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The first principles investigation of structural, electronic, mechanical and lattice dynamical properties of the B and N doped M_2AX type MAX phases $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds

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ABSTRACT

$Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds which are called M_2AX type MAX phases referred to as 211 and have hexagonal crystal structure with conform to $P6_3/mmc$ space group, have been examined by using Generalized Gradient Approximation (GGA) in the Density Functional Theory (DFT) as implemented in CASTEP software package. In this study, the electronic, elastic, and lattice dynamical properties of these compounds have been investigated within the *ab initio* study. These compounds show metallic behavior since there is no band gap in the calculated electronic band structures. The estimated elastic constants of these compounds indicate that they are mechanically stable and their bonding nature is ionic and also, $Ti_2AlN_{0.5}C_{0.5}$ compund has anisotropic character in mechanically whereas the behavior of $Ti_2AlB_{0.5}C_{0.5}$ compound is nearly isotropic. Moreover, both of our compounds are brittle materials. Also, these compounds are dynamically stable since there are no soft modes in their plotted phonon dispersion curves.

1. Introduction

Among the nanolaminated materials MAX phases which have hexagonal crystal structure and comform to $P6_3/mmc$ space group, are determined by the general chemical formula $M_{n+1}AX_n$ (n = 1,2, and 3) which are often referred to as 211 (n = 1) or 312 (n = 2), herein M is an early transition metal, A is an A-group element and X is either carbon (C) or nitrogen (N) [1,2]. The MAX phases are thermodynamically stable materials and candidate for many industrial applications such as high-temperature structural, electrical, and tribological applications [3-5], due to have unique physical, chemical, electrical, and mechanical properties some of which are good thermal and electrical conductivity [6,7], strength and stiffness mechanically [8,9], readily machinable [6,10], relatively soft [6,11], and high thermal shock resistance and good damage tolerance [1,6] properties. Therefore, since the discovery of metallic and ceramic behaviors of MAX phases by Barsoum and El-Raghy [12], these materials have attracted the attention of many scientists up to now [13-20] since they have.

Although there are a lot of theoretical and experimental study about the discovery physical properties of *MAX* phases in the literature until now, to the best of our knowledge, there is no study on the mechanical and dynamic stability, electronic band structure of $Ti_2AlB_{0.5}C_{0.5}$ compound. Therefore, the focus of this study is about the structural, mechanical, electronic, and lattice dynamic properties of Ti and Al based M_2AX type $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds while B or N element is substitutied with C element in our compositions.

In the present work, we have investigated the structural, electronic, mechanical, and vibrational properties of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds which have hexagonal crystal structure ($P6_3/mmc$) in detail. The computational methods are given in the second section. The discussion about the calculated some structural parameters, estimated mechanical properties and electronic and lattice dynamical behaviors of these compounds is given in the third section. Finally in the last section, the obtained results are summarized. To the extend we know in the literature, especially for $Ti_2AlB_{0.5}C_{0.5}$ compound, there is no such a detailed study before in theoretically.

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2. Computational methods

In this present work, we have utilized linear augmented-plane-wave basis set and pseudopotential approximation using the CASTEP (Cambridge Serial Total Energy Package) [21] software package to calculate some physical parameters of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds which have hexagonal crystal structure conforms to $P6_3/mmc$ space group. For *ab* initio calculations, the electronic exchange-correlation energy has been treated according to Perdew-Burke-Ernzerhof type generalized gradient approximation (PBE-GGA) [22-24]. Also, the valence electron configurations of *Ti, Al, B, C,* and *N* atoms in compositions are considered as $3d^24s^2$, $3s^23p^1$, $2s^22p^1$, $2s^22p^2$ and $2s^22p^3$, respectively.

The Brillouin zone integrations have been performed with automatically generated 6×6×2 **k**-point mesh used in the irreducible Brillouin zone, all centered at Γ-point, following the convention of Monkhorst and Pack [25]. To determine the number of plane-waves in expansion, the kinetic energy cut-off value is chosen as 650 eV. For minimizing the force and the pressure successfully in the unit cell and also obtaining optimal lattice parameters, the cystal structures of these compounds have been optimizied conducting until the successive change in the total energy is less than 10^{-8} eV/Å. The primitive cells of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds are modelled with 8-atom primitive cell and the three dimensional (3D) crystallographic representation of these optimizied structures is presented in Figure 1.

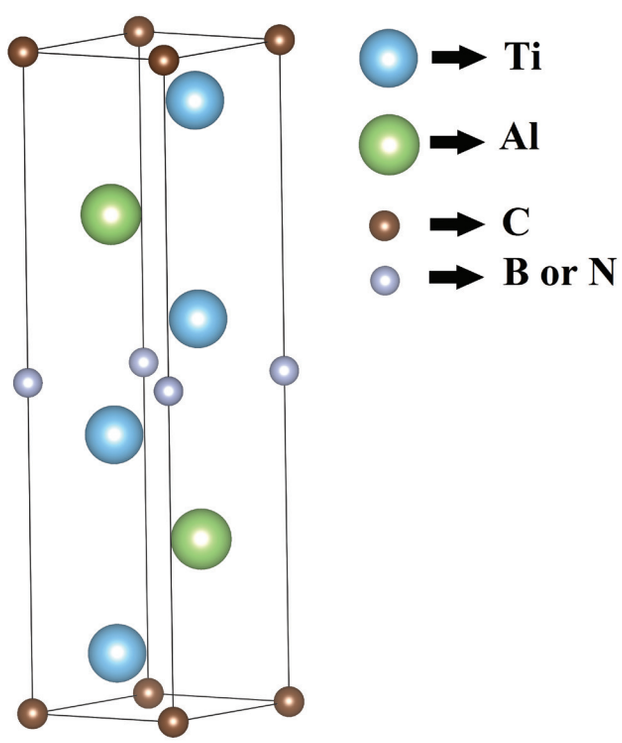

Figure 1. The three dimensional (3D) crystallographic shape of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds where blue atoms represent *Ti*, green atoms represent *Al*, brown atoms represent *C*, and grey atoms represent *B* or *N* element.

3. Results and discussion

3.1. Structural parameters and metallicity of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds

Firstly, the hexagonal unit cell of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds have been optimizied to obtain optimal lattice parameters from well-converged ground state and also to examine structural stability and synthesizability of them. Then, formation enthalpies (ΔH_f) [26] of these compounds have been calculated from internal energy changes of atoms in the composition and also the obtained ground state energy of bulk crystal, as shown in Eq. 1, below. The formation enthalpy of a crystal can be calculated with a chemical formula A_xB_y are given, by

$$\Delta H_f = E_{tot} - \left(xE_A^{bulk} + yE_B^{bulk}\right) \quad (1)$$

where, is the ground state energy of the bulk crystal. E_A^{bulk} and E_B^{bulk} are the ground state energy values of A and B atoms in their bulk crystal form. The calculated formation enthalpies and optimal lattice parameters of these compounds are presented in Table 1.

Table 1. The calculated formation enthalpies and optimal lattice parameters of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds.

Compound	ΔH_f (eV/f.u.)	a (Å)	c (Å)
$Ti_2AlB_{0.5}C_{0.5}$	-0.71622	3.090	13.777
$Ti_2AlN_{0.5}C_{0.5}$	-1.06074	3.020	13.540

$Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds are structurally stable and synthesizable materials since the calculated formation enthalpies of them are negative, as seen in Table 1. The calculated lattice parameters of $Ti_2AlN_{0.5}C_{0.5}$ compound within PBE-GGA approximation (a = 3.020 Å and c = 13.540 Å), are very close to the experimental results (a = 3.021 Å [27], a = 3.023 Å [28] and c = 13.610 Å [27,28]). The obtained lattice parameters (a and c) of this compound are different approximately % 0.1 and % 0.5 from experimental results, respectively. To the best of our knowledge, there is no previous experimental or theoretical study about $Ti_2AlB_{0.5}C_{0.5}$ compound in the literature, so the obtained lattice parameters (a and c) for this compound can not be compared with other results.

The electronic behaviour of a material is more important for technological applications and it can be decided whether a material is metallic, semi-metallic or insulating from the obtained electronic band structure and density of states (DOS). The calculated total density of states of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds within PBE-GGA, also the calculated orbital projected partial density of electronic states of atoms in compositions are presented in Figure 2.a and Figure 2.b, respectively. The plotted graphics indicate that, all

of these compounds have metallic character since total density of states (TDOS) and also orbital projected partial density of electronic states of atoms (PDOS) values are not equal to zero almost at the Fermi level.

For both of these metallic compounds, the calculated orbital projected partial density of electronic states of atoms indicate that, d and p states of *Ti* atoms and p states of *Al* and *B* atoms cross the Fermi level (E_F), yielding a metallic behavior as seen in Figure 2.a and Figure 2.b For all of our compounds, the d-orbitals of *Ti* atoms are almost located between at -6 eV below E_F and 5 eV above E_F. For $Ti_2AlB_{0.5}C_{0.5}$ compound, the p-orbitals of *Ti* atom are almost located between 5 eV and -10 eV, the p-orbitals of *Al* atom are almost located between 5 eV and -8 eV, the p-orbitals of *B* atom are located between 4 eV and -5 eV, also d-orbitals of *Ti* atom and p-orbitals of these atoms cross the Fermi level. For this compound, the p-orbitals of *C* atom are located between -2 eV and -5 eV below E_F, as seen in Figure 2.a. For $Ti_2AlN_{0.5}C_{0.5}$ compound, the location of the p-orbitals of *Ti* atom are almost the same with $Ti_2AlB_{0.5}C_{0.5}$ compound. The p-orbitals of *Al* atom are almost located between 2 eV and -8 eV, the p-orbitals of *N* atom are located between -4 eV and -7.5 eV below E_F, also d-orbitals of *Ti* atom and p-orbitals of *Ti* and *Al* atoms cross the Fermi level. For this compound, the p-orbitals of *C* atom are located between -1 eV and -5 eV below E_F, as seen in Figure 2.b. Therefore, d- and p-orbitals of *Ti* atoms and p-orbitals of *Al* have remarkable effect on metallicitiy of these compounds. Also for $Ti_2AlB_{0.5}C_{0.5}$ compound, p-orbitals of B atom have lower effect. The s-orbitals of *Ti*, *Al*, *B*, *C* and *N* elements have no remarkable effect on bonding nature of these compounds. Therefore, the bonding properties and metallicity of these systems are due to the hybridization between d-orbitals of *Ti* and p-orbitals of *Al* atoms.

3.2. The elasticity and some mechanical properties

The mechanical stability of a solid is a much important information and it can be decided whether a crystal is stable or unstable mechanically from the calculated elastic constants (C_{ij}). Also, some important mechanical properties such as hardness or stiffness, sound velocities and also Debye temperature, can be estimated from these valuable constants which can be calculated with high accuracy and precision in first principles by using the “stress–strain” method [29]. For a hexagonal crystal, there are five independent elastic constants which are C_{11}, C_{12}, C_{13}, C_{33}, and C_{44} [30] and these calculated constants of our compounds are presented in Table 2.

Where C_{66} constant ($C_{66} = (C_{11} - C_{12})/2$) is added for comparison with C_{44}. Also the calculated Cauchy pressure (C_p) values are added to table.

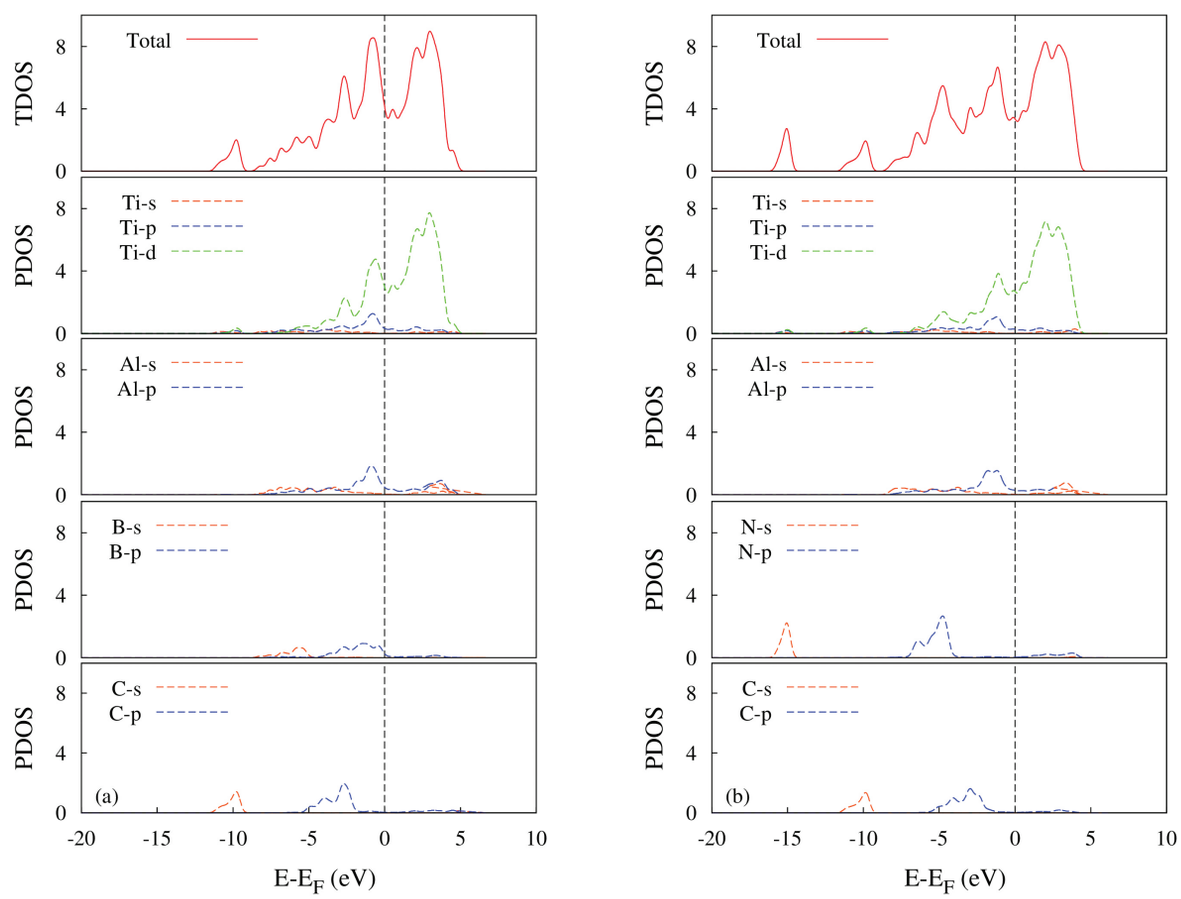

Figure 2. The total and orbital projected partial density of electronic states of atoms within PBE-GGA for (a) $Ti_2AlB_{0.5}C0_{.5}$ compound and (b) $Ti_2AlN_{0.5}C_{0.5}$ compound

Table 2. The calculated elastic constants of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds.

Compounds	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	C_{66} (GPa)	C_p (GPa)
$Ti_2AlB_{0.5}C_{0.5}$	266.928	69.531	64.932	257.301	102.098	98.699	-32.567
$Ti_2AlN_{0.5}C_{0.5}$	298.644	49.777	94.159	274.108	127.783	124.434	-78.006

For a crystal, the mechanical stability or the durability of against external forces is a desirable situaiton for ensuring its sustainability for endustrial or scientific applications. In order for a crystal to be mechanically stable, there are certain conditions which are known Born-Huang criterias [30-33]. According to the this, the calculated elastic constants for a stable hexagonal crystal structure should satisfy these criterias which are shown in below in Eq. 2.

$$(C_{11}+2C_{12})C_{33}>2C_{13}^2;\quad C_{11}>|C_{12}|\ \text{ and }\ C_{44}>0 \qquad (2)$$

In this study, both of compounds are found to be stable in mechanically since their calculated elastic constants satisfy these stability criterias. The bonding strength of a crystal in some crystallographic directions depends on its calculated elastic constants. For a hexagonal crystal, C_{11} and C_{33} give information about the stiffness against changes in the principal strain in $[01\bar{1}0]$ and [0001] directions, respectively, C_{66} is referred to the resistance to shear of the {100} plane in the <110> direction, and C_{44} represents the resistance to shear of the {010} or {100} plane in the <001> direction [34]. In this study, the calculated C_{11} values of compounds are greater than C_{33} values as seen in Table 2. This situation shows that the incompressibility and the bonding strength in $[01\bar{1}0]$ and [1010] directions of our compounds are stronger than in the [0001] direction [20] and also, it is even lower when *B* element is doped to these materials instead of *N* element, as seen in Table 2.

The calculated Cauchy pressure (C_p) which is given below in Eq. 3, can give information about ductility of a crystal,

$$C_p = C_{12} - C_{44} \qquad (3)$$

When the calculated Cauchy pressure of a crystal is negative ($C_{12} < C_{44}$), it is expected that, this material is brittle, on the other hand, if this value is positive ($C_{44} < C_{12}$) the material is ductile [35]. In this respect, our compounds are brittle materials since they have negative C_p values. Also, it is clearly seen that, the brittleness of $Ti_2AlN_{0.5}C_{0.5}$ compound is greater than the $Ti_2AlB_{0.5}C_{0.5}$ compound since the absolute value of of $Ti_2AlN_{0.5}C_{0.5}$ compound is highest value and therefore, it can be said that, the brittleness increase when *N* element is doped to materials instead of *B* element.

Additionally, some mechanical properties of a material can be estimated from the calculated elastic constants. The bulk (*B*) moduli of a crystal is the resistance to a volume change of a material to a hydrostatic pressure, and also shear moduli (*G*) is the resistance against a shape change of a material. The upper, lower and average values of these modulus can be estimated by Voigt, Reuss, and Hill approximations [36-38], as seen in Eq.4-7, respectively.

$$B_V = (2/9)[C_{11}+C_{12}+2C_{13}+(C_{33}/2)] \qquad (4)$$

$$B_R = 1/[(2S_{11}+S_{33})+2(S_{12}+2S_{13})] \qquad (5)$$

$$G_V = [(2C_{44}+C_{66})/5]+[(2C_{11}+C_{33}-C_{12}-2C_{13})/15] \qquad (6)$$

$$G_R = 15/[4(2S_{11}+S_{33})-4(S_{12}+2S_{13})+3(2S_{44}+S_{66})] \qquad (7)$$

where S_{ij} are the elastic compliance constants. The average values of bulk and shear moduli of a material can be calculated from Hill approximation which are given by $B=(1/2)(B_V + B_R)$ and $G=(1/2)(G_V + G_R)$ In addition, Poisson's ratio (ν) can give information about bonding property of a crystal and also Young's modulus (*E*) define the stiffness of a solid is given as the ratio of stress and strain of a crystal [39]. These can be estimated from Eq. 8 and Eq. 9, respectively.

$$\nu = (3B-2G)/[2(3B+G)] \qquad (8)$$

$$E = (9BG)/(3B+G) \qquad (9)$$

The another important mechanical property of a crystalline solid is Vickers hardness (H_v) which can be calculated from a semi-empirical method [40] as given in Eq. 10,

$$H_v = 2(k^2G)^{0.585}-3 \qquad (10)$$

where k = G/B is Pugh's modulus ratio. The calculated bulk (B_V, B_R and *B*) and shear modulus (G_V, G_R and *G*) and estimated Poisson's ratio (ν), Young's moduli (*E*), *B/G* and Pugh's ratios and also Vickers hardness (H_v) of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds have been tabulated in Table 3.

The calculated *G*, *E* and H_v values of our compounds indicate that, both of compounds are hard materials (H_v > 10 GPa) and also, $Ti_2AlN_{0.5}C_{0.5}$ compound is the harder material than the other. In addition, the upper and lower limits of bulk (*B*) and shear moduli (*G*) values of these compounds show that there is comparatively small difference between them as seen in Table 3.

Table 3. The calculated upper and lower limits, average values of bulk and shear moduli, Young's moduli (in GPa) and Poisson's ratios, B/G and Pugh's ratios and also Vickers hardness (H_v) of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds.

Compound	B_V	B_R	B	G_V	G_R	G	B/G	k	v	E	H_v
$Ti_2AlB_{0.5}C_{0.5}$	132.22	132.14	132.18	100.03	99.99	100.01	1.32	0.76	0.198	239.60	18.35
$Ti_2AlN_{0.5}C_{0.5}$	149.73	149.56	149.65	118.22	115.54	116.88	1.28	0.78	0.190	278.21	21.29

Also, B/G value is an another important parameter which can give much important information about ductility of a crystal. The ductile materials have large B/G ratios (larger than approximately 1.75 and 1.75 is a critical value which separates ductile and brittle materials from each other [41]), whereas brittle materials have low B/G ratios (smaller than approximately 1.75). In this respect, the calculated B/G values of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds are almost 1.32 and 1.28 respectively, and these values indicate that both of compounds are brittle and this result is consistent with the results in subsection where the Cauchy press (C_p) is discussed.

The estimated Poisson's ratios of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds are 0.198 and 0.190, respectively as given in Table 3. The calculated these values indicate that the bonding nature of our materials are close to ionic [41].

The shear anisotropic factor (A) can give about isotropic or anisotropic character of a solid and for a hexagonal crystal, this important mechanical parameter can be calculated from Eq. 11 [42,43]. In this study, the estimated shear anisotropic factors of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds are found to be 1.036 and 1.330, respectively as seen in Table 4. It is known that, for a hexagonal crystal, the calculated shear anisotropic factor value for the $\{10\bar{1}0\}$ shear planes between the $<01\bar{1}1>$ and $<01\bar{1}0>$directions which is identical to the shear anisotropic factor for the $\{01\bar{1}0\}$ shear planes between the $<10\bar{1}1>$ and <0001> directions. In this respect, the behavior of $Ti_2AlB_{0.5}C_{0.5}$ compound closes to isotropic whereas $Ti_2AlN_{0.5}C_{0.5}$ compound has anisotropic character.

$$A = 4C_{44}/(C_{11} + C_{33} - 2C_{13}) \quad (11)$$

The another anisotropy parameter (k_c/k_a) of a hexagonal crystal can be defined from the ratio between the linear compressibility coefficients along the c- and a-axis as given in Eq. 12.

$$k_c/k_a = (C_{11} + C_{12} - 2C_{13})/(C_{33} - C_{13}) \quad (12)$$

The calculated values by using this formula show that, along the a-axis the compressibilities of $Ti_2AlN_{0.5}C_{0.5}$ compound is larger than that along the c-axis whereas the compressibility of $Ti_2AlB_{0.5}C_{0.5}$ compound along the c-axis is larger than that along the a-axis.

Navier's equations [44] can be used to calculate the longitudinal and transverse wave velocities inside of a crystalline solid as seen in Eqs. 13 and 14 and also average wave velocity [45] can be calculated from Eq. 15.

$$\mathrm{v_l} = \left[\left(\mathrm{B} + (4\mathrm{G}/3)\right)/\rho\right]^{1/2} \quad (13)$$

$$\mathrm{v_t} = [\mathrm{G}/\rho]^{1/2} \quad (14)$$

$$\mathrm{v_m} = \left\{(1/3)\left[\left(2/(\mathrm{v_t^3})\right) + \left(1/(\mathrm{v_l^3})\right)\right]\right\}^{-1/3} \quad (15)$$

where ρ is the density of the crystal. The calculated velocity values imply that, the sound conductivity of $Ti_2AlN_{0.5}C_{0.5}$ compound is greater than $Ti_2AlB_{0.5}C_{0.5}$ compound as seen in Table 4.

Among the calculated mechanical properties the Debye temperature (Θ_D) is an important another pysical parameter for a crystal. This parameter is in relation with many physical properties such as lattice vibrations, specific heat and melting temperature [46]. In this study, the Debye temperatures (Θ_D) of our compounds have been calculated from Eq. 16 as given below,

$$\theta_D = (\mathrm{h}/\mathrm{k})[(3\mathrm{n}/4\pi)(\mathrm{N_A}\rho/\mathrm{M})]^{1/3}\mathrm{v_m} \quad (16)$$

where h is the Planck's constant, k the Boltzmann's constant, N_A is the Avogadro's number, M is the molecular weight and n is the number of atoms in the

Table 4. The calculated shear anisotropy factor (A), k_c/k_a ratio and longitudinal (v_l), transverse (v_t), and average (v_m) wave velocities in crystal and also Debye temperatures (Θ_D) of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds.

Compound	A	k_c/k_a	v_l (m/s)	v_t (m/s)	v_m (m/s)	Θ_D (K)
$Ti_2AlB_{0.5}C_{0.5}$	1.036	1.074	8240	5057	5582	685.8
$Ti_2AlN_{0.5}C_{0.5}$	1.330	0.890	8513	5266	5807	728.6

molecule. The calculated Debye temperature values of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds have been tabulated in Table 4. It is obviously seen that, the value of $Ti_2AlB_{0.5}C_{0.5}$ compound is (685.8 K) lower than the value of $Ti_2AlN_{0.5}C_{0.5}$ compound (728.6 K). For $Ti_2AlN_{0.5}C_{0.5}$ compound, the estimated shear moduli (G), Young moduli (E), Poisson's ratio (v), sound velocities and also Debye temperature (Θ_D) values are consistent with other obtained results in the literature [28].

3.3. The lattice dynamic stability

In this subsection, the calculated thermal conductivity by using different two methods, the obtained some thermodynamic by using quasi-harmonic Debye model and vibrational properties by using finite-displacement method of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds have been discussed in detail.

3.3.1. Thermal conductivity

The heat conduction property of a material can be estimated from the calculated thermal conductivity and also, this calculated parameter is much important for the suitability of the material for thermal barrier coating application. The total thermal conductivity is a much important physical property for a solid and this parameter is sum of the lattice thermal and the electronic thermal conductivity. In generally, for low temperatures, the electronic thermal conductivity is only less than 10% of the total. Therefore, the total thermal conductivity of a cystal is mainly due to the lattice thermal conductivity [47]. For a crystalline solid, the minimum limit of the thermal conductivity (λ_{min}) can be calculated from Clarke's [48] and Cahill's model [49] which are different theoretical models from each other, as shown below Eqs. 17-18, respectively.

Clarke's model:

$$\lambda_{min} = 0.87 k_B \overline{M_a}^{-2/3} E^{1/2} \rho^{1/6} \qquad (17)$$
$$\overline{M_a} = \left(M/(mN_A)\right)$$

Cahill's model:

$$\lambda_{min} = (k_B/2.48) n^{2/3} (v_l + 2v_t) \qquad (18)$$

where M_a is the average mass per atom, E is the Young's modulus, ρ is the density, M is the molar mass, m is the total number of atoms per formula, k_B is Boltzmann's constant, N_A is Avogadro's number, n is the density of number of atoms per volume and also v_l and v_t are the longitudinal and transverse wave velocities, respectively. The calculated minimum limits of thermal conductivity of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds from these methods have been presented in Table 5. It is obviously seen that, for both of compounds, the calculated values from Clarke's model is slightly lower than Cahill's model and also, the thermal conductivity of $Ti_2AlN_{0.5}C_{0.5}$ compound is greater than the other compound, as given in Table 5. These compounds are good candidate for thermal barrier coating applications since these materials have dynamic stability which will be discussed in *Vibrational Properties* subsection, and a low minimum thermal conductivity values which are comparable to typical thermal barrier coatings [50].

3.3.2. Thermodynamic Properties

In this subsection, some thermodynamic properties which have been calculated by using quasi-harmonic Debye model [51], of these compounds have been presented. In this approximation, the calculated Poisson's ratios of our compounds have been used, which have been estimated as 0.198 and 0.190 from the elastic constants, respectively. For all calculations, the temperature range taken in obtaining thermodynamic properties were between 0 and 1000 K since the crystal structures are destroyed at larger values. Temperature dependence of heat capacity (C_V), entropy (S), Gibbs free energy (G) and enthalpy (H) curves of compounds are shown in Figure 3.a-d, respectively.

The thermodynamic behaviors of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds are so close to the each other. The change of entropy, Gibbs free energy and enthalpy with temperature has exponential behavior. The heat capacity shows T^3 dependence for small temperatures and rises to the Delong-Petit limit faster. Similarly, the entropy and Gibbs free energy rise rapidly whereas the enthalpy decreases for above almost 150 K.

3.3.3. Vibrational Properties

Finally, the full phonon dispersion curves along the high symmetry directions in the irreducible Brillouin zone with formed 2×2×1 super-cells for $Ti_2AlB_{0.5}C_{0.5}$

Table 5. The calculated lower limits of the thermal conductivity of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds by using Clarke's and Cahill's models.

Compound	Clarke's model		Cahill's model	
	$\overline{M_a}(10^{-26}kg)$	$\lambda_{min}(Wm^{-1}K^{-1})$	$n\ (10^{28}m^{-3})$	$\lambda_{min}(Wm^{-1}K^{-1})$
$Ti_2AlB_{0.5}C_{0.5}$	5.569	1.559	5.650	1.694
$Ti_2AlN_{0.5}C_{0.5}$	5.635	1.671	5.940	1.407

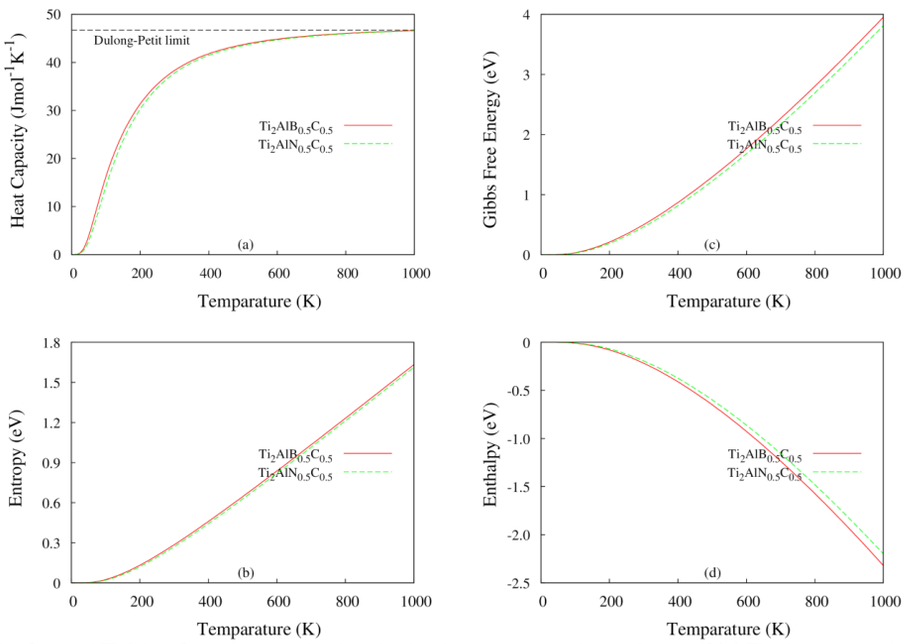

Figure 3. For $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds, the obtained temperature dependence of (a) The heat capacity, (b) Entropy, (c) Gibbs free energy and (d) Enthalpy curves.

and $Ti_2AlN_{0.5}C_{0.5}$ compounds, have been obtained to investigate information about the dynamic stability of these compounds. The finite-displacement method with CASTEP software package [52] has been used to obtain the phonon frequencies of these compounds based on the interatomic force constants. The calculated phonon dispersion spectras of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds have been presented along with the high symmetry directions in the first Brillouin zone as seen in Figure 4.a-b, respectively. To the best of our knowledge, there is no study experimentally or theoretically about the lattice dynamic properties of these compounds in the literature to compare with the obtained datas.

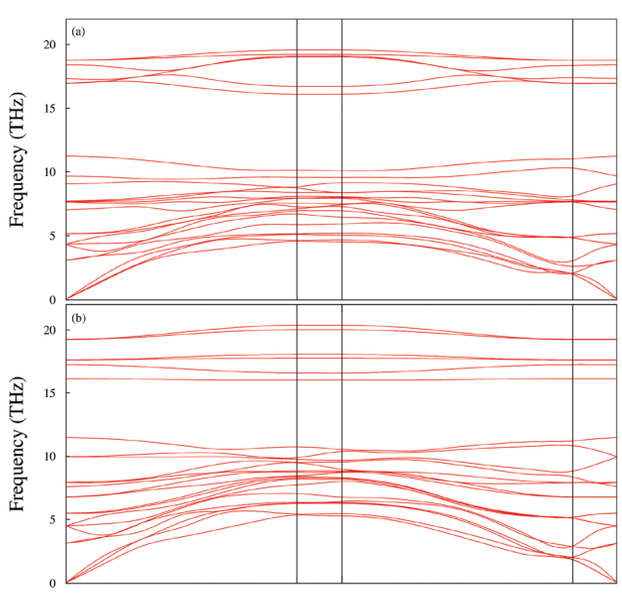

Figure 4. Phonon dispersion curve along high symmetry directions in the first Brillion zone of (a) $Ti_2AlB_{0.5}C_{0.5}$ and (b) $Ti_2AlN_{0.5}C_{0.5}$ compounds.

The obtained phonon dispersion curves of $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds clearly show that, these compounds are dynamically stable since all phonon branches of them are real as given in Figure 6 and 7. The primitive cell of each compound is composed of 8 atoms and therefore there are 24 phonon branches with 3 acoustics and 21 optical branches in obtained phonon dispersion curves. Moreover, it is clearly seen that, there are clear gaps in the whole Brillouin zone dynamically stable $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds between the optic and acoustic branches almost 4.78 THz and 4.51 THz, respectively.

4. Conclusion

The structural, mechanical, electronic and lattice dynamic properties of M_2AX type MAX phase $Ti_2AlB_{0.5}C_{0.5}$ and $Ti_2AlN_{0.5}C_{0.5}$ compounds which have hexagonal crystal structure conforming to $P6_3/mmc$ space group, have been investigated theoretically within *ab initio* methods. These compounds show metallic behavior since total density of states (TDOS) and also orbital projected partial density of electronic states of atoms (PDOS) values are not equal to zero almost at the Fermi level. The calculated elastic constants indicate that, these compounds have stability in mechanical due to satisfy Born-Huang stability criterias. Moreover, the calculated shear anisotropy factors indicate that, the behavior of $Ti_2AlB_{0.5}C_{0.5}$ compound closes to isotropic whereas $Ti_2AlN_{0.5}C_{0.5}$ compound has anisotropic character mechanically. Finally, thermal conductivity, some thermodynamic properties and vibrational properties in lattice dynamic behaviors have been investigated and the obtained phonon dispersion curves of these compounds show that, both of compounds have dynamically stability since all of phonon modes are real in the obtained dispersion spectras.

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