Structural, Elastic and Electronic Properties of Nitride Ti$_2$CdN Phase in Comparison with the Carbide Ti$_2$CdC Phase from First-principles Study

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Abstract. First-principles studies were conducted to investigate the structural, elastic and electronic properties of the Cd-containing 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; the lattice constant a remains almost unchanged. All the 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 higher in comparison with Ti$_2$CdN. Both the two nanolaminates are brittle in nature. The calculated electronic band structures and density of states imply that the chemical bonding in these two compounds is a combination of covalent, ionic and metallic nature. Electrically, Ti$_2$CdC is more conducting than Ti$_2$CdN.

1. Introduction

The MAX phases, a class of layered ternary carbides and nitrides, are expressed 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, 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 combination of physical, chemical, electrical, and mechanical properties, some of which have characteristics of metals and some of ceramics [1]. Due to their simultaneous metallic and ceramics properties, 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 material strength at high temperature [2-9].

Among more than 70 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 [11]. In spite of that, Ti$_2$CdC is 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 was done by Bai et al. [13] to characterize the chemical bonding by means of electronic density of states (EDOS). They also calculated the elastic properties of Ti$_2$CdC and the structural parameters. An earlier theoretical study predicted Ti$_2$CdN as a stable nanolaminate [14] from the calculated values of the elastic constants. Surprisingly, this predicted phase has not drawn any attention from either the experimentalists or the theorists. This motivates us to perform the present study on the structural, elastic, electronic, and optical properties of these Cd-containing MAX phases. We have shed light on the effect of substitution of C by N in Ti$_2$CdC phase, in particular.

The organization of the rest of the paper is as follows. In section 2, a brief description of the computational procedure used in this investigation has been presented. The important results are analyzed in section 3. Finally, section 4 summarizes the main conclusions of the present study.

2. Computation procedures

The first-principles investigations have been conducted by using the CAmbridge Serial Total Energy Package (CASTEP) code [15] based on the density functional theory (DFT) [16,17]. The electronic exchange-correlation energy has been treated according to the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [18]. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultra-soft pseudopotential [19]. 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 various ground state properties by independently modifying the lattice parameters and internal atomic coordinates. The geometry optimizations were performed through minimizing the total energy and internal forces by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique [20]. 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 [21] 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 Ti$_2$CdC and Ti$_2$CdN were taken to achieve the ground-states.

The elastic constants have been determined by applying a set of finite homogeneous deformations and calculating the resulting stresses with respect to optimized the internal degrees of freedom [22], as implemented in the CASTEP code.

3. Results and discussion

3.1. Structural properties

The MAX compounds Ti$_2$CdC and Ti$_2$CdN considered in this study belong to the hexagonal crystallographic system with space group $P6_3/mmc$ (No. 194). There are two formula units and eight atoms per unit cell (Fig. 1). The optimized Ti atom is located on the 4$f$ Wyckoff position, with fractional coordinates $(1/3, 2/3, 0.077)$ and $(1/3, 2/3, 0.076)$ in Ti$_2$CdC and Ti$_2$CdN, respectively. The Cd atoms are positioned in the 2$d$ Wyckoff site, with fractional coordinates $(1/3, 2/3, 3/4)$ in Ti$_2$CdC and Ti$_2$CdN. The C and N atoms are situated in the 2$a$ Wyckoff position, with fractional coordinates $(0, 0, 0)$ and $(0, 0, 0)$. The lattice constants $a$ and $c$, internal atomic coordinate $z$, equilibrium unit cell volume $V$, Bulk modulus $B$, and pressure derivative of bulk modulus $B\theta$ for Ti$_2$CdC and Ti$_2$CdN at 0 K are given in Table 1. Calculated structural parameters agree quite well with both experimental (where applicable) and theoretical values. As can be noted from Table 1, the substitution of C by N mostly affects the $c$ values; the $a$ values remain almost unchanged. This is opposite to the general trend (as C is replaced by N, $a$-axis lattice parameter changes more in comparison with the $c$ values [26]). To understand this intriguing discrepancy more theoretical work is required. The bulk modulus increases by 12.5% as the C is substituted by N.
Figure 1. Crystal structure of Ti$_2$CdN.

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

| Compound  | $a$  | $c$  | $c/a$ | $z$  | $V$  | $B$  | $B'$ | Reference   |
|-----------|------|------|-------|------|------|------|------|-------------|
| Ti$_2$CdC | 3.103| 14.57| 4.696 | 0.077| 121.50| 112  | 4.9  | This study  |
|           | 3.099| 14.41| 4.650 | 0.086| 119.84| -    | -    | Expt. [11]  |
|           | 3.091| 14.528| 4.700 | -    | 120.21| -    | -    | Theo. [12]  |
|           | 3.104| 14.55| 4.687 | 0.077| 121.40| 116  | -    | Theo. [13]  |
|           | 3.106| 14.54| 4.681 | -    | 121.47| 116  | -    | Theo. [14]  |
| Ti$_2$CdN | 3.078| 14.19| 4.610 | 0.076| 116.48| 126  | 5.4  | This study  |
|           | 3.082| 14.15| 4.591 | -    | 116.40| 130  | -    | Theo. [14]  |

3.2. Elastic properties
Table 2 lists the calculated elastic constants $C_{ij}$, together with other theoretical results of Ti$_2$CdC and Ti$_2$CdN. Calculated results for both nanolaminates agree well with the values found in literatures [12-14]. The elastic constants are positive and satisfy the well-established Born criteria [27], which suggests that the two 211 MAX phases under study are mechanically stable. It is observed that the elastic constants $C_{11}$ and $C_{33}$ increase when C is substituted with N. Thus, we may conclude that the Ti-N bonds are stronger than Ti-C bonds. The average difference between $C_{11}$ and $C_{33}$ for Ti$_2$CdC is about 51.5 GPa, whereas for Ti$_2$CdN, this is found to be 33 GPa. It suggests that the elastic anisotropy in Ti$_2$CdC is high in comparison with Ti$_2$CdN. Besides, the calculated shear anisotropy factor, defined by $A = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$, also implies that Ti$_2$CdC possesses larger anisotropy compared to Ti$_2$CdN for the shear planes {1 0 1 0} between the directions (0 1 1) 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 crystal differ largely.
Another anisotropy parameter defined by the ratio between the linear compressibility coefficients along the c- and a-axis for hexagonal crystal: \( k_c/k_a = (C_{11} + C_{12} - 2C_{13})/(C_{11} - C_{13}) \) has also been evaluated. The results imply that the compressibility along the c-axis is larger than that along the a-axis for both the phases. 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 gives the values of bulk modulus \( B \), shear modulus \( G \), Young modulus \( Y \) and Poisson’s ratio \( \nu \) of two compounds. For comparison, other theoretical values available in the literatures [12-14] are also listed in the table. Not surprisingly, all elastic constants and moduli increase when C is replaced by N. Bulk and shear moduli are the most important parameters for estimating the material hardness. The small moduli of Ti\(_2\)CdX show that they can be grouped into high compressibility materials. Young’s modulus is used to measure the stiffness of a solid. A large \( Y \) indicates a stiff material. As a result, Ti\(_2\)CdN (212 GPa) is stiffer than Ti\(_2\)CdC (162 GPa). 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 be ductile. The Poisson’s ratio for a ductile metallic material is typically 0.33 and for brittle material, it is less than 0.33 [29]. So, according to Pugh’s criteria and the values of Poisson’s ratio, both Ti\(_2\)CdC and Ti\(_2\)CdN are brittle in nature, which is the general trend of all MAX phases [30-32]. The relatively low values of the Poisson’s ratios for two studied MAX phases indicate their high degree of directional covalent bonding. The directional covalent bonding is helpful for materials’ shear moduli. This may be the reason why Ti\(_2\)CdN (87 GPa) has the larger shear modulus compared to Ti\(_2\)CdC (64 GPa).

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

| Compound | \( C_{11} \) | \( C_{12} \) | \( C_{13} \) | \( C_{44} \) | \( B \) | \( G \) | \( Y \) | \( G/B \) | \( \nu \) | \( A \) | \( k_c/k_a \) | Ref. |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| Ti\(_2\)CdC | 257   | 68    | 44    | 205   | 36    | 114   | 64    | 162   | 0.56  | 0.26  | 0.385 | 1.472 | This study |
|           | 263   | 64    | 45    | 212   | 39    | 114   | 74    | 183   | 0.65  | 0.23  | 0.405 | 1.419 | Theo.[12] |
|           | 258   | 68    | 46    | 205   | 33    | 116   | 70    | 174   | 0.60  | 0.25  | 0.356 | 1.465 | Theo.[13] |
|           | 253   | 71    | 47    | 203   | 31    | 116   | 67    | 168   | 0.58  | 0.26  | 0.343 | 1.474 | Theo.[14] |
| Ti\(_2\)CdN | 266   | 76    | 56    | 235   | 74    | 127   | 87    | 212   | 0.68  | 0.22  | 0.761 | 1.285 | This study |
|           | 270   | 83    | 58    | 235   | 68    | 130   | 84    | 208   | 0.65  | 0.23  | 0.699 | 1.339 | Theo.[14] |

3.3. Electronic properties
The band structures of Ti\(_2\)CdC and Ti\(_2\)CdN at equilibrium lattice parameters along the high symmetry directions in the first Brillouin zone are illustrated in Fig. 2. The Fermi level of both the nanolaminate lies below the valence band maximum near the Γ point. The occupied valence bands of Ti\(_2\)CdC lie in the energy range from -6.9 eV to Fermi level \( E_F \). On the other hand, in Ti\(_2\)CdN the valence bands extend widely from -7.2 eV to Fermi level. Moreover, for both the phases, a lot of valence bands go across the Fermi level and overlap with conduction bands. Consequently, no band gap is found at the Fermi level and Ti\(_2\)CdC as well as Ti\(_2\)CdN shows metallic conductivity.

The total and partial density of states (DOS) of Ti\(_2\)Cd\(_X\) (\( X = C \) or \( N \)) are presented in Fig. 3. It is seen that the lowest-lying valence bands in Ti\(_2\)CdC, 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 C 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 Ti\(_2\)CdC. At the Fermi level, the DOS mainly arises from the Ti 3d states. The calculated DOSs at the Fermi level \( N (E_F) \) is
Figure 2. Electronic band structure of (a) Ti$_2$CdC and (b) Ti$_2$CdN.

Figure 3. Total and partial-density of states of (a) Ti$_2$CdC and (b) Ti$_2$CdN.

5.63 states per unit cell per eV, which explain the metallic behavior of Ti$_2$CdC. Our result is consistent with the value of 5.59 states per unit cell per eV calculated by Bai et al. [13]. The conduction properties
of Ti$_2$CdC results in due to the Ti 3$d$ 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 5$p$ 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 Ti$_2$CdN phase though the lowest-lying valence bands disappear in Ti$_2$CdC 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 Ti$_2$CdC is more conducting than Ti$_2$CdN. This is consistent with the results observed in Ti$_2$AlX [34, 35] and Ti$_2$InX [36], but not in agreement with the calculations conducted for Ti$_2$AlX by Du et al. [37] and for Ti$_2$InX 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 Ti$_2$CdC has the energy range from -5.4 to -2 eV, whereas the covalent Ti-N bond in Ti$_2$CdN 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 Ti$_2$CdN are larger than that of Ti$_2$CdC. The Ti-Cd bonds in both Ti$_2$CdC and Ti$_2$CdN 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, due to the difference in electronegativity between the constituting elements, ionic.

4. Conclusion
We have performed the first-principles calculations to investigate the structural, elastic and electronic properties of the Cd-containing MAX phase, Ti$_2$CdC and Ti$_2$CdN. Our results show that the substitution of C by N in Ti$_2$CdC affects all properties. The replacement of C by N increases all the elastic constants and moduli of Ti$_2$CdC. The phase Ti$_2$CdC is more compressible along the c-axis compared to Ti$_2$CdN. The phase Ti$_2$CdN appears to be more important than Ti$_2$CdC in many engineering applications since it is found to be stiffer than Ti$_2$CdC. The elastic anisotropy of Ti$_2$CdC is higher than that of Ti$_2$CdN. Both these MAX phases are brittle in nature and Ti$_2$CdN is more brittle than Ti$_2$CdC. The chemical bonding in two nanolaminates is seen to be a combination of covalent, ionic and metallic nature. Ti$_2$CdN is less conducting than Ti$_2$CdC and consequently the ceramic properties of it are more suitable for high temperature applications. Finally, we hope that these theoretical findings will stimulate experimental research to synthesize the Ti$_2$CdN Max phase, which has several properties of interest for a range of applications.

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