Remarkable class of materials: Band structures and optical properties of non-superconducting and superconducting MAX phases

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Abstract. The MAX phases, due to their nanolaminated crystal structure, are found to be exciting materials which combine certain best attributes of metals (good electrical and thermal conductivity, low hardness, machinability, damage tolerance and thermal shock resistance) with those of ceramics (high temperature strength, high elastic moduli, oxidation and corrosion resistance). Over 70 MAX phases are in existence, amongst which there are eight low-temperature superconductors. Thus a vast majority of the MAX phases are not superconductors. In the present review, emphasis will be made on the theoretical works conducted in recent years in our laboratory to understand the band structure and optical properties of several non-superconducting (particularly Zr-metal based phases) and the available superconducting MAX phases.

1. Review of fundamentals

The so-called nanolaminates (or MAX) phases after their discovery during 1960s by Nowotny and coworkers [1-8] and discovery of superconductive molybdenum carbide family of compounds [6] have, since the work of Barsoum group and others, attracted a lot of interest among the research community due to their remarkable properties having unusual attributes of both ceramic and metal [9-31]. Ceramic properties include among others lightweight, elastically rigid, and high temperatures strength, whereas metallicity attributes show the phases to be quasiductile, thermally and electrically conductive, and damage tolerant.

In 1996 Barsoum et al. [10] for the first time synthesized and characterized the ternary compound, $\text{Ti}_3\text{SiC}_2$, and showed that it possesses some of the best attributes of metals and ceramics. After about one year or so they showed that this compound belonged to a group of over 60 phases majority of which was discovered and produced in powder form in 1960s in Vienna by H. Nowotny and coworkers [2–8]. One year after the successful synthesis of $\text{Ti}_3\text{SiC}_2$, Barsoum and his group [11] discovered hexagonal nitride $\text{Ti}_4\text{AlN}_3$ which indicated a much larger family of compounds showing similar behaviour. All the ternary carbides and nitrides can be described by the general formula $\text{M}_{n+1}\text{AX}_n$, (MAX) where $n = 1$ to $3$. Here M is an early transition metal, A is an A-group (mostly IIIA and IVA) element and X is either C and/or N. These phases are layered hexagonal (space group $D_{6h}^1 - P6_3/mmc$ ) with two formula units per unit cell [10].
Figure 1: Early transition metals, group A and C (and or N) elements in the periodic table (top) that combine together to form the MAX phases. Table 1 below lists the currently known 211, 312 and 413 phases mostly obtained in bulk form by Barsoum and group [9]. MAX phases marked in black are superconductors. Nowotny and co-workers during 1960’s [6] discovered most of the phases shown in bottom boxes under 211 and 312.

Table 1: Commonly known MAX phases. Phases marked in blocks are superconductors.
The research on the MAX phases has shown an almost exponential increase in the past decade. As a result the existence of further MAX phases has been reported or proposed. In this endeavour a large number of authors contributed to this field which has been acknowledged in several reviews [32-36].

More recently Aryal et al. [36] reported a comprehensive study on the elastic and electronic properties of 792 possible MAX ($M_{n+1}AX_n$, $n = 1−4$) phases with using first principles methods. A screening of these crystals was then made on the basis of their elastic and thermodynamic stability which still resulted in 665 viable phases. All the experimentally verified MAX phases passed the screening. They also studied various correlations among and between these crystals. A list of 211, 312 and 413 MAX phases that are mostly obtained in bulk form is given in figure 1. Figures 2a, b, c compare the unit cells of the 211, 312 and 413, respectively. Here near close-packed layers of M layers are interleaved with layers of pure group A-element, with the X-atoms filling the octahedral sites between the former. The A group elements are located at the center of trigonal prisms that are larger than the octahedral sites and thus better able to accommodate the larger A-atoms. The M6X octahedra are edge sharing and are identical to those found in the rock salt structure of the corresponding binary carbides [10]. Recently 514 phase (figure 2d) has been discussed by Aryal et al. [36] which has been screened for elastic and thermodynamic stability.

We have over 70 MAX phases [32], amongst which there are eight low-temperature superconductors e.g., $Mo_2GaC$ [7], $Nb_2SC$ [13], $Nb_2SnC$ [14], $Nb_2AsC$ [15], $Ti_2InC$ [16], $Nb_2InC$ [17], $Ti_2InN$ [18], and $Ti_2GeC$ [19]. The phase $Mo_2GaC$ became the first MAX compound, for which superconductivity with $T_C ≈ 4$ K was discovered [7]. Beckmann et al. [5] synthesized $Nb_2AsC$ first in powder form. Lofland et al. [15] reported the discovery of its superconducting behavior with a transition temperature of 2 K. Bortolozo et al. [17] showed
that \( Nb_2InC \) compound superconducts at 7.5 K. Jeitschko et al. [2, 3] first synthesized the \( Nb_2InC \) phase.

2. Computational Methodology
The computational methodology employed in the study of various properties of non-superconducting Zr-based and other MAX phases and the superconducting MAX phases have been published as described in ref. [37-45]. The plane wave pseudopotential approach with the generalized gradient approximation (GGA) developed by Perdew-Burke-Ernzerhof [46] within the DFT [47, 48] as implemented in the CASTEP code [49] has been used. Vanderbilt-type ultrasoft pseudopotentials [50] are used to treat the electron-ion interaction for most cases. The optical properties are calculated using the norm-conserving pseudopotential instead of the Vanderbilt-type ultrasoft pseudopotential [37-45]. The plane-wave cutoff energy of 500 eV was employed to determine the number of plane waves within the expansion. The geometry optimizations for unit cell with two formula units were achieved using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique [51]. The convergence thresholds used were: \( 5 \times 10^{-6} \) eV/atom for total energy, 0.01 eV/Å for maximum force, 0.02 GPa for maximum stress and \( 5 \times 10^{-4} \) Å for maximum atomic displacement. The tolerance in the self-consistent field calculation is set to \( 5 \times 10^{-7} \) eV/atom. For the sampling of the Brillouin zone, the Monkhorst-Pack scheme [52] is used to produce a uniform grid of k-points along the three axes in reciprocal space of crystal [37-45]. For example, \( 10 \times 10 \times 2 \) k-points for Zr\(_2\)AlC and Zr\(_2\)SC, \( 11 \times 11 \times 2 \) k-points for Zr\(_2\)SiC and \( 12 \times 12 \times 3 \) k-points for Zr\(_2\)PC, \( 10 \times 10 \times 2 \) k-points for Nb\(_2\)InC and \( 16 \times 16 \times 4 \) k-points for Nb\(_2\)AsC and Mo\(_2\)GaC are used in the ground-states.

The optical properties of MAX phases under consideration with different photon energies are investigated by the frequency-dependent dielectric function
\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)
\]
which is closely related to the electronic band structure. The imaginary part \( \varepsilon_2(\omega) \) of the dielectric function can be expressed as the momentum matrix elements between the occupied and the unoccupied electronic states and can be calculated directly using [53]:

\[
\varepsilon_2(\omega) = \frac{2e^2}{\Omega \varepsilon_0} \sum_{k,\nu,\sigma} |\langle \psi_{\nu k}^c | \hat{u} \cdot \vec{r} | \psi_{\nu k}^v \rangle|^2 \delta (E_{\nu k}^c - E_{\nu k}^v - E),
\]

where \( \omega \) is the frequency of light, \( e \) is the electronic charge, \( \hat{u} \) is the vector defining the polarization of the incident electric field, and \( \omega_{\nu k}^c \) and \( \omega_{\nu k}^v \) are the conduction and valence band wave functions at \( k \), respectively. From the imaginary part \( \varepsilon_2(\omega) \), the real part of the dielectric function is extracted through the Kramers-Kronig relations. The remaining optical properties, such as refractive index, absorption spectrum, loss-function, reflectivity, and conductivity (real part) are derived from \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) [53, 54].

3. Band structure and optical properties
3.1. Non-superconducting MAX phases
The dielectric function for the metallic compounds depends on both inter-band and intra-band transitions. The formalism mentioned in the methodology section include interband excitations but does not include an intra-band contribution from the conduction electrons. Hence a conventional Drude term [55, 56] is added with unscreened plasma frequency of 5 eV and damping of 0.05 eV. Its effect is to enhance the low energy part of the spectrum. We first assure that that Zr\(_2\)AC (A = Al, Si, P and S) behave like metallic compounds through band structure calculations.
The calculated electronic band structures for $\text{Zr}_2\text{AC}$ along the high-symmetry directions in the first Brillouin zone are depicted in figure 3 [37]. Since many valence bands are crossing the Fermi level ($E_F$) and overlapping with conduction bands, metallic conductivity of the four phases are indicated. The densities of states (DOS) of the compounds are shown in figure 4 [37]. As a trend of MAX phases [57], M d (here Zr 4d) states are mainly contributing to the DOSs at $E_F$. It is clear that there is a small increasing trend in the DOSs at $E_F$ as the A-group element moves from left to right across the periodic table followed by a decrease for S. Consequently, a sharp transition to a more ceramic-like character occurs in the column S, this behavior is also observed in S-containing other MAX phases [24]. Just below the Fermi level, it is seen that A 3p states interact with Zr 4d states and in deeper energy C 2p as well as C 2s states hybridize with Zr 4d states. As a result, the covalent Zr-A and Zr-C bonds occur and strong Zr 4d-C 2p hybridization stabilizes the structures of $\text{Zr}_2\text{AC}$. The overall bonding nature in four MAX phases may be described as a mixture of metallic, covalent and ionic - the last one is due to the difference in electronegativity between the comprising elements.

Figure 5 depicts the evaluated optical functions of the MAX phases $\text{Zr}_2\text{AC}$ ($A = \text{Al, Si, P and S}$) [37] for photon energies up to 20 eV for [100] polarization direction. The real and imaginary parts of the dielectric function of $\text{Zr}_2\text{AC}$ are presented in figures 5a and 5b along with other calculated values [58] for comparison. In the range of $\varepsilon_1 < 0$, the real part of the dielectric function goes through zero from below, which is the characteristic of metal and declares $\text{Zr}_2\text{AC}$ as metallic compounds. In the real part, a sharp peak is seen to be centered at around 0.72, 0.68, 0.83 and 0.77 eV for $\text{Zr}_2\text{AlC}$, $\text{Zr}_2\text{SiC}$, $\text{Zr}_2\text{PC}$ and $\text{Zr}_2\text{SC}$, respectively. The imaginary part of the dielectric functions of four ternary carbides (figure 5b) approaches zero from above, which also implies that $\text{Zr}_2\text{AC}$ are metallic in nature. The present results for both real and imaginary parts of the dielectric function differ from the previous calculations due to taking only
Figure 4: Total and partial density of states of (a) Zr$_2$AlC, (b) Zr$_2$SiC, (c) Zr$_2$PC and (d) Zr$_2$SC. The vertical dashed line denotes the Fermi level [37].

The refractive indices of Zr$_2$AlC, Zr$_2$SiC, Zr$_2$PS and Zr$_2$SC for the electric polarization vector [100] are shown in figure 5c. The variation of the refractive index of Zr$_2$AC for [100] polarization direction with incident photon energy is almost same in the entire energy region. Except in the 1−6 eV regions, the extinction coefficients of Zr$_2$AC (figure 5d) exhibit the same qualitative features in entire energy range. Figure 5e demonstrates the absorption spectra of Zr$_2$AC, which begin at zero photon energy due to their metallic nature. The absorption spectra ascend sharply below 5.4 eV and the highest peaks for Zr$_2$AlC, Zr$_2$SiC, Zr$_2$PS and Zr$_2$SC appear at 6.02, 7.02, 7.51 and 7.21 eV, respectively, and then continue to decrease up to 13.2 eV.

The energy loss function of Zr$_2$AC (A = Al, Si, P and S) for polarization direction [100] is elucidated in figure 5f. The frequency associated with the highest peak of energy loss spectrum that appears at $\varepsilon_2 < 1$ and $\varepsilon_1 = 0$ is defined as the bulk plasma frequency $\omega_p$ of the material [56, 59]. The plasma frequencies of Zr$_2$AlC, Zr$_2$SiC, Zr$_2$PS and Zr$_2$SC are found from the energy loss spectra to be equal to 13.2, 14.6, 14.9 and 14.6 eV, respectively. Thus these four
MAX phase materials will be transparent if the incident light has frequency greater than their respective plasma frequency and will change from metallic to dielectric response.

The reflectivity of Zr$_2$AC shown in figure 5g increases drastically in the moderate-infrared region as well as in the ultraviolet region of the energy range 4.8–9.8 eV. The spectra for Zr$_2$AC (excluding the phase Zr$_2$SC) show no significant change in the visible light region (energy range ∼1.8–3.1 eV) and the degree of reflectivity is always above 44%. The MAX phases Zr$_2$AlC, Zr$_2$SiC and Zr$_2$PC should appear as metallic gray due to this nearly constant reflectivity in the visible light region. Again for the polarization direction [100] the reflectivity increases expeditiously to reach the maximum value of ∼0.89–0.95 in the ultraviolet region (between 9 and 10 eV). The MAX compounds with the average reflectivity about 44% in the visible light region are capable of reducing solar heating [55]. So, it may be concluded that Zr$_2$AlC, Zr$_2$SiC and Zr$_2$PC may be used as coating materials for reducing solar heating.

That the optical conductivity is a good gauge of photoconductivity was in fact seen in Nd$_2$Cu$_4$−σ [60] via synchronous measurements of both the optical and photoconductivity. The photoconductivity could also shed light on the electrical conductivity of the materials [61]. Figure 5h illustrates the real part of the optical conductivity of Zr$_2$AC (A = Al, Si, P and S). It is observed that for all the four compounds the optical conductivity increases rapidly as photon energy goes to zero. This is an indication for higher electrical conductivity in the [100] polarization direction, which has already been observed in Nb$_2$AlC [62]. The optical conductivity exhibits a sharp dip from 0 to 0.34 eV and then moves upward to reach the maximum value of ∼5.3–6.0 for polarization direction [100] in the energy range 2.6–5.0 eV. Accordingly, Zr-based MAX phases under consideration will be highly electrically conductive when the incident photon has energy within the range of ∼2.6 to 5.8 eV. The electrical conductivity is enhanced with a small amount by the absorption of electromagnetic radiation of photon energy within 9.8 to 14.7 eV.

3.2. Superconducting MAX phases
3.2.1. Nb$_2$AsC, Nb$_2$InC and Mo$_2$GaC The electronic band structures for Nb$_2$AsC, Nb$_2$InC, and Mo$_2$GaC at equilibrium lattice parameters along the high symmetry directions in the
Brillouin zone are shown in figure 6 [38] in the energy range from $-8$ eV to 6 eV. The valence and conduction bands overlap considerably and there is no band gap at the Fermi level for all the phases under study. As a result the three superconducting phases show the metallic conductivity.

As the materials under study are metallic, which is evident from our calculated band structures, a Drude term [55, 56] with unscreened plasma frequency 5 eV and damping 0.05 eV has been used as before. We have used a 0.5 eV Gaussian smearing for all calculations.

The calculated optical parameters of $Nb_2AsC$, $Nb_2InC$, and $Mo_2GaC$ for photon energies up to 20 eV for polarization vectors [100] and [001] are shown in figure 7 [38]. The real and imaginary parts of dielectric functions of the three nanolaminates for a limited energy range are shown in figure 7a and 7b along with the measured values for $NbC_{0.87}$ [63]. All phases exhibit metallic characteristics in the energy range for which $\varepsilon_1(\omega) < 0$. In the real part we observe that the highest peak centered at 3.7 eV for $NbC_{0.87}$ is shifted to the left with a sharp peak at around 2.66 eV for $Nb_2AsC$, and 2.20 eV for $Nb_2InC$ for the polarization direction [100]. We also see that the same peak for $Mo_2GaC$ at around 2.77 eV. In figure 7b, the imaginary part of the dielectric function of the three nanolaminates for both polarization directions approaches zero from above at about 10.5−11.75 eV. The peak of the imaginary part of the dielectric function is related to the electron excitation. In imaginary part $\varepsilon_2$, the peak for $<1.2$ eV is due to the intraband transitions.
The refractive index and extinction coefficient are shown in figure 7c and 7d. The nature of the variation of the refractive indices of Nb$_2$AsC, Nb$_2$InC, and Mo$_2$GaC with incident light energy is almost same but the extinction coefficient shows different qualitative features for different phases in the energy range 0.6–5.8 eV. The static refractive indices of the three phases for polarization direction [100] are 10.46, 7.98, and 17.53, respectively. On the other hand, the corresponding values for the three phases for [001] direction are 7.88, 6.06, and 7.49, respectively. In figure 7e the three nanolaminates confirm their metallic nature showing absorption band in the low energy range. For Nb$_2$AsC, Nb$_2$InC, and Mo$_2$GaC the absorption spectra for both directions arise sharply below 7 eV and their highest peaks for the polarization direction [100] arise at 8.1, 7.4, and 7.7 eV, respectively.

The energy loss spectrum describes the energy loss of a fast electron moving inside the sample [64]. The frequency associated with the highest peak of energy loss spectrum is defined as the bulk plasma frequency $\omega_p$, which appears at $\omega_2 < 1$ and $\omega_1 = 0$ [56, 58]. The energy loss functions for phases under study are displayed in figure 7f. In the energy loss spectra, we find that the plasma frequency of Nb$_2$AsC, Nb$_2$InC, and Mo$_2$GaC are equal to 16.5, 14.8, and 17.2 eV, respectively. These three materials will be transparent if the incident light has frequency greater than their respective plasma frequency.

Figure 7g represents the reflectivity spectra as a function of incident light energy. For comparison the measured spectra of NbC$_{0.98}$ [63] are displayed in the plot. It is seen that the reflectivity spectra for the three phases exhibit no significant changes in the energy range 1.8–6.0 eV and the values are always above 44%. The real part of photocconductivity for the three compounds is shown in Fig. 7(h). For all the phases the conductivity occurs at zero photon
energy. Hence the phases have no band gap. These three nanolaminates have their highest peaks in photoconductivity at 3.48, 4.70, and 5.71 eV, respectively. The measured photoconductivity of $\text{NbC}_{0.98}$ [63] is also shown in the figure for comparison.

3.2.2. $\text{Nb}_2\text{AC}$ ($A = S, \text{Sn}$) Figures 8a,b show the energy bands of $\text{Nb}_2\text{SC}$ and $\text{Nb}_2\text{SnC}$ [40] along the high symmetry directions of the Brillouin zone. The band structures of the two nanolaminates are to some extent similar. As observed before [64] they mainly differ in the energy positions of the s and p bands of S or Sn and in the population of the common valence band (VB) due to different electron concentrations, being 40e and 36e per unit cell for $\text{Nb}_2\text{SC}$ and $\text{Nb}_2\text{SnC}$, respectively. The valence and conduction bands of $\text{Nb}_2\text{SC}$ and $\text{Nb}_2\text{SnC}$ are seen to overlap, thus indicating metallic behavior of both the phases.

Figures 9a,b present the total and partial densities of states for the two superconducting $\text{Nb}_2\text{SC}$ and $\text{Nb}_2\text{SnC}$ nanolaminates. The density of states at the Fermi level are 3.54 and 3.82 states/eV which predominantly contain contributions from the Nb 4d states of 2.88 and 2.90 states/eV of $\text{Nb}_2\text{SC}$ and $\text{Nb}_2\text{SnC}$ (more conducting) respectively.

The valence band (VB) of $\text{Nb}_2\text{SC}$ has several energy bands (figure 9a): the quasi-core S 3s bands (from $-16$ to $-13.5$ eV) are located below the C 2s bands ($-12.5$ to $-11.8$ eV). These are nonbonding quasi-core bands with small energy dispersion. The upper part of the VB (from $-8$ eV to Fermi level) is contributed to by the C 2p, S 3p, and Nb 4d states. The lower part of the VB is characterized by mixing of the C 2p, S 3p, and Nb 4d states, whereas the near-Fermi region (from $-3.6$ to Fermi level) is mostly of Nb 4d character. These may now be compared with those for $\text{Nb}_2\text{SnC}$ (i.e. when S is replaced by Sn) (figure 9b). Here the lower band consisting mainly of C 2s states is from $-12.3$ to $-10.5$ eV below the Fermi level. These are again quasi-core nonbonding bands with small dispersion. In agreement with the results obtained using different computational methodology [64] the next two bands, of Sn 5s type (from $-11$ to $-6.5$ eV), are of quasi-2D character along the M—K direction, but with a maximum dispersion along the Γ-K and Γ-M directions. This indicates that the Sn 5s orbitals are involved in Sn-Sn bonding (in the plane of tin networks) of atoms from neighboring Nb networks [64]. The top of the VB (from $-6.8$ eV to Fermi level) is formed by several hybrid bands mainly made up of the Nb 4d, C 2p,
and Sn 5p orbitals. It may be mentioned here that the VB part for Nb$_2$SC is 1.2 eV wider than that for Nb$_2$SnC as a result of filling of Nb 4d bands due to increase in electron concentration. Further, the Fermi level for both the phases falls in the region of nonbonding Nb 4d states.

The top of the VB (from $-8$ eV to Fermi level) is formed by hybridizing bands made up of the Nb 4d, C 2p, and S 3p orbitals in case of Nb$_2$SC. But for Nb$_2$SnC the top of the VB (from $-6.8$ eV to Fermi level) is formed by hybridizing bands made up of the Nb 4d, C 2p, and Sn 5p orbitals. These Nb 4d - S 3p (Nb 4d - Sn 5p for Nb$_2$SnC) hybrids are closer to Fermi level than the Nb 4d - C 2p ones suggesting that Nb-C bonds are stronger than Nb-S(Sn) bonds. These results are in agreement with the bond lengths obtained from an analysis of Mulliken bond population. The bond lengths in Å are: Nb-C (2.2061, 2.2006), Nb-S (2.6207), Nb-Sn (3.0008); Nb-Nb (2.9330, 2.9568), S-C (3.4835), Sn-C (3.9541).

Figure 10 shows the optical functions of Nb$_2$SC and Nb$_2$SnC [40] calculated for photon energies up to 20 eV for polarization vectors [100] and [001] (only spectra for [100] shown), along with a lone theoretical spectrum of dielectric function of Nb$_2$SnC [65].

The real and imaginary parts of dielectric function of the two nanolaminates are shown in figures 10a and 10b [40] along with the curve from Kanoun et al. [65] which is for a limited energy range. Nb$_2$SC and Nb$_2$SnC exhibit metallic characteristics in the energy ranges for which $\varepsilon_1(\omega) < 0$. As can be seen the result of Nb$_2$SnC is somewhat different as regards the energy ranges for negativity of $\varepsilon_1(\omega)$. For the imaginary part $\varepsilon_2(\omega)$ of the dielectric function, the peak for Nb$_2$SC around 0.55 eV (0.83 eV for Nb$_2$SnC) eV is due to transitions within Nb 4d bands. In the energy range of 1.8–6 eV, $\varepsilon_2(\omega)$ curve due to Kanoun et al. [65] has nearly similar characteristics as regards peak positions but the magnitude is quite different from our data. The nanolaminates Nb$_2$SC and Nb$_2$SnC both have positive static dielectric constant $\varepsilon_1(0)$ of 130 and 66. The refractive index and extinction coefficient are displayed in Figs. 10 (c, d) from which the static values of refractive indices are found to be 11.3 and 8.1 for the two phases, respectively.

The absorption spectra shown in figure 10e reveal the metallic nature of the nanolaminates
Figure 10: (a) Real part of dielectric function, (b) imaginary part of dielectric function, (c) real part of refractive index, (d) extinction coefficient, (e) absorption, (f) loss function, (g) reflectivity, and (h) real part of conductivity of Nb$_2$SC and Nb$_2$SnC in [100] direction [40].

since the spectra starts from 0 eV. Nb$_2$InC has three peaks at 1.6, 6.8, 8.8 eV, besides having a shoulder at ~14 eV, whereas Nb$_2$SnC has a broad main peak at ~7 eV. The function $L(\omega)$ shown in figure 10f describes the energy loss of a fast electron traversing in the material. Its peak is defined as the bulk plasma frequency $\omega_P$, which occurs at $\varepsilon_2(\omega) < 1$ and $\varepsilon_1(\omega) = 0$. In the energy-loss spectrum, we see that the plasma frequency $\omega_P$ of the two phases are equal to 16 and 15.3 eV. When the incident photon frequency is higher than $\omega_P$, the material becomes transparent.

The reflectivity spectra as a function of photon energy are shown in figure 10g. It is found that the reflectivity of both the compounds, having nearly similar characteristics, starts with a value of ~0.6–0.68, decreases and then rises again to reach maximum value of ~0.7 to 0.9 between 9–15.5 eV. Thus both the phases, with roughly similar reflectivity spectra, show promise as good coating materials between 9–15 eV regions. Since the material has no band gap as evident from band structure, the photoconductivity starts with zero photon energy as shown in figure 10h. The photoconductivity and hence electrical conductivity of the materials increases as a result of photon absorption.

3.2.3. Ti$_2$InX ($X=\text{C, N}$) The band structures of both the superconducting phases [39] reveal 2D-like behaviour with smaller energy dispersion along the c-axis and in the K-H and L-M directions (figure 11). The 2-D behaviour does not differ much from one superconductor to the other, except that the bands of the nitride phase are shifted more towards the Fermi level. The
occupied valence bands of Ti$_2$InC and Ti$_2$InN lie in the energy range from $-8.8$ eV to Fermi level and $-9.5$ eV to Fermi level, respectively. Further, the valence and conduction bands are seen to overlap, thus indicating metallic-like behaviour of both the phases. This conductivity increases as C is replaced by N. The In 4d and C 2s-type quasi-core bands with a small dispersion can be seen in the energy intervals $\sim -13.7$ to $-14.4$ eV and from $-11$ to $-10$ eV, respectively below the Fermi level. The corresponding energy intervals are about $-14$ to $-15$ eV for In 4d and N 2s-type quasi-core bands. As seen in ref. [22] the multiband character of the systems can be inferred from three near Fermi bands which intersect the Fermi level.

The total and partial densities of states for the two superconducting phases are illustrated in figures 12a,b. The values of DOS at the Fermi level are 2.78 and 4.98 states/eV which predominantly contain contributions from the Ti 3d states of 2.22 and 4.06 states/eV of the two phases Ti$_2$InC and Ti$_2$InN, respectively. The diffuse character of both s and p states of In atoms causes larger dispersion of In bands than those due to C and N. A covalent interaction occurs ($-9$ eV to Fermi level) between the constituting elements as a result of the degeneracy of the states with respect to both angular momentum and lattice site. C p, N p, and Ti d as well as In p and Ti d states are all hybridized. All these indicate that Ti-In bond is weaker than either Ti-C or Ti-N bond. The population analysis shows that bond lengths in Å for Ti$_2$InC and Ti$_2$InN in increasing order are as: Ti-C (2.1277), Ti-Ti (2.8661), Ti-In (3.0456), In-C (3.9908) and Ti-N (2.1010), Ti-Ti (2.8416), Ti-In (3.0013), In-N (3.9439). The bands associated with N atoms are narrower and lower in energy. This is attributed to the large electronegativity of N compared to that of C.
The C atom is less electronegative than N, and the chemical bond between Ti-C is less polarized than Ti-N. It is thus hypothesized [23] that the electrons of the basal plane rather than the d-electrons of Ti may be responsible for the superconducting behaviour in nanolaminates. One also notes that Tc value is more than doubled when C atoms are replaced by N atoms in the Ti$_2$InX compound.

The optical functions of Ti$_2$InC and Ti$_2$InN for photon energies up to 20 eV for polarization vectors [100] and [001] (only spectra for [100] shown) along with measured spectra of TiC and TiN (where available) are shown in figure 13 [39]. We have used a 0.5 eV Gaussian smearing for all calculations. As before, a Drude term [55, 56] with plasma frequency 3 eV and damping (relaxation energy) 0.05 eV was used.

Despite some variation in heights and positions of peaks, the overall features of our calculated optical spectra of Ti$_2$InC and Ti$_2$InN are roughly similar. In the energy range for which $\varepsilon_1(\omega) < 0$, Ti$_2$InC and Ti$_2$InN exhibit the metallic characteristics (figure 13a). The result of Ti$_2$InC is somewhat different as regards the energy range for negativity of $\varepsilon_1(\omega)$. The dielectric function of Ti$_2$InC is compared with that of TiC$_{0.9}$ [66]. We see that the double peak structure centred at 1.7 eV for TiC$_{0.9}$ is replaced with a sharp peak at around 0.7 eV for Ti$_2$InC. The spectra differ at low energy due to the electronic structure change near the Fermi level, induced by the addition of In layer in TiC. The same inference can be made when one compares low energy spectra of Ti$_2$InN and TiN [67]. On the other hand, no maxima are seen in $\varepsilon_2$ for the two MAX phases, although the values are large in the low energy region (figure 13b). The corresponding spectra for TiC$_{0.9}$ [66] and TiN [67] are shown for comparison. The refractive index and extinction coefficients of the nanolaminates are displayed in figure 13c,d.

The absorption coefficient provides data about optimum solar energy conversion efficiency and it indicates how far light of a specific energy (wavelength) can penetrate into the material before being absorbed. Figure 13e shows the absorption coefficients of both the phases which begin at 0 eV due to their metallic nature. Ti$_2$InC has two peaks, one at $\sim 4.3$ eV (same for Ti$_2$InN) and the other at 6.3 eV (8 eV for Ti$_2$InN), besides having a shoulder at lower energy.

Figure 12: Total and partial DOSs of (a) Ti$_2$InC and (b) Ti$_2$InN [39].
Figure 13: Energy dependent (a) real part of dielectric function, (b) imaginary part of dielectric function, (c) refractive index, (d) extinction coefficient, (e) absorption, (f) loss function, (g) reflectivity and (h) real part of conductivity of Ti$_2$InC and Ti$_2$InN along [100] direction [39]. Experimental data shown for TiC and TiN are from ref. [66] and [67, 68], respectively.

Both the nanolaminates show rather good absorption coefficient in the 4–10 eV region. The energy loss L(ω) of a fast electron traversing in the material is depicted in figure 13f. The bulk plasma frequency ω$_{P}$ is at the peak position which occurs at ε$_2$(ω) < 1, and ε$_1$(ω) = 0. In the energy-loss spectrum, we see that ω$_{P}$ of the two phases Ti$_2$InC and Ti$_2$InN are ∼13.2 eV and ∼12.8 eV, respectively.

Figure 13g shows the reflectivity spectra as a function of photon energy in comparison with measured spectra of TiC$_{0.97}$ [66] and TiN [68]. The reflectance for TiC$_{0.97}$ is nearly constant over the energy range considered. With addition of In to TiC the reflectivity is much higher in the infrared region, it then decreases sharply to 0.55 which becomes almost steady till 5 eV. After an increase with photon energy up to ∼10 eV, the reflectivity falls again. On the other hand we find that the reflectivity in Ti$_2$InN is high in IR-visible-UV up to ∼12.8 eV region (reaching maximum between 10 and 12.8 eV). Compared to this the reflectivity of TiN starts with a higher value in the infrared and there is a sharp drop between 2 and 3 eV, which is characteristics of high conductance [68]. The low reflectivity in the region of visible blue and violet light (2.8–3.5 eV) increases to a value of 0.36 at 6 eV (ultraviolet). The analysis shows that the nitride phase would be a comparatively better material as promising candidate for use as coating material. The photoconductivity here starts with zero photon energy due to the reason that the materials have no band gap which is evident from band structure (figure 13h). Moreover, the photoconductivity and hence electrical conductivity of a material increases as a result of absorbing photons.

3.2.4. Recently discovered superconducting Ti$_2$GeC

The electronic structure of Ti$_2$GeC shown in figure 14a [42] reveals that it is a metal and exhibits covalent nature. Moreover, the Ti-C bonds possessed stronger covalent bonding than the Ti–Ti bonds. At around the Fermi level,
Figure 14: Calculated (a) band structures and (b) DOS of Ti$_2$GeC [42].

the DOS (figure 14b) mainly originates from the Ti 3d states. Ti 3d-C 2p hybridization is the driving force in the structure and the presence of Ge changes the Ti-C–Ti-C covalent bond chain into a Ti-C–Ti-Ge bond chain, forming a layered structure. The calculated Fermi surface (not shown here) is formed mainly by the low-dispersive bands, which should be responsible for the presence of superconductivity in Ti$_2$GeC.

For Ti$_2$GeC a Drude term [55, 56] with unscreened plasma frequency 3 eV and damping of 0.05 eV with a Gaussian smearing of 0.5 eV have been used. The optical properties of the new superconducting phases Ti$_2$GeC for phonon energies up to 20 eV for two different polarization directions [100] and [001] are depicted in figure 15 [42]. The real and imaginary parts of the dielectric functions of Ti$_2$GeC are displayed in figure 15a and 15b along with the measured values of TiC$_{0.9}$ [66] for comparison. In the range of $\varepsilon_1<0$, the real part of the dielectric function goes through zero from below, indicating the metallic characteristic of Ti$_2$GeC. In the real part, it is seen that the double peak structure centered at 1.7 eV for TiC is replaced with a sharp peak at around 1.0 eV and 1.5 eV for Ti$_2$GeC with polarization directions [100] and [001], respectively. In figure 15b, the imaginary part of the dielectric function for both directions approaches zero from above, which also indicates that Ti$_2$GeC is metallic in nature. In $\varepsilon_2(\omega)$, the spectra differ at low energy, due to the change of electronic structure near the Fermi level, caused by the addition of Ge layer in TiC.

The real part of the refractive index of Ti$_2$GeC is shown in Fig. 15c. The static refractive indices of Ti$_2$GeC for the polarization vectors [100] and [001] are seen to have the values 84.56 and 84.58, respectively. The nature of the variation of the refractive index of Ti$_2$GeC for two different polarization directions with incident light energy is almost same between 6.2 and 20 eV but differs slightly in the low energy region. The extinction coefficient i.e. imaginary part of the refractive index indicates the amount of absorption loss when the electromagnetic wave propagates through the material. The extinction coefficients of Ti$_2$GeC for two different propagation directions are presented in figure 15d. For two different polarization directions, the extinction coefficients of Ti$_2$GeC show the same qualitative features in entire energy range.
except 1–7 eV regions.

Figure 15e illustrates the absorption spectra of $Ti_2GeC$ for both polarization directions, which starts at zero photon energy due to its metallic nature. The absorption spectra for two polarization directions arise sharply below 5.5 eV and the highest peaks for polarization directions [100] and [001] appear at 6.28 and 5.99 eV, respectively and then decrease drastically up to 13.7 eV. Again, the absorption spectra show a sharp dip from 13.7 to 14.6 eV. The highest peak is associated with the transition from Ge/C p to Ti d states [42].

![Figure 15: (a) Real and (b) imaginary part of dielectric function, (c) real and (d) imaginary part of refractive index, (e) absorption coefficients, (f) loss function, (g) reflectivity, and (h) real part of photoconductivity of $Ti_2GeC$ in both [100] and [001] directions [42]. Experimental data shown for TiC are from ref. [66]](image)

The energy loss function of $Ti_2GeC$ for both polarization directions is presented in figure 15f [42]. From the energy loss spectra, it is seen that the plasma frequency of $Ti_2GeC$ is equal to 14.5 eV, which means that the superconducting phase $Ti_2GeC$ will be transparent if the incident light has frequency greater than 14.5 eV and will change from a metallic to a dielectric response.

The reflectivity spectra of $Ti_2GeC$ as a function of incident light energy are presented in figure 15g. For comparison, the measured spectra of $TiC_{0.97}$ [66] are shown in the plot. The reflectance of $TiC_{0.97}$ is roughly constant in the energy region from 0 to 8.5 eV. A gradual decrease starts at 8.5 eV and ends at 10.4 eV. Again, the reflectivity of $TiC_{0.97}$ increases to reach another almost constant value. By addition of Ge to TiC, the reflectivity increases rapidly in the moderate-infrared region as well as in the ultraviolet region of the energy range 4.6–8.5 eV and decreases drastically from 14.2 to 15.1 eV. In the visible light region (energy range $\sim$1.8–3.1 eV), it is observed that for both polarization orientations there is no significant change in reflectivity spectra for $Ti_2GeC$ and the amount of reflectivity is always above 44%. Due to this nearly constant reflectivity in the visible light region the superconducting phase $Ti_2GeC$ should appear as metallic gray. Further, the reflectivity spectra for the two different polarization directions increase expeditiously to reach maximum value of $\sim$ 0.93–0.95 in the
ultraviolet region (between 8.46 and 8.53 eV).

The real part of the photoconductivity of $Ti_2GeC$ for two different polarization directions is shown in figure 14h [42]. It is seen that photoconductivity occurs at zero photon energy due to the overlapping of the valence and conduction bands at the Fermi level. Therefore, photocurrent can be generated within a wide range of photon energies. The photoconductivity shows a sharp dip from 0 to 0.3 eV and then inclines upward to reach maximum value of $\sim 6.9-8.3$ for polarization directions [100] and [001] in the ultraviolet region (between $\sim 4.0$ and 5.0 eV). Therefore, $Ti_2GeC$ will be highly electrically conductive when the incident radiation has energy within the range of $\sim 4.0$ to 5.0 eV. The enhancement of electrical conductivity due to absorption of electromagnetic radiation of photon energy within 8.5 to 16.2 eV is so small. There is no photoconductivity when the photon energy is $> 16.2$ eV.

4. Conclusion
Recent first-principles calculations based on DFT on band structures and optical properties of the MAX compounds $Zr_2AlC$, $Zr_2SiC$, $Zr_2PC$ and $Zr_2SC$ and the eight superconducting phases, e.g. $Mo_2GaC$, $Nb_2SC$, $Nb_2SnC$, $Nb_2AsC$, $Ti_2InC$, $Nb_2InC$, $Ti_2InN$, and $Ti_2GeC$ have been reviewed.

The electronic structures of $Zr_2AC$ reveal that they are metal and exhibit covalent nature. At around the Fermi level, the DOS mainly originates from the Zr 4d states. The Zr 4d-C 2p hybridization is the prominent feature in the structure. The optical properties such as dielectric function, refractive indices, absorption spectrum, energy-loss function, reflectivity and optical conductivity are reported. The reflectivity spectra imply that except $Zr_2SC$, all $Zr_2AC$ compounds are potential candidate materials for coating to reduce solar heating. plasma frequency of the MAX phases $Zr_2AC$ as A-group atom moves from left to right across the periodic table followed by a decrease for S.

Optical properties of the three 211 MAX superconducting phases $Nb_2AsC$, $Nb_2InC$, and $Mo_2GaC$ are discussed. The reflectivity spectra of all three nanolaminates imply that they are potential candidate materials for coating to avoid solar heating. The optical properties such as refractive index, reflectivity, and conductivity are found to be polarization dependent. The results provide clear indications of the anisotropy in the optical properties of the three MAX phases under consideration.

The band structure and total densities of states analysis of two superconducting MAX phases $Nb_2AC$ (A = S, Sn) suggest that both materials exhibit metallic conductivity which increases as A is changed from S to Sn in $Nb_2AC$. The bonding is achieved through hybridizing bands made up of the Nb 4d, C 2p, and S 3p/Sn 5p orbitals for $Nb_2SC$ and $Nb_2SnC$. From an analysis of optical functions, it is found that $Nb_2SC$ is a better dielectric material. Further the reflectivity is seen to be high in visible-ultraviolet regions between 9–15 eV for both $Nb_2SC$ and $Nb_2SnC$, showing promise as good coating materials.

The electronic structure reveals that it is a metal and the Ti-C bonds possessed stronger covalent bonding than the Ti-Ti bonds. Near Fermi level, the DOS mainly originates from the
Ti 3d states. Ti 3d-C 2p hybridization is the driving force in the structure and the presence of Ge changes the Ti–C–Ti–C covalent bond chain into a Ti–C–Ti–Ge bond chain, forming a layered structure. The Fermi surface of $\text{Ti}_2\text{GeC}$ is formed mainly by the low-dispersive bands, which is responsible for the presence of superconductivity in it. The optical properties such as refractive index, reflectivity, and photoconductivity are found to be polarization dependent. The reflectivity spectra imply that $\text{Ti}_2\text{GeC}$ is a potential candidate material for coating to reduce solar heating.

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References

[1] Kudielka H and Rohde H 1960 Z. Kristallogr. 114 (1–6) 447
[2] Jeitschko W, Nowotny H and Benesovsky B 1964 Monatsh. Chem. 95 178
[3] Jeitschko W et al 1964 Monatsh. Chem. 95 431
[4] Jeitschko W, Nowotny H and Benesovsky B 1963 Monatsh. Chem. 94 1198
[5] Beckmann O, Boller H and Nowotny H 1968 Monatsh. Chem. 99 1580
[6] Nowotny H 1970 Prog. Solid State Chem. 2, Pergamon Press, New York, NY, USA, edited by H. Reiss.
[7] Toth L E 1967 J. Less-Common Metals 13 (1) 129
[8] Jeitschko W, Nowotny H and Benesovsky F 1963 Monatsh. Chem. 94 (6) 1201
[9] Barsoum M W, El-Raghy T 2001 American Scientist 89 (4) 334
[10] Barsoum M W 2000 Prog. Solid State Chem. 28 (1–4) 201
[11] Barsoum M W, El-Raghy T and Procopio A 2000 Metallur. Mater. Transac. A 31 (2) 373
[12] Eklund P, Beckers M, Jansson U, Högborg H, and Hultman L 2010 Thin Solid Films 518 (8) 1851
[13] Sakamaki K, Wada H, Nozaki H, Onuki Y and Kawai M 1999 Solid State Commun. 112 (6) 323 14
[14] Sakamaki K, Wada H, Nozaki H, Onuki Y and Kawai M 2006 Solid State Commun. 139 (2) 57 15
[15] Lofland S E, Hettlinger J D and Meehan T et al 2006 Phys. Rev. B 74 (17) 174501 16
[16] Bortolozo A D, Sant’Anna O H, Dos Santos C A M and Machado A J S 2007 Solid State Commun. 144 (10-11) 419 17
[17] Bortolozo A D, Fisk Z, Sant’Anna O H, Dos Santos C A M and Machado A J S 2009 Physica C 469 (7-8) 256 18
[18] Bortolozo A D, Serrano G, Serquis A et al 2010 Solid. State Commun. 150 (29-30) 1364 19
[19] Bortolozo A D, Sant’Anna O H, Dos Santos C A M and Machado A J S 2012 Mater. Sci.-Poland 3092 20
[20] Barsoum M W, Golczewski J, Seifert H J, and Aldinger F 2002 J. Alloys Comp. 340 (1-2) 173 21
[21] Manoun B, Leaffer O D and Gupta S et al 2009 Solid State Commun. 149 (43–44) 1978 22
[22] Shein I R and Ivanovskii A L 2009 Phys. Solid State 51 (8) 1608 23
[23] Ivanovskii A L, Sabiryanov R F, Skazkin A N, Zhukovskii V M and Shevekin G P 2000 Inorg. Mater. 36 (1) 28 24
[24] Hug G 2006 Phys. Rev. B 74 (18) 184113 25
[25] Medkour Y, Bouhemadou A and Roumili A 2008 Solid State Commun. 148 (9-10) 459 26
[26] He H, Bai Y, Li Y, Zhu C and Li M 2009 Solid State Commun. 149 (13-14) 564 27
[27] Shein I R and Ivanovskii A L 2011 Phys. Stat. Soli. B 248 (1) 228 28
[28] Leaffer O D, Gupta S, Barsoum M W and Spanier J E 2007 J. E. Spanier, 22 (10) 2651 29
[29] Benayad N, Rached D and Khnata R et al 2011 Mod. Phys. Lett. B 25 (10) 747 30
[30] Liu B, Wang J Y, Zhang J, Wang J M, Li F Z and Zhou Y C 2009 Appl. Phys. Lett. 94 (18) 181906 31
[31] Haines J, Léger J M and Bocquillon G 2001 Annu. Rev. Mater. Res. 31 1 32
[32] Wang J and Zhou Y 2009 Annu. Rev. Mater. Res. 39 (1) 415 33
[33] Sun Z M 2011 Int. Mater. Res. 56 143 34
[34] Barsoum M W and Radovic M 2011 Annu. Rev. Mater. Res. 41 (1) 195 35
[35] Barsoum M W 2013 MAX Phases: Properties of Machinable Ternary Carbides and Nitrides (Wiley-VCH, Weinheim) 36
[36] Aryal S, Sakidja R, Barsoum M W, and Ching W M 2014 Phys. Status Solidi B 251 (8) 1480 37
[37] Nasir M T, Hadi M A, Naqib S H, Parvin F, Islam A K M A, Roknuzzaman M and Ali M S 2014 Int. J. Mod. Phy. B 28 (32) 1550022 38
[38] Hadi M A, Ali M S, Naqib S H and Islam A K M A 2013 Int. J. Comp. Mater. Sci. Eng. 2 (2) (2013) 1350007 39
[39] Roknuzzaman M and Islam A K M A 2013 ISRN Cond. Matter Phys. 2013 (2013) 646042 40
[40] Nasir T M and Islam A K M A 2012 Comput. Mater. Sci. 65 365 41
[41] Ali M S, Islam A K M A, Hossain M M and Parvin F 2012 Physica B: Condensed Matter. 407 (21) 4097 42
[42] Rayhan M A, Ali M A, Naqib S H and Islam A K M A 2015 J. Sci. Res. 7 (3) 53 43
[43] Islam M S and Islam A K M A 2011 Physica B 406 275 44
[44] Ali M S, Parvin F, Islam A K M A and Hossain M A 2013 Comput. Mater. Sci. 74 119 45
[45] Hadi M A, Roknuzzaman M, Parvin F, Naqib S H, Islam A K M A and Aftabuzzaman M 2014 J. Sci. Res. 6 (1) 11 46
[46] Perdew P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865 47
[47] Hohenberg P and Kohn W 1994 Phys. Rev. B 136 864 48
[48] Kohn W and Sham L J 1965 Phys. Rev.140 A 1133 49
[49] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M J, Refson K and Payne M C 2005Z. Kristallogr. 220 567 50
[50] Vanderbilt D 1990 Phys. Rev. B 41 7892 51
[51] Fischer T H and Almlof J 1992 J. Phys. Chem. 96 9768 52
[52] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188 53
[53] Materials Studio CASTEP manual© Accelrys 2010. http://www.tcm.phy.cam.ac.uk/castep/documentation/WebHelp/CASTEP.html 54
[54] Saha S, Sinha T P and Mookerjee A 2000 Phys. Rev. B 62 8828. 55
[55] Li S, Aluia R, Barsoum M W, Jena P and Johansson B 2008 Appl. Phys. Lett. 92 221907 56
[56] Saniz R, Ye L H, Shishidou T and Freeman A J 2006 Physical Review B 74 014209 57
[57] Hug G and Fries E 2002 Phys. Rev. B 65 131104 58
[58] Kanoun M B, Goumri-Said S, Reshak A H and Merad A H 2010 Solid State Sci. 12 887. 59
[59] De Almeida J S and Aluia R 2006 Phys. Rev.B 73 165102 60
[60] Yu G, Lee C H, Heeger A J and Cheong S W 1992 Physica C 203 419 61
[61] Mo Y, Rulis P and Ching W Y 2012 Phys. Rev. B 86 165122 62
[62] Scabrozi T H, Roche J, Rosenfeld A, Lim S H, Salamanca-Riba L, Yong G, Takeuchi I, Barsoum M W, Hettlinger J D and Lofland S E 2009 Thin Solid Films 517 2920 63
[63] Allison C Y, Modine FA and French R H 1987 Phys. Rev. B 35 2573 64
[64] Shein I R, Bamburov V G and Ivanovskii A L 2006 Doklady Phys. Chem. 411 (Part 1) 317 65
[65] Kanoun M B, Goumri-Said S and Reshak A H 2009 Comput. Mater. Sci. 47 491 66
[66] Lynch D W, Olson C G, Peterman D J and Weaver J H 1980 Phys. Rev. B 22 (8) 3991 67
[67] Eibler R, Dorrer M and Neckel A 1983 J. Phys. C 16 16 68
[68] Karlsson B 1981 Ph.D. thesis, Acta Universitatis Upsaliensis, Uppsala, Sweden