ELECTRONIC STRUCTURE AND MECHANICAL PROPERTIES OF 20 MAX PHASE COMPOUNDS

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ABSTRACT

A relatively new class of transition metal layered compounds $M_{n+1}AX_n$, (MAX phases) where M is an early transition metal, A a group A element most likely Al, and X is C or N with n = 1, 2, 3 or 4. Due to their unique structural arrangements and directional bonding, these ternary compounds possess some very outstanding mechanical and chemical properties such as damage-resistance, oxidation resistance, excellent thermal and electric conductivity, machinability, and fully reversible dislocation-based deformation. These properties can be explored in the search for new phases and their composites to meet the performance goals of advanced materials with applications in fossil energy conversion technology. Systematic and detailed computational studies on MAX phase compounds can provide fundamental understanding of the key characteristics that lead to these desirable properties and to the discovery of other new and better alloys.

In this paper, we present results on the electronic structure and mechanical properties of 20 MAX phase compounds using first-principles methods. They are: Ti_3AC_2 (A = Al, Si, Ge), Ti_2AC (A = Al, Ga, In, Si, Ge, Sn, P, As, S), Ti_2AlN, M_2AlC (M = V, Nb, Cr), and $Ta_{n+1}AlC_n$ (n = 1 to 4). The calculated results include: band structures, total and partial density of states, effective charges on each atom, quantitative bond order values, interband optical conductivities, elastic coefficients, bulk modulus, shear modulus, Young's modulus, Poisson's and Pugh ratios. By systematically analyzing these results and in comparison with available experimental data, several important features on structural stability, interatomic bonding and optical conductivities are identified. These results form part of the data base that will enable us to explore and predict new MAX phases and new composite alloys with better physical properties as advanced materials for various applications at extreme conditions.

INTRODUCTION

A new project titled *Large-Scale Simulation of the Mechanical Properties of Layered Transition Metal Ternary Compounds for Fossil Energy Power System Application* was initiated a year ago under DOE-NETL support. The main objective is to develop advanced materials for applications in fossil energy conversion technology under extreme conditions such as high temperature, high pressure, and corrosive environments. This project focuses on the computational development of a new class of materials called MAX phases, or $M_{n+1}AX_n$ [1]. Due to their unique structural arrangements, different types of elements in M and A and a variety of special bonding configurations including metallic, covalent and even ionic bonds, many of these alloys possess some of the most outstanding properties such as damage-resistance, oxidation resistance, excellent thermal and electric conductivity, machinability, and fully reversible dislocation-based deformation [2-5]. These properties can be explored in the search for new phases and their composites that have potential to meet the performance goals for materials to be used in the next generation of fossil energy power systems at a significantly reduced cost.

There are more than 70 known phases of MAX compounds and this number is rapidly growing. In this paper, we present results on the electronic structure and mechanical properties of 20 MAX phase compounds using first-principles methods. They are: Ti_3AC_2 (A = Al, Si, Ge), Ti_2AC (A = Al, Ga, In, Si, Ge, Sn, P, As, S), Ti_2AlN, M_2AlC (M = V, Nb, Cr), and $Ta_{n+1}AlC_n$ (n = 1 to 4). Most of them are Ti-containing phases, since they are the most common in MAX phases. They are chosen for a wide representation and for studying specific trends. The first 12 vary only by the A element and involve three (3 1 2) phases and the nine (2 1 1) phases. In addition to carbides, one example of nitride, Ti_2AlN is also included. This is followed by three other (2 1 1) phases, $(V, Nb, Cr)_2AlC$ where the transition metal M have different d-electron configurations. The Ta-Al-C group is chosen to study the effect of the number of MX layers (see Fig.1). The calculated results include: band structures, total and partial density of states, effective atomic charges, quantitative bond order values, interband optical conductivities, elastic coefficients, bulk modulus, shear modulus, Young's modulus, and Poisson's ratio. By systematically analyzing these results and in comparison with available experimental data, several important features on structural stability, interatomic bonding and optical conductivities are identified. These results enable us to build a data base to facilitate the search for new MAX phases and new composite alloys with the potential of having better physical properties as advanced materials.

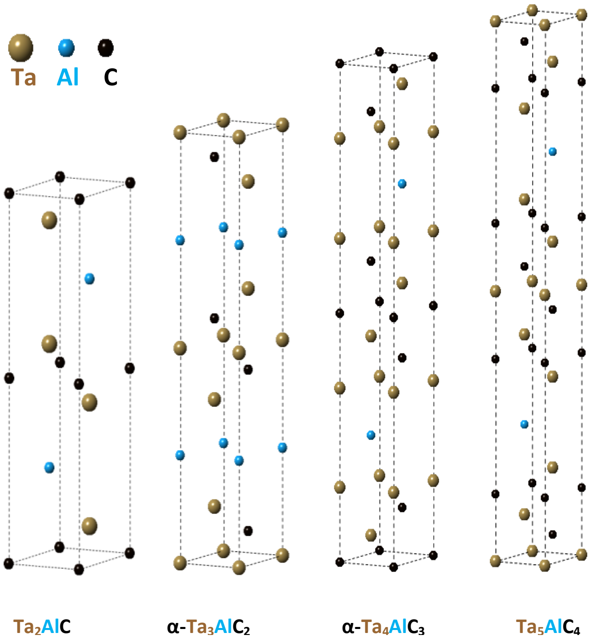

Fig. 1. Crystal structure of 211, 312, 413, 514 phases of M=Ta, A=Al and X=C.

COMPUTATIONAL PROCEDURES

We used two well established computational methods based on density functional theory in our study: the orthogonalized linear combination of atomic orbitals (OLCAO) method [6,7] and the Vienna *Ab initio* Simulation Package (VASP) [8]. The OLCAO method was developed at the University of Missouri-Kansas City and is used mainly for the calculation of electronic structure, bonding and optical properties. The use of atomic orbitals in the OLCAO method for the basis expansion makes it easy to obtain accurate effective charge $Q^{*}{}_{\alpha}$ on each atom and bond order values $\rho_{\alpha\beta}$ between a pair of atoms which is a quantitative measure of the bond strength using the Mulliken scheme [9]. This feature is particularly useful for investigating complex ternary compounds with different types of bonding such as the MAX phases.

$$Q_{\alpha}^{*} = \sum\nolimits_{i} \sum\nolimits_{n,occ} \sum\nolimits_{j,\beta} C_{i\alpha}^{n^*} C_{j\beta}^{n} \left\langle b_{i\alpha}(\vec{k},\vec{r}) \middle| b_{j\beta}(\vec{k},\vec{r}) \right\rangle \tag{1}$$

$$\rho_{\alpha\beta} = \sum\nolimits_{n,occ} \sum\nolimits_{i,j} C_{i\alpha}^{n^*} C_{j\beta}^{n} \left\langle b_{i\alpha}(\vec{k},\vec{r}) \middle| b_{j\beta}(\vec{k},\vec{r}) \right\rangle \tag{2}$$

In Eq. (1) and (2), i and j are the orbital quantum numbers and the C's are the eigenvector coefficients of the Bloch function $b(\vec{k},\vec{r})$ constructed from the linear combination of atomic orbitals [7] and n is the band index.

VASP is a plane-wave based method using pseudopotentials and is most effective for force calculation and geometry optimization [8]. It is mainly used for structural relaxation, elastic and mechanical properties calculations in conjunction with other available methods [10]. The elastic constants are obtained using a strain vs. stress analysis scheme on fully relaxed structure and the Ruess-Voigt-Hill (RVH) approximation [11] for polycrystals. The combination of these two methods has proven to be extremely effective for studying the properties of many complex materials.

RESULTS AND DISCCUSSION

(1) ELECTRONIC AND OPTICAL PROPERTIES

Details of electronic structure and optical conductivity calculations for the 20 MAX phases specified in the Introduction using the OLCAO method were reported elsewhere [12]. Only some selected results are presented here due to page limitation. Fig. 2 shows the total density of states (TDOS) and atom-resolved partial DOS (PDOS) of the 20 MAX phases. The local feature of the TDOS curve around the Fermi-level (E_f) is a reasonable indicator of the intrinsic stability of a crystal. A local minimum at E_f implies higher structural stability because it signifies a barrier for electrons below the E_f ($E < 0$ eV) to move into unoccupied empty states ($E > 0$ eV); whereas a local maximum at E_f is usually a sign of structural instability. This semi-quantitative criterion works reasonably well for the results of Fig.1. Ti_2InC, Ti_2SC, and Cr_2AlC have a local minimum at E_f, suggesting a higher level of stability. Ti_2PC, Ti_2AsC, and Ta_5AlC_4 show a peak in the TDOS at E_f. These facts correlate quite well with the observation that the first group of MAX phases are easier to synthesize whereas those in the second group are not [12].

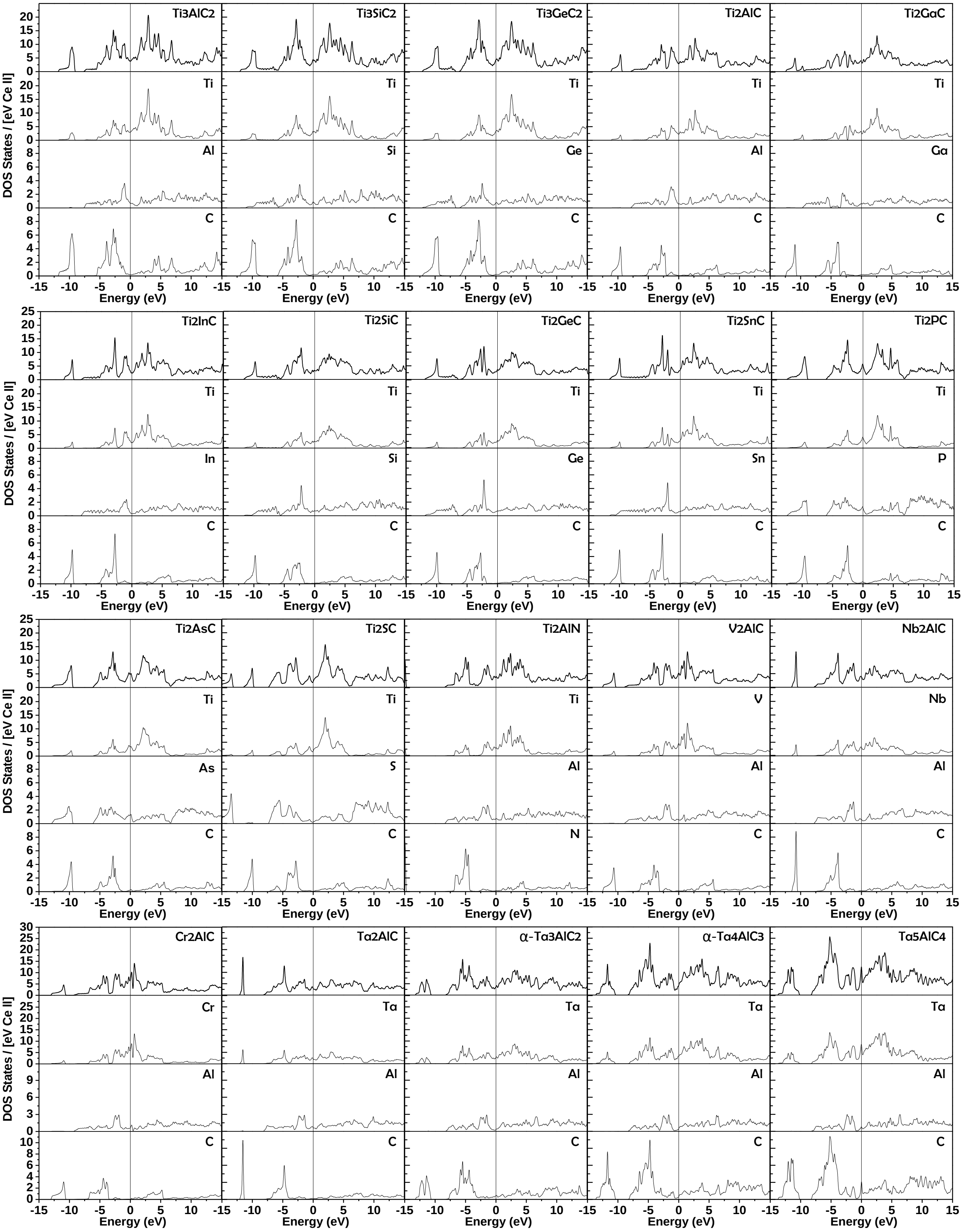

Fig. 2: Calculated DOS and atom-resolved PDOS of 20 MAX phase compounds.

An important physical quantity in MAX phases is the direction of charge transfer between layered atoms. This can be easily obtained from calculated effective charge Q^*_α . Fig. 3 shows the charge transfer $\Delta Q = Q^*_\alpha - Q_0$ where Q_0 is the charge of the neutral atom α. It shows that the metal atoms M always lose charge and C or N always gains charge (more negative). For the A atoms, most of them also gain charge but Al loses a tiny amount. An exception is Cr_2AlC where Al loses almost 0.33 electron with a concomitant large gain of 0.52 electron by C and a small charge loss from Cr element (0.09 electron). This is in sharp contrast with Nb_2AlC where Nb loses 0.51 electron and C and Al gain 0.74 and 0.28 electron respectively. Thus, from the charge-transfer point of view, Cr_2AlC is clearly an outlier and to a less extent Nb_2AlC among the 20 MAX phases. A trend in the Ta-Al-C series is also observed. As the stoichiometric ratio of Ta to C decreases or n increases, there are more C atoms per Ta such that in the limit of large n the degree of electron transfer approaches that of TaC.

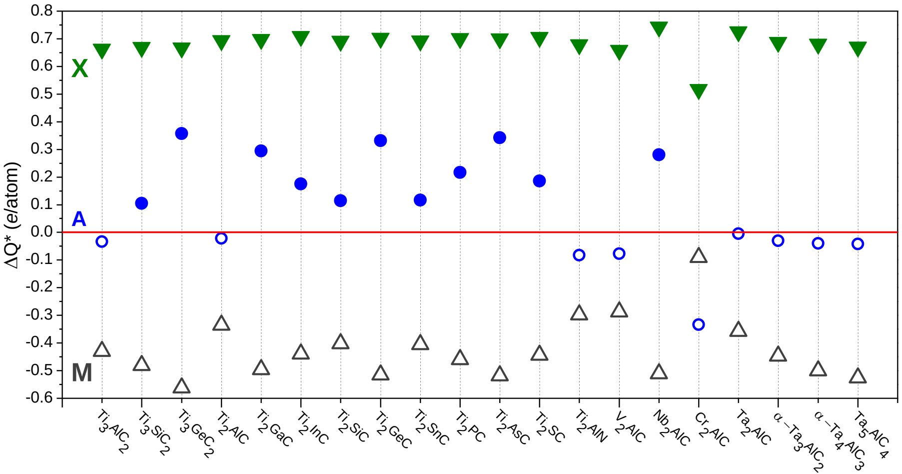

Fig. 3. Charge transfer between composing elements in 20 MAX phase compounds showing M is losing charge, X gain charge and A can lose or gain charge.

The calculated optical conductivities in the 20 MAX phase compounds for frequency range between 0 and 10 eV are shown in Fig. 4. The spectra are resolved into the planar (*a*-*b* plane) and the axial (*c*-direction) components, or $\sigma_{1,\ planar}$ and $\sigma_{1,\ axial}$ for short. The number indicated in each plot is the anisotropy ratio, or the averaged ($\sigma_{1,\ planar}/\sigma_{1,\ axial}$) ratio over all the data points. From these plots, several interesting observations can be made [12]. Most of the MAX phases have the maximum optical conductivities around 5 eV and several phases show sharp peak structures with considerable anisotropy especially in the Ta series. The optical conductivity may be related to the electric conductivity in MAX phases if intra-band contribution at the frequency near 0. eV can be accounted for. It is conceivable that the anisotropy in optical conductivity in the low energy range could also imply that there may be similar trends in the electrical conductivity. The optical anisotropy in the low energy range of our calculation is quite low for the majority of the 20 phases which correlates well with the low anisotropy in the measured electrical conductivities. A notable exception is Nb_2AlC. Indeed, experiments by T. H. Scabarozi et al. [13] showed that Nb_2AlC has a significantly larger anisotropy in its electrical conductivity than other MAX-phase compounds.

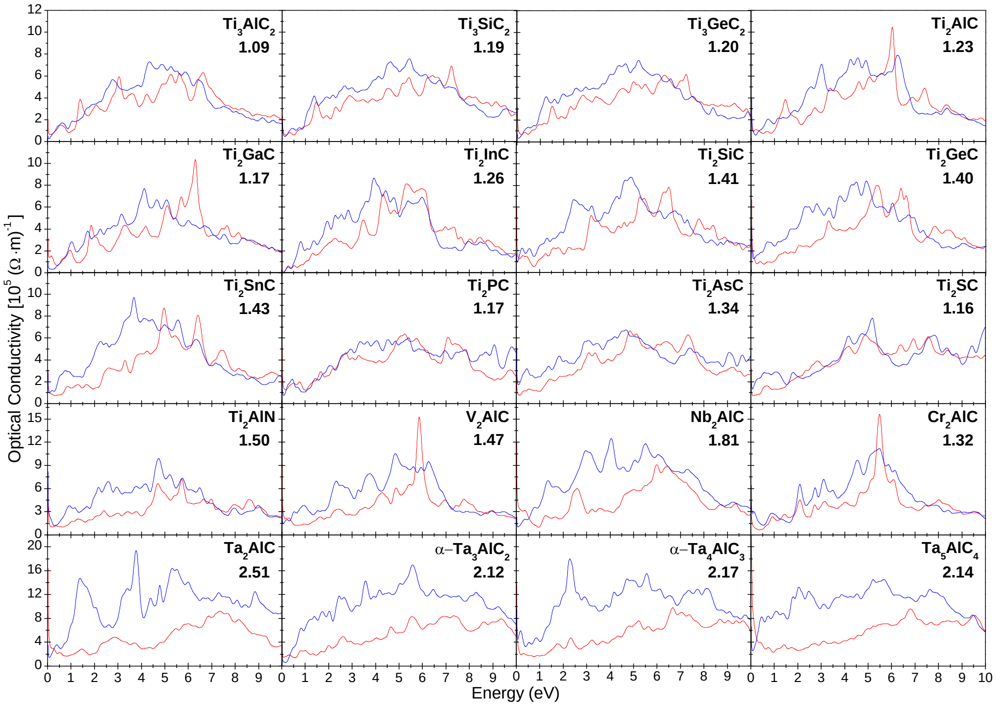

Fig. 4: Optical conductivities of 20 MAX phases compounds. Blue (red) curves show the planer (axial) direction.

(2) MECHANICAL AND ELASTIC PROPERTIES

More recently, we have obtained the complete set of the elastic constants of the same 20 phases of the MAX phases. From the elastic constants, bulk mechanical properties (bulk modulus K, shear modulus G, Young's modulus E, and Poisson ratio η can be obtained using Voigt-Reuss-

Table 1. Calculated elastic coefficients and mechanical properties of 20 MAX phase compounds.

Crystals	**C_{11}**	**C_{12}**	**C_{13}**	**C_{33}**	**C_{44}**	**C_{66}**	**K**	**G**	**E**	**η**	**G/K**
Ti_3AlC_2	355.8	81.4	75.3	293.4	120.3	137.2	162.5	126.7	301.7	0.191	0.78
Ti_3SiC_2	369.6	96.2	107.6	358.3	155.0	136.7	191.1	141.3	340.0	0.204	0.74
Ti_3GeC_2	362.0	97.2	97.7	332.0	137.3	132.4	182.2	132.2	319.3	0.208	0.73
Ti_2AlC	301.9	68.0	63.0	267.9	105.1	117.0	139.7	110.5	262.3	0.187	0.79
Ti_2GaC	300.8	79.2	63.8	246.5	92.4	110.8	139.3	101.4	244.9	0.207	0.73
Ti_2InC	284.4	69.3	55.2	235.5	83.9	107.5	128.6	96.0	230.5	0.201	0.75
Ti_2SiC	312.9	82.1	110.4	329.2	149.6	115.4	173.0	124.9	302.0	0.209	0.72
Ti_2GeC	296.6	85.7	96.8	297.1	121.5	105.5	161.0	110.0	268.8	0.222	0.68
Ti_2SnC	262.6	88.6	73.1	255.2	96.8	87.0	138.8	92.4	226.8	0.228	0.67
Ti_2PC	256.8	144.8	155.0	339.5	166.3	56.0	191.8	93.1	240.4	0.291	**0.49**
Ti_2AsC	212.9	180.4	123.7	289.5	146.3	16.2	150.7	57.2	152.3	0.332	**0.38**
Ti_2SC	339.8	101.4	109.7	361.9	159.5	119.2	186.8	134.4	325.2	0.210	0.72
Ti_2AlN	312.9	73.0	95.5	290.7	126.1	120.0	160.5	117.4	283.1	0.206	0.73
V_2AlC	334.4	71.5	106.0	320.8	149.8	131.5	172.9	132.1	315.9	0.196	0.76
Nb_2AlC	316.6	86.3	117.0	288.6	137.6	115.2	173.6	116.4	285.5	0.226	0.67
Cr_2AlC	366.3	85.8	111.3	356.9	142.9	140.2	189.6	137.0	331.2	0.209	0.72
Ta_2AlC	344.5	112.2	137.1	327.9	152.3	116.1	198.8	124.1	308.1	0.242	0.62
αTa_3AlC_2	453.6	130.5	135.6	388.4	175.0	161.5	232.8	161.1	392.8	0.219	0.69
αTa_4AlC_3	459.2	149.1	148.7	383.1	170.5	155.0	243.0	155.3	384.1	0.237	0.64
Ta_5AlC_4	481.5	149.6	158.1	423.6	188.8	165.9	257.2	169.1	416.0	0.231	0.66

Hill approximation [10]. Table 1 lists the calculated elastic tensors and mechanical properties. Fig. 4 shows the comparison of the calculated K, G, E and η with the available experimental data or calculated by others as listed in ref. [5]. For most compounds the agreements are very good. (The data points are close to the diagonal line.) The only exceptions are Cr_2AlC, Ti_2SC and V_2AlC, especially Cr_2AlC and Ti_2SC. These same compounds also show deviations in other properties from most MAX phases and deserve a closer scrutiny in the way they were measured and the nature of the samples used, and the reason behind for such deviations.

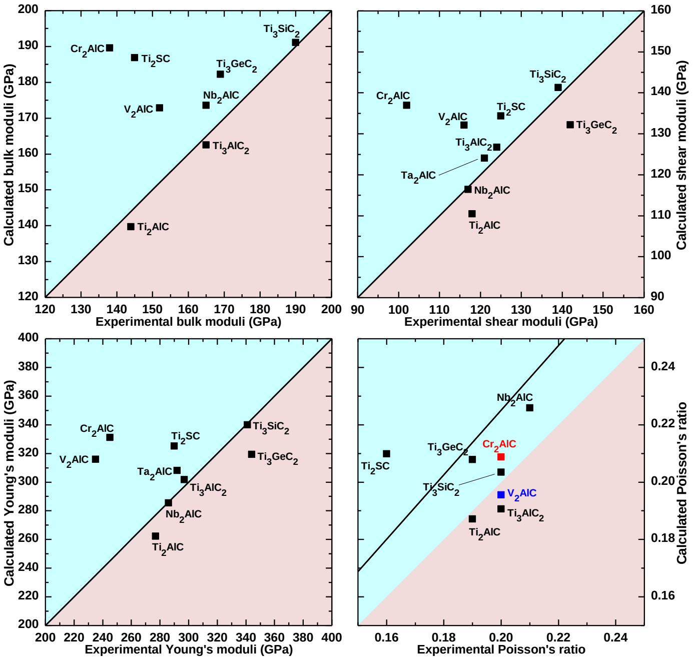

Fig. 5: Comparison between calculated and experimental values of K, G, E and η in some MAX phase compounds (data from ref. 5).

An important parameter, the Pugh ratio k = G/K is also listed in Table 1. According to the prevailing theory on mechanical properties of metallic systems [13], larger (smaller) k implies the materials to be relatively brittle (ductile). Table 1 shows that the Pugh ratios for Ti_2AsC and Ti_2PC to be much lower than other phases, indicating that these crystals to be more ductile than other MAX phase compounds.

For MAX phase compounds to be applied as viable fossil energy materials, structural safety is a critical issue in addition to other physical properties. Thus damage tolerant and avoidance of premature failure is most important. It is not clear if some of the reported fracture energy of the MAX phases which are widely scattered and much dependent on the samples and experimental conditions can be somehow be correlated with calculated k or Poisson's ratio η. On the other hand, our data in Table 1 shows a clear inverse correlation between k and η. Thus one of the goals is to use the calculated mechanical parameters to relate to the strength and toughness of the compounds. This certainly requires a large data base and a credible empirical relation as recently used for many crystalline superhard materials and metallic glasses [15].

CONCLUSTION

We are currently near the middle of the three-year project which is roughly divided into two phases. The first phase consists of the fundamental electronic structure and mechanical properties of the five most important MAX phases. In this paper, we have reported results on 20 MAX phases, well beyond the original expectation. Due to page limitations, only some selected results are presented in this paper and more will be reported later. In the second part of the project, we will move toward the more complex calculation related to surfaces, interfaces and absorption of gas molecules on the surfaces with the goal of using MAX phases compounds for coating to protect the main alloys used in fossil energy at high temperature and pressure. We are also contemplating of performing additional calculations on more MAX phases so as to enlarge the data base with a much larger number of MAX compounds and different physical and chemical properties.

ACKNOLEDGEMENTS

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