

## ***Ab Initio* Calculations for Properties of MAX Phases $\text{Ti}_2\text{TlC}$ , $\text{Zr}_2\text{TlC}$ , and $\text{Hf}_2\text{TlC}$**

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### **Abstract**

Using *ab initio* calculations we have computed the lattice constants, bulk moduli, and local and total density of states of the MAX phases,  $\text{Ti}_2\text{TlC}$ ,  $\text{Zr}_2\text{TlC}$ , and  $\text{Hf}_2\text{TlC}$  in the hexagonal  $P6_3/mmc$  space group. The results for lattice constants are within 2% of experimental results. The bulk moduli are predicted to be 125, 120, and 131 GPa respectively. These are the lowest values of bulk moduli amongst all MAX phases studied to date. The electronic density of states shows that all three materials are conducting. These low values of their bulk moduli are attributed to weak metal M (M= Ti, Zr, Hf) bonding with the A element thallium.

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## 1. Introduction

$M_{n+1}AX_n$  phases were discovered about 35 years ago by Nowotny and his coworkers.<sup>1</sup> In the chemical formula, M is an early transition metal, A is an A-group element, and X is either carbon (C) or nitrogen (N). When  $n=1$  these phases are called 211 MAX phases, signifying the ratio of the constituent elements. These structures are unique in that they have attributes of metals and ceramics, allowing for some fascinating possibilities for these materials as conductors at very high temperatures.<sup>1</sup> More recently these studies gained renewed interest by the production of a single phase of  $Ti_3SiC_2$  by Barsoum and co-workers.<sup>2</sup> Subsequently, many of these phases have been studied experimentally and theoretically.<sup>3,4</sup>

Sun *et al.*,<sup>5</sup> recently studied the  $M_2AC$  MAX phases, where  $M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W$  and  $A = Al, Ga, Ge, Sn$ . They discovered that the phases  $M_2AC$  with group IV B elements  $M = Ti, Zr, \text{ and } Hf$  give significantly lower bulk moduli (B) than other MAX phases in their data set, attributing this to weaker M d-orbital C p-orbital bonding in these materials. Motivated by their work and in the quest for MAX phases with the lowest bulk moduli we explored the bulk modulus and structural and electronic properties of  $M_2TiC$ , with  $M = \text{titanium (Ti), zirconium (Zr) or Hafnium (Hf)}$ . These MAX phases have been synthesized by Nowotny and co-workers.<sup>6,7</sup> Our theoretically computed lattice constants are in reasonable agreement with experiment.<sup>6,7</sup> We predict the bulk modulus (B), local- and total- electronic density of states for these MAX phases. Our computations show that these materials indeed show the smallest values of B amongst MAX phases experimentally or theoretically studied so far. They are electrical conductors.

## 2. Crystal Structure

The three MAX phases studied in this paper are 211 phases with a layered hexagonal, close-packed structure. They belong to the space group  $P6_3/mmc$ .<sup>8</sup> In each unit cell there are two M layers, with  $M = \text{Ti, Zr, or Hf}$ , interleaved with layers of thallium (Tl). The carbon (C) atoms fill the octahedral locations between the M layers.<sup>9,10</sup> The repeating structure of the planes in the unit cell can be further defined by the  $A_C C_M B_{Ti} C_M A_C B_M C_{Ti} B_M$  close-pack stacking along the Z-axis.<sup>8,9,10</sup> The letters A, B, and C stand for the three distinct positions for atoms to occupy, in the close-packed  $\langle 0001 \rangle$  plane.<sup>11</sup> The subscripts denote the type of atom that sits at the site, e.g.  $B_M$  means the metal atom M sits at a B site. The Z- coordinate increases as we go from left to right. Table I gives a precise description of the specific positions of each atom in the unit cell corresponding to this type of stacking.

## 3. Computational Method

We performed first-principles total energy calculations within the generalized gradient approximation (GGA) to density functional theory<sup>12</sup> (DFT) using the suite of codes VASP.<sup>13,14,15,16</sup> Core electrons are implicitly treated by ultra soft Vanderbilt type pseudopotentials<sup>17</sup> as supplied by G. Kresse and J. Hafner.<sup>18</sup> For each calculation, irreducible  $k$ -points are generated according to the Monkhorst-Pack scheme.<sup>19</sup> The convergence is achieved with 60  $k$ - points in the irreducible part of Brillouin zone for the eight atom unit cell described in Table I. The single-particle wave functions have been expanded in a plane-wave basis using a 300 eV kinetic energy cutoff. All atoms are allowed to relax until a force tolerance of 0.001 eV/Å is reached for each atom. The

calculations for the total density of states (DOS) were performed with the tetrahedron method with Blöchl corrections for the energy.<sup>20</sup> Tests using a higher plane-wave cutoff and a larger k-point sampling indicate that a numerical convergence better than  $\pm 1.0$  meV is achieved for relative energies.

To obtain the absolute minimum in total energy for each crystal structure, the equilibrium lattice constants  $a$  and  $c$  were varied independently. Once the equilibrium constants and volume  $V_0$  were established for each structure, external strains  $\delta$  of  $\pm 1\%$ , and  $\pm 2\%$  were applied to the structure, while allowing full relaxation of the ions. This ionic relaxation allowed the value of  $z_M$  to change with the strain. We thus obtained the total minimum energies  $E(V)$  at these strained volumes  $V$ , corresponding to each value of  $\delta$ . These energies and strains were fit with the corresponding parabolic equation<sup>21</sup>

$$\Delta E = \frac{9}{2} V_0 B \delta^2, \text{ where } \Delta E \equiv E(V) - E(V_0).$$

#### 4. Results

Our calculated values for the constants  $a$ ,  $c$ ,  $z_M$ , and  $c/a$  are shown in Table II. The deviation from the experimental values of  $c$  and  $a$  for  $Ti_2TlC$  was 1.3% and 0.9%, respectively. For  $Zr_2TlC$ , the change from experimental values was 1.4% and 0.6%, while for  $Hf_2TlC$  it was 1.1% and 0.6%, respectively.

The bulk moduli ( $B$ ) of  $Ti_2TlC$ ,  $Zr_2TlC$ , and  $Hf_2TlC$  were found to be 125, 120 and 131 GPa respectively. Sun *et al.*,<sup>5</sup> have calculated  $B$  for  $Ti_2AlC$ ,  $Ti_2GaC$ ,  $Zr_2AlC$ ,  $Zr_2GaC$ ,  $Hf_2AlC$  and  $Hf_2GaC$  to be approximately 166, 165, 148, 146, 158 and 158 GPa respectively. We notice that as we go from  $A = Al$ , to  $Ga$  to  $Tl$  for a fixed element  $M$  ( $M=Ti, Zr, Hf$ ), the bulk modulus of  $M_2AC$  decreases though the decrease in  $B$  from

$M_2AlC$  to  $M_2GaC$  is very small. The decrease in  $B$  from  $M_2AlC$  to  $M_2TiC$  is however quite significant (a maximum of approximately 25% decrease in  $B$ ). Sun *et al*<sup>5</sup> showed that  $M_2AC$  MAX phases can be divided into two groups. The first group with V-B and VI-B transition metals where the bulk modulus of  $M_2AC$  is approximately same as  $MC$  and the second group with IV-B transition metals where the bulk modulus of  $M_2AC$  is significantly lower than  $MC$ . Our calculations show that the three MAX phases studied in this report belong to the second group with their bulk moduli significantly lower than their binary carbides.

The local density of states (LDOS) showing the hybridization of the various  $M$ ,  $Tl$ , and  $C$  electronic states is shown in Fig. 1. LDOS shows two interesting features: (i) The peak of the  $C$   $p$  electronic states (dashed lines in Fig. 1) corresponding to the hybridization of  $M$   $d$  and  $C$   $p$  electrons, increases monotonically as we go down the  $M$  group from  $Ti$  to  $Hf$ . This suggests that as we go down this group from  $Ti$  to  $Hf$  more  $C$   $p$  electrons participate in the  $M$   $d$  and  $C$   $p$  bonding. (ii) The hybridization peaks of  $M$   $d$  ( $M = Ti, Zr, Hf$ ) and carbon  $p$  lie between  $-2$  eV and  $-3$  eV, while those of  $M$   $d$  and  $Tl$   $p$  are between  $-1$  eV and  $-2$  eV. This suggests that the  $M$  and carbon bonds are stronger than  $M$  and  $Tl$  bonds. This trend in LDOS is also seen in the data of Sun *et al*.<sup>5</sup> for  $Ti_2AlC$ ,  $Cr_2AlC$  and  $Cr_2GeC$ .

Our calculated total density of states (DOS) is shown in Fig. 2. At the fermi level  $E_f$ , the DOS for  $Ti_2TiC$ ,  $Zr_2TiC$ , and  $Hf_2TiC$ , were 2.5, 2.1, and 1.8 states per unit cell per eV, respectively. Thus there is a small decreasing trend in the DOS at  $E_f$  with increasing atomic numbers of the transition metal ( $M$ ). Hence it is tempting to conclude that  $Ti_2TiC$  is more conducting than  $Zr_2TiC$  and  $Zr_2TiC$  is more conducting than  $Hf_2TiC$ . However as

stated by Barsoum<sup>22</sup>, the mobilities of charge carriers for all MAX phases except for  $\text{Ti}_4\text{AlN}_3$  are inversely proportional to the DOS at Fermi level.

In summary we have performed *ab initio* computations of the structural, elastic, and electronic properties of  $\text{M}_2\text{TiC}$ ,  $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ . All three materials are found to be conducting with the DOS at Fermi energy decreasing with the increase in the atomic number of the transition metal. These materials have the *lowest* bulk moduli amongst the MAX phases experimentally or theoretically studied so far. The LDOS shows that there is an increase in carbon p electrons participation in M d and C p bonds with the increase in the atomic number of transition metal. For all the three MAX phases investigated, the M d and C p bond is stronger than M d and Ti p bond.

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## Table and Figure captions

### Table captions:

#### Table I.

The table lists the 8 atom basis for the unit cell  $M_2TIC$  phase<sup>8,9,10</sup> with  $M = Ti, Zr, \text{ or } Hf$ .

The lattice vectors of this hexagonal unit cell with lattice constants  $a$  and  $c$  are:

$\mathbf{a}_1 = 2c_2a(1, -c_3, 0)$ ,  $\mathbf{a}_2 = 2c_2a(1, c_3, 0)$ , and  $\mathbf{a}_3 = c(0, 0, 1)$ . The constants are  $c_1 \equiv \frac{1}{3}$ ,  $c_2 \equiv \frac{1}{4}$ , and  $c_3 \equiv \frac{1}{\sqrt{c_1}}$ . The constant “ $z_M$ ” corresponding to the internal degree of freedom is given in Table II for each phase.

#### Table II.

Equilibrium values of the hexagonal unit cells in Table I: the lattice constants  $a$  and  $c$ , their ratio  $c/a$ ,  $z_M$ , equilibrium volume  $V$ , and bulk modulus  $B$  for the three phases calculated with GGA, compared with experimental values. The internal degree of freedom  $z_M$  in the unit cells is defined in Table I.

### Figure captions

#### Fig 1.

Local density of states (LDOS) for  $M_2TIC$  ( $M = Ti, Zr, Hf$ ). The LDOS for the  $s$  states are not shown since they do not contribute much to bonding.

#### Fig 2.

The total density of states (DOS) is shown as a function of energy for the three phases studied. The zero of the energy is taken at the Fermi energy  $E_f$  shown by a dotted line.

Atom Type	Position Vector
C	$0$
M	$c_1(\mathbf{a}_1 + 2\mathbf{a}_2) + z_M\mathbf{a}_3$
Tl	$c_1(2\mathbf{a}_1 + \mathbf{a}_2) + c_2\mathbf{a}_3$
M	$c_1(\mathbf{a}_1 + 2\mathbf{a}_2) + (2c_2 - z_M)\mathbf{a}_3$
C	$2c_2\mathbf{a}_3$
M	$c_1(2\mathbf{a}_1 + \mathbf{a}_2) + (2c_2 + z_M)\mathbf{a}_3$
Tl	$c_1(\mathbf{a}_1 + 2\mathbf{a}_2) + 3c_2\mathbf{a}_3$
M	$c_1(2\mathbf{a}_1 + \mathbf{a}_2) + (1 - z_M)\mathbf{a}_3$

Table I of J. A. Warner *et al.*

<b><u>Property</u></b>	<b><u>Ti<sub>2</sub>TiC</u></b>		<b><u>Zr<sub>2</sub>TiC</u></b>		<b><u>Hf<sub>2</sub>TiC</u></b>	
	<u>Theory</u>	<u>Expt.<sup>1, 23</sup></u>	<u>Theory</u>	<u>Expt.<sup>1, 24</sup></u>	<u>Theory</u>	<u>Expt.<sup>1, 24</sup></u>
a (Å)	3.18	3.15	3.38	3.36	3.34	3.32
c (Å)	14.16	13.98	14.99	14.78	14.78	14.62
z <sub>M</sub> (Å)	0.0777		0.0817		0.0811	
c/a	4.45	4.42	4.43	4.40	4.42	4.40
$V = \left(\frac{\sqrt{3}}{2}\right)a^2c$	124.36	119.64	148.57	144.54	142.88	139.44
B (GPa)	125		120		131	

Table II of J. A. Warner *et al.*

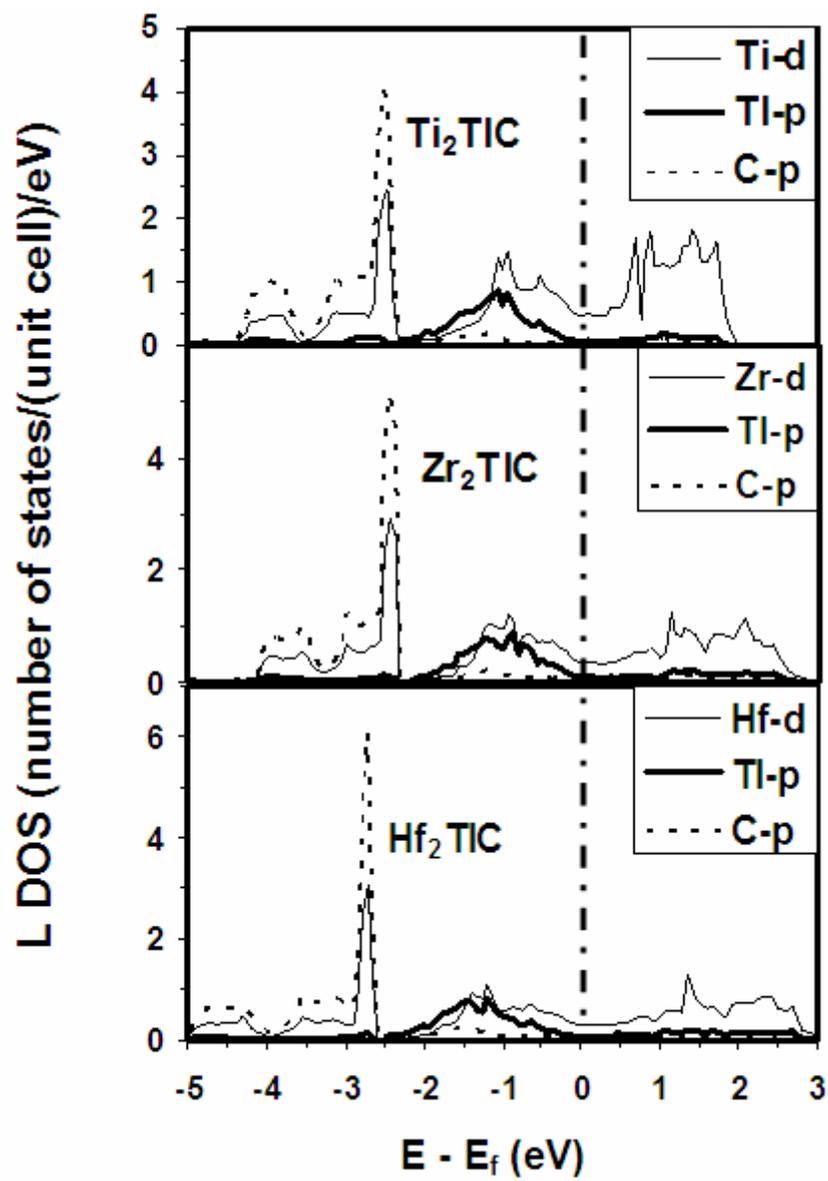


Fig 1. of J. A. Warner *et al.*

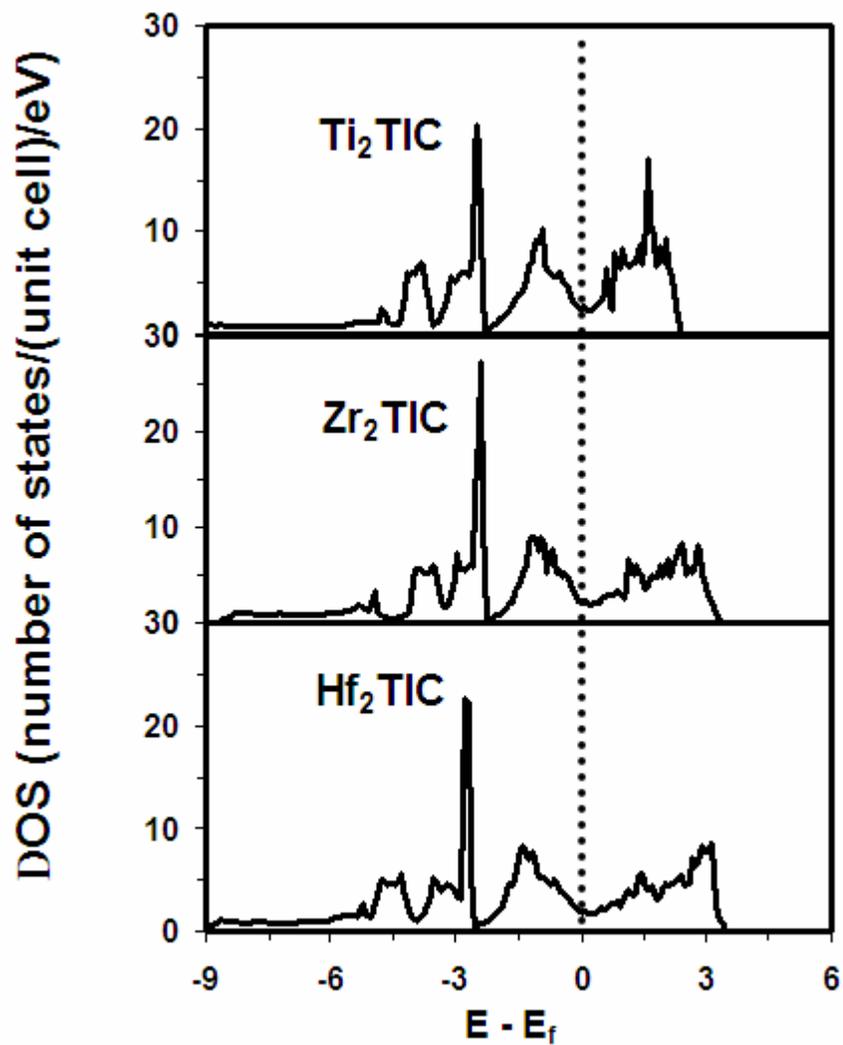


Fig 2. of J. A. Warner *et al.*

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