

Ab initio calculations for properties of MAX phases Ti₂TiC, Zr₂TiC, and Hf₂TiC

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Using *ab initio* calculations we have computed the lattice constants, bulk moduli, and local and total density of states of the MAX phases, Ti₂TiC, Zr₂TiC, and Hf₂TiC in the hexagonal *P6₃/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 among 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. © 2006 American Institute of Physics.

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M_{n+1}AX_n phases were discovered about 35 years ago by Nowotny and his co-workers.¹ 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.² More recently these studies gained renewed interest by the production of a single phase of Ti₃SiC₂ by Barsoum and co-workers.³ Subsequently, many of these phases have been studied experimentally and theoretically.^{4,5} Owing to many advantageous material properties of MAX phases, single crystal thin films⁶ of Ti₂AlN have been grown recently for possible engineering applications like wear protective coatings for cutting tools and diffusion barriers in microelectronics.

Sun *et al.*⁷ recently studied the M₂AC MAX phases, where M=Ti,Zr,Hf,V,Nb,Ta,Cr,Mo,W and A=Al,Ga,Ge,Sn. They discovered that the phases M₂AC with group IV B elements M=Ti, Zr, 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 M₂TiC, with M=titanium (Ti), zirconium (Zr) or Hafnium (Hf). These MAX phases have been synthesized by Nowotny and co-workers.^{8,9} Our theoretically computed lattice constants are in reasonable agreement with experiment. 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 among

MAX phases experimentally or theoretically studied so far. They are electrical conductors.

The three MAX phases studied in this letter are 211 phases with a layered hexagonal, close-packed structure. They belong to the space group *P6₃/mmc*.¹⁰ In each unit cell there are two M layers, with M=Ti, Zr, or Hf, interleaved with layers of thallium (Tl). The carbon (C) atoms fill the octahedral locations between the M layers.^{11,12} The repeating structure of the planes in the unit cell can be further defined by the A_CC_MB_{Tl}C_MA_CB_MC_{Tl}B_M close-pack stacking along the Z axis.¹⁰⁻¹² The letters A, B, and C stand for the three distinct positions for atoms to occupy, in the close-packed <0001> plane.¹³ 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.

We performed *ab initio* total energy calculations within

TABLE I. The table lists the eight atom basis for the unit cell M₂TiC phase (see Refs. 10–12) with M=Ti, Zr, 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 $c_3\equiv\frac{1}{\sqrt{3}}$. The constant “z_M” corresponding to the internal degree of freedom is given in Table II for each phase.

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	$c_1(2\mathbf{a}_1+\mathbf{a}_2)+(1-z_M)\mathbf{a}_3$

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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.

Property	Ti ₂ TiC		Zr ₂ TiC		Hf ₂ TiC	
	Theory	Expt. (Refs. 2 and 24)	Theory	Expt. (Refs. 1 and 2)	Theory	Expt. (Refs. 1 and 2)
a (Å)	3.18		3.15	3.38	3.36	3.34
c (Å)	14.16		13.98	14.99	14.78	14.78
z_M	0.0777			0.0817		0.0811
c/a	4.45		4.42	4.43	4.40	4.42
$V=(\sqrt{3}/2)a^2c$	124.36		119.64	148.57	144.54	142.88
B (GPa)	125			120		131

the generalized gradient approximation (GGA) to density functional theory¹⁴ using the suit of codes VASP.^{15–18} Core electrons are implicitly treated by ultrasoft Vanderbilt-type pseudopotentials¹⁹ as supplied by Kresse and Hafner.²⁰ For each calculation, irreducible k points are generated according to the Monkhorst–Pack scheme.²¹ The convergence is achieved with 60 k points in the irreducible part of the 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.²² Tests using a higher plane-wave cutoff and a larger k -point sampling indicate that a numerical convergence better than ± 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 δ 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 (the ratio of z coordinate of M atoms to the lattice constant c) to change with the strain. We thus obtained the total minimum energies $E(V)$ at these strained volumes V , corresponding to each value of δ . These energies and strains were fit with the corresponding parabolic equation²³ $\Delta E = \frac{9}{2}V_0B\delta^2$, where $\Delta E \equiv E(V) - E(V_0)$.

Our calculated values for the constants a , c , z_M , and c/a are shown in Table II. The deviation from the experimental²⁴ values of c and a for Ti₂TiC was 1.3% and 0.9%, respectively. For Zr₂TiC, the change from experimental² values was 1.4% and 0.6%, while for Hf₂TiC it was² 1.1% and 0.6%, respectively.

The bulk moduli (B) of Ti₂TiC, Zr₂TiC, and Hf₂TiC were found to be 125, 120 and 131 GPa, respectively. Sun *et al.*⁷ have calculated B for Ti₂AlC, Ti₂GaC, Zr₂AlC, Zr₂GaC, Hf₂AlC and Hf₂GaC 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 M₂AC decreases though the decrease in B from M₂AlC to M₂GaC is very small. The decrease in B from M₂AlC to M₂TiC is, however, quite significant (a maximum of approximately 25% decrease in B). Sun *et al.*⁷ showed that M₂AC MAX phases can be divided in to two groups. One group with V-B and VI-B transition metals where the bulk modulus of M₂AC is approximately same as

MC and the second group with IV-B transition metals where the bulk modulus of M₂AC is significantly lower than MC. Our calculations show that the three MAX phases studied in this letter 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, Ti, 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 and -3 eV, while those of M d and Ti p are between -1 and -2 eV. This suggests that the M and carbon bonds are stronger than M and Ti bonds. This trend in LDOS is also seen in the data of Sun *et al.*⁷ for Ti₂AlC, Cr₂AlC and Cr₂GeC.

Our calculated total density of states (DOS) is shown in Fig. 2. At the fermi level E_f , the DOS for Ti₂TiC, Zr₂TiC,

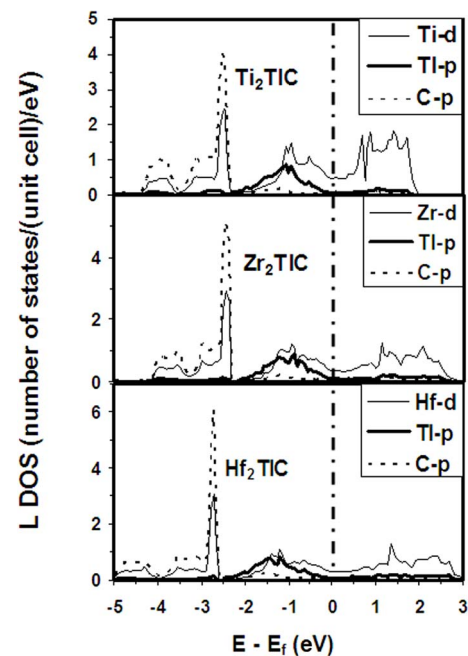


FIG. 1. Local density of states (LDOS) for M₂TiC (M=Ti, Zr, Hf). The LDOS for the s states are not shown since they do not contribute much to bonding. The zero of the energy is taken at the Fermi energy E_f shown by a dotted line.

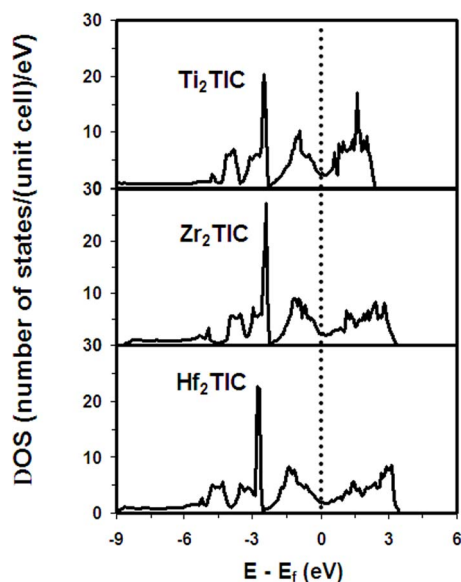


FIG. 2. The total density of states (DOS) is shown as a function of energy for the three phases studied. The zero of the energy is taken at the Fermi energy E_f shown by a dotted line.

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,²⁵ the mobilities of charge carriers for all MAX phases except for Ti_4AlN_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 M_2TIC , $\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$. 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 among 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 *Tl p* bond.

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