Ab initio predictions of structure and physical properties of the Zr₂GaC and Hf₂GaC MAX phases under pressure

Muhammad Waqas Qureshi¹,², Xinxin Ma¹,²*, Guangze Tang² & Ramesh Paudel³

The electronic structure, structural stability, mechanical, phonon, and optical properties of Zr₂GaC and Hf₂GaC MAX phases have been investigated under high pressure using first-principles calculations. Formation enthalpy of competing phases, elastic constants, and phonon calculations revealed that both compounds are thermodynamically, mechanically, and dynamically stable under pressure. The compressibility of Zr₂GaC is higher than that of Hf₂GaC along the c-axis, and pressure enhanced the resistance to deformation. The electronic structure calculations reveal that M₂GaC is metallic in nature, and the metallicity of Zr₂GaC increased more than that of Hf₂GaC at higher pressure. The mechanical properties, including elastic constants, elastic moduli, Vickers hardness, Poisson’s ratio anisotropy index, and Debye temperature, are reported with fundamental insights. The elastic constants C₁₁ and C₃₃ increase rapidly compared with other elastic constants with an increase in pressure, and the elastic anisotropy of Hf₂GaC is higher than that of the Zr₂GaC. The optical properties revealed that Zr₂GaC and Hf₂GaC MAX phases are suitable for optoelectronic devices in the visible and UV regions and can also be used as a coating material for reducing solar heating at higher pressure up to 50 GPa.

MAX phase materials (with general formula Mₙ₊₁AXₙ n = 1–3) are the transition metal ternary carbides and nitrides, which provides the bridge between metals and ceramics in terms of properties, and have been attracted significant attention of the scientific community since they were discovered. ‘M’ is denoted as early transition metals, ‘A’ represents the IIIA or IVA elements in the periodic table, and ‘X’ is either carbon or nitrogen. The MAX phases crystallize in P₆₃/mmc hexagonal structure, having the combination of strong covalent M–X bonds and relatively weak metallic M–A bonds, which are responsible for their hybrid properties. The unit cell of the MAX phase consists of edge-shared M₆X octahedra is sandwiched by an A-atom sheet. To be specific, these compounds are machinable, thermal and electrical conductor, damage and irradiation tolerant, corrosion and oxidation resistant, possess high strength and stiffness at high temperature, and having low densities. These outstanding attributes make MAX phase materials potential candidates applicable for wear, oxidation, and corrosion resistant coating materials, superconducting materials, and the cladding material in a nuclear reactor. Moreover, the MXenes are the 2D derivatives of MAX phases possessing useful application in Li-ion and sodium-ion batteries and supercapacitors.

In order to take the full advantages of MAX phase materials in technological applications, a series of experimental and theoretical calculations have been done so far. For example, T. Lapauw et al. synthesized Zr₄AlC and Hf₄AlC (n = 1, 2) experimentally, and their lattice parameter was in good agreement with first-principle investigations and Hu et al. fabricated Nb₄AlC, by using the spark plasma sintering (SPS) technique and investigated the thermal expansion and electrical conductivity. In addition, Petruhins et al. predicted the phase stability, and the magnetic state of Cr₂GaC and thin film of Cr₂GaC was also prepared using the magnetron sputtering technique, and Hoffman et al. investigated the neutron irradiation tolerance behavior of Tiₙ₊₁ACₙ (A = Al, Si, n = 1, 2) MAX phases and found that their radiation-hard is similar to that of SiC which is mostly used material in nuclear reactors. Moreover, it is experimentally proved that Al-based MAX phase materials are excellent oxidation resistant as bulk material and thin-film form because a protective Al₂O₃ layer formed, which...

¹State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China. ²School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China. ³Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur 44700, Nepal. *email: maxin@hit.edu.cn
further hinders the oxidation of core material. The theoretical research on the MAX phase material is mainly based on density functional theory (DFT) calculations, and numerous studies can be found in literature. The theoretical studies related to MAX phase materials are enormous, and it’s growing abruptly compared to experimental work. Recently, the electronic, elastic, thermodynamic, and vibrational properties of $M_2GaC$ phases with $M = Ti, Mo, V, Nb, Mn$, and $Cr$ have been studied theoretically. Romero et al. investigated the structural, elastic, and electronic properties of $Nb_2AC$ (where $A = Sn, In, and S$) under pressure range from 0 to 10 GPa and found the linear compressibility of unit cell along the $c$ axis compared with the increase in pressure. Similarly, Boughemadou et al. investigated the structural, electronic, and elastic of a wide range of $M_2AX$ phases, and pressure effect on structural and elastic properties was comparatively studied. Among numerous computed investigations, the $M_2GaC$ ($M = Zr, Hf$) MAX phases are the least studied 211-type MAX phases. Recently, the structural stability, elastic, phonon, and thermodynamic properties of $Zr_2GaC$ and $Hf_2GaC$ have been studied, and computed elastic properties are in excellent agreement with the available data. However, the properties of $Zr_2GaC$ and $Hf_2GaC$ MAX phases need to be studied under high pressure, and the stability of these compounds with respect to their competing phases should be explored further.

These above mentioned experimental and theoretical studies motivated us to investigate the electronic structure, mechanical, dynamical, and optical characteristics of $Zr_2GaC$ and $Hf_2GaC$ MAX phases under high pressure. In the present work, the structural stability, electronic, mechanical, phonon, and optical properties of the $M_2GaC$ ($M = Zr, Hf$) MAX phase materials have been investigated under pressure ranging from 0 to 50 GPa using the first-principles plane-wave pseudopotential DFT within the generalized gradient approximation (GGA). The results showed that the $M_2GaC$ MAX phases are electronically, elastically, and optically anisotropic in nature and suitable for high-temperature application, coating material, and optoelectronic devices. The paper is organized as follows: detailed computational methods is second section, the obtained results and discussion of $M_2GaC$ are presented in third section, and in fourth section summary of this research is given.

**Computational details**

The Density Functional Theory (DFT) is an ideal quantum mechanical tool to determine the ground state properties and electronic structures of the molecules and solid materials. The calculations presented in this work were performed using the Cambridge Serial Total Energy Package (CASTEP) based on DFT. The exchange-correlation was treated within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) with the plane-wave pseudopotential code. Exchange correlation in GGA is a function of charge density $\rho(r)$ and spatial gradient and empirically written as $E_{XC} = \int \rho \nabla \rho \, d^3r$. The accuracy of calculations depends on two parameters, i.e., first, the kinetic energy cut-off, which determines the number of plane waves in the expansion, and second, the special $k$-points used for the Brillouin zone (BZ) integration. For both $M_2GaC$ ($M = Zr, Hf$) MAX phases, plane waves cut off energy was set at 600 eV, and the Monkhorst-pack scheme of $15 \times 15 \times 3k$-points was employed, respectively. The ground state structural parameters were determined using Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique while the convergence tolerance were set as follows: total energy tolerance less than $5 \times 10^{-6}$ eV/atom, stress component less than 0.02 GPa, maximum force tolerance 0.01 eV/Å, and maximum displacement of the atom during the geometric optimization was less than 0.0005 Å. Finally, Debye’s temperature, mean, transverse, and longitudinal sound velocities were calculated using elastic constants. For the dynamical stability of $M_2GaC$ MAX phases, the phonon dispersion was computed using a finite displacement method implemented in Material Studio. The crystal orbital Hamilton population (COHP) calculations are performed using an open-source Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) code to investigate the chemical bonding.

The enthalpy of formation of $M_2GaC$ phase was calculated through the linear optimization procedure as:

$$\Delta H_{FP} = H_{211} - H_{\text{competing phases}}$$

(1)

where $H_{211}$ is the enthalpy of the 211-$M_2GaC$ MAX phases and $H_{\text{competing phases}}$ is the total enthalpy of the set of competing phases.

The energy of formation per atom ($E_{\text{for}}^{M_2GaC}$) for $M_2GaC$ MAX phases can be calculated as:

$$E_{\text{for}}^{M_2GaC} = \left( \frac{E_{\text{total}}^{M_2GaC} - \left( x E_{\text{M}}^{\text{solid}} + y E_{\text{Ga}}^{\text{solid}} + z E_{\text{C}}^{\text{solid}} \right) }{ x + y + z } \right)$$

(2)

where $E_{\text{total}}^{M_2GaC}$, $E_{\text{M}}^{\text{solid}}$, $E_{\text{Ga}}^{\text{solid}}$, and $E_{\text{C}}^{\text{solid}}$ are the total energy of $M_2GaC$ MAX phase, $M, Ga, and C$ atoms in the solid form, and $x, y, z$ is the number of atoms for $M, Ga, and C$ elements in the unit cell, respectively.

The distortion parameter for octahedra ($a_o$) and that of trigonal prism ($p_r$) can be defined as follow:

$$a_o = \frac{\sqrt{3}}{2 \sqrt{4z^2 \left( \frac{x}{y} \right)^2 + \frac{1}{11}}}$$

(3)

$$p_r = \frac{1}{\sqrt{(0.25 - z)^2 \left( \frac{x}{y} \right)^2 + \frac{1}{5}}}$$

(4)

The DOS at Fermi level is used to investigate the metallic at ambient temperature using following expression:

$$\text{DOS}_{F} = \ldots$$

(5)
where \( n_m \) is the thermally excited number of electrons and \( n_e \) is the total number of valence electrons in the unit cell. \( k_B \) and \( N(E_F) \) are the Boltzmann constant, and value of DOS at Fermi level in unit states/eV/unit cell, respectively.

The Fermi energy of \( \text{M}_2\text{GaC} \) MAX phases are used to estimate the velocity of electron \((v_F)\) near the Fermi level:

\[
v_F = \sqrt{\frac{2E_F}{m}}
\]

Then use this value to estimate the conductivity \((\sigma)\) as:

\[
\sigma = \frac{n e^2 \tau}{m} = \frac{n e^2 l}{m v_F}, \quad \tau = \frac{l}{v_F}
\]

where \( \tau, m, n, e, \) and \( l \) are the time between two collisions, mass of electron, number of electrons, electron's charge, and mean free path of electron, respectively.

To calculate the bulk, shear, and Young's modulus, the following equations used within the Voigt (V)\(^{57}\), Russ (R)\(^{58,59}\), and Voigt-Russ and Hill (VRH)\(^{60,61}\) approximation scheme:

\[
B_V = \frac{1}{9} (2C_{11} + C_{12} + 4C_{13} + C_{33})
\]

\[
B_R = \frac{((C_{11} + C_{12})C_{33} - 2C_{13}^2)}{(C_{11} + C_{12} + 2C_{33} - 4C_{13})}
\]

\[
G_V = \frac{1}{30} (C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66})
\]

\[
G_R = \frac{\frac{5}{7} \left( (C_{11} + C_{12})C_{33} - 2C_{13}^2 \right)^2 C_{55}C_{66}}{3B_VC_{55}C_{66} + ((C_{11} + C_{12})C_{33} - 2C_{13}^2) (C_{55} + C_{66})}
\]

\[
B = \frac{1}{2} (B_V + B_R)
\]

\[
G = \frac{1}{2} (G_V + G_R)
\]

where \( B_V \), \( G_V \), and \( B_R \), \( G_R \) are the bulk and shear modulus in terms of Voigt and Russ approximation, respectively. The Values of Young's modulus and Poisson's ratio obtained by:

\[
E = \frac{9BG}{3B + G}
\]

\[
\sigma = \frac{3B - 2G}{2(3B + G)}
\]

The mechanical Anisotropy \((A)\) calculated as follows:

\[
A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}
\]

To calculate the hardness, the semi-empirical method based on Pugh's ratio, which is proposed by the Chen et al.\(^{62}\), was adopted as:

\[
H_P = 2 \left( k^2 G \right)^{0.585} - 3
\]

where \( k \) is the Pugh's ratio \((G/B)\), and \( G \) is the shear modulus. The Debye temperature determined by the Anderson method\(^{63}\):

\[
\theta_D = \frac{h}{k_B} \left( \frac{3\pi}{4\pi V_a} \right)^{\frac{1}{2}} V_m
\]

The transverse sound velocity \((V_t)\), longitudinal sound velocity \((V_l)\), and mean sound velocity \((V_m)\) calculated by:
where \( h \) is Planck’s constant, \( k_B \) is Boltzmann’s constant, \( n \) represents the number of atoms per unit cell, \( V_a \) is the atomic volume, respectively. The melting temperature (\( T_m \)) of MAX phase materials having hexagonal crystal structure was calculated from the elastic constants as follows:

\[
T_m = 3C_{11} + 1.5C_{33} + 354
\]

The 3D Young’s modulus surface was obtained using the following equation:

\[
\frac{1}{E} = S_{11} \left( l_1^4 + l_2^4 + 2l_1^2l_2^2 \right) + S_{13}l_3^4 + (S_{44} + 2S_{13}) \left( l_1^2 + l_2^2 \right) l_3^2
\]

where \( S_{ij} \) and \( l_i \) represent the elastic compliance tensor of \( M_2GaC \) MAX phases and direction cosine in the sphere coordination, respectively.

The value of the imaginary part can be calculated from the moment matrix element between the occupied and unoccupied electronic states as:

\[
\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\hbar\delta} \sum_{k,v,c} |\psi_k^{c}|u.r.|\psi_k^{v}|^2 \delta(E_k^c - E_k^v - E)
\]

where \( e \) is the electronic charge, \( \omega \) is the light frequency, \( u \) is the vector defining the polarization of the incident electric field, \( \psi_k^{c} \) and \( \psi_k^{v} \) are the conduction and valence band wave function at \( k \), respectively.

**Results and discussion**

**Structural properties and compressibility.** The considered \( M_2GaC \) (\( M = Zr, Hf \)) MAX phase crystallizes in the hexagonal structure with a space group \( P6_3/mmc \) (No. 194) in which \( M_6C \) (\( M = Zr, Hf \)) edge shared octahedron is interleaved by atomic layer of Ga atom. There are eight atoms per unit cell in MAX phase compounds, and the unit cell contains two formula units. The atoms in the \( M_2GaC \) MAX phase are placed as follows: C atoms in 2a (0, 0, 0), Ga atoms are at 2d (2/3, 1/3, 1/4), and \( M \) atoms are at 4f (1/3, 2/3, \( z_M \)), respectively, where \( z_M \) is known as the internal parameter. Figure 1 shows the optimized unit cell of the \( M_2GaC \) MAX phase.

The thermodynamic stability of \( M_2GaC \) MAX phase materials is predicted in terms of formation enthalpy (\( \Delta H_f \)) by comparing the total energy \( M_2GaC \) MAX phase to the energy of non-MAX competing phases (single elements, binary and ternary compounds). Table 2 shows the most competing phases considered for \( M_2GaC \) MAX phases determined by using linear optimization procedure. This linear optimization procedure has been successfully used for predicting many MAX phases in which a phase is considered to be stable if \( \Delta H_f < 0 \). Based on identified competing phases, the Eq. (1) for \( Zr_2GaC \) and \( Hf_2GaC \) MAX phases can be rewritten as:

![Figure 1. The unit cell of the \( M_2GaC \) MAX phase (\( M = Zr, Hf \)). An edge shared \([M_6X]\) octahedra and a \([M_6A]\) trigonal prism are outlined.](image-url)
The distortion parameters for IV-B and V-B group transition metal MAX phases are thermodynamically stable and can be formed experimentally. Moreover, the calculated formation energy per atom for $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ at 0 GPa is $-7.59$ eV/atom and $-7.45$ eV/atom, respectively. There has been an increase in energy of formation for $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ as pressure is increased.

Figure 2 shows the effect of pressure on the normalized lattice parameters $a$, $c$, internal parameter $z$, no. of DOS at $E_F$ (states/eV/unit cell), formation energy $E_f$ (eV/atom), metallicity ($f_m$), and Fermi energy $E_F$ (eV) for $\text{M}_2\text{GaC}$ MAX phase ($\text{M} = \text{Zr}, \text{Hf}$) obtained by GGA-PBE at 0–50 GPa pressure.

![Table 1](image)

Table 1. Calculated lattice parameters (a) and (c) in Å, unit cell volume ($V^3$), c/a, internal parameter (z), no. of DOS at $E_F$ (states/eV/unit cell), formation energy $E_f$ (eV/atom), metallicity ($f_m$), and Fermi energy $E_F$ (eV) for $\text{M}_2\text{GaC}$ MAX phase ($\text{M} = \text{Zr}, \text{Hf}$) obtained by GGA-PBE at 0–50 GPa pressure.

$$
\Delta H_{\text{cp}} = E(\text{Zr}_2\text{GaC}) - E(\text{Zr}_2\text{Ga}) - E(\text{C}) < 0
$$

$$
\Delta H_{\text{cp}} = E(\text{Zr}_2\text{GaC}) - E(\text{ZrC}) - E(\text{Ga}) - E(\text{Zr}) < 0
$$

$$
\Delta H_{\text{cp}} = E(\text{Hf}_2\text{GaC}) - E(\text{Hf}_2\text{Ga}) - E(\text{C}) < 0
$$

Both the $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ phases fulfill the criterion $\Delta H_{\text{cp}} < 0$, indicating that the $\text{M}_2\text{GaC}$ MAX phases are thermodynamically stable and can be formed experimentally. Moreover, the calculated formation energy per atom for $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ at 0 GPa is $-7.59$ eV/atom and $-7.45$ eV/atom, respectively. There has been an increase in energy of formation for $\text{Zr}_2\text{GaC}$ and $\text{Hf}_2\text{GaC}$ as pressure is increased.

As mentioned earlier that the crystal structure of the MAX phase is hexagonal and constituted by $[\text{M}_6\text{X}]$ octahedron and $[\text{M}_6\text{A}]$ trigonal prism. For an ideal structure, the octahedra and trigonal parameters should be equal. However, in reality, the distortion is observed due to the mutual repulsion of atoms. The distortion parameters for IV-B and V-B group transition metal MAX phases are deduced from their optimized lattice parameters in the literature for comparison. It is worth noticing that at high pressure, the volume ratio curve becomes steady, indicating that change in atomic distance is smaller, which results in stronger mutual repulsion as atoms come further closer; eventually, compression of the crystal becomes more difficult. Similarly, the reduction in lattice parameter ratios ($c/a$) results in stronger mutual repulsion as atoms come further closer; eventually, compression of the crystal becomes more difficult.

The bond lengths of $\text{Zr}$–$\text{Ga}$ and $\text{Zr}$–$\text{C}$ reduced more than $\text{Hf}$–$\text{Ga}$ and $\text{Hf}$–$\text{C}$, exhibiting that the $\text{Zr}_2\text{GaC}$ MAX phase is more compressible than $\text{Hf}_2\text{GaC}$ along the $\text{Zr}$–$\text{Ga}$ direction. Furthermore, the $c/a$ and the internal parameter $z$ were used to calculate the distortion within the structure.
element in M₂GaC MAX phases, distortion in octahedra decreases and tends to be stable while distortion in trigonal prisms increases. The distortion in [M₆X] octahedron and [M₆A] trigonal prisms can be observed in other MAX phases with different A-site elements.

### Electronic properties.

The band structure for the M₂GaC MAX phase at equilibrium lattice parameter within the GGA-PBE was calculated and discussed. Figure 4 shows the band structures from −15 to 8 eV energy range along the high symmetry lines of the Brillouin zone (Γ–A–H–K–Γ–M–L–H) at 0, 30, and 50 GPa. The conduction bands overlap with the valance band at the Fermi level without having a bandgap in the vicinity of the Fermi level resulting in the metallic behavior of the M₂GaC MAX phase compounds. Moreover, band structures' appearance resembles other metallic MAX phases, i.e., Cr₂AlC and Ti₂AlC. The small energy dispersion along the K–H and L–M directions indicates the strong anisotropic behavior. In other words, the conductivity of MAX phase compounds is lower along the c-axis than to their basal planes. There is no apparent difference in band associated with Zr and Hf atoms in terms of energy level because electronegativity for Zr (1.33) and Hf (1.30) is almost the same. At different pressure, the increase in bandwidth was observed within the mentioned pressure limit. We found that with the increase in pressure from 0 to 50 GPa, the bands become looser, i.e., the bands

| Phase    | Space group   | a (Å)    | b (Å)    | c (Å)   | V (Å³)   | E (eV/μ) |
|----------|---------------|----------|----------|---------|----------|----------|
| C        | P6₃/mmc (194) | 2.467    | 2.467    | 8.685   | 45.80    | −155.09682 |
| Ga       | Fm-3m (222)   | 3.405    | 3.405    | 5.405   | 38.40    | −102.40728 |
| Ga       | Fm-3m (222)   | 3.320    | 3.320    | 5.405   | 38.40    | −102.40728 |
| Ga       | Fm-3m (222)   | 3.320    | 3.320    | 5.405   | 38.40    | −102.40728 |
| Ga       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Ga       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |
| Zr       | Fm-3m (222)   | 3.330    | 3.330    | 5.405   | 38.40    | −102.40728 |

**Table 2.** Lattice parameter, unit cell volume, and total energies of M₂GaC and its competing phases considered. The phases in bold are the non-MAX competing phases obtained from the linear optimization to calculate the formation enthalpy of the M₂GaC MAX phase.
above the Fermi level move upward while the bands below the Fermi level move downward. Moreover, the bands at the Fermi level increases with the increase in pressure.

To explain the bonding behavior of \( \text{M}_2\text{GaC} \) (M = Zr, Hf) MAX phases, we examine the density of states (DOS). The partial and total density of states (TDOS) for \( \text{M}_2\text{GaC} \) MAX phase compounds at pressure 0 GPa, 30 GPa, and 50 GPa are depicted in Fig. 5. In our previous work\(^{42}\), the hybridization of M (4d, 4p, 5s), Ga (3d, 4p, 4s), and C (2p, 2s) orbitals for \( \text{M}_2\text{GaC} \) is explained at 0 GPa. The TDOS at Fermi level at 0 GPa for \( \text{Zr}_2\text{GaC} \) and \( \text{Hf}_2\text{GaC} \) are 3.00 states/eV/unit and 2.47 states/eV/unit, respectively. In the \( \text{Zr}_2\text{GaC} \) MAX phase, the lowest valence bands of TDOS is formed by C-s with Zr-d, Zr-p in the energy ranges from −10.85 to −9.11 eV. The states range from −8.01 to −5.1 eV, and −5 to −1.90 eV are formed by Ga-s states and strong hybridization of Zr-d and C-s states, respectively. The highest valence bands in the created by Zr-d and Ga-p hybridization, which is relatively weaker.
Figure 4. Band structure for Zr₂GaC at a 0 pressure, b 30 GPa, and c 50 GPa, and for Hf₂GaC at d 0 pressure, e 30 GPa, and f 50 GPa. Fermi level is set to 0 eV.

Figure 5. The total and partial density of states (PDOS) for Zr₂GaC at pressure a 0 GPa, b 30 GPa, and c 50 GPa, and for Hf₂GaC at pressure d 0 GPa, e 30 GPa, and f 50 GPa. Fermi level is set to 0 eV.
than of Zr-d and C-s states. These results are consistent with that of Cr$_2$AlC MAX phase material, which has the maximum DOS at $E_F$, i.e., 6.46 states/eV cell/unit$^{75}$.

Moreover, the density of states at the Fermi level increased with increased pressure, and obtained results are tabulated in Table 1. It is observed that the increase in TDOS for the Zr$_2$GaC MAX phase is more significant than that of Hf$_2$GaC. The TDOS values for M$_2$GaC illustrate that these MAX phase materials are metallic, and their metallicity is in the order of Zr$_2$GaC > Hf$_2$GaC in the given range of pressure. However, there is an increase in bandwidth, and correspondingly, the intensity decreased with the increase in pressure. The density of states on the right side of the Fermi level moves rightwards, whereas the density of states on the left side of the Fermi level moves leftwards under pressure (See Fig. 6), which is in good agreement with the analysis of band structure. It is worth noticing that the main contribution at the Fermi level is from the M-4d electrons in both MAX phases, which is not affected by the pressure. This implies that Zr-d and Hf-d electrons mainly contribute to the conduction properties of MAX phase materials under pressure.

To understand the chemical bonding of Zr$_2$GaC and Hf$_2$GaC MAX phase, we investigate the Crystal Orbital Hamilton Population (COHP) for M–C, M–Ga, and Ga–C bonds, respectively. The COHP method has been widely applied to investigate the bonding and antibonding analysis of many MAX phases$^{26-79}$. Figure 7 shows the COHP at the ground state of Zr$_2$GaC and Hf$_2$GaC MAX phases. It is observed that the COHP curves for both

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**Figure 6.** Total density of states (DOS) from GGA-PBE for M$_2$GaC MAX phase (M = Zr, Hf) at different pressure. Figure inserted showing the effect of pressure in TDOS at Fermi level. Fermi level is set to 0 eV.

**Figure 7.** The calculated crystal orbital Hamilton population (COHP) showing the pair interactions of M–C, M–Ga, and Ga–C in a Zr$_2$GaC and b Hf$_2$GaC. Positive values in the y-axis (–COHP) indicating the bonding states. Fermi level is set to 0 eV.
MAX phases have well-defined bonding and antibonding regions with crossover points near the Fermi level, which is an indication of covalent bonding nature. There is no occupation of antibonding orbitals in the M–C bonds of Zr$_2$GaC and Hf$_2$GaC MAX phases. Moreover, the occupied region below the Fermi level is dominated by strong M–C interaction, while at the Fermi level, the M–Ga bonding character was dominant. There is almost zero bonding interaction for Ga–C atoms due to the absence of orbital overlapping. The COHP curves are similar to the most studied Al-containing MAX phases. Furthermore, the calculated values for metallicity and Fermi energy in the pressure range 0–50 GPa are tabulated in Table 1. It is observed that the metallicity of both Zr$_2$GaC and Hf$_2$GaC phases increases with increasing pressure. According to Eq. (6), the conductivity mainly depends upon $n/vF$ ratio because $e$, $l$, and $m$ are constants. In the given pressure range, the $n/vF$ ratio of M$_2$GaC MAX phases is in order of $(n/vF)_{\text{Hf}_2\text{GaC}} > (n/vF)_{\text{Zr}_2\text{GaC}}$, hence we may conclude that the conductivity of Hf$_2$GaC > Zr$_2$GaC.

To insight the chemical bonding of M$_2$GaC MAX phases under pressure, the charge density distributions mapping along the (100) plane at 0 GPa, 30 GPa, and 50 GPa are plotted in Fig. 8. The bonding character of MAX phases is essential to understand the chemical bonding of their 2D derivatives (MXenes). The preferential accumulation of charges (positive regions at the scale bar) between two atoms indicates the covalent bonds, while balancing the positive or negative (depleted regions) charges at atomic position exhibits the ionic bonding. At 0 GPa, the strong charge accumulation regions were observed at C and M = Zr, Hf atoms, indicating the formation of a strong covalent bond between C–Zr and C–Hf atoms. The charge accumulation at these atomic positions increases with an increase in pressure due to the decrease in atomic distance and an increase in internal

![Figure 8. Electronic charge density mapping along the (100) plane for Zr$_2$GaC at a 0 pressure, b 30 GPa, and c 50 GPa, and for Hf$_2$GaC at d 0 pressure, e 30 GPa, and f 50 GPa.](image-url)
parameters (z) (See Fig. 3). Furthermore, there is a sign of charge balancing around the Zr and Hf atoms, with the C indicating the small degree of ionic bonding. It is also seen that another covalent bond is formed between the Ga–M = Zr, Hf atoms, which is comparatively weaker than that of C–M = Zr, Hf atoms. Therefore, the chemical bonding in the M2GaC MAX phase is predicted to be a mixture of covalent and ionic nature and degree of bonding increases with the increase in pressure.

Mechanical stability and dynamical properties. The mechanical properties of material help to predict the material’s response under the application of load. The mechanical properties of MAX phase materials also contribute to predicting the usefulness in service and are critical in the fabrication process. The elastic constants (Cij) for M2GaC MAX phase materials calculated in the pressure range from 0 to 50 GPa are shown in Fig. 9, and calculated mechanical properties are listed in Table 4. As we know that the M2GaC MAX phase has the hexagonal crystal structure, and there are six stiffness constants (C11, C12, C13, C33, C44 = C55, and C66), but five of them are independent since C66 = (C11 − C12)/2. Our results are consistent with other MAX phases.

The elastic moduli versus pressure for the M2GaC MAX phase are plotted in Fig. 10. It is found that the elastic constants and moduli increase monotonically with an increase in pressure, and the values of C11, C33, Young’s modulus (E), and bulk modulus (B) increased significantly compared to other elastic constants. Contrary, the values of C66 and shear modulus (G) vary slowly. It can also be noticed that C11 and C66 for the Zr2GaC MAX

| M2AX | Pressure | C11 | C12 | C13 | C33 | C44 | Bv | Br | Gv | Gr | B | G | Hv | Ref |
|------|----------|-----|-----|-----|-----|-----|----|----|----|----|----|----|----|-----|
| Zr2GaC | 0 | 266 | 59 | 59 | 218 | 91 | 123 | 122 | 95 | 94 | 18.23 | 42 |
|       | 10 | 325 | 85 | 99 | 283 | 112 | 167 | 167 | 112 | 111 | 16.77 | 42 |
|       | 20 | 377 | 115 | 138 | 340 | 130 | 208 | 208 | 125 | 124 | 15.47 | 42 |
|       | 30 | 419 | 142 | 171 | 388 | 142 | 244 | 244 | 134 | 132 | 14.28 | 42 |
|       | 40 | 444 | 174 | 204 | 436 | 153 | 276 | 276 | 138 | 136 | 12.63 | 42 |
|       | 50 | 440 | 216 | 236 | 462 | 155 | 302 | 301 | 128 | 124 | 9.27 | 42 |
| Hf2GaC | 0 | 305 | 65 | 72 | 251 | 112 | 142 | 141 | 112 | 111 | 20.99 | 42 |
|       | 10 | 366 | 97 | 113 | 318 | 138 | 188 | 188 | 130 | 129 | 19.36 | 42 |
|       | 20 | 417 | 128 | 150 | 374 | 153 | 229 | 229 | 142 | 140 | 17.56 | 42 |
|       | 30 | 467 | 159 | 193 | 426 | 171 | 272 | 272 | 153 | 150 | 16.14 | 42 |
|       | 40 | 508 | 186 | 236 | 470 | 188 | 312 | 312 | 162 | 162 | 14.84 | 42 |
|       | 50 | 552 | 212 | 273 | 506 | 204 | 347 | 347 | 172 | 164 | 14.20 | 42 |
| Zr2AlC | 266 | 55 | 63 | 226 | 87 | 124 | 94 | 17.59 | 69 |
| Zr2GaB | 178 | 69 | 65 | 263 | 101 | 139 | 109 | 86 |
| Hf2GaB | 213 | 76 | 62 | 176 | 66 | 111 | 66 | 9.79 | 85 |
| Ti2GaC | 314 | 66 | 29 | 122 | | 140 | 121 | 85 |
| Ti2GaC | 303 | 66 | 63 | 263 | 101 | 139 | 109 | 85 |
phase increases uniformly up to 40 GPa and then decreases when pressure is exceeded to 50 GPa. A similar trend can be seen for Young’s and shear modulus of Zr$_2$GaC. On the other hand, the Hf$_2$GaC MAX phase shows a linear trend, consistent with the other MAX phase studies under pressure$^{55,83}$. The mechanical stability of M$_2$GaC MAX phases are predicted from the Born stability criteria$^{84}$, i.e., $C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{66} > 0$, ($C_{11} + C_{12}$)$C_{33} - 2C_{13}^2 > 0$. Both MAX phases satisfy the mechanical stability criteria in the mentioned range of pressure. The elastic constant $C_{33}$ for Zr$_2$GaC and Hf$_2$GaC increases by up to 462 GPa and 506 GPa, while the values for $C_{66}$ for both materials increased only by 112 GPa and 169 GPa, respectively. The rapid increase in $C_{33}$ and moderate $C_{66}$ infers the increasing insensitivity of the compression strain along the c axis, not the shear strain.

It is known that the moduli (B, G, and E) measure the resistance of the material to fracture, plastic deformation, and stiffness and are essential to understand the solid-state properties, i.e., structural stability, ductility, stiffness, and brittleness. In this work, the elastic moduli (B, G, and E) increased with an increase in pressure from 0 to 50 GPa, i.e., for Zr$_2$GaC increase in moduli are B (122–302 GPa), G (94–126 GPa), and E (226–333 GPa) and that of Hf$_2$GaC are B (142–347 GPa), G (112–168 GPa), and E (266–435 GPa), respectively. The elastic moduli for the M$_2$GaC MAX phase are in the order of $(B, G, E)_{Hf_2GaC} > (B, G, E)_{Zr_2GaC}$ in the given pressure range.

The brittle/ductile behavior of the M$_2$GaC MAX phase is predicted from the Poisson’s ratio ($\sigma$). It is the ratio between the transverse strain to longitudinal strain under tensile stress. It is an important tool to quantify the failure state in the solids. Frantsveich et al.$^{85}$ proposed a borderline value $\sigma \sim 0.26$, which separates the ductile and brittle materials. For the brittle materials, this value is small, whereas the material is considered to be ductile if Poisson’s ratio is greater than 0.26. Our calculated values for $\sigma$ for Zr$_2$GaC and Hf$_2$GaC are 0.192 and 0.187 at 0 GPa, respectively. These values increase linearly with an increase in pressure, as shown in Fig. 11a. There is a sharp increase in $\sigma$ noticed for the Zr$_2$GaC MAX phase when pressure increase from 40 to 50 GPa. In the pressure

![Figure 10. Variation of elastic moduli of M$_2$GaC MAX phase (M = Zr, Hf) with pressure.](image1)

![Figure 11. Variation of a Poisson's ratio (\(\sigma\)), and b Anisotropic Index (A) for the M$_2$GaC MAX phase (M = Zr, Hf) in function of pressure. The horizontal line in (a) is the proposed borderline between brittle and ductile transition.](image2)
range mentioned, the $M_2GaC$ MAX phase behaves in a brittle manner at 0 GPa pressure, similar to many other MAX phases. Both MAX phases exhibit ductile nature when pressure is increased from 30 GPa. Moreover, the microscopic hardness model proposed by Chen et al. was used to calculate the Vickers hardness of $M_2GaC$ MAX phases, and the obtained results are listed in Table 4. The theoretical Vickers hardness for $(Zr_2GaC)_{HV} = 18.23$ GPa < $(Hf_2GaC)_{HV} = 20.99$ GPa at 0 GPa pressure, respectively, and Vickers hardness decreases with an increase in pressure. It is worth noticing that the grain size of the material has an essential effect on hardness, yield strength, tensile, and fatigue strength according to the Hall–Petch relation because grain boundaries hinder the movement of dislocations. The effect grain size on the compressive strength of bulk Ti$_2$AlC MAX phase followed the Hall–Petch relation under the dynamic and quasi-static loads. Moreover, the oxidation resistance and mechanical properties of MAX phase thin films can be improved by increasing the grain boundaries.

Figure 11b illustrates the anisotropic index ($A$) of the $M_2GaC$ MAX phase in the function of pressure. Typically, a material is called to be isotropic if anisotropic index $A = 1$ and the deviation from 1 indicates the anisotropic nature of the material. Figure 11b shows that the values of $A$ do not satisfy the isotropic criteria, and an increase in pressure results in a higher anisotropic index for both $Zr_2GaC$ and $Hf_2GaC$ MAX phases suggesting the anisotropic nature of $M_2GaC$ MAX phases in the given pressure range. In other words, the properties for the $M_2GaC$ MAX phases, i.e., higher compressibility along the c-axis compared to other basal planes.

According to Pugh’s criteria, a material will behave ductile if the $B/G > 1.75$ and $G/B < 0.57$, otherwise it should be brittle. For 0 GPa these ratios for $M_2GaC$ MAX phases are in the order $(Hf_2GaC)_{B/G} = 1.26 < (Zr_2GaC)_{B/G} = 1.29$ and $(Hf_2GaC)_{G/B} = 0.78 > (Zr_2GaC)_{G/B} = 0.77$, respectively. This indicates that the $M_2GaC$ phases behave in a brittle manner at 0 GPa: however, with an increase in pressure, $M_2GaC$ phases likely to be ductile (See Fig. 12). These results are consistent with studies available in the literature.

For the dynamical stability of $M_2GaC$ MAX phases, phonon calculation was performed along the high-symmetry directions in the Brillouin zone. The calculated phonon dispersion curves at 0 GPa, 30 GPa, and 50 GPa are shown in Fig. 13. There are eight atoms per unit cell in the 211 family of MAX phases. So, 24 phonon branches are produced; three are acoustic, and the rest are for optical modes. The optical branches are situated at the upper part of the dispersion curves, responsible for the optical behavior of MAX phase materials. These optical modes originate from the out-of-phase oscillations of atoms in lattice when one atom goes to the left and its neighbor to the right. In contrast, the acoustic branches are located at the lower part of phonon dispersion curves.
and arise from the coherent vibration of atoms in a lattice outside their balance position. The absence of negative frequencies in the phonon dispersion curves within the whole Brillouin zone robustly indicates the dynamical stability of M₂GaC MAX phases under normal and high pressure against mechanical perturbation. The phonon dispersion curves become loose with the increase in pressure, which is consistent with band structures. At point Γ, the values of transverse optical (TO) and longitudinal optical (LO) frequencies and the separation between TO and LO increases with an increase in pressure. At 0 GPa, the values of LO (lower dispersion curve) and TO frequencies at Γ are 14.58, 16.56 THz for Zr₂GaC and 16.00, 18.32 THz for Hf₂GaC, respectively. Moreover, at the center zone point (Γ), the acoustic mode frequency is zero for all pressures, which is another indication of the stability of M₂GaC MAX phases within the given pressure range.

As mentioned earlier that the MAX phases compounds studied in this work have an elastic anisotropic nature, while the elastic anisotropy is not apparent. Figure 14 plots the 3D Young's modulus surfaces obtained by an open-source software package (AnisioVis)⁹⁰ of Zr₂GaC (a, b, c) and Hf₂GaC (d, e, f) at 0, 10, and 50 GPa, respectively. It can be observed that the shape begins to deviate from the sphere with an increase in pressure, and color varies in different regions, which indicates the elastic anisotropy of M₂GaC MAX phases. The color variation (dark blue to yellow) exhibits that elastic modulus increases with an increase in pressure, and obtained values are mentioned at the top of each 3D plot, which agrees well with the previously calculated results (see Fig. 10). The Young's modulus at 0 GPa pressure for Zr₂GaC and Hf₂GaC are 226.57 GPa and 266.68 GPa respectively. The pressure effect on the degree of spherical shape, the anisotropy of Hf₂GaC is bigger than Zr₂GaC (See Fig. 11b).

### Optical properties

The optical properties for the M₂GaC MAX phase (M = Zr, Hf) were determined for the first time by frequency-dependent dielectric functions within the photon energies up to 20 eV. The optical properties for the MAX phases are optically anisotropic⁹⁹,100. Thus, two polarization directions, <100> and <001>, were chosen to investigate the optical properties. The MAX phase compounds under this study are metallic in nature (see band structure) so, the term Drude (plasma frequency 3 eV and damping 0.05 eV) has a close relation to the band structure. Once the imaginary part is known, the real part can be derived using the Kramers–Kronig equation. Later, all the optical properties can be obtained using the Drude model. The optical properties for M₂GaC phases (M = Zr, Hf) at 0–50 GPa pressure.

| M₂AX  | Pressure (GPa) | ρ (g/cm³) | V₉ (10³ m/s) | V₅ (10³ m/s) | V₆ (10³ m/s) | T₉(K) | T₅(K) | References |
|-------|----------------|-----------|--------------|--------------|--------------|-------|-------|-----------|
| Zr₂GaC | 0              | 6.407     | 3.85         | 6.24         | 4.24         | 788   | 1481  |           |
|       | 10             | 6.683     | 4.03         | 6.79         | 4.46         | 816   | 1757  |           |
|       | 20             | 7.235     | 4.15         | 7.20         | 4.60         | 843   | 1997  |           |
|       | 30             | 7.558     | 4.20         | 7.47         | 4.67         | 868   | 2195  |           |
|       | 40             | 7.852     | 4.18         | 7.65         | 4.66         | 892   | 2343  |           |
|       | 50             | 8.128     | 3.94         | 7.61         | 4.41         | 915   | 2371  |           |
| Hf₂GaC | 0              | 10.85     | 3.21         | 5.18         | 3.54         | 720   | 1648  |           |
|       | 10             | 11.53     | 3.36         | 5.60         | 3.71         | 739   | 1931  |           |
|       | 20             | 12.09     | 3.42         | 5.88         | 3.79         | 757   | 2170  |           |
|       | 30             | 12.58     | 3.47         | 6.14         | 3.85         | 774   | 2395  |           |
|       | 40             | 13.02     | 3.50         | 6.35         | 3.90         | 791   | 2586  |           |
|       | 50             | 13.42     | 3.54         | 6.53         | 3.95         | 807   | 2769  |           |
| Nb₂AlC | 0              | 6.35      | 4.40         | 7.31         | 4.87         | 592   | 1800  |           |
|       | 10             | 6.88      | 4.35         | 7.46         | 4.93         | 612   | 1944  |           |
|       | 20             | 7.26      | 4.26         | 7.56         | 4.99         | 627   | 1976  |           |
| Hf₂AlN | 0              | 10.10     | 3.38         | 5.50         | 3.73         | 439   |       | 101      |
|       | 10             | 10.64     | 3.36         | 5.67         | 3.72         | 445   |       | 101      |
| Zr₂AlC | 0              | 5.56      | 4.22         | 6.89         | 4.66         | 544   |       | 101      |

Table 5. The computed density (ρ), transverse (V₉), longitudinal (V₅), mean (V₆) sound velocities, and Debye’s temperature (θ_D) for the M₂GaC phase (M = Zr, Hf) at 0–50 GPa pressure.

Dielectric constant. The real part of the dielectric constant ε₁(ω) is essential for optoelectronic devices because it corresponds to the primitivity component that measures the stored energy. The imaginary part of the dielectric constant ε₂(ω) gives the information about the optical system's energy reduction in the function of frequency. Figure 15a,b shows the real ε₁(ω) and imaginary part ε₂(ω) of dielectric constants calculated for the <100> and <001> polarization directions for M₂GaC. It is observed that the real part of dielectric constant (ε₁) approaches to zero from below, while the imaginary part (ε₂) gets to zero from above, which implies that the M₂GaC MAX phases are metallic in nature. In the real part of the dielectric constant, the spectra within the infrared region (1R ≤ 1.7 eV) has the highest dielectric constant for <100> polarization compared to <001> polarization due to intra-band transition of electron. The sharp peaks were observed in ε₁(ω) for Zr₂GaC and Hf₂GaC.

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phases along the <100> polarization at ∼1.01 eV and ∼1.04 eV, respectively. It is worth noticing that the spectra of $\varepsilon_1(\omega)$ for different polarization directions exhibit different features in the photon energy range. There is no significant difference observed for both MAX phases in the $\varepsilon_2(\omega)$ spectra for <100> and <001> polarization. Thus, we can deduce that the MAX phases studied here are optically anisotropic. Moreover, the value $\varepsilon_1(\omega)$ approached zero from below for polarization <100> at around 12.8–13.7 eV and for polarization <001> at photon energy ranges from 12.5 to 16.7 eV.

**Figure 13.** The phonon dispersion curve for Zr$_2$GaC at pressure a 0 GPa, b 30 GPa, and c 50 GPa, and for Hf$_2$GaC at pressure d 0 GPa, e 30 GPa, and f 50 GPa.
Loss function. The loss function is peak corresponds to the bulk plasma frequency ($\omega_p$), which appears where $\varepsilon_2 < 1$ and $\varepsilon_1$ approaches to zero. It is the energy loss of the first electron traversing through a material, and bulk plasma frequency ($\omega_p$) is obtained from the loss function spectrum. The studied $M_2GaC$ MAX phases become transparent if the frequency of incident light is higher than that of plasma frequency. By analyzing, the energy-loss function peaks of $Zr_2GaC$ and $Hf_2GaC$ phases was occurred at around 12.79 eV and 13.7 eV, respectively, for <100> polarization: and corresponding 14.00 eV and 15.61 eV for <001> polarization as shown in Fig. 16. It is noticed that the plasma frequent ($\omega_p$) of $M_2GaC$ for the <001> polarization is larger than that for <100> polarization. Moreover, energy loss spectra for $M_2GaC$ MAX phases show no peaks in the photon energy range of 0–10 eV due to large $\varepsilon_2(\omega)$ (see Fig. 15b).

Figure 14. 3D plot of Young's modulus (E) surface of $M_2GaC$ MAX phase ($M = Zr, Hf$) at various pressure.
Absorption coefficient. The absorption coefficient gives the knowledge about the efficiency of the solar energy conversion, which is important for solar cell material. It corresponds to the amount of light of a specific wavelength into a solid before getting absorbed. Figure 17 depicts the energy-based absorption ($\alpha$) spectra of $M_2GaC$ MAX phases. It is observed that the absorption spectra for both MAX phases are weak in the infrared region (I.R), increases monotonously in the visible region and dominant ultraviolet (UV) regions. The maximum value of $\alpha$ was observed for $Zr_2GaC$ and $Hf_2GaC$ at around 6.09 eV and 6.86 eV, respectively, for $<100>$ polarization; and corresponding 6.34 eV and 6.97 eV for $<001>$ polarization. Moreover, the light absorption of $M_2GaC$ in the $<001>$ polarization direction is larger than that for $<100>$ polarization, indicating their optically anisotropic nature. The rise in $\alpha$ was observed in the direction of the UV region, exhibits the high absorbent feature of the material. Based on the calculated absorption spectra of $M_2GaC$ MAX phases, it can be deduced that these materials are competing candidates for optoelectronic devices in both visible and UV regions.

Photoconductivity. Photoconductivity ($\sigma$) of material can be described as the increase in the electric conductivity due to absorbing photos. For $M_2GaC$ MAX phases $\sigma$ is shown in Fig. 18. It is noticed that for both MAX phases under this study, photoconductivity increases exponentially when the photo energy goes to 0 eV as expected for metals because there is no band gap present in the $M_2GaC$ MAX phases. A sharp dip in photoconductivity of $Zr_2GaC$ and $Hf_2GaC$ for $<100>$ polarization was observed at 0.37 eV and 0.39 eV, and that for polarization $<001>$ was observed at 0.26 eV and 0.20 eV, respectively. Peak heights for different polarization

![Figure 15.](image1.png)  
*Energy dependence of dielectric function a real part b imaginary part of $M_2GaC$ MAX phase ($M = Zr, Hf$).*

![Figure 16.](image2.png)  
*Loss function of $M_2GaC$ MAX phase ($M = Zr, Hf$) for $<100>$ and $<001>$ polarization.*
are different at various photon energies, and Zr$_2$GaC <001> gives the highest peak at 4.98 eV. It is concluded that M$_2$GaC MAX phases are photoconductive at near I.R, visible, and UV regions.

Reflectivity. Finally, reflectivity spectra of M$_2$GaC MAX phases for <100> and <001> polarization, as a function of incident light are demonstrated in Fig. 19. The reflectivity for M$_2$GaC MAX phases shows the highest reflectivity in the I.R region and visible region ranges from 4.4 to 13.10 eV and then approaches zero for both phases in the incident photon energy ranges from 19 to 22 eV. However, it is worth noticing that the reflectivity is almost constant for <100> polarization of Zr$_2$GaC and Hf$_2$GaC MAX phases within the visible region, and values are above 45% and should appear as a metallic gray color. It is known that materials having constant reflectivity in the visible regions with an average value of about 44% are capable of reflecting the solar light, which results in a reduction in solar heating in the visible light region$^{104}$. So, it may be concluded that Zr$_2$GaC and Hf$_2$GaC MAX phases can be used as the coating material for the purpose of solar heating reduction. However, the variable reflectivity within the visible region of different polarization indicated the optical anisotropy M$_2$GaC MAX phase$^{105}$.

The dependence of reflectance on the pressure of M$_2$GaC MAX phases was studied as well, and results for polarization <100> at a pressure range from 0 to 50 GPa is shown in Fig. 20. For the M$_2$GaC MAX phase, the reflectance exhibits less change in the moderate range of the I.R region ranging from 0 to 0.48 eV at all pressures and show variable reflectivity in the rest I.R region. It is noticed that the reflectivity increases with an increase in pressure in the I.R region. However, the reflectivity of M$_2$GaC decreased at higher pressure, but almost the same in the visible region then increases in the UV region more quickly and exhibits a higher value at 0 GPa.
reflectance at pressure range 0–50 GPa remains above 40% in the visible zone. Thus, it is concluded that M2GaC MAX phase materials are ideal for coating materials under high-pressure conditions to avoid solar heating in the <100> polarization direction.

**Conclusion**

The effect of pressure on structural stability, mechanical, electronic, phonon, and optical properties of M2GaC MAX phases (M = Zr and Hf) in the pressure range from 0 to 50 GPa were calculated by using first-principles calculations. The formation of enthalpy with respect to its most competing phases showed that M2GaC MAX phases are thermodynamically stable. The band structure and total density of states exhibited that M2GaC MAX phases are metallic in nature, with an increase in bandgap at the Fermi level with an increase in pressure. The DOS at EF in the pressure range of 0–50 GPa are Zr2GaC = 2.96–4.27 states/eV/unit > Hf2GaC = 2.47–2.60 states/eV/unit, which implies that the metallicity of Zr2GaC increased more than that of Hf2GaC with increasing the internal pressure. According to COHP analysis, M–C bonds are stronger than that M–Ga in both Zr2GaC and Hf2GaC MAX phases. The volume ratio and lattice parameters Zr2GaC and Hf2GaC decrease with increasing pressure, and the compressibility of Zr2GaC is better than that of Hf2GaC. Besides, the normalized bond lengths show that crystals compressed more easily along the M–Ga (Zr, Hf) direction under pressure. The effect of pressure on the mechanical properties of M2GaC MAX phases is pronounced. Both the Zr2GaC and Hf2GaC MAX phases revealed the brittleness behavior at 0 GPa pressure and tended to ductile when pressure increased from 10
to 50 GPa. Moreover, there is a linear increase in elastic constants, elastic moduli, Poisson’s ratio, and a decrease in Vickers hardness was observed with the increase in pressure. The calculated Vickers hardness is found to be 18.23 GPa and 20.99 GPa for Zr$_2$GaC and Hf$_2$GaC, respectively. The phonon dispersion curves have confirmed the dynamical stability of compounds in the given pressure range. The optical properties of the MAX phase compounds reveal some interesting information. The absorption spectra of M$_6$GaC increased to the maximum value in the visible region, and the UV region indicates its high absorbance capability and is suitable for optoelectronic devices in the visible and UV regions. Moreover, the reflectance curves show the constant values in the visible region with an average value above 44%. We conclude that these compounds can also be used as a coating material to avoid solar heating at even high pressure. To the author’s best knowledge, no study had been made to predict the mechanical, electronic, thermal, phonon, and optical properties of M$_6$GaC MAX phases under pressure. Hence, these results can serve as a reference for future theoretical and experimental research.

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Author contributions
Conceptualization, M.W.Q. and X.M.; methodology, M.W.Q and R.P.; software, X.M.; validation M.W.Q., X.M., G.T., and R.P.; formal analysis, M.W.Q., X.M., and R.P.; investigation, M.W.Q., G.T.; writing—original draft preparation, M.W.Q., and X.M.; writing—review and editing, M.W.Q., X.M., and R.P.; supervision, X.M. All authors have read and agreed to the published version of the manuscript.

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Competing interests
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Additional information
Correspondence and requests for materials should be addressed to X.M.

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