First principles investigations of Ta₄AlX₃ (X= B, C, N) MAX phase ceramics

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ABSTRACT

Ta₄AlX₃ (X=B, C, N) MAX phase ceramics have been examined using first principles calculations in this study. Ta₄AlX₃ MAX phase ceramics have hexagonal crystal structure and the formation energies have been determined for the optimized crystal structures. The elastic constants of Ta₄AlX₃ MAX phase ceramics have been determined and these constants satisfy the mechanical stability criteria. In addition, the mechanical properties such as bulk modulus, shear modulus, etc. have been obtained to reveal the detailed properties of these compounds. The anisotropic elastic properties have been visualized in both 3D and 2D. Moreover, the thermal properties of Ta₄AlX₃ MAX phase ceramics such as thermal expansion coefficient, heat capacity etc. have been studied in 0 to 1000 K temperature range and 0 to 40 GPa pressure range. In this study, Ta₄AlB₃ has been considered for the first time along with Ta₄AlC₃ and Ta₄AlN₃ compounds and the effect of X atom to the properties of these compounds have been discussed in detail.

1. Introduction

MAX phases are interesting compounds due having both metallic and ceramic properties [1]. MAX phases get their name from the M, A and X elements in their structures where M is a transition metal, A is an A group element and X is C and/or N [2]. The chemical formula of MAX phases is Mₙ₊₁AXₙ with n=1, 2 and 3. Moreover, MAX phases with n=4, 5 and 6 are also investigated in the literature [3-5]. MAX phases have hexagonal crystal structure in the P6₃/mmc space group and MX slabs are interleaved with A layers [6]. This crystal structure results with the strong covalent bonds between M and X atoms and weak bonds between M and A atoms. After the discovery of the MAX phases by Nowotny [7], the MAX phases are synthesis using different methods such as reactive hot pressing [8], self-propagating high-temperature synthesis [9] and spark plasma sintering [10].

MAX phases have high oxidation resistance as a result of their ceramic properties [11]. Also, MAX phases have excellent thermal and electrical conductivities, high shock resistance and great damage tolerance due to their metallic properties [12-14]. MAX phases have been employed for magnetic materials [15], fuel cells [16], nuclear industry [12] that are some examples of the technological applications of the MAX phases. Moreover, the removal of the A atoms in the MAX phases produce a new class of materials as called MXenes [17]. The MXenes are 2D materials and the interest of these materials comes from their special properties for several applications such as photocatalyst [18], energy storage [19] and spintronics [20], etc.

The MAX phases have been investigated in detail with X atom as C and/or N. Theoretically, MAX phases could be formed with X atom as B. A limited number of studies have been performed for MAX phase borides where X atom is chosen as B [21-26]. These studies have shown that B substitution for the X atom results with energetically, mechanically and thermodynamically stable MAX phase borides. With the motivation of these studies, Ta₄AlB₃ MAX phase boride with Ta₄AlC₃ MAX phase carbide and Ta₄AlN₃ MAX phase nitride have been studied using density functional theory and the effect of the B substitution for the X atom in Ta₄AlX₃ MAX phase ceramics have been investigated in this study. Recently, Ta₄AlC₃ have been synthesized using hot pressing and spark plasma sintering methods [27] and there are several studies both experimentally and theoretically for Ta₄AlC₃ ceramic [28-37] and only one theoretical study for Ta₄AlN₃ ceramic [38] in the literature. The electronic and mechanical properties of Ta₄AlC₃ ceramic were investigated while the mechanical properties of Ta₄AlN₃ ceramic was investigated before this study. In the following sections, structural, mechanic, anisotropic elastic and thermal properties of Ta₄AlX₃ MAX phase ceramics will be presented and the effect of the B, C and N to these properties will be discussed in detail.

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2. Computational details

The Ta₄Alₓ₃ (X= B, C, N) MAX phase ceramics have been studied using the Vienna Ab-initio Simulation Package (VASP) \[39,40\] that is based on the Density Functional Theory. The projector augmented wave method (PAW) \[41,42\] has been utilized for the electron-ion interaction with an energy cut off as 550 eV. The electron-electron interactions have been considered using the Generalized Gradient Approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional \[43\]. The k-points have been sampled using a gamma centered mesh \[44\] and 20 x 20 x 2 k-points have been obtained. The structural optimizations have been performed with an energy convergence criterion as 10⁻¹¹ eV per unit cell and a force convergence criterion as 10⁻¹⁰ eV/Å. The valence electron configurations of B, C, N, Al and Ta have been taken as 2s²2p¹, 2s²2p², 2s³2p³, 3s²3p¹ and 6s²5d³, respectively. The crystal structure visualization and X-ray diffraction patterns have been obtained using Vesta software \[45\]. The mechanical properties have been investigated with the elastic constants that are obtained with stress-strain method within the VASP \[46\]. Also, the direction dependent mechanical properties have been visualized using ELATE software \[47\]. The thermal properties have been determined using the GIBBS software \[48\] where the quasi-harmonic Debye model \[49\] is employed.

3. Structural properties of Ta₄Alₓ₃ MAX phase ceramics

Ta₄Alₓ₃ (X= B, C, N) MAX phase ceramics have hexagonal crystal structure (P6₃/mmc, 194 space group) as shown in Figure 1a. In the literature, Ta₄AlC₃ has two phases as called α phase and β phase and the only difference between these phases are the positions of the Ta atoms \[27\]. Moreover, it was found that the α phase of Ta₄AlC₃ was more stable than the β phase \[28\]. So, the α phase of Ta₄AlC₃ has been considered in this study. In addition, Ta₄AlB₃ and Ta₄AlN₃ also have the same crystal structure with Ta₄AlC₃. These structures have been optimized and the obtained lattice parameters and Wyckoff positions have been listed in Table 1 as well as literature results. The lattice parameters of Ta₄AlC₃ are closer to the previous theoretical results and the determined lattice parameters are higher than the experimental results. For Ta₄AlN₃, the calculated results are lower than the previous theoretical result that could be due to the different simulation software. Furthermore, the change of the X atom affects the lattice parameters and if X atom changes from B to N, a lattice parameter decreases due to the reduction the atomic radius of the X element and c lattice parameter increases due to the longer bond length between Ta and X atom. As can be concluded from Table 1, the lattice parameters of Ta₄AlC₃ and Ta₄AlN₃ is consistent with the literature and the lattice parameters of Ta₄AlB₃ have been determined for the first time and it could be useful for the future studies. In addition, the X-ray diffraction patterns of Ta₄Alₓ₃ MAX phase ceramics have been obtained using a Cu Kα source with 1.541 Å wavelength and the X-ray diffraction patterns are similar for these compounds as shown in Figure 1b. Also, the 2θ values are 7.35°, 7.29° and 7.19° for Ta₄AlB₃, Ta₄AlC₃ and Ta₄AlN₃, respectively.

The thermodynamic stability of these compounds should be considered and the formation energy as listed in Table 1 could be employed for this determination. The formation energy could be calculated using the equation given in Ref. \[22\] with the total energies of Ta₄Alₓ₃ ceramics and the ground state energies of Ta, Al, B, C and N atoms. The calculated formation energies for Ta₄Alₓ₃ MAX phase ceramics have negative values as listed in Table 1 that indicate the thermodynamic stability and synthesizability. As known from the literature, Ta₄AlC₃ has already been synthesized and these results also demonstrate that Ta₄AlB₃ and Ta₄AlN₃ could be synthesized as well. The formation energy difference for Ta₄AlN₃ could be arisen from the different simulation software. The thermodynamic stability of Ta₄Alₓ₃ MAX phase ceramics increases when the X atom changes from B to N.

![Figure 1](image1.png)  
Figure 1. (a) Crystal structure and (b) X-ray diffraction patterns of Ta₄Alₓ₃ (X= B, C, N) MAX phase ceramics.
4. Anisotropic elastic and mechanical properties of $\text{Ta}_4\text{AlX}_3$ (X = B, C, N) MAX phase ceramics

The mechanical stability of $\text{Ta}_4\text{AlX}_3$ (X = B, C, N) MAX phase ceramics could be determined using the elastic constants. Table 2 lists the calculated elastic constants for these compounds with the available literature results. In order to be a mechanically stable compound, the elastic constants of that compound must satisfy the Born stable criteria [50,51] that can be found in Ref. [52]. The listed elastic constants for $\text{Ta}_4\text{AlX}_3$ MAX phase ceramics are satisfied the Born stability criteria; therefore, they are mechanically stable compounds. In addition, the results are coherent with the previous results.

The calculation of the elastic constants is also useful to determine the mechanical properties as listed in Table 3 for $\text{Ta}_4\text{AlX}_3$ MAX phase ceramics. The bulk modulus (B) gives the information of the stiffness of a material and it is defined as the volume change of a material under hydrostatic pressure. The bulk modulus of $\text{Ta}_4\text{AlX}_3$ MAX phase ceramics is increased from $\text{Ta}_4\text{AlB}_3$ to $\text{Ta}_4\text{AlN}_3$. The shear modulus (G) is defined as the ratio of the shear strain to shear stress and it is important for transverse deformations. As can be seen from Table 3, $\text{Ta}_4\text{AlC}_3$ has the highest shear modulus among these compounds and it has highest resistance to transverse deformations. Young’s modulus (E) also called modulus of elasticity is defined as the length change of a material due to a push or pull. Similar to shear modulus, $\text{Ta}_4\text{AlC}_3$ has the highest Young’s modulus among these compounds. Poisson’s ratio ($\nu$) is an important parameter to determine the bonding type of a material. The value of 0.25 for the Poisson’s ratio indicates the dominantly ionic bonding and 0.1 value indicates the dominantly covalent bonding [22]. Moreover, the Poisson’s ratio around 0.33 indicates the metallic bonding and when the value approaches to 0.5, the plasticity increases for the material [53]. As can be seen from Table 3, $\text{Ta}_4\text{AlB}_3$ and $\text{Ta}_4\text{AlC}_3$ have the Poisson’s ratio around 0.25 and they have dominantly ionic bonding while $\text{Ta}_4\text{AlN}_3$ having the Poisson’s ratio as 0.332 has metallic bonding. G/B ratio is useful to determine the bonding of the compounds. The G/B ratio around 0.3, 0.6 and 1.1 corresponds to metallic bonding, ionic bonding and covalent bonding for the material [22,53]. Using these parameters, the same results with the Poisson’s ratio have been obtained. The brittle or ductile nature of the materials are crucial and it can be determined using B/G ratio. For this determination,
Table 3. Bulk modulus (B in GPa), Shear modulus (G in GPa), Young’s modulus (E in GPa), Poisson’s ratio (υ), G/B ratio and B/G ratio for Ta₄AlX₃ (X= B, C, N) MAX phase ceramics.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
<th>B</th>
<th>G</th>
<th>E</th>
<th>υ</th>
<th>G/B</th>
<th>B/G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta₄AlB₃</td>
<td>This study</td>
<td>197.20</td>
<td>133.30</td>
<td>326.30</td>
<td>0.224</td>
<td>0.675</td>
<td>1.479</td>
</tr>
<tr>
<td>Ta₄AlC₃</td>
<td>This study</td>
<td>243.40</td>
<td>149.80</td>
<td>372.80</td>
<td>0.245</td>
<td>0.615</td>
<td>1.624</td>
</tr>
<tr>
<td>Ta₄AlN₃</td>
<td>Theory [28]</td>
<td>247.00</td>
<td>161.00</td>
<td>397.00</td>
<td>0.230</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Minimum and maximum values of Young’s modulus (E in GPa), linear compressibility (β), shear modulus (G in GPa) and Poisson’s ratio (υ) for Ta₄AlX₃ (X= B, C, N) MAX phase ceramics.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E_.min</th>
<th>E_max</th>
<th>β_.min</th>
<th>β_max</th>
<th>G_.min</th>
<th>G_max</th>
<th>υ_min</th>
<th>υ_max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta₄AlB₃</td>
<td>242.18</td>
<td>366.13</td>
<td>1.60</td>
<td>1.74</td>
<td>99.00</td>
<td>166.60</td>
<td>0.09</td>
<td>0.37</td>
</tr>
<tr>
<td>Ta₄AlC₃</td>
<td>302.60</td>
<td>397.84</td>
<td>1.24</td>
<td>1.65</td>
<td>128.47</td>
<td>175.53</td>
<td>0.12</td>
<td>0.31</td>
</tr>
<tr>
<td>Ta₄AlN₃</td>
<td>184.29</td>
<td>312.41</td>
<td>1.28</td>
<td>1.34</td>
<td>62.31</td>
<td>161.79</td>
<td>-0.05</td>
<td>0.64</td>
</tr>
</tbody>
</table>

1.75 value is important for B/G ratio. The brittle materials have B/G ratio lower than 1.75 while the ductile materials have higher than 1.75 [22]. As can be seen from Table 3, Ta₄AlB₃ and Ta₄AlC₃ are brittle materials having B/G ratios as 1.479 and 1.624 while Ta₄AlN₃ is a ductile material having B/G ratio as 2.636.

The direction dependent mechanical properties are crucial for technological applications and they give information for the microcracks, plastic deformations, etc. Figure 2 shows the direction dependent Young’s modulus, linear compressibility, shear modulus and Poisson’s ratio for Ta₄AlB₃ in 3D and 2D. The direction dependent mechanical properties of Ta₄AlC₃ and Ta₄AlN₃ have not been presented here due to save space in the journal. The spherical or the circular shape indicates the isotropy for that mechanical property while the distorted shapes indicates the anisotropy. Also, the maximum values are shown in blue and the minimum ones are shown in green. For Ta₄AlB₃, Young’s modulus is isotropic in xy plane while it is anisotropic in xz and yz planes. Ta₄AlC₃ and Ta₄AlN₃ have similar behavior with Ta₄AlB₃ for the direction dependent Young’s modulus. Also, the direction dependent linear compressibility is isotropic in all planes for Ta₄AlB₃. Ta₄AlN₃ has similar behavior with Ta₄AlB₃ for direction dependent linear compressibility while the linear compressibility of Ta₄AlC₃ is anisotropic in xz and yz planes. The shear modulus and the Poisson’s ratio of Ta₄AlB₃ have similar behavior and they are isotropic in xy plane while they are anisotropic in xz and yz planes. Ta₄AlC₃ and Ta₄AlN₃ have similar behavior with Ta₄AlB₃ for the direction dependent shear modulus and Poisson’s ratio. In addition, the minimum and the maximum values for Ta₄AlX₃ (X= B, C, N) MAX phase ceramics have been presented in Table 4. Ta₄AlC₃ has the highest maximum values for Young’s modulus and shear modulus among these compounds as listed in Table 4 consistent with Table 3. Also, Ta₄AlN₃ has the highest maximum value for Poisson’s ratio as listed in Table 4 and consistent with Table 3. For the linear compressibility, Ta₄AlB₃ has the highest maximum value as listed in Table 4.

The thermal properties of Ta₄AlX₃ MAX phase ceramics have been investigated using the quasi-harmonic Debye model. The non-equilibrium Gibbs function (G*(V, T, P)) is given in Equation 1 where total energy per unit cell is E(V), the constant hydrostatic pressure is PV, the Debye temperature is θ(V) and the vibrational Helmholtz free energy is A_vib.

\[ G^*(V, T, P) = E(V) + PV + A_{vib}(\theta(V); Y) \]  (1)

The A_vib could be determined as [54]

\[ A_{vib}(\theta, T) = nkT \left[ \frac{\theta}{\theta T} + 3 \ln(1 - e^{-\theta / T}) - D\left(\frac{\theta}{T}\right) \right] \]  (2)

Where n is the number of atoms per formula unit and D(θ/T) is the Debye integral. Also, the minimization of the non-equilibrium Gibbs function with respect to volume gives the equation of state and the heat capacity at constant volume (C_v), thermal expansion coefficient (α) and entropy (S) could be determined using Equation 4, Equation 5 and equation 6. In Equation 5, y is the Grüneisen parameter.

\[ \frac{\partial G^*(V, T, P)}{\partial V} \bigg|_{P, T} = 0 \]  (3)

\[ C_v = nk \left[ 4D \left( \frac{\theta}{T} \right) - \frac{3\theta}{e^{\theta/T} - 1} \right] \]  (4)

\[ \alpha = \frac{\gamma C_v}{B V} \]  (5)

\[ S = nk \left[ 4D \left( \frac{\theta}{T} \right) - 3 \ln(1 - e^{-\theta / T}) \right] \]  (6)
The thermal properties such as heat capacity at constant volume, free energy, etc. have been studied in 0 to 1000 K temperature range and 0 to 40 GPa pressure range using GIBBS software for Ta₄Alₓ MAX phase ceramics. Figure 3a shows the thermal expansion coefficient for Ta₄Alₓ for 0, 10, 20, 30 and 40 GPa pressure values. The thermal expansion coefficient increases as the temperature increases while it decreases.
with the pressure increment. This behavior was also observed for Ta₄AlC₃ and Ta₄AlN₃ compounds and in order to save space, they are not given in here. But, Figure 3b shows the thermal expansion coefficient for Ta₄AlX₃ compounds at zero GPa pressure to investigate the effect of the change of the X atom to the thermal expansion coefficient. As can be seen from Figure 3b, Ta₄AlN₃ has the highest thermal expansion among these compounds for low temperature about 500 K and Ta₄AlN₃ and Ta₄AlB₃ have thermal expansion coefficients very close to each other at high temperature.

The heat capacity at constant volume is shown in Figure 4a for Ta₄AlB₃ for 0, 10, 20, 30 and 40 GPa pressure values. The heat capacity increases as the temperature increases and it reaches the Dulong-Petit limit. The pressure effect on the heat capacity is reverse than the temperature and the heat capacity decreases as the pressure increases as can be seen from Figure 4a. The heat capacity at zero pressure for Ta₄AlX₃ MAX phase ceramics are shown in Figure 4b to reveal the effect of X atom to the heat capacity. As can be seen from the figure, Ta₄AlN₃ has higher heat capacity than Ta₄AlB₃ and Ta₄AlC₃ at temperature lower than 800 K and at the high temperature region, both compounds have similar heat capacities.

The entropy change of Ta₄AlB₃ with temperature and pressure change are shown in Figure 5a. As can be seen from the figure, the entropy increases with the temperature increment while it decreases with the pressure increase. Figure 5b shows the entropy for Ta₄AlX₃ MAX phase ceramics at 0 GPa pressure and Ta₄AlN₃ has higher entropy than Ta₄AlB₃ and Ta₄AlC₃ for all temperatures.

Figure 6a shows the free energy for Ta₄AlB₃ and the free energy decreases as the temperature increases. Also, the free energy increase when the pressure increases as can be seen from the Figure. Figure 6b shows the free energy for Ta₄AlX₃ ceramics at 0 GPa pressure and Ta₄AlC₃ has the highest free energy among these compounds. This result is consistent with the entropy because Ta₄AlC₃ has the lowest entropy among these compounds.

![Figure 3](image3.png)

**Figure 3.** (a) Thermal expansion coefficient for Ta₄AlB₃ for 0, 10, 20, 30 and 40 GPa pressure values and (b) thermal expansion coefficient for Ta₄AlX₃ (X= B, C, N) MAX phase ceramics at 0 GPa pressure.

![Figure 4](image4.png)

**Figure 4.** (a) Heat capacity at constant volume for Ta₄AlB₃ for 0, 10, 20, 30 and 40 GPa pressure values and (b) heat capacity at constant volume for Ta₄AlX₃ (X= B, C, N) MAX phase ceramics at 0 GPa pressure.
5. Conclusion

$Ta_4AlX_3$ ($X = B, C, N$) MAX phase ceramics have been examined for the electronic, mechanical and thermal properties using Density Functional Theory in this study. $Ta_4AlX_3$ MAX phase ceramics have been optimized and it has been found that as the X atom changes from B to N, a lattice parameter decreases while c lattice parameter increases. The thermodynamic stability of these compounds has been determined with the calculated formation energies that indicate the thermodynamic stability and synthesizability. Also, the thermodynamic stability increases when the X atom changes from B to N. Moreover, the mechanical stability of $Ta_4AlX_3$ MAX phase ceramics has been established using the calculated elastic constants with satisfying the mechanical stability. In addition, it has been found that $Ta_{4AlB_3}$ and $Ta_{4AlC_3}$ are brittle materials while $Ta_{4AlN_3}$ is a ductile material. The direction dependent Young’s modulus of $Ta_{4AlB_3}$ is isotropic in xy plane and anisotropic in xz and yz planes while the linear compressibility is isotropic in all planes. Also, the shear modulus and Poisson’s ratio of $Ta_{4AlB_3}$ have similar behavior with Young’s modulus and they are isotropic in xy plane and anisotropic in xz and yz planes. In addition, the temperature and pressure dependent thermal properties have been studied in 0 to 1000 K temperature range and 0 to 40 GPa pressure range. $Ta_{4AlN_3}$ has the highest thermal expansion coefficient for temperatures about 500 K and the temperature higher than 500 K, $Ta_{4AlB_3}$ has the highest thermal expansion coefficient among these compounds. For the heat capacity at constant volume, $Ta_{4AlN_3}$ has the highest value lower than 800 K and for the high temperature, all compounds have similar heat capacity values. $Ta_{4AlN_3}$ has the highest entropy while $Ta_{4AlC_3}$ has the highest free energy among these compounds. These study presents the detailed electronic and mechanical properties of $Ta_4AlX_3$ MAX phase ceramics and $Ta_{4AlB_3}$ is a promising MAX phase boride.

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