

Ab-initio study of hypothetical Ti_3AlB_2 and two new designed layered ordered double-transition metals MAX compound Ti_2ZrAlB_2

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Abstract

We have designed Ti_3AlB_2 and two new layered ordered double-transition metals MAX compound Ti_2ZrAlB_2 based on the structure of Ti_3AlC_2 . By first-principles calculations with density functional theory, their structure, phase stability, elastic properties, electronic properties and thermal properties have been further investigated. Results show that they are all energetic, thermodynamically and mechanically stable. The bulk modulus, shear modulus, Young's modulus, Poisson's ratio and Debye temperature were computed to discuss their elastic and thermal properties. Results show that they are all good ductile materials with high melting points. Density of states and electron localization function of these three phases were presented to research the chemical bonds and explore the reason limiting their melting points.

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Abstract: We have designed Ti_3AlB_2 and two new layered ordered double-transition metals MAX compound Ti_2ZrAlB_2 based on the structure of Ti_3AlC_2 . By first-principles calculations with density functional theory, their structure, phase stability, elastic properties, electronic properties and thermal properties have been further investigated. Results show that they are all energetic, thermodynamically and mechanically stable. The bulk modulus, shear modulus, Young's modulus, Poisson's ratio and Debye temperature were computed to discuss their elastic and thermal properties. Results show that they are all good ductile materials with high melting points. Density of states and electron localization function of these three phases were presented to research the chemical bonds and explore the reason limiting their melting points.

Keywords: first-principles calculations, ordered double-transition metals MAX, phase stability, thermal properties

Introduction

Since Nowotny *et al* synthesized the first member of $M_{n+1}AX_n$ (MAX) compounds— Ti_3SiC_2 in 1965 [1]. Hundreds of new carbides of this class were synthesized in the past several decades [2-7]. As a new class of ceramic compounds, $M_{n+1}AX_n$ crystallizes in the form of with layered structures, where n varies from 1 to 3, M is an early transition metal, A is primarily an element in group IIIA or IVA, X is the element of C, B or N. This new class of ceramic materials usually have the advantages of both metal and traditional ceramic materials, such as good conductivity, thermal conductivity and easy processing similar to metal, high temperature resistance, light weight, creep resistance and fatigue resistance similar to traditional ceramic materials. These excellent characteristics make them as potential candidates in a wide range of technological applications [8-10]. In addition, based on the structure of MAX compounds, a new class of 2D materials—MXenes, can be gotten by selectively etching the A-layers and leaving the $M_{n+1}X_n$ layers intact [11-13]. This will greatly increase the variety of 2D materials. What's more, theoretical and experimental studies show that the performance and stability of double transition metal MXenes are better than that of single transition metal MXenes. However, the double transition metal MXenes should be obtained by chemical etching the corresponding double transition metal MAX. For example, Rose *et al* [14] obtained a set of novel MXenes— $Mo_{1.33}C$ from their independently synthesized $(Mo_{2/3}Sc_{1/3})_2AlC$ structure (Mo and Sc are chemically ordered in the same plane) by selective etching of the Al and Sc elements. Anasori *et al*[15] have obtained 2D MXenes structures $Mo_2TiC_2T_x$, $Mo_2Ti_2C_3T_x$ and $Cr_2TiC_2T_x$ based on the parent ordered double transition metal MAX phases.

In view of its application prospect in the industrial field and the design requirements of two-dimensional double transition metal MXenes, the design of double transition metal MAX structures has an important scientific significance. Now many double transition metal MAX [16-17], such as $(V_{0.5}Cr_{0.5})_{n+1}AlC_n$ ($n=2, 3$) and $(Ti_{0.5}Nb_{0.5})_5AlC_4$, have been successfully synthesized by introducing another solid solution metal into the layered ceramic compounds in the laboratory. Liu *et al* [18-19] also reported the crystal structure of two newly ordered double transition metal MAX phases, Cr_2TiAlC_2 and $Cr_{5/2}Ti_{3/2}AlC_3$, by various techniques. By mixing and heating different elemental powder mixtures method, Anasori *et al* [20] has successfully obtained two newly double ordered transition metal MAX phases Mo_2TiAlC_2 and $Mo_2Ti_2AlC_3$. And more and more chemical ordered double transition metal MAX structures have been synthesized in the laboratory [21]. However, both theoretical and experimental studies focus on MAX ($X=C, N$), but there are few studies on MAX ($X=B$) [22], and no report on the double transition metal MAB. Ti_3AlC_2 is the most typical representative of MAX phase, and the research on this phase is also the most. Therefore, we design the aimed structures on the basis of Ti_3AlC_2 structure.

As an effective way to predict condensed material structures and properties, first-principles calculations can reproduce experimental data at a high accuracy. So this method has been widely used in the study field of material science [23-26]. In this study, based on the structure of Ti_3AlC_2 , we predicted Ti_3AlB_2 and two Ti_2ZrAlB_2 double transition metal MAX phases and further investigate the phase stability and potential properties of them by first-principle calculations.

2. Computational methods and details

In this work, we set up the theoretical models of chemically ordered MAX phase compositions Ti_3AlB_2 and two Ti_2ZrAlB_2 structures based on the structure of Ti_3AlC_2 reported by Pietzka *et al* [27]. The predicted structural parameters of these three new compounds are presented in the Supplement Material. Then first-principles calculations were carried out by VASP software to study the structural stability, electronic, elastic and thermophysical properties of the ternary ceramic Ti_3AlB_2 and two quaternary ceramic Ti_2ZrAlB_2 . The crystal structures of these ceramic compounds were optimized by the conjugate gradient (CG) algorithm. The plane-wave pseudopotential method within the PBE-GGA designed by Perdew, Burke, and Ernzerhof [28-29] is employed in the calculations. The cut-off energy for the plane wave basis set was configured as 520 eV. A $12 \times 12 \times 2$ Monkhorst-pack grid [30] of k-point sampling was set for the first electronic Brillouin zone (BZ). In the structural optimizations, the calculated systems are relaxed until the total energy change and the band structure energy change between two steps are both smaller than 1×10^{-6} eV in the relaxation of the

electronic degrees of freedom, and the forces of all atoms are smaller than 0.02 eV/Å in the ionic relaxation. Phonon dispersions were calculated in the Phonopy software based on the density functional linear-response method [31].

3. Results and discussion

3.1. Determination of Crystal Structure

In present study, based on the structure of Ti_3AlC_2 , we set up the structure of Ti_3AlB_2 and tried to design layered ordered double-transition metals MAX compound for Ti_2ZrAlB_2 . Two stable phases were determined via calculations of formation enthalpy, elastic constants and phonon dispersion curves (This would be discussed later). Here we recorded them as Ti_2ZrAlB_2 -1 and Ti_2ZrAlB_2 -2 respectively, and their structures were shown in Figure 1. Lattice constants and atomic coordinates for new predicted Ti_3AlB_2 , Ti_2ZrAlB_2 -1 and Ti_2ZrAlB_2 -2 are presented in Supplemental Material Table S1. The formation enthalpies are defined by $E = E(Ti_3AlB_2) - 3E(Ti) - E(Al) - 2E(B)$ and $E = E(Ti_2ZrAlB_2) - 2E(Ti) - E(Zr) - E(Al) - 2E(B)$ for Ti_3AlB_2 and Ti_2ZrAlB_2 , respectively; in which $E(Ti_3AlB_2)$ and $E(Ti_2ZrAlB_2)$ are the energy of Ti_3AlB_2 and Ti_2ZrAlB_2 (Ti_3AlB_2 , Zr (spacegroup : $P6_3/mmc$), Al (spacegroup : $Fm - 3m$) and B (spacegroup : $R - 3m$). The formation enthalpies of them were recalculated and listed in Table 1. It can be seen that the formation enthalpy of Ti_3AlB_2 , Ti_2ZrAlB_2 -1 and Ti_2ZrAlB_2 -2 are negative, so these phases can be considered as stable ones in energy, and are thereby expected to be synthesized.

Table 1. Calculated equilibrium structural data, bond lengths and formation enthalpy E for Ti_3AlB_2 , $Ti_2ZrAlB_2 - 1$ and $Ti_2ZrAlB_2 - 2$

Structures	a(Å)	c(Å)	Ti(1)-B/ Zr(1)-B	Ti(2)-B/ Zr(2)-B	Ti(2)-Al/ Zr(2)-Al	Ti(1)- Ti(2)/ Ti(1)- Zr(2)/ Ti(2)-Zr(1)	E (eV/f.u.)	Ref
Ti_3AlC_2	3.075	18.578						[27]
Ti_3AlC_2	3.072	18.732	2.207	2.089	2.878	2.997		[32]
$Tl_3Al_{1.1}C_{1.8}$	3.065	18.487						[33]
Ti_3AlB_2	3.138	19.549	2.264	2.193	2.924	3.163	-2.051	
Ti_2ZrAlB_2 - 1	3.265	19.739	2.431	2.210	2.932	3.283	-1.880	
Ti_2ZrAlB_2 - 2	3.229	19.973	2.289	2.360	3.071	3.344	-1.955	

Based on the designed structures, the calculations of geometry optimization are performed in first principle theory VASP code. After full geometry optimization, the structures of Ti_3AlB_2 and two designed Ti_2ZrAlB_2 keep their symmetry as shown in Figure 1. And the calculated equilibrium structural data and the bond lengths are listed in Table 1. For two Ti_2ZrAlB_2 structures, it is easy to understand that the bond lengths of Zr-B and Ti-B are different. But for Ti_3AlB_2 , the bond lengths of Ti(1)-B and Ti(2)-B are different, and the former is slightly longer than the latter. Similar phenomena have been found in Ti_3AlC_2 and Ti_3SiC_2 [33-34]. Ti_3AlB_2 can be regarded as formed by introducing Al element into Ti-B compound. The introduction of this element changes the bonding environment of Ti atom, and it leads to the increase of partial bond length and the decrease of partial bond length of Ti-B bond in the structure. Thus, two types of Ti-B bonds with different bond lengths appeared in Ti_3AlB_2 structure.

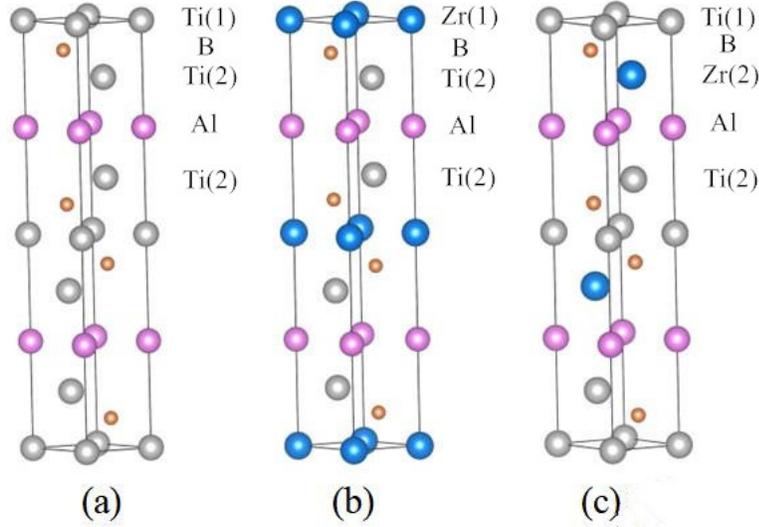


Figure 1. Structural model of (a) Ti_3AlB_2 and two new layered ordered double-transition metals MAX compound (b) Ti_2ZrAlB_2-1 and (c) Ti_2ZrAlB_2-2 , where the Ti atoms are in gray, Zr atoms are in blue, Al atoms are in pink and B atoms are in orange.

Phonon dispersion curve is an important criterion to measure the stability of a crystal structure in lattice dynamics. So we calculated the phonon spectrum of Ti_3AlB_2 and two designed Ti_2ZrAlB_2 , and results were shown in following Figure 2. It can be seen that the phonon frequencies are positive for all the considered structures. There is no imaginary frequency in the phonon dispersion curves, which means that Ti_3AlB_2 and the designed Ti_2ZrAlB_2 structures are stable in lattice dynamics. In addition, formation enthalpy of the ground state can be used to analyze the thermodynamic stability of crystals. The lower formation enthalpy is, the more thermodynamically stable the structure has. In Table 1, we listed the formation enthalpy of two designed Ti_2ZrAlB_2 . Result indicates that the Ti_2ZrAlB_2-2 is more stable than Ti_2ZrAlB_2-1 at 0 GPa.

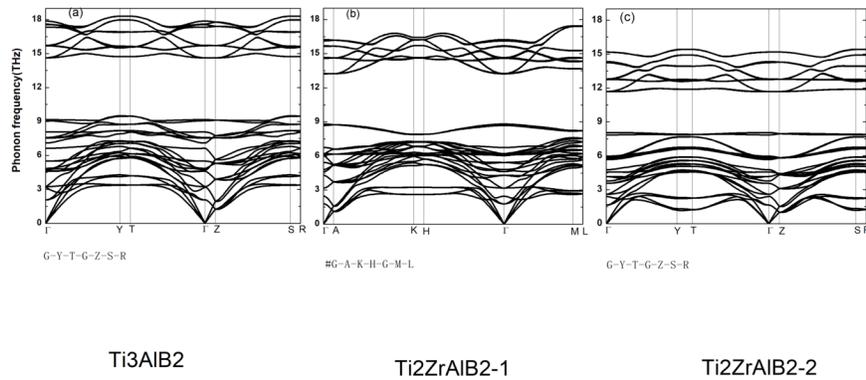


Figure 2. Phonon dispersion curves of (a) Ti_3AlB_2 , (b) $\text{Ti}_2\text{ZrAlB}_2$ -1 and (c) $\text{Ti}_2\text{ZrAlB}_2$ -2 at atmospheric pressure.

3.2. Mechanical Stability and Mechanical properties

To discuss the mechanical stability of Ti_3AlB_2 and two designed $\text{Ti}_2\text{ZrAlB}_2$ structures, we calculated the elastic constants of them on the basis of the energy-strain method. Results of this method were listed in following Table 2.

Table 2. Calculated elastic constants of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2

Structures	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{55}	C_{66}
Ti_3AlC_2	354	76	69	296	115	115	139
Ti_3AlB_2	181.8	107.8	72.0	240.2	98.0	97.9	35.5
$\text{Ti}_2\text{ZrAlB}_2$ -1	163.8	92.6	83.5	164.8	35.6	88.1	88.1
$\text{Ti}_2\text{ZrAlB}_2$ -2	186.8	102.6	73.3	218.0	85.7	85.7	42.0

According to the mechanical stability criterion for hexagonal crystals [35] and the calculated elastic constants of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2 listed in Table 2, it can be said that they are all stable in mechanics.

Based on the investigation of formation enthalpy, phonon dispersion curve and elastic constants of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2, it can be concluded that these three compounds are stable at normal pressure. However, we still know little about their performance, which needs further exploration. Here, we first studied their bulk modulus B and shear modulus G according to the Voigt-Reuss-Hill approximation [36-37] and listed the results in Table 3.

The B/G ratio is a parameter to evaluate the brittleness of materials proposed by Pugh [38-39]. In present work, the B/G ratio of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2 are larger than 1.75, which means they have good ductility. This is an obvious advantage that the MAX materials studied previously does not have. This excellent characteristic shows that the three layered ceramic materials have good toughness and are not fragile. Fragile is the weakness of traditional ceramic materials, none of the three materials in this study has this disadvantage.

The Poisson ratio values, $\nu=(3B-2G)/2(3B+G)$, are calculated to evaluate the degree of the covalent bonding [40]. For Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2, their Poisson ratios are larger than 0.25, which means ionic bonds dominate in these three crystal materials. And the specific bonding characteristics will be discussed in the following study of electronic properties.

Table 3. Calculated bulk Modulus B (GPa), Shear Modulus G (GPa), Young's Modulus E (GPa), Poisson's Ratio ν , and B/G of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2 at atmospheric pressure.

	B_v	B_R	B	G_v	G_R	G	ν	B/G	Ref
Ti_3AlC_2	159	158	159	126	125	126	0.19		this work
$\text{Ti}_3\text{Al}_{1.1}\text{C}_{1.8}$						124	0.2		[33]
Ti_3AlB_2	123.5	122.8	122.9	69.7	56.7	63.2	0.28	1.95	this work
$\text{Ti}_2\text{ZrAlB}_2$ -1	112.4	112.3	112.4	57.9	48.7	53.3	0.30	2.11	this work
$\text{Ti}_2\text{ZrAlB}_2$ -2	121.1	121.1	121.1	65.5	59.0	62.2	0.28	1.95	this work
ScAl_3C_3			164			139		1.18	[41]
UAl_3C_3			167			114		1.46	[41]

3.3. Electronic properties

To study the conductivity and bonding characteristics, we further studied the electronic properties of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2. As is shown in Figure 3, the finite positive values of density of states near Fermi level shows that they all have good electrical conductivity. From the case of partial density of states, it can be seen the conductivity are mainly contributed by Ti-d and B-p electron orbitals for Ti_3AlB_2 , and Ti-d, Zr-d and B-p electron orbitals for two $\text{Ti}_2\text{ZrAlB}_2$. For Ti_3AlB_2 and $\text{Ti}_2\text{ZrAlB}_2$ -2, the similar shape of partial density of states for Ti-d and B-p electron near Fermi level means show there is strong orbital hybridization between these two types of electrons. And the shape of Ti-d and Zr-d orbitals are similar for $\text{Ti}_2\text{ZrAlB}_2$ -2, it indicates that metal bonds can also be formed between Zr and Ti atoms. While for $\text{Ti}_2\text{ZrAlB}_2$ -1, Zr atoms also participate in bonding, which reduces the similarity of PDOS between Ti and B atoms compared with Ti_3AlB_2 and $\text{Ti}_2\text{ZrAlB}_2$ -2. It indicates the ionic bonds in Ti_3AlB_2 and $\text{Ti}_2\text{ZrAlB}_2$ -2 are stronger than that in $\text{Ti}_2\text{ZrAlB}_2$ -1, this is also consistent with the result of Poisson ratio discussed earlier.

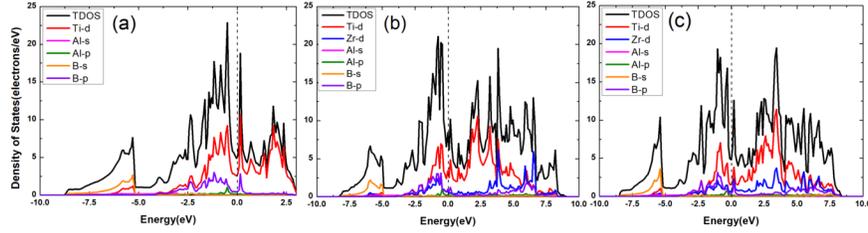


Figure 3. Density of States for (a) Ti_3AlB_2 , (b) $\text{Ti}_2\text{ZrAlB}_2$ -1 and (c) $\text{Ti}_2\text{ZrAlB}_2$ -2.

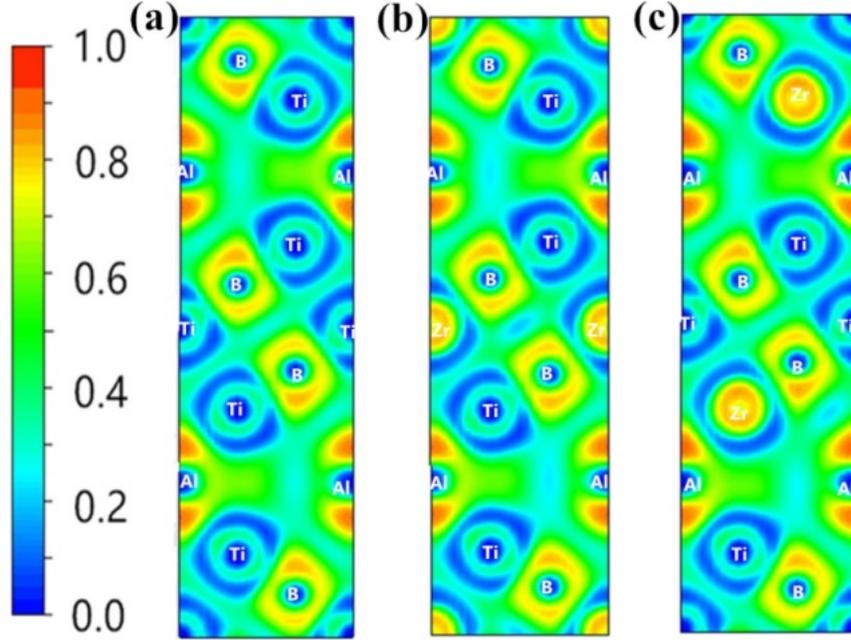


Figure 4. Electron localization function (ELF) in (110) plane for (a) Ti_3AlB_2 , (b) $\text{Ti}_2\text{ZrAlB}_{2-1}$ and (c) $\text{Ti}_2\text{ZrAlB}_{2-2}$.

In Figure 4, the electron localization function in (110) plane for Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_{2-1}$ and $\text{Ti}_2\text{ZrAlB}_{2-2}$ are given. It can be seen the electron localization function on Ti and B atoms are almost zero, which mean there is almost no charge. But on Zr atoms, the electron localization function is about 0.8, which means there is strong charge localization. This charge distribution shows that the ionic bonds between Ti and B are similar to covalent bonds to some extent. There is almost no local charge on the atoms, and the charges are distributed between two atoms, and the interaction between atoms by sharing electron pairs. While the chemical bonds between Zr and B are typical ionic bonds which formed by one party loses electrons and the other gets electrons, the charge distribution of the two electrons is obviously different. This difference further results in that the different binding strength of the chemical bond formed between Ti and B and between Zr and B. Another obvious difference is, compared with Ti_3AlB_2 and $\text{Ti}_2\text{ZrAlB}_{2-2}$, there is a small uncharged or almost no charge region between closest B-B atoms in $\text{Ti}_2\text{ZrAlB}_{2-1}$, which indicates that this structure is not so closely as the other two structures. This also leads to the fact that $\text{Ti}_2\text{ZrAlB}_{2-1}$ is easier to be compressed and deformed than the other two structures, so its bulk modulus and shear modulus are also lower than them, which is in good agreement with the results given in Table 3. This will further affect its thermal performance, which we will discuss in the Section 3.4.

3.4 Thermal properties

High melting point is an advantage of ceramic materials. Debye temperature is an important parameter to evaluate this thermal property and it can be calculated by the Debye model which have been stated in detail in Ref[42].

Based on this theoretical model, the Debye temperatures Θ_D of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_{2-1}$ and $\text{Ti}_2\text{ZrAlB}_{2-2}$ are calculated and listed in following Table 4. Compared with transition metal carbides MAX-phase, the Debye temperatures Θ_D of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_{2-1}$ and $\text{Ti}_2\text{ZrAlB}_{2-2}$ are not high, which means the high temperature resistance of them are not as good as these carbides. It is mainly caused by their low shear modulus. As shown in Table 1, the distance between Al and Ti or Zr atoms in Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_{2-1}$ and $\text{Ti}_2\text{ZrAlB}_{2-2}$ are larger than the Ti-C lengths in Ti_3AlC_2 . It indicates relatively weak bonding between Al

and the M(2)-B-M(1)-C-M(2) (M=Ti or Zr), so it is easier slip between two layers and lead to their low shear modulus.

But compared with ordinary materials, these Debye temperatures are still very high, it indicates that their high temperature resistance is also good. Compared with Ti_3AlB_2 and $\text{Ti}_2\text{ZrAlB}_2$ -2, the Debye temperatures Θ_D of $\text{Ti}_2\text{ZrAlB}_2$ -1 is lower. According to the Debye model, it is due to the lower bulk modulus and shear modulus of $\text{Ti}_2\text{ZrAlB}_2$ -1 than other two compounds. Combined the discussion in Section 3.3, this is ultimately due to the strength and mode of chemical bond bonding in the structure.

Table 4. Our calculated density; longitudinal, transverse sound, mean sound velocities, and the Debye temperatures obtained from the mean sound velocities of Ti_3AlB_2 , $\text{Ti}_2\text{ZrAlB}_2$ -1 and $\text{Ti}_2\text{ZrAlB}_2$ -2; and corresponding data for $\text{Zr}_2\text{Al}_3\text{C}_4$ and $\text{Zr}_3\text{Al}_3\text{C}_5$ obtained from previous studies.

Compounds	B(GPa)	G(GPa)	v_l (m/s)	v_t (m/s)	v_a (m/s)	Θ_D (K)	Ref
Ti_3AlB_2	122.9	63.2	7356.9	4063.3	4527.6	560.7	this work
$\text{Ti}_2\text{ZrAlB}_2$ -1	112.4	53.3	6536.4	3523.7	3933.5	472.9	this work
$\text{Ti}_2\text{ZrAlB}_2$ -2	121.1	62.2	6857.1	3786.9	4219.6	509.1	this work
$\text{Zr}_2\text{Al}_3\text{C}_4$			9249	5792	6379	830	[40]
$\text{Zr}_3\text{Al}_3\text{C}_5$			8954	5607	6175	806	[40]
ScAl_3C_3	164	139	10311	6505	7158	939	[41]
UAl_3C_3	167	114	6943	4151	4593	593	[41]

4. Conclusion

In summary, based on the structure of Ti_3AlC_2 , possible structures for layered ordered double-transition metals MAX compound $\text{Ti}_2\text{ZrAlB}_2$ have been searched by *ab initio* calculations. One Ti_3AlB_2 and two new $\text{Ti}_2\text{ZrAlB}_2$ structures have been successfully designed. The calculations of formation enthalpy, phonons and elastic constants all confirmed the phase stabilities of them. High B/G ratios indicate that they are all good ductile materials. Study of their mechanical properties show their Poisson ratios are larger than 0.25, which means ionic bonds dominate in these three crystal materials. The electron localization functions have also demonstrated that the ionic Ti-B and Zr-B bonding play a key role in their chemical properties, but metal bonds also exist in the structures. Results of electronic densities of states show that they all have good electrical conductivity, and the conductivity are mainly contributed by Ti-d and B-p electron orbitals for Ti_3AlB_2 , and Ti-d, Zr-d and B-p electron orbitals for two $\text{Ti}_2\text{ZrAlB}_2$. Although the high temperature resistance of these three MAX compounds in present study is not as good as the MAX carbides, they also have not low melting points. In particular, they also have good ductility. The unusual combination of these properties of these compounds makes them promising candidates in the field of engineering application. At the end of present work, we also explored the factors limiting its heat resistance, it is due to the weak bonding between Al and the M(2)-B-M(1)-C-M(2) (M=Ti or Zr).

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Reference

- [1] V. H. Nowotny, Strukturchemie einiger Verbindungen der Übergangsmetalle mit den elementen C, Si, Ge, Sn, *Prog. Solid. State. Chem.* 5 (1971) 27.
- [2] M. W. Barsoum, M. Radovic, Elastic and Mechanical Properties of the MAX Phases, *Ann. Rev. Mater. Res.* 41 (2011) 195.
- [3] M. W. Barsoum, T. El-Raghy, Synthesis and Characterization of a Remark-able Ceramic: Ti_3SiC_2 , *J. Am. Ceram. Soc.* 79 (1996) 1953.
- [4] M. W. Barsoum and T. El-Raghy, A Progress Report on Ti_3SiC_2 , Ti_3GeC_2 and the H-Phases, M_2BX , *J. Mater. Synth. Process.* 5 (1997) 197.
- [5] J. Y. Wang, Y. C. Zhou, Polymorphism of ceramic: First-principles investigations, *Phys. Rev. B* 69 (2004) 144108.
- [6] S. Gupta, M.W. Barsoum, On the tribology of the MAX phases and their composites during dry sliding: a review, *Wear* 271 (2011) 1878.
- [7] P. Eklund, M. Beckers, U. Jansson, H. Hogberg, L. Hultman, The $\text{M}_{n+1}\text{AX}_n$ phases: Materials science and thin-film processing, *Thin. Solid. Films.* 518 (2010) 1851.
- [8] I. Salama, T. El-Raghy, M. W. Barsoum, Synthesis and mechanical properties of Nb_2AlC and $(\text{Ti,Nb})_2\text{AlC}$, *J. Alloys. Compd.* 347 (2002) 271.
- [9] N. J. Lane, S. C. Vogel, M. W. Barsoum, Temperature-Dependent Crystal Structures of Ti_2AlN and Cr_2GeC as Determined from High Temperature Neutron Diffraction, *J. Am. Ceram. Soc.* 94 (2011) 3473.
- [10] W. Sun, W. Luo, R. Ahuja, Role of correlation and relativistic effects in MAX phases, *J. Mater. Sci.* 47 (2012) 7615.
- [11] M. Naguib, J. Come, B. Dyatkin, V. Presser, P.-L. Taberna, P. Simon, M. W. Barsoum, Y. Gogotsi, MXene: A Promising Transition Metal Carbide Anode for Lithium-Ion Batteries, *Electrochem. Commun.* 16 (2012) 61.
- [12] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 , *Adv. Mater.* 23 (2011) 4248.
- [13] M. Naguib, V. N. Mochalin, M. W. Barsoum, Y. Gogotsi, MXenes: A New Family of Two-Dimensional Materials, *Adv. Mater.* 26 (2014) 982.
- [14] B. Anasori, Y. Xie, M. Beidaghi, J. Lu, B. C. Hosler, L. Hultman, P. R. C. Kent, Y. Gogotsi, M. W. Barsoum, Two-Dimensional, Ordered, Double Transition Metals Carbides (MXenes), *ACS. Nano.* 9 (2015) 9507.
- [15] Q. Tao, M. Dahlqvist, J. Lu, S. Kota, R. Meshkian, J. Halim, J. Palisaitis, L. Hultman, M. W. Barsoum, P. O. A. Persson, J. Rosen, Two-dimensional $\text{Mo}_{1.33}\text{C}$ MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering, *Nat. Commun.* 8 (2017) 14949.
- [16] Y. C. Zhou, F. L. Meng, J. Zhang, New MAX-Phase Compounds in the V-Cr-Al-C System, *J. Am. Ceram. Soc.* 91 (2008) 1357.
- [17] L. Y. Zheng, J. M. Wang, X. P. Lu, F. Z. Li, J. Y. Wang, Y. C. Zhou, $(\text{Ti}_{0.5}\text{Nb}_{0.5})_5\text{AlC}_4$: A New-Layered Compound Belonging to MAX Phases, *J. Am. Ceram. Soc.* 93 (2010) 3068.
- [18] Z. M. Liu, L. Y. Zheng, L. C. Sun, Y. H. Qian, J. Y. Wang, M. S. Li, G. P. Bei, $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ and $(\text{Cr}_{5/8}\text{Ti}_{3/8})_4\text{AlC}_3$: New MAX-phase Compounds in Ti-Cr-Al-C System, *J. Am. Ceram. Soc.* 97 (2014) 67-69.

- [19] Z. M. Liu, E. D. Wu, J. M. Wang, Y. H. Qian, H. M. Xiang, X. C. Li, Q. Q. Jin, G. G. Sun, X. P. Chen, J. Y. Wang, M. S. Li, Crystal structure and formation mechanism of $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2\text{MAX}$ phase, *Acta Mater.* 73 (2014) 186.
- [20] B. Anasori, M. Dahlqvist, J. Halim, E. J. Moon, J. Lu, B. C. Hosler, E. N. Caspi, S. J. May, L. Hultman, P. Eklund, Experimental and theoretical characterization of ordered MAX phases $\text{Mo}_2\text{TiAlC}_2$ and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$, *J. Appl. Phys.* 118 (2015) 094304.
- [21] M. Dahlqvist, J. Lu, R. Meshkian, Q. Z. Tao, L. Hultman, J. Rosen, Prediction and synthesis of a family of atomic laminate phases with Kagome-like and in-plane chemical ordering, *Sci. Adv.* 3 (2017) e1700642.
- [22] M. Khazaei, M. Arai, T. Sasaki, M. Estili, Y. Sakka, Trends in electronic structures and structural properties of MAX phases: a first-principles study on M_2AlC ($\text{M} = \text{Sc}, \text{Ti}, \text{Cr}, \text{Zr}, \text{Nb}, \text{Mo}, \text{Hf}, \text{or Ta}$), M_2AlN , and hypothetical M_2AlB phases, *J. Phys.: Condens. Matter.* 26 (2014) 505503.
- [23] Y. L. Bai, N. Srikanth, C. K. Chua, K. Zhou, Density Functional Theory Study of $\text{M}_{n+1}\text{AX}_n$ Phases: A Review, *Crit. Rev. Solid. State.* 44 (2019) 56.
- [24] A. Togo, L. Chaput, I. Tanaka, G. Hug, First-principles phonon calculations of thermal expansion in Ti_3SiC_2 , Ti_3AlC_2 , and Ti_3GeC_2 , *Phys. Rev. B* 81 (2010) 174301.
- [25] A. Togo, F. Oba, I. Tanaka, First-principles calculations of the ferroelastic transition between rutile-type and CaCl_2 -type SiO_2 at high pressures, *Phys. Rev. B* 78 (2008) 134106.
- [26] N. J. Lane, S. C. Vogel, G. Hug, A. Togo, L. Chaput, L. Hultman, M. W. Barsoum, Neutron diffraction measurements and first-principles study of thermal motion of atoms in select $\text{M}_{n+1}\text{AX}_n$ and binary MX transition-metal carbide phases, *Phys. Rev. B* 86 (2012) 214301.
- [27] M. A. Pietzka, J. C. Schuster, Summary of Constitutional Data on the Al-C-Ti System, *J. Phase Equilib.* 15 (1994) 392.
- [28] Z. G. Wu, R. E. Cohen, More accurate generalized gradient approximation for solids, *Phys. Rev. B* 73 (2006) 235116.
- [29] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865.
- [30] H. J. Monkhorst, J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* 13 (1976) 5188.
- [31] A. Togo, I. Tanaka, First principles phonon calculations in materials science, *Scr. Mater.* 108 (2015) 1.
- [32] Y. C. Zhou, X. H. Wang, Z. M. Sun, S. Q. Chen, Electronic and structural properties of the layered ternary carbide Ti_3AlC_2 , *J. Mater. Chem.* 11 (2001) 2335.
- [33] N. V. Tzenov, M.W. Barsoum, Synthesis and Characterization of Ti_3AlC_2 , *J. Am. Ceram. Soc.* 83 (2000) 825.
- [34] M. W. Barsoum, T. El-Raghy, C. J. Rawn, W. D. Porter, A. Payzant, C. R. Hubbard, Thermal properties of Ti_3SiC_2 , *J. Phys. Chem. Solids.* 60 (1999) 429.
- [35] S. Q. Feng, Y. Yang, F. Guo, L. Su, X. R. Cheng, C. S. Yuan, K. Yang, Structural, Elastic, Electronic and Hardness Properties of Osmium Diboride Predicted from First Principles Calculations, *J. Alloy. Compd.* 844 (2020) 156098.
- [36] Z. Wu, E. Zhao, H. Xiang, X. Hao, X. Liu, J. Meng, Crystal structures and elastic properties of superhard IrN_2 and IrN_3 from first principles, *Phys. Rev. B* 76 (2007) 054115.
- [37] R. Hill, The Elastic Behaviour of a Crystalline Aggregate, *Proc. Soc. London. A* 65 (1952) 349.

- [38] S. F. Pugh, XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals, *Phil. Mag.* 45 (1954) 833.
- [39] Z. J. Wu, E. J. Zhao, H. P. Xiang, X. F. Hao, X. J. Liu, J. Meng, Crystal structures and elastic properties of superhard and from first principles, *Phys. Rev. B* 76 (2007) 054115.
- [40] J. Haines, J. M. Leger, G. Boequillon, Synthesis and Design of Superhard Materials, *Annu. Rev. Matter. Res.* 31 (2001) 1.
- [41] S. Q. Feng, J. L. Zhao, Y. Yang, W. B. Zhang, J. Y. Li, X. L. Cheng, X. R. Cheng, First Principle Study on Electronic, Thermophysical and Optical Properties of ScAl_3C_3 and UAl_3C_3 under high pressure, *J. Mater. Res. Technol.* 8 (2019) 5774.
- [42] S. Q. Feng, F. Guo, F. Miao, Z. Wang, C. S. Yuan, K. Yang, Nb-based double transition metal silicides MAX-phase: a first-principle study, *Chem. Phys.* 551 (2021) 111321.

Supplement Material

Table S1. Lattice constants and atomic coordinates for three new predicted compounds.

Structure	Group	Parameter(Å)	$\Delta E(\text{eV/f.u.})$	Atom	x	y	z
Ti_3AlB_2	P6 ₃ /mmc	a=b=3.138 c=19.549	-2.051	Ti(4f)	0.33333	0.66667	0.86738
				Ti(2a)	0.00000	0.00000	0.00000
				Al(2b)	0.00000	0.00000	0.25000
				B(4f)	0.66667	0.33333	0.93056
$\text{Ti}_2\text{ZrAlB}_2\text{-1}$	P6 ₃ /mmc	a=b=3.265 c=19.739	-1.880	Ti(4f)	0.33333	0.66667	0.86380
				Zr(2a)	0.00000	0.00000	0.00000
				Al(2b)	0.00000	0.00000	0.25000
				B(4f)	0.66667	0.33333	0.92225
$\text{Ti}_2\text{ZrAlB}_2\text{-2}$	P6 ₃ mc	a=b=3.229 c=19.973	-1.955	Zr(2b)	0.33333	0.66667	0.86525
				Ti(2b)	0.66667	0.33333	0.12927
				Ti(2a)	0.00000	0.00000	0.00423
				Al(2a)	0.00000	0.00000	0.24307
				B(2b)	0.66667	0.33333	0.57048
				B(2b)	0.66667	0.33333	0.93769