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Ab-initio Calculations of the Structural and Electronic Properties of Zr_2AC

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Abstract
In this work we have used ab-initio investigations to calculate the structural and electronic properties of Zr_2AC (A = In, Pb, Sn, Tl), using density functional theory (DFT). The substitution between Pb, Sn, In, Tl causes changes in their lattice parameters and electronic properties. The optimized lattice parameters *a(*Å), *c*(Å), and volume, *V*(Å)^3, were found to be consistent with available experimental data. From the calculated band structures, and density of states, (DOS), results show that materials have no bandgap. This shows the materials are metallic conductors. Calculated DOS shows Zr_2SnC has the highest DOS, and Zr_2InC has the lowest of the four phases. The top of the valence band and lower conduction band are dominated by Zr-4d and In-5p, Tl-6p, while Pb-6p, Sn-5p, C-2p are dominant at the lowest energy zone in each phase respectively. A complete understanding of the layered carbides would require research into their structural stability. A great design may fail in the choice of parent materials if the working environment is subjected to a higher temperature. The ability of materials to sustain defacing in such conditions like shielding wall for nuclear reactors, jet engine nuzzles requires materials test for structural stability.
Keywords: Ab-initio; density functional theory; lattice parameters; band structures; density of states

Introduction

MAX phase is a group of layered ternary carbides and nitrides having a fascinating stoichiometry $M_{n+1}AX_n$ where n is an integer of magnitudes 1 to 3; The constituent elements of MAX phases as enshrined in their general relation are; M representing early transition metals from either group III (Sc), IV (Ti, Zr, Hf), V (V, Nb, Ta) and VI (Cr, Mo); A an A-group element from groups XII (Cd), XIII (Al, Ga, In, Tl), XIV (Si, Ge, Sn, Pb), XV (P, As), or XVI (S), and X represents carbon (C) or nitrogen (N) [1,2,3]. The Zr_2AC (A = In, Pb, Sn, Tl), MAX-phase crystals, also called 2 1 1 MAX phases, have a hexagonal symmetry in space group *P*63/*mmc* (#194) with Wyckoff positions: M (4*f*), A (2*d*), and X (2*a*). This class of compounds has dual characteristic properties of metal and ceramic and they possess most of the potentials needed today in the field of modern technologies. The ability to understand their stoichiometry and their unique crystal family structure is a gateway to exploiting their engineering potentials and hence the need to accurately determine their characteristic ground state properties [4,5].

The history of MAX phases can be viewed from two perspectives. The time of their discovery from early to mid-1960s, and the tail end of the mid-1990s. Since then, the study on the MAX phase compounds has grown exponentially [6,7]. This was followed by the growing interest in MAX phases because of their great potentials about a decade and a half later. In these great search the ternary compound, Ti_3SiC_2, was synthesized and characterized by Dr. Michel Barsoum's Research group at Drexel University in the late 1990s [8]. A year later the unit presented Ti_3SiC_2 as one of well over sixty phases synthesized mostly discovered and fashioned in powder form in the 1960s by H. Nowotny and co-workers [9] Ti_4AlN_3 was discovered In the late 20th century and it realized that a much larger family of solids that all behaved similarly is being dealt with. Since then tremendous efforts have been made to calculate the properties of MAX phases [10,11]. In the current study, we looked through the structural and electronic properties of Zr_2AC, (A = In, Pb, Sn, and Tl) and compared results of substitution of the A elements on the A site of MAX phase to enrich the computational data base for future studies .

Although materials belong to the same 211 group of MAX phases, each substitution affects their lattice parameters, electronic bands, and density of states. A complete understanding of such materials would require additional research into their structural stability[12]. A great design may fail with the choice of the wrong material if the working environment is subjected to a higher temperature.

Computational inputs

Ab-initio calculations were used in conjunction with the plane-wave pseudopotential methods enshrined in the density functional theory (DFT) framework as implemented in Quantum Espresso (QE) simulation package [13]. The exchange-correlation (*XC),* energy functional used is the generalized gradient approximation(GGA) as parameterized by Perdew-Burke Ernzerhof (PBE) formalism [14]. Throughout this study, ultrasoft pseudopotentials (UPP) were used and an energy cut-off of 500 Ry was used to limit the number of components in the plane wave expansion. A Gaussian smearing technique was used to a smearing width of 0.02 Ry. For the Brillouin zone integration, a 14 × 14 × 14 k-points mesh was generated using the Monkhorst-Pack scheme to produce a uniform grid of k-points along the three axes in reciprocal space. Lattice parameters were fully optimized by relaxing atomic positions through various volumes until the total energy difference for the four phases were smaller or less than 10^{-8} Ry[15].

Results and discussion

Structural properties

In this research, we have achieved a general optimization and convergence tests of the lattice parameters, cut-off energy, and k-points respectively for the four MAX compounds: Zr_2InC, Zr_2PbC, Zr_2SnC, and Zr_2TlC. Total energy is converged in terms of the expansion of the charge density, wave function until it reached equilibrium. The crystal structures of the studied MAX phases are shown in Figure 1. The Energy (eV) versus Volume, *V* $(a.u)^3$ curves in Figure 2 (a), (b), (c), and (d) shows optimized volumes of the studied materials, respectively.

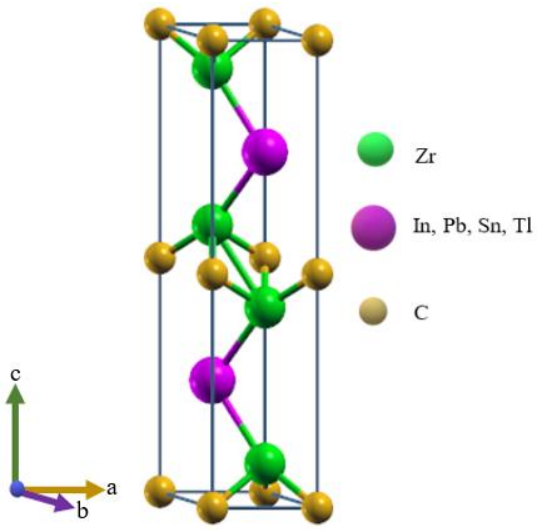


Figure 1 Crystal structure of Zr2AC, (A = In, Pb, Sn, Tl)

The discrepancy of our calculated results with theory and experimental data are: *a* (1.4%), *c* (2.2%) and *c/a* (0.8%) for Zr_2InC; *a* (0.1%), *c* (1.6%) and *c/a* (1.4%)for Zr_2PbC; *a*(0.7%), *c* (0.7%) and *c/a* (1.4%) for Zr_2SnC while for Zr_2TlC we have *a* (0.2%), *c* (0.6%) and *c/a* (0.03%) respectively.

Lattice optimization

From the fully optimized structures, the calculated lattice parameters, *a*(Å), *b*(Å); *V*(Å^3), and the ratio, *c*/*a* are recorded alongside theoretical and experimental results [10], [18], [17], and [18] for comparisons in Table 1.

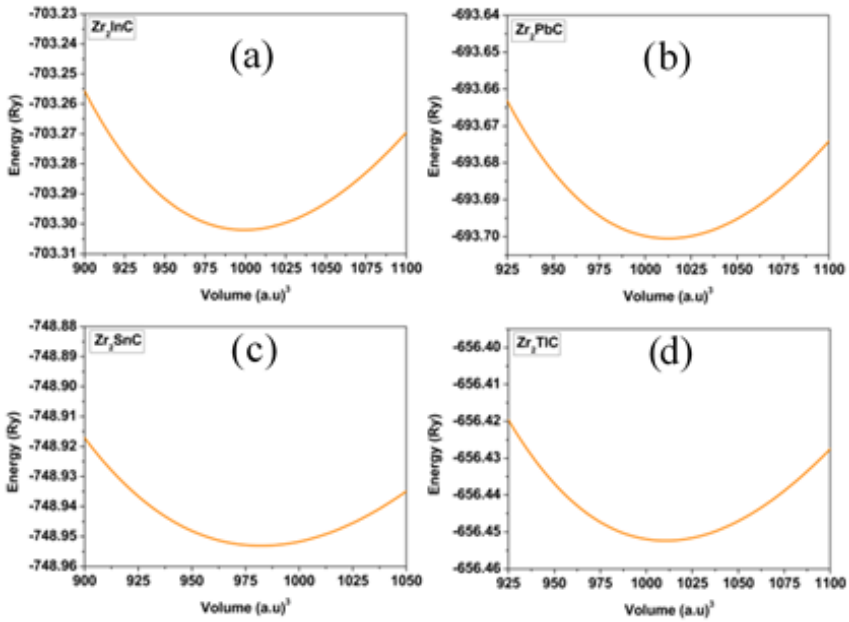


Figure 2 Optimized Volume (a) Zr2InC (b) Zr2PbC (c) Zr2SnC and (d) Zr2TlC

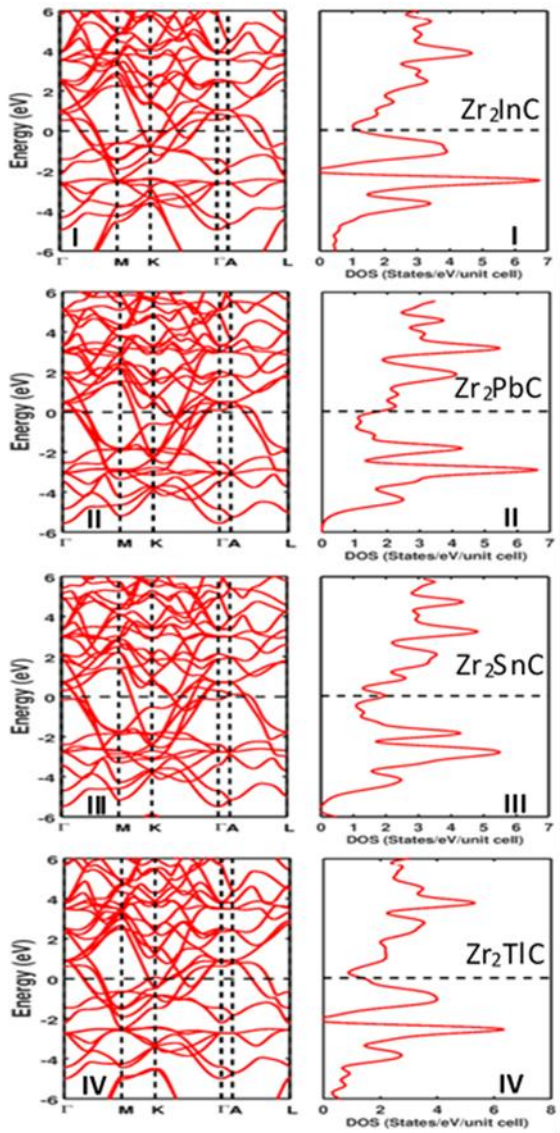
Electronic properties.

The calculated energy bands of Zr_2AC MAX phases along high symmetry path are presented in Figure 3(a) I to IV, and the total density of states (DOS) in Figure 3 (b) I to IV respectively. The Fermi energy level (E_F) is represented by the dash lines and labelled as zero, (0) respectively. E_F is chosen as a starting point of the energy bands, and DOS Figure 3(a) and (b) respectively, and partial density of states (PDOS) in Figure 4 (a), (b), (c), and (d) respectively on the energy scale. The bands show considerable hybridization of the energy states from the valence to the conduction bands. For this singular reason, studied materials have zero, (0) bandgap. This behaviour shows that materials are metallic conductors.

Total density of states

In this work, we have split the energy states into three energy zones: (i) The zone of lowest energy: from -6 *eV* to -2 *eV*. This zone is dominated by Zr-4d, C-2p, In-5s; Pb-6p, and Sn-5p and Tl-6s energy states. A lot of hybridization of the energy states is manifest in this zone. This shows the presence of a covalent structure. (ii) The valence energy zone from -2 eV to 0 eV: this zone is mostly dominated by Zr-4d, with reasonable contributions from In- 5p, Pb-6p, Sn-5p, and Tl -6p. (iii) The conduction energy zone which starts from 0 eV the Fermi energy level, and above into the conduction band is attributed to the Zr-4d, In -5p, Pb -6p, Sn -5p, Tl-6p. The Zr- 4d dominates throughout the energy zones from -6 *eV* to 6 *eV* from the lowest energy zone, through the valence zone to the conduction band and is a backbone in the conduction properties of studied materials.

In general, multiple hybridizations are eminent from the lowest energy zone, the valence zone, through the conduction energy zone. The energy states between -6 *eV* and 6 *eV* show significant contribution at E_F are due to the Zr -4d energy states dominating. The C- 2p states in the four compounds have no contribution to the total DOS at the E_F. Therefore, it does not participate in the conduction properties of either of the materials. The PDOS shows interesting features of hybridization right from the lower energy zone through the valence zone to the conduction zone.



(a) (b)

Figure 3 Energy band structures (a)I Zr_2InC (a)II Zr_2PbC (a)III Zr_2SnC (a)IV Zr_2TlC and Density of states DOS (b)I Zr_2InC (b)II Zr_2PbC (b)III Zr_2SnC (b)IV Zr_2TlC.

The hybridization peaks of in the DOS Figure 3 (b) I to IV are as a result of the dominant effect of Zr -4d and C-2p in the valence zone with only Zr-4d dominating elsewhere in the remaining energy zones. However, very little contributions are noticed coming from In-5s, In -5p, Pb -6p, Sn- 5p, Tl-6s, and Tl -6p energy states respectively Figure 4 (a)-(d). We have calculated the density of states (DOS) at the Fermi energy level, E_F. The calculated DOS is inherent to materials electrical conduction properties which have seen the studied phases in the order of their conduction properties from the highest to the lowest as: Zr_2SnC> Zr_2PbC >Zr_2TlC >Zr_2InC, respectively. The calculated density of states (DOS), for each of the materials are: Zr2InC, 1.151 states /eV, Zr_2PbC, 1.783 states/eV, Zr_2SnC, 1.951 states /eV and Zr2TlC 1.355 states /eV, respectively.

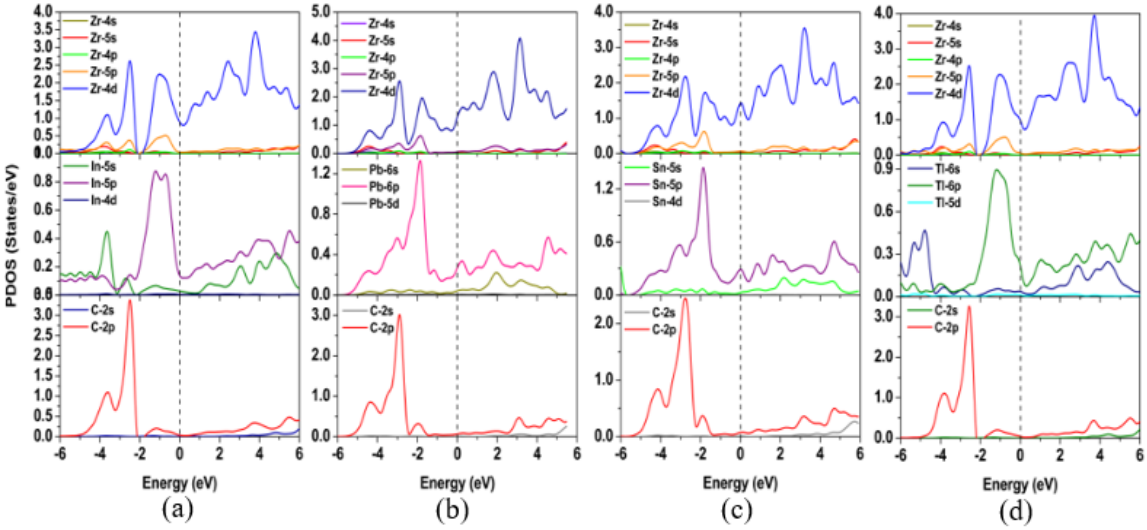


Figure 4 Partial density of states (a) Zr2InC (b) Zr2PbC (c) Zr2SnC (d) Zr2TlC

Table 1: Calculated lattice parameters *a* (Å), *c* (*Å*), and *V* (*Å*^{3}) of the four MAX-phase compounds

Compound	***XC***	***a***	***c***	***c/a***	***V***	**Reference**
Zr_2InC	PBE	3.3867	15.2403	4.5	148.14	This work
Experiment		3.34	14.91	4.46407		[17]
Zr_2PbC	PBE	3.3867	14.9016	4.4	150.29	This work
Experiment		3.38	14.66	4.33728		[17]
Zr_2SnC	PBE	3.3338	14.6687	4.4	145.14	This work
Theory	XRD*			4.337		[10]
Experiment	NPD**			4.341		[10]
Zr_2TlC	PBE	3.3867	14.9016	4.4	149.87	This work
Theory	GGA	3.38	14.99	4.43491		[18]
Experiment	GGA	3.36	14.78	4.39881		[18]

*X-Ray Diffraction. **Neutron Powder Diffraction

Conclusion

The effects of substituting on the A site of the 211 MAX phases Zr_2AC, (A = In, Pb, Sn, and Tl) have been studied using ab-initio calculations as implemented in DFT and results compared alongside available theoretical and experimental data. The substitution has effects on the lattice parameters and electronic properties. The Zr-4d orbital is the major contributor in the DOS of each studied material. In general, the Zr-4d state dominates at and around the E_F.

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References

[1] Arróyave, R., Talapatra, A., Duong, T., Son, W., & Radovic, M. (2018). Out-of-plane ordering in quaternary MAX alloys: an alloy theoretic perspective. *Materials Research Letters*, *6*(1), 1-12.

[2] Yu, W., Mauchamp, V., Cabioc'h, T., Magne, D., Gence, L., Piraux, L., Gauthier-Brunet, V. & Dubois, S. (2014). Solid solution effects in the Ti_2Al (CxNy) MAX phases: Synthesis, microstructure, electronic structure and transport properties. *Acta Materialia*, *80*, 421-434.

[3] Ng, W.H., Gnanakumar, E.S., Batyrev, E., Sharma, S.K., Pujari, P.K., Greer, H.F., Zhou, W., Sakidja, R., Rothenberg, G., Barsoum, M.W. and Shiju, N.R. (2018). The Ti_3AlC_2 MAX phase as an efficient catalyst for oxidative dehydrogenation of n-Butane. *Angewandte Chemie*, *130*(6), 1501-1506.

[4] Hadi, M. A., Panayiotatos, Y., & Chroneos, A. (2017). Structural and optical properties of the recently synthesized $(Zr_{3-x}Ti_x)AlC_2$ MAX phases. *Journal of Materials Science: Materials in Electronics*, *28*(4), 3386-3393.

[5] Bouhemadou, A. (2008). Calculated structural and elastic properties of M_2InC (M= Sc, Ti, V, Zr, Nb, Hf, Ta). *Modern Physics Letters B*, *22*(22), 2063-2076.

[6] Jeitschko, W., Nowotny, H., & Benesovsky, F. (1963). Ti_2AlN, eine stickstoffhaltige H-phase. *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften*, *94*(6), 1198-1200.

[7] Anirudh, C., Vaibhav Koushik, A. V., & Kempaiah, U. N. (2014). MAX phase materials-Review of an exciting class of ternary carbides and nitrides. *International Journal of Emerging Technology and Advanced Engineering, 4*(8), 624-628.

[8] Barsoum, M.W. (2000). The $M_{N+1}AX_N$ phases: A new class of solids: Thermodynamically stable nanolaminates. *Progress in Solid State Chemistry*, 28: 201–281.

[9] Wang, H., Han, H., Yin, G., Wang, C. Y., Hou, Y. Y., Tang, J., Dai, J.X., Ren, C.L., Zhang, W. and Huai, P. & Huai, P. (2017). First-principles study of vacancies in Ti_3SIC_2 and Ti_3ALC_2. *Materials*, *10*(2), 103.

[10] Lapauw, T., Tunca, B., Potashnikov, D., Pesach, A., Ozeri, O., Vleugels, J., & Lambrinou, K. (2018). The double solid solution $(Zr, Nb)_2(Al, Sn)C$ MAX phase: a steric stability approach. *Scientific Reports*, *8*(1), 1-13.

[11] Lane, N. J., Naguib, M., Lu, J., Hultman, L., & Barsoum, M. W. (2012). Structure of a new bulk $Ti_5Al_2C_3$ MAX phase produced by the topotactic transformation of Ti_2AlC. *Journal of the European Ceramic Society*, *32*(12), 3485-3491.

[12] Candan, A., Akbudak, S., Uğur, Ş., & Uğur, G. (2019). Theoretical research on structural, electronic, mechanical, lattice dynamical and thermodynamic properties of layered ternary nitrides Ti_2AN (A= Si, Ge and Sn). *Journal of Alloys and Compounds*, *771*, 664-673.

[13] Clark, S. J., Segall, M. D., Pickard, C. J., Hasnip, P. J., Probert, M. I., Refson, K., & Payne, M. C. (2005). First principles methods using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials*, *220*(5-6), 567-570.

[14] Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Physical review letters*, *77*(18), 3865.

[15] Monkhorst, H. J., & Pack, J. D. (1976). Special points for Brillouin-zone integrations. *Physical review B*, *13*(12), 5188.

[16] Mo, Y. (2014). *Electronic, Optical, Structural, and Elastic Properties of MAX Phases and* $(Cr_2Hf)_2Al_3C_3$ (Doctoral dissertation).

[17] Rahman, A., & Rahaman, Z. (2015). Study on structural, electronic, optical and mechanical properties of MAX phase compounds and applications. American Journal of Modern Physics, *4*(2), 75-91.

[18] Warner, J. A., Patil, S. K. R., Khare, S. V., & Masiulaniec, K. C. (2006). Ab initio calculations for properties of MAX phases Ti_2TlC, Zr_2TlC, and Hf_2TlC. *Applied Physics Letters*, *88*(10), 101911.