First-principles Studies of the Structural, Elastic, Electronic and Optical Properties of Ti$_2$CdC and Ti$_2$CdN

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Abstract

First-principles studies were conducted to investigate the structural, elastic, electronic and optical properties of the Cd-containing only synthesized MAX phase Ti$_2$CdC in comparison with the predicted phase Ti$_2$CdN. Our calculations show that the substitution of C by N in Ti$_2$CdC mostly affects the lattice constant $c$ but the lattice constant $a$ almost remains unchanged. All elastic constants and moduli increase when C is replaced by N. In comparison with the Ti$_2$CdN phase, Ti$_2$CdC is more compressible along the c-axis. The elastic anisotropy in Ti$_2$CdC is high in comparison with Ti$_2$CdN. Both nanolaminates are brittle in nature. The calculated electronic band structures and density of states imply that the chemical bonding in two compounds is a combination of covalent, ionic and metallic nature. Ti$_2$CdC is more conducting than Ti$_2$CdN. The obtained reflectivity spectra show that the MAX phases Ti$_2$CdC and Ti$_2$CdN have the potential to be used as coating materials for reducing solar heating.

Keywords: First principles, elastic properties, electronic properties, optical properties.

1. Introduction

The MAX phases, a class of layered ternary carbides and nitrides, are described by the chemical formula $M_{n+1}AX_n$, with the different MAX stoichiometries often referred to as 211, 312, and 413 phases for $n = 1, 2, \text{ and } 3$, respectively. In the periodic table of elements, $M$ is an early transition metal from groups 3 (Sc), 4 (Ti, Zr, Hf), 5 (V, Nb, Ta), or 6 (Cr, Mo), $A$ is an A-group element from groups 12 (Cd), 13 (Al, Ga, In, Tl), 14 (Si, Ge, Sn, Pb), 15 (P, As), or 16 (S), and $X$ is C and/or N. The MAX phases are thermodynamically stable nanolaminates which have the potential for industrial applications owing to their conspicuous combination of physical, chemical, electrical, and mechanical properties, some of which are characteristics of metals and ceramics [1]. Due to their simultaneous metallic and ceramics characteristics, the MAX phases are also termed as metallic ceramics [2]. These technologically important ceramics have drawn sufficient attention of material scientists, physicists, and chemists because of their good electrical and thermal conductivities, exceptional damage tolerance, good machinability, excellent thermal shock resistance, fully reversible plasticity, high resistance to oxidation and corrosion, good elastic rigidity, and ability to maintain the strengths to high temperature [2-9].

Among the known 85 synthesized MAX compounds [10], only Ti$_2$CdC phase contains Cd as A-group element. Moreover, this material is synthesized at the early period of discovery of the MAX phases by their discoverers’ group [11]. Inspite of that Ti$_2$CdC is, up to date, a relatively little studied member of 211 phases. Liu et al. [12] carried out a theoretical study on structural and mechanical properties of Ti$_2$CdC along with other Ti$_2$AC (A = Sn, Ga, In, and Pb) phases. An ab initio study is accomplished by Bai et al. [13] to evaluate the chemical bonding by means of density of states (DOS) and the elastic properties of Ti$_2$CdC, providing the structural parameters. Yang et al. [14] investigated the dielectric function as optical property of Ti$_2$CdC including other MAX phases Ti$_2$AC (A = In, Sn, Al, and Pb). On the other hand, after a theoretical prediction by calculating the elastic coefficients of Ti$_2$CdN as a stable nanolaminate [15], this phase has not drawn any attention.
from either the experimentalists or the theorists. These motivate us to perform the present study on the structural, elastic, electronic, and optical properties of these Cd-containing MAX phases. We have also shed light on the effect of substitution of C by N in Ti2CdC phase.

2. Theoretical Methods

The first-principles investigations have been conducted by using the Cambridge Serial Total Energy Package (CASTEP) code [16] in which the plane-wave pseudopotential total energy calculation approach based on the density functional theory (DFT) [17,18] is applied. The electronic exchange-correlation energy has been treated according to Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [19]. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultrasoft pseudopotential [20]. To determine the number of plane-waves in expansion, a plane-wave cutoff energy of 500 eV was employed throughout the calculations. The crystal structures were fully optimized to calculate the ground state various properties by independently modifying the lattice parameters and internal atomic coordinates with no core correction or spin effect. The geometry optimizations were acquired through minimizing the total energy and internal forces by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique [21]. The convergence criteria were chosen as the difference in total energy being less than $5 \times 10^{-6}$ eV/atom, the maximum ionic Hellmann-Feyman force being less than 0.01 eV/Å, maximum ionic displacement being less than $5 \times 10^{-4}$ Å, and the maximum stress being less than 0.02 GPa. The tolerance in the self-consistent field calculation was set to $5 \times 10^{-7}$ eV/atom. For the sampling of the Brillouin zone, the Monkhorst-Pack scheme [22] is used to produce a uniform grid of k-points along the three axes in reciprocal space of crystal, and $15 \times 15 \times 3$ k-points for both Ti2CdC and Ti2CdN were taken to achieve the ground-states. In optical properties calculations, the Vanderbilt-type ultrasoft pseudopotential was replaced by the norm-conserving pseudopotential remaining the other set up unchanged.

The elastic constants have been determined by applying a set of finite homogeneous deformations and calculating the resulting stresses with respect to optimizing the internal degrees of freedom [23], as implemented in the CASTEP code. The intraband contribution to the optical properties of metallic compounds like MAX phases affects mainly the low-energy part of the spectra. It can be

The imaginary part $\varepsilon_2(\omega)$ of the dielectric function has been calculated by the formula:

$$
\varepsilon_2(\omega) = \frac{2e^2n}{\Omega \varepsilon_0} \sum_{k, \alpha, \beta} \left| \langle \psi_k | \mathbf{p} | \psi_\alpha \rangle \right|^2 \delta(E_k - E_\alpha - E_\beta)
$$

where $\Omega$ is the primitive cell volume, $\omega$ is the frequency of light, $e$ is the electronic charge, $\mathbf{p}$ is the vector defining the polarization of the incident electric field and $\psi_k$ and $\psi_\alpha$ are the conduction and valence band wave functions at $k$, respectively. The Kramers-Kronig relations provide the real part $\varepsilon_1(\omega)$ of the dielectric function and reflectivity.

3. Results and Discussion

3.1. Structural Properties:

Fig. 1. Crystal structure of Ti2CdX ($X = $ C, N).

The MAX compounds Ti2CdC and Ti2CdN considered in this study belong to the hexagonal crystallographic system with space group P63/mmc (No. 194). There are two formula units and eight atoms per unit cell (Fig. 1). Fully relaxed structures for both layered nanolaminates are obtained by optimizing the geometry structure including lattice constants and internal atomic positions, starting from an eight atoms unit cell. The optimized Ti atom located on the 4f Wyckoff position, fractional coordinates (1/3, 2/3, 0.077) and (1/3, 2/3, 0.076) in Ti2CdC and Ti2CdN, respectively. The Cd atoms are positioned in the 2d Wyckoff site, fractional coordinates (1/3, 2/3, 3/4) in Ti2CdC and Ti2CdN, respectively. The C and N atoms are situated in the 2a Wyckoff position, fractional coordinates (0, 0, 0) and (0, 0, 0). The obtained lattice constants $a$ and $c$, internal atomic coordinate $z$, equilibrium unit cell volume $V$, Bulk modulus, and pressure derivative of bulk
modulus $B$ for Ti$_2$CdC and Ti$_2$CdN at 0K are given in Table 1. Our calculated structural parameters agree quite well with both experimental (where applicable) and theoretical values; the deviations for the lattice constants and volumes are 1.11% and 1.39%, respectively. As noted from the calculated data, the substitution of C by N mostly affects the $c$ values; this, the calculated shear anisotropy factor, defined by $A = 4C_{44}/(C_{11} + C_{13} - 2C_{12})$, also implies that Ti$_2$CdC possesses large anisotropy compared to Ti$_2$CdN for the shear planes $\{1 0 1 0\}$ between the directions $<0 1 1 0>$ and $<0 1 1 0>$. The large anisotropy for Ti$_2$CdC indicates that the in-plane and out-of-plane inter-atomic interactions in Ti$_2$CdC differ largely. Another anisotropy parameter defined by the ratio between the linear compressibility coefficients along the $c$- and $a$-axis for hexagonal crystal: $k_c/k_a = (C_{11} + C_{12} - 2C_{13})/(C_{11} - C_{12})$ has also been evaluated. The obtained results imply that the compressibility along the $c$-axis is larger than that along the $a$-axis for both the phases. But in comparison with the Ti$_2$CdN phase, Ti$_2$CdC is more compressible along the $c$-axis. As noted above, the elastic anisotropy decreases as C is replaced by N. In fact, the elastic anisotropy for Ti$_2$CdN is quite mild and as a result, this phase is almost cubic in its lack of elastic anisotropy [26].

Table 2 also tabulates the values of bulk moduli $B$, shear moduli $G$, Young moduli $Y$ and Poisson’s ratio $\nu$ of two compounds. For comparison, other theoretical values available in the literatures [12,13,15] are also listed in the table. Not surprisingly, all elastic constants and moduli increase when C is replaced by N. The bulk materials can be classified into two groups according to the Pugh’s criteria [28]: ductile and brittle materials. A material should be brittle if its $G/B > 0.5$, otherwise it should

### Table 1. Calculated lattice parameters $a$ and $c$ (in Å), hexagonal ratio $c/a$, internal parameter $z$, unit cell volume $V$ (in Å$^3$) and bulk modulus $B$ (in GPa) and its pressure derivative $B'$ for Ti$_2$CdC and Ti$_2$CdN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$z$</th>
<th>$V$ (Å$^3$)</th>
<th>$B$ (GPa)</th>
<th>$B'$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.091</td>
<td>14.528</td>
<td>4.700</td>
<td>-</td>
<td>120.21</td>
<td>-</td>
<td>-</td>
<td>Theo. [12]</td>
</tr>
<tr>
<td></td>
<td>3.104</td>
<td>14.55</td>
<td>4.687</td>
<td>0.077</td>
<td>121.40</td>
<td>116</td>
<td>-</td>
<td>Theo. [13]</td>
</tr>
<tr>
<td>Ti$_2$CdN</td>
<td>3.078</td>
<td>14.19</td>
<td>4.610</td>
<td>0.076</td>
<td>116.48</td>
<td>126</td>
<td>5.4</td>
<td>Present</td>
</tr>
</tbody>
</table>

The $a$ values almost remain unchanged, which is the opposite of the general trend as C is replaced by N results in a more affected $a$ values in comparison with the $c$ values [26]. To better understand this intriguing discrepancy more work, especially theoretical work, is required. The bulk modulus increases by 12.5% as the C is substituted with N.

### Table 2. Calculated elastic constants $C_{ij}$ (GPa), bulk moduli $B$ (GPa), shear moduli $G$ (GPa), Young’s moduli $Y$ (GPa), Poisson’s ratio $\nu$, elastic anisotropic factor $A$ and $k_c/k_a$ of Ti$_2$CdC and Ti$_2$CdN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$B$</th>
<th>$G$</th>
<th>$Y$</th>
<th>$G/B$</th>
<th>$A$</th>
<th>$k_c/k_a$</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Ti$_2$CdC</td>
<td>257</td>
<td>68</td>
<td>44</td>
<td>205</td>
<td>36</td>
<td>114</td>
<td>64</td>
<td>162</td>
<td>0.56</td>
<td>0.26</td>
<td>0.385</td>
<td>1.472</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>64</td>
<td>45</td>
<td>212</td>
<td>39</td>
<td>114</td>
<td>74</td>
<td>183</td>
<td>0.65</td>
<td>0.23</td>
<td>0.405</td>
<td>1.419</td>
</tr>
<tr>
<td></td>
<td>258</td>
<td>68</td>
<td>46</td>
<td>205</td>
<td>33</td>
<td>116</td>
<td>70</td>
<td>174</td>
<td>0.60</td>
<td>0.25</td>
<td>0.356</td>
<td>1.465</td>
</tr>
<tr>
<td></td>
<td>253</td>
<td>71</td>
<td>47</td>
<td>203</td>
<td>31</td>
<td>116</td>
<td>67</td>
<td>168</td>
<td>0.58</td>
<td>0.26</td>
<td>0.343</td>
<td>1.474</td>
</tr>
<tr>
<td>Ti$_2$CdN</td>
<td>266</td>
<td>76</td>
<td>56</td>
<td>235</td>
<td>74</td>
<td>127</td>
<td>87</td>
<td>212</td>
<td>0.68</td>
<td>0.22</td>
<td>0.761</td>
<td>1.285</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>83</td>
<td>58</td>
<td>235</td>
<td>68</td>
<td>130</td>
<td>84</td>
<td>208</td>
<td>0.65</td>
<td>0.23</td>
<td>0.699</td>
<td>1.339</td>
</tr>
</tbody>
</table>
be ductile. The Poisson's ratio for a ductile metallic material is typically 0.33 and for brittle material, it is small and less than 0.33 [29]. So, according to Pugh's criteria and the values of Poisson's ratio, both Ti2CdC and Ti2CdN are brittle in nature, which is the general trend of MAX phases [30-32].

3.3. Electronic Properties

The investigated band structures of Ti2CdC and Ti2CdN at equilibrium lattice parameters along the high symmetry directions in the first Brillouin zone are illustrated in Fig. 2. The Fermi level of both which is high and inherently, explain the metallic behavior of the phase Ti2CdC. Our result is consistent with the value of 5.595 states per unit cell per eV calculated by Bai et al. [13]. The conduction properties of Ti2CdC results in due to the Ti 3d contribution. There is no contribution to the DOS at the Fermi level from C and therefore C is not involved in the conduction properties. A poor contribution from Cd 5p states participate in formation of DOS at the Fermi level. These results are consistent with the reports published on MAX phases [31, 33]. The almost similar features are found in Ti2CdN phase though the lowest-lying valence bands disappear in Ti2CdC when C is substituted by N. However, the DOSs at the Fermi level decrease from 5.63 to 4.57 states per unit cell per eV as C is replaced with N, indicating that Ti2CdC is more conducting than Ti2CdN. This is consistent with the results observed in Ti2AlX [34,35] and Ti2InX [36], but not in agreement with the calculations conducted for Ti2AlX by Du et al. [37] and for Ti2InX by Benayad et al. [38], where X is C or N. By comparing Figs. 3(a) and 3(b), it is seen that the covalent Ti-C bond in Ti2CdC has the energy range from -5.4 to -2 eV, whereas the covalent Ti-N bond in Ti2CdN occupies the energy range from -7.2 to 4 eV. Obviously, the Ti-N bond is stronger than Ti-C bond, since the former appears at a lower energy. For this reason, all elastic moduli of Ti2CdN are larger than that of Ti2CdC. The Ti-Cd bonds in both Ti2CdC and Ti2CdN correspond to the peaks of states at around -0.34 and -0.76 eV, respectively, which essentially suggest that the Ti-Cd bonds are weaker than Ti-C and Ti-N bonds. The overall bonding character in two MAX phases may be described as a mixture of metallic, covalent and ionic.

![Fig. 2. Electronic band structure of (a) Ti2CdC and (b) Ti2CdN with equilibrium optimized structure.](image-url)

The total and partial density of states (DOS) of Ti2CdC and Ti2CdN are presented in Fig. 3. It is seen that the lowest-lying valence bands in Ti2CdC, from -11.5 to -9.4 eV, are formed by the C 2s states with a small mixture of the Ti 3p and Ti 3d states. The highest valence bands occupied the energy range from -9.4 to -7.2 eV are derived almost entirely from Cd 4d states. The valence bands located between -7.2 and -5.4 eV below the Fermi level arise mainly from mixed Ti 3s, 3p and Cd 5s, 5p states. An intense peak in the total DOS in the range -5.4 to -2 eV are originated from the strong hybridization of Ti 3d and C 2p states indicating the covalent Ti-C bonds in Ti2CdC. At the Fermi level, the DOS mainly arises from the Ti 3d states. The calculated DOSs at the Fermi level \(N(E_F)\) is 5.63 states per unit cell per eV,
3.5. Optical Properties

The calculated optical properties such as dielectric function and reflectivity of two MAX compounds for incident photon energies up to 20 eV for two polarization vectors [100] and [001] are depicted in Fig. 4. Dielectric function is the most general property of a material, which modifies the incident electromagnetic wave of light. The real and imaginary parts of the dielectric function are illustrated in Figs. 4(a) and 4(b). The real part of the dielectric function $\varepsilon_1$ (a) of the phase Ti$_2$CdC for the polarization along [100] direction exhibit two peaks at around 0.8 and 2.3 eV, whereas for [001] direction no peak is found.

In case of Ti$_2$CdN, a peak is observed at 0.88 eV for the direction [100] and at 1.1 eV for the direction [001]. It is seen that the peak intensity increase expeditiously when C is replaced with N in Ti$_2$CdC.

In the range of $\varepsilon_1 < 0$, the real part of the dielectric function goes through zero from below, which implies...
the metallic nature of the two studied phases. The imaginary part of the dielectric function approaches zero from above that also confirms the metallic characteristics of the two compounds. In fact, this is the general feature of the MAX phase compounds [25, 31, 32, 39]. In the range of high energies, the real part of the dielectric function tends to be unity and the imaginary part reaches nearly zero. It means that in this region where the materials become almost transparent with a small absorption.

The reflectivity spectra as a function of incident photon energy are plotted in Fig. 4(c) for two polarization directions. It is observed that the reflectivity spectra for two different polarization directions do not exhibit great changes in the entire energy range in case of each phase. But the scenario is different for two different phases. At around 4.5 eV a gradual increase starts for Ti2CdC but a rapid decrease occurs in reflectivity spectra of Ti2CdN. An intense peak observed at around 8.5 eV in the reflectivity spectra of Ti2CdC is shifted at around 9.8 eV when C is replaced with N. In the moderate-infrared region, the reflectivity spectra of both MAX materials increase drastically and rise to reach the maximum value of 0.98. It is seen that the reflectivity spectra for two polarization directions for two phases exhibit no significant change in the energy range 1.8-5.1 eV and the amount of reflectivity is always above 44%. Due to almost constant reflectance in the visible light region (1.8-3.1 eV), the two nanolaminates Ti2CdC and Ti2CdN should appear as metallic gray. Moreover, for the same reason, the two MAX compounds show the nonselective characteristic that makes them capable of reducing solar heating. So, we may conclude as Li et al. [25] that the MAX phases have the potential to be used as a coating on spacecraft to avoid solar heating.

4. Conclusion

We have performed the first-principles calculations to investigate the structural, elastic, electronic and optical properties of the Cd-containing MAX phase Ti2CdC and Ti2CdN. Our results show that the substitution of C by N in Ti2CdC affects the all properties such as structural, elastic, electronic, etc. The replacement of C with N reduces all the elastic constants and moduli of Ti2CdC. The phase Ti2CdC is more compressible along the c-axis compared to Ti2CdN. The elastic anisotropy of Ti2CdC is higher than that of Ti2CdN. The studied two MAX phases are brittle in nature. Via the calculation of electronic band structures and density of states, the chemical bonding in two nanolaminates are seen to be a combination of covalent, ionic and metallic nature. Ti2CdC is more conducting than Ti2CdN. The MAX phases Ti2CdC and Ti2CdN are potential candidate materials for coating to reduce solar heating.

References