Comparison of structural, mechanical and optical properties of tantalum hemicarbide with tantalum monocarbide: \textit{ab initio} calculations

M Jubair, A M M Tanveer Karim, M Nuruzzaman and M A K Zilani
Department of Physics, Rajshahi University of Engineering & Technology, Rajshahi-6204, Bangladesh
E-mail: nzaman79@gmail.com

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Abstract

First-principles calculations are employed to investigate and compare the structural, elastic and optical properties of tantalum hemicarbide Ta\textsubscript{2}C and tantalum monocarbide TaC. Calculated lattice constants of these carbides are in good agreement with available theoretical and experimental results. The mechanical stability of these carbides is affirmed by the estimated values of elastic constants. The estimated values of Vickers hardness indicate that TaC is harder than Ta\textsubscript{2}C. The values of Pugh’s ratio and Poisson’s ratio suggest the brittle nature of both Ta\textsubscript{2}C and TaC. The optical properties of Ta\textsubscript{2}C along two polarization directions [001] and [100] are studied in details for the first time. Our study shows that the optical properties of both Ta\textsubscript{2}C and TaC compounds compliment the electronic structure calculations. Optical constants of Ta\textsubscript{2}C show significant dependence of the state of polarization of the incident electric field, and predict this material as optically anisotropic.

1. Introduction

Tantalum carbides with chemical formula Ta\textsubscript{x}C\textsubscript{y} [1], where \(x \approx 0.44\) and 1.0, have achieved much attention because of their interesting applications in providing surface toughness [2], as cutting tools in improving shock resistance, and as oxidation resistance materials [3]. These materials are chemically resistive, very hard and thermodynamically stable [3]. Hardness of tantalum carbides is affected by carbon contents [4]. Their metallic properties like high melting point (\(\sim 3880^\circ\text{C}\) [5, 6]), high electrical and thermal conductivities make them industrially applicable as ceramic coating materials [7, 8]. Scientists are also encouraged by the superconducting properties of these materials \((T_\text{c} = 10 \text{ K})\) [6]. Production of tantalum carbide is done by various experimental methods such as heating tantalum in dilute hydrocarbon atmosphere [9] and chemically-activated combustion synthesis reactions [10]. Ultrafine TaC powders are synthesized through mechanochemical process [11]. These powders are compressed and sintered to produce small tantalum carbide objects [9]. Sometimes multiwall carbon nanotube is used to synthesize tantalum carbide nanofibers [7].

Leon \textit{et al} investigated deformation mechanism in Ta\textsubscript{2}C at higher temperatures by Transmission Electron Microscopy technique [12]. A laser melting study is carried out to investigate the melting nature of these materials [13]. The outcome of these studies is useful in the operation of hypersonic flight vehicles in extreme environments [13]. Both experimental and computational techniques are applied to study the electronic and elastic properties of tantalum carbides [14, 15]. Hua Xiang \textit{et al} used x-ray diffraction and scanning tunneling microscopy to characterize the microstructure and phase composition of tantalum carbide materials [16]. Phase stability of tantalum carbide is studied by Xiao-Xiang \textit{et al} using Density Functional Theory (DFT) calculation [17]. Surface stability of tantalum carbides Ta\textsubscript{2}C, Ta\textsubscript{4}C\textsubscript{3} and Ta\textsubscript{8}C\textsubscript{13} is investigated by Wen-Li Yan \textit{et al} [1]. Peng \textit{et al} investigated elastic and thermodynamic properties of transition metal carbide TaC under pressure by applying DFT [18]. The reflectivity, dielectric function, refractive index and optical conductivity of TaC are studied experimentally by reflectance and ellipsometry measurements in the infrared to near ultraviolet region [6]. Optical properties of TaC are also investigated computationally using DFT calculations by Sahnoun \textit{et al} [8].
We would like to extend our computational work on optical properties of Ta$_2$C. To the best of our knowledge till to date there is no experimental or theoretical data available on the optical properties of Ta$_2$C. In this paper, we also pay attention to revisit the existing theoretical data of TaC and Ta$_2$C for various physical properties (e.g. structural, elastic, electronic etc).

2. Computational procedure

DFT $^{[20, 21]}$ calculations are executed on tantalum carbides Ta$_2$C and TaC by using the Cambridge Serial Total Energy Package (CASTEP) code $^{[22]}$. Here the electron-ion interaction is considered by ultrasoft pseudopotentials for both Ta$_2$C and TaC $^{[23]}$. Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation (GGA) is used to treat the exchange correlation energy $^{[24]}$. Minimization of total energy is achieved by the technique proposed by Broyden, Fletcher, Goldfrab and Shanno $^{[25]}$. The optimization of crystal structure is done with a plane wave cut off energy of 850 eV and 18 $\times$ 18 $\times$ 10 Monkhorst-Pack grid $^{[26]}$ for Ta$_2$C. In case of TaC, plane wave cut off energy of 950 eV and 19 $\times$ 19 $\times$ 19 Monkhorst-Pack grid are used for optimization. Convergence threshold of $1 \times 10^{-5}$ eV atom$^{-1}$ for the total energy, 0.03 eV Å$^{-1}$ for the maximum force, 0.05 GPa for maximum stress, and 0.001 Å for maximum displacement are taken for all calculations.

3. Results and discussion

3.1. Structural properties

Tantalum hemicarbide $^{[27]}$ Ta$_2$C has hexagonal structure with space group $P\bar{6}m1$ (No. 164) $^{[1]}$. The Ta atom is positioned on the 2d Wyckoff position having fractional coordinates (0.3333, 0.6667, 0.2559). The 1a Wyckoff position with fractional coordinates (0, 0, 0) is inhabited by C atom. The crystal structure of Tantalum monocarbide TaC belongs to the face-centered cubic (fcc) system with space group $Fm\bar{3}m$ (No.225) $^{[1]}$. The atoms have the following positions: C atoms in 4a Wyckoff position having fractional coordinates (0,0,0) and Ta atoms in 4b Wyckoff position with fractional coordinates (0.5, 0.5, 0.5). The optimized crystal structures of Ta$_2$C and TaC with respect to lattice constants are shown in figures 1(a) and (b), respectively. The calculated equilibrium lattice parameters and unit cell volume of Ta$_2$C and TaC are listed in table 1 along with previous data for comparison. It is evident that our results are closely matched with other computational and experimental values. Other phases of TaC are also found in literature with space groups $F\bar{4}3m$, No. 216 (cubic) $^{[28]}$, and $P\bar{6}m2$, No. 187 (hexagonal), respectively $^{[29]}$, those are not focused in this work. Here the calculated equilibrium lattice parameters $a$, and $c$ for Ta$_2$C overestimate the experimental values by 2.3% and 1.5%, respectively. The calculated lattice parameter of TaC, $a$ underestimates the experimental value by 2.4% (cf. table 1).

3.2. Elastic properties

Elastic properties are important because many fundamental solid state properties are linked with elastic properties of solids. To compute different elastic constants ($C_{ij}$) for both Ta$_2$C and TaC, we apply the finite strain

Figure 1. Crystal structures of (a) TaC and (b) Ta$_2$C. Two diagrams are in different scales.
theory [32] with the linear strain-stress relations given by $\sigma_i = C_{ij}\varepsilon_j$. The necessary number of elastic constants is determined by the symmetry of the materials, and it is 3 and 5 for cubic and hexagonal crystals, respectively.

The elastic constants are determined by a Taylor expansion of the total energy of the system $E(V, \delta)$, with respect to a small strain $\delta$ of the lattice of volume $V$. The Bravais lattice for hexagonal crystal structure is spanned by three vectors $(\frac{\sqrt{3}a}{2}, -\frac{a}{2}, 0), (0, a, 0)$ and $(0, 0, c)$. In matrix form the Bravais lattice vectors are expressed as:

$$R = \begin{pmatrix} \sqrt{3}a/2 & -a/2 & 0 \\ -a/2 & a & 0 \\ 0 & 0 & c \end{pmatrix}$$

We express the energy of the strained system by means of a Taylor expansion in the distortion parameters [33]:

$$E(V, \delta) = E(V_0, 0) + V_0 \left[ \sum_\delta \tau_{ij} \delta_i \delta_j + \frac{1}{2} \sum_i C_{ij} \xi_i \xi_j \right]$$

(2)

Where $E(V_0, 0)$ is the energy of the unstrained system with equilibrium volume $V_0$, $\tau_{ij}$ is an element in the stress tensor and $\xi_i$ is a factor to take care of Voigt index. The linear terms vanish if the strain causes no changes in the volume of the crystal. Otherwise, $\tau_{ij}$ is related to the strain on the crystal. Five different strains (distortions) are needed to determine five independent elastic constants $C_{11}, C_{12}, C_{13}, C_{33}$, and $C_{44}$ for hexagonal Ta$_2$C. The first distortion is given by

$$D_1 = \begin{pmatrix} 1 & \delta & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(3)

This changes the size of the basal plane, maintaining the $z$-axis constant. The symmetry of the strained lattice is therefore still hexagonal and the energy for this distortion can be obtained as:

$$E(V, \delta) = E(V_0, 0) + V_0[(\tau_1 + \tau_2)\delta + (C_{11} + C_{12})\delta^2]$$

(4)

The second type of distortion elongates the cell along $x$-axis and compresses along the $y$-axis while conserving the volume and leads to monoclinic symmetry:

$$D_2 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 & -\delta \\ 0 & 0 & 1 \end{pmatrix}$$

(5)

The energy for this type of distortion is as follows:

$$E(V, \delta) = E(V_0, 0) + V_0[(\tau_1 - \tau_2)\delta + (C_{11} - C_{12})\delta^2]$$

(6)

The third distortion stretches or compresses the $z$-axis while keeping the other axis unchanged. The volume changes but the symmetry is preserved. The distortion is expressed as:

$$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 + \delta \end{pmatrix}$$

(7)

The corresponding energy relation, from which elastic constant can be obtained, is given by

$$E(V, \delta) = E(V_0, 0) + V_0\left[\tau_3\delta + \frac{1}{2}C_{33}\delta^2\right]$$

(8)
In the fourth distortion, the $c/a$ ratio is assumed to be constant under a small strain, gives compression or expansion to the system. The symmetry is conserved but the volume changes. The distortion is given by:

$$D_4 = \begin{bmatrix}
1 + \delta & 0 & 0 \\
0 & 1 + \delta & 0 \\
0 & 0 & 1 + \delta
\end{bmatrix}$$

(9)

The energy relation can be written as

$$E(V, \delta) = E(V_0, 0) + V_0 \left[ (\tau_1 + \tau_2 + \tau_3)\delta + \frac{1}{2}(2C_{11} + 2C_{12} + 4C_{13} + C_{33})\delta^2 \right]$$

(10)

The last one is the volume conserving triclinic distortion and is given by:

$$D_5 = \begin{bmatrix}
1 & 0 & \delta \\
0 & 1 & 0 \\
\delta & 0 & 1
\end{bmatrix}$$

(11)

The elastic constant can be obtained from the energy relation:

$$E(V, \delta) = E(V_0, 0) + V_0 [\tau_3 \delta + 2C_{44} \delta^2]$$

(12)

The five independent elastic constants $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$ and $C_{44}$ are derived from the relations (4), (6), (8), (10) and (12), respectively.

The three elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ for cubic TaC can be obtained by calculating the total energy as a function of the shears described below. For $C_{11}$ and $C_{12}$ one considers the following shears $[34, 35]$, \[ C_{11} \]

$$E(V, \delta) = E(V_0, 0) + V_0 [(C_{11} - C_{12})\delta^2 + 0(\delta^4)]$$

(14)

and

$$E(V, \delta) = E(V_0, 0) + V_0 \delta(\tau_1 + \tau_2 + \tau_3) + V_0 \left\{ \frac{3}{2}(C_{31} + 2C_{32})\delta^2 + 0(\delta^4) \right\}$$

(16)

$C_{44}$ can be determined in cubic-elastic by

$$E(V, \delta) = E(V_0, 0) + (2C_{44})\delta^2 + 0(\delta^4)$$

(18)

The calculated elastic constants for both $\text{Ta}_2\text{C}$ and $\text{TaC}$ are shown in table 2 with other available computational and experimental results. There is a good agreement between our calculated results and other existing results with few exceptions. Both the compounds are mechanically stable, because elastic constants of the hexagonal $\text{Ta}_2\text{C}$ satisfy the Born criteria: $C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$ and fcc $\text{TaC}$ compound satisfy the same criteria for cubic crystal: $C_{11} + 2C_{22} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$. The bulk ($B$) and shear ($G$) moduli of these compounds can be obtained from the estimated values of elastic constants. The Voigt-Reuss-Hill approximation is applied to calculate the bulk modulus $B$ and shear modulus $G$ $[36, 37]$. Two widely used equations $Y = (9GB)/(3B + G)$ and $\nu = (3B - 2G)/(6B + 2G)$ are used to calculate Young’s modulus $Y$ and Poisson’s ratio $\nu$. There are two types of solids based on Pugh’s ratio ($k$): brittle and ductile. The ratio of shear to bulk modulus ($G/B$) is called Pugh’s ratio ($k$) $[38]$. A brittle material has a Pugh’s ratio greater than 0.5 while the value is less than 0.5 for ductile one. The critical limit of Poisson’s ratio is 0.33. If the value of Poisson’s ratio is less than 0.33, the material is brittle otherwise the material is ductile. The values of Pugh’s and Poisson’s ratio in table 2 indicate the brittle nature of both $\text{Ta}_2\text{C}$ and $\text{TaC}$.

Hardness of any material is a parameter which indicates the ability of the material to resist the indentation. We have calculated the Vickers hardness of these materials using the approximations given by: (i) Teter et al $[42]$,
H_{v-Teter} = 0.151G, in which hardness depends on shear modulus only; (ii) Tian et al.\[43\], \(H_{v-Tian} = 0.92k^{1.37}G^{0.708}\) and (iii) Chen et al.\[38\], \(H_{v-Chen} = 2(k^2G)^{0.585} - 3\).

The theoretically calculated values of the Vickers hardness by using above mentioned methods for Ta\(_2\)C and TaC phase are listed in table 3. Vickers hardness estimations indicate that TaC phase is relatively harder than Ta\(_2\)C phase. We note that all the values of elastic constants and Vickers hardness in our calculations (tables 2 and 3) are slightly scattered from the experimental results which are likely due to the limitations of GGA\[44,45\].

### 3.3. Electronic properties

We now briefly discuss the electronic structure of TaC and Ta\(_2\)C to interpret the optical properties of these materials. Figures 2 and 3 show the band structure at equilibrium lattice parameters along the high symmetry directions within the Brillouin zone, and the total and partial density states (DOS) for TaC and Ta\(_2\)C, respectively. Some of the valence bands with varying degrees of dispersions cross the Fermi level, \(E_F\) indicate the metallic nature of both carbides (figures 2(a) and (b)).

Figure 3(a) shows the calculated total and partial DOS of TaC. Metallic behaviour of TaC is also ensured by the non-zero value of DOS (2.8 states/eV) at the Fermi level. The inspection of the partial DOS reveals that C-2p and Ta-5d states are donating to the DOS at the Fermi level. It is also seen from figure 3(a) that the low energy structure in the energy range from \(-14.5\) to \(-10.2\) eV are originated from the major contribution of C-2s with a
little admixture of Ta-6s and Ta-5d states. Then DOS in the energy range from $-8.4$ to $-2.0$ eV has a significant contribution from C-2p and Ta-5d states and a little contribution from Ta-5p states. The overall behavior of electronic structure for TaC in our calculation agrees well with the corresponding results obtained from other research groups [8, 48, 49].

In the case of Ta$_2$C, due to the large number of Ta and C atoms in the unit cell, a large number of energy bands are observed (figure 2(b)). From figure 3(b) it is seen that major contribution to the total DOS at EF is from the Ta-5d state. Below the Fermi level, there are five peaks, located at $-0.7$, $-1.6$, $-4.4$, $-6.0$ and $-11.0$ eV. The major peak in the DOS for TaC at around $-4.8$ eV (figure 3(a)) is associated with the hybridization of 2p- and 5d- states of C and Ta atoms, which is covalent in nature. This peak seems to decrease for Ta$_2$C with carbon content which reveals that it has less contribution to the bonding characteristics in the metal-rich carbide Ta$_2$C. The decrease of the weight of interaction between the C-2p and Ta-5d states near the Fermi level can be interpreted as an increase of d-d bonding or metallic bonds between the tantalum atoms. The change from the p-d bonding (covalent) to the d-d bonding (metallic) with carbon content might result in a collective decrease in bond strength for the carbides. This corresponds to the decrease in Vickers hardness and elastic constants obtained for the metal-rich carbide, Ta$_2$C shown in tables 2 and 3. The overall discussion of DOS for Ta$_2$C is fairly agreed with the previous report [17].

3.4. Optical properties

The energy dependent optical properties, namely, dielectric function, refractive index, absorption coefficient, loss function, reflectivity and photoconductivity for Ta$_2$C and TaC are presented in figure 4. All the calculations are done along polarization directions [001] and [100]. The incident photon energies are considered in the range 0 to 30 eV. Response of a material to the incident electromagnetic wave is related to the dielectric function. The dielectric function is given by the relation,

$$
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) .
$$

Here $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are respectively the real and imaginary part of dielectric function.

The local field effects (related to the fact that the electric field experienced at a particular site of a crystal lattice is screened by the polarizability of the system itself) are neglected in this work. In the long wavelength limit ($q \rightarrow 0$), the imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ is calculated from the momentum matrix elements between the occupied and unoccupied electronic states and given by [50],

$$
\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{k,v} \psi_v^* \psi_v^* | \mathbf{u} \cdot \mathbf{r} |^2 \delta(E_v^* - E_k - E)
$$

Here $\mathbf{u}$ is the vector defining the polarization of the incident electric field, $\omega$ is the light frequency, $e$ is the electronic charge, $\psi_v^*$ and $\psi_v^*$ are the conduction and valence band wave functions at $k$, $\Omega$ is the volume of the unit cell, and $\varepsilon_0$ is the permittivity of free space, respectively. The real part $\varepsilon_1(\omega)$ of the dielectric function is
derived from the imaginary part through the Kramers-Kronig relations [50]:

\[ \varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)} \]  

(20)

Where \( P \) represents the principle value of the integral.

The free-electron region can be classically described by the Drude model, yielding the following dielectric functions:

\[ \varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \]  

(21)

\[ \varepsilon_2(\omega) = \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)} \]  

(22)

Here \( \omega_p \) means the plasma frequency, \( \omega_p = \left( \frac{4\pi N e^2}{m^*} \right)^{1/2} \), with \( N \), the free charge density and \( m^* \), the effective optical mass. The parameter \( \Gamma \) describes the damping of the electron motion due to impurities, phonons etc. It is related to the relaxation time \( \tau \) by \( \tau = \frac{\epsilon}{\Gamma} \).

At low frequencies (\( \omega \tau \ll 1 \)), \( \varepsilon_1(\omega) \) becomes large and negative, and \( \varepsilon_2 \) is very large and positive. In this case, \( \varepsilon_2 \) will dominate the optical behavior. On the other hand, when \( \omega \tau \gg 1 \) (high frequency region), the real part approaches unity and the imaginary part becomes very small. This region is characterized by the inductive nature of electronic motion induced by high-frequency incident electromagnetic radiation.

All other optical constants can be derived in terms of \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \), such as static refractive index \( n(\omega) \), extinction coefficient \( k(\omega) \), absorption coefficient \( \alpha(\omega) \), loss function \( L(\omega) \), reflectivity \( R(\omega) \), and
photoconductivity $\sigma(\omega)$ by using following equations [6, 8, 50],

$$
n(\omega) = \frac{1}{\sqrt{2}} \sqrt{\left[ \varepsilon_{\text{r}}(\omega) \right]^2 + \left[ \varepsilon_{\text{i}}(\omega) \right]^2}$$  \hspace{1cm} (23)

$$
k(\omega) = \frac{1}{\sqrt{2}} \sqrt{\left[ \varepsilon_{\text{r}}(\omega) \right]^2 + \left[ \varepsilon_{\text{i}}(\omega) \right]^2} \varepsilon_{\text{r}}(\omega)$$  \hspace{1cm} (24)

$$
\alpha(\omega) = \sqrt{2} \omega \left[ \varepsilon_{\text{r}}(\omega) \right] \left[ \varepsilon_{\text{r}}(\omega) \right]^2 \varepsilon_{\text{i}}(\omega)$$  \hspace{1cm} (25)

$$
L(\omega) = \frac{\varepsilon_{\text{r}}(\omega)}{\left[ \varepsilon_{\text{r}}(\omega) \right]^2 + \left[ \varepsilon_{\text{i}}(\omega) \right]^2}$$  \hspace{1cm} (26)

$$
R(\omega) = \frac{\sqrt{\varepsilon_{\text{r}}(\omega) - 1}}{\sqrt{\varepsilon_{\text{r}}(\omega) + 1}}$$  \hspace{1cm} (27)

$$
\sigma(\omega) = \frac{\omega \varepsilon_{\text{r}}(\omega)}{4\pi}$$  \hspace{1cm} (28)

The variations of real and imaginary parts of the dielectric functions of Ta$_2$C and TaC with incident photon energy are shown in figures 4(a) and (b), respectively. A Drude term with unscreened plasma frequency 10 eV and damping 0.05 eV is used [51] in our calculations. The large negative value of $\varepsilon_{\text{r}}(\omega)$ is observed for both Ta$_2$C and TaC phases in figure 4(a), indicates a clear sign of Drude-like behavior as seen in metals. The variations of $\varepsilon_{\text{r}}(\omega)$ with energy for TaC along two polarization directions [001] and [100] are exactly similar in nature. However, the peak positions are different and distinguishable with height as well for Ta$_2$C for two polarization directions. The polarization dependent response of the dielectric constants yields information regarding optical anisotropy of Ta$_2$C. The imaginary part of the dielectric function $\varepsilon_{\text{i}}(\omega)$ for both compounds increases abruptly at the low energy, where intraband transition occurs, (figure 4(b)), indicating the low energy divergence characteristics as seen in metals. This property also complements the electronic band structure characteristics of both carbides. On the other hand, in higher frequency region, the real part approaches unity and the imaginary part becomes very small. This region is characterized by the inductive nature of electronic motion induced by high-frequency incident electromagnetic radiation as mentioned earlier. The imaginary part of the dielectric function exhibits a minimum near 2.0 eV before increasing which mark the onset of dominance by interband transitions rather than intraband effects. We observe several peaks in the spectra of $\varepsilon_{\text{i}}(\omega)$ for TaC at energies 4.0 eV, 6.4 eV and 8.0 eV, respectively. The peaks of the imaginary part of the dielectric function are originated from the electron excitation. The momentum matrix elements between the occupied and unoccupied electronic states are involved to eventually obtain peaks in the imaginary part of the dielectric function. For example, the major peak at around 4.0 eV for TaC arises due to electronic transition from the high density of states at $\sim$4.7 eV to the empty states above the Fermi level. Our results agree well with the previous theoretical data by Sahnoun et al [8] and also with the experimental data below 6.0 eV where the comparison can be made [5]. The peaks for Ta$_2$C become flat which might be associated with decrease of the strength of hybridization between the C-2p and Ta-5d states near the Fermi level. The imaginary part of dielectric function approaches zero in the high energy region ($\sim$18 eV) for both compounds along two polarization directions [001] and [100]. It hints that in the higher energy range both compounds are almost transparent with little absorption.

The static refractive index, $n$ and extinction coefficient, $k$ of these compounds along polarization directions [001] and [100] are plotted in figures 4(c) and (d), respectively. The refractive index exhibits the low energy divergence characteristics of metals and reveals optical properties similar to those of transition metals [6]. The static refractive index determines the phase velocity of the electromagnetic wave inside the compound, while the imaginary part, often termed as extinction coefficient, is related with the absorption loss encountered by electromagnetic waves travelling through a medium. In the long wavelength limit, the static refractive index $n(\omega)$ of Ta$_2$C is found to be 9.5 and 11.5 for polarization directions [001] and [100], respectively. The polarizing vector dependence of static refractive index of TaC, hints its optically anisotropic nature. The nature of the variations of the refractive index and extinction coefficient roughly follows the imaginary and real part of complex dielectric function, respectively.

The absorption spectra for TaC and Ta$_2$C along polarization directions [001] and [100] are shown in figure 4(e). The absorption coefficient, $\alpha$ measures the penetration for light of a certain wavelength before absorption. The absorption coefficient starts at low energy for both compounds due to their metallic nature. The absorption coefficient is weak in the IR region and continuously increases toward the UV region. It is clearly seen from the figure 4(e) that the absorption spectra in Ta$_2$C in UV region are significantly wider than that in TaC. These results indicate that the compound Ta$_2$C is more promising than TaC as absorbing materials in the UV region. The different behaviors of absorption spectra for two polarizing directions reveal the optically anisotropic character of Ta$_2$C.

The energy loss functions, $L$ along the polarization directions [001] and [100] are plotted in figure 4(f) for both materials. The incident light frequency at the peak of loss spectrum is characterized by the bulk plasma
frequency. Along the polarization direction [001], the plasma frequencies of Ta$_2$C and TaC are located at 23 eV and 17.2 eV, respectively; while those values of Ta$_2$C and TaC along polarization direction [100] are located at 22.5 and 17.2, respectively. Therefore, the materials are likely to become transparent to incident radiation when the frequency of the incident light is higher than that of plasma frequency. The resonance amplitude is evidently higher in TaC compound than that in Ta$_2$C compound.

Reflectivity, $R$ denotes the part of incident energy of a wave that is reflected from the surface of materials. Figure 4(g) shows the variations of reflectivity with incident photon energy for two carbides along polarization directions [001] and [100]. The peaks of energy loss function correspond to the trailing edge in the reflection spectra [52]. For example, the pronounced peaks observed at 23 eV and 17.2 eV along polarization direction [001] for Ta$_2$C and TaC, respectively as mentioned earlier which are consistent with the rapid fall in the reflectivity data (figures 4(f) and (g)). For Ta$_2$C, $R$ flattens in the ultraviolet region over an extended energy range (5–15 eV) along [001] polarization direction whereas several small peaks are observed in the same range for [001] polarization direction.

The real part of optical conductivity, $\sigma$ for both carbides along the polarization directions [001] and [100] are presented in figure 4(h). The band structures of TaC and Ta$_2$C show no band gap which indicate that the photoconductivity starts at low photon energy (figure 4(h)). The very good metallic nature of these compounds is pointed out by this type of nature of photoconductivity. Ta$_2$C has relatively higher conductivity than TaC for both polarization directions. Conductivity spectra of Ta$_2$C depend on the state of polarization of the electric field of the incident light waves. It is mentioned that all the optical constants data for TaC are exactly same for both polarization directions [001] and [100] (figures 4(a)–(h)), and are presented with a single curve.

All the calculated optical parameters of Ta$_2$C show significant dependence of the state of electric field polarization. Among the two carbides under study, Ta$_2$C possesses noticeable optical anisotropy.

4. Conclusion

First-principles calculations based on DFT are executed to elucidate the structural, elastic, and optical properties of tantalum carbides Ta$_2$C and TaC. A gentle agreement in lattice constants and elastic properties between our calculated and existing experimental and theoretical results is observed. The calculated elastic constants satisfy the mechanical stability criteria of both Ta$_2$C and TaC compounds. Vickers hardness estimations indicate that TaC phase is harder than Ta$_2$C phase. Pugh’s ratio and Poisson’s ratio suggest the brittle nature of both Ta$_2$C and TaC compounds. The optical properties (dielectric function, refractive index, absorption coefficient, loss function, reflectivity and photoconductivity) of the tantalum carbides Ta$_2$C and TaC are calculated along two polarization directions [001] and [100]. Our optical results show that the state of polarization of the electric field has appreciable effect on the magnitude of all the optical constants for Ta$_2$C. Both the carbides exhibit strong absorption in the UV region and the absorption spectra in Ta$_2$C are significantly wider than that in TaC.

Declarations

Author contribution statement

M Jubair: Conceived and performed the computational work, analyzed and interpreted the data, and wrote the manuscript.

A M M Tanveer Karim: Conceived and performed the computational work, analyzed and interpreted the data, and wrote the manuscript.

M Nuruzzaman: Analyzed and interpreted the data and wrote the manuscript.

M A K Zilani: Analyzed and interpreted the data and wrote the manuscript.

Competing interest statement

The authors declare no conflict of interest.

ORCID iDs

M Nuruzzaman @ https://orcid.org/0000-0003-2569-8022
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