Density functional theory study of structural, mechanical, electronic and optical properties of MoAlX (X = B, C, N and O) compounds

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Abstract
The structural, mechanical, electronic and optical properties of MoAlX (X = B, C, N and O) were studied by density functional theory calculations. The hardness of MoAlB and MoAlN is 20.45 GPa and 9.03 GPa with softer and machinable character as opposed to other borides. The analysis of the band structure and density (DOS) of states shows that MoAlX compounds have a metallic nature. The electronic density difference plots show a spherical charge distribution with ionic bonding in MoAlB and oblate charge distribution in MoAlX (X = C, N and O) indicating covalent bonding. The optical properties of MoAlX are investigated. In the energy range up to ~15 eV, MoAlX possesses high reflectivity with the strongest absorption in the energy range of 0–35 eV. Furthermore, the plasma frequencies of MoAlX ranges from 21–24 eV and have the ability to change from metallic to dielectric response should the frequency of the incident light be greater than 24 eV.

1. Introduction

Binary transition metals borides (MB) are a group of transition metals with light covalent bonding elements, where M denotes transition metals and B is boron respectively. The combination of metals with non-metal often leads to novel materials that can be used in different spheres of applications. The transition metal borides (MB) are currently applied in high-temperature structural applications and this attributes to their phenomenal properties namely: high melting point, high hardness, outstanding thermal stability and electrical conductivity [1–3]. Despite their advantages, they possess poor oxidation resistance and brittleness that hampers the application. In recent years, the addition of group 3A to 4A elements to the MB structures forming a ternary Nano-laminated borides (MAB) are predicted to manage the above problem. MoAlB consists of an orthorhombic structure with the space group of Cmcm similar to MAX phases, where, A is a group IIIA–IVA element and X indicate nitrogen or carbon [4–6]. In addition, alternative layers of MoB and Al can be formed [7]. The layered ternary MoAB structure provides exceptional physical and mechanical properties, such as good radiation tolerance, high-electrical conductivity and thermal stability at elevated temperatures [4, 7–9]. Furthermore, MoAlB indicates enhanced oxidation resistance at high-temperature environments due to its alumina scale formation in the air [7–9] and this is confirmed experimentally by Koto et al [7]. Since then, theoretical and experimental studies have been conducted on MoAlB structure [3, 4, 6, 8, 10–17]. The calculated hardness values of MoAlB are 12.71 GPa [10] and 11.6 GPa [12] consistent with the MoAlB experimental hardness of 13.6 GPa [17] and 10.3 GPa [7]. All the MoAlB hardness are relatively low compared to other borides such as: MoB (23 GPa and MoB2, (21–27 GPa) [18]. Therefore, MoAlB is soft and radiation tolerant as opposed to other borides. To improve and understand the mechanical and optical properties of MB, other elements from group 3A to 7A such as MoAlX (X = C, N and O) are considered for the first time. This study is worthy to be conducted to produce novel materials for various industrial applications. We substitute X with B, C, N and O elements because they belong to the same group (XIII-XVI) across the periodic table with similar chemical and physical properties and can improve the MoAlX properties. On the other hand, these compounds have not been studied in detail. For example, analysis of the heats of formation, Cauchy pressure, shear modulus, bulk modulus, Young’s modulus, machinability index, hardness, anisotropy in elastic moduli and optical properties

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are still sparse. In this article, the mechanical, electronic and optical properties of MoAlX ternaries are calculated and compared with the available experimental values using the \textit{ab-initio} density functional theory method.

2. Computational details

The density functional theory (DFT) \cite{19} calculations implemented in Cambridge Serial Total Energy Package (CASTEP) code \cite{20} were performed for structural, mechanical, electronic and optical properties of MoAlX (X = B, C, N and O) compounds in an orthorhombic crystal phase. The calculations are based on generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) \cite{21} functional for the exchange and correlation energies. The core and valence interactions are represented by the ultra-soft pseudopotentials \cite{22}. In order to perform pseudo atomic calculations, the following valence electron configurations have been considered: [Kr] 4d\(^5\) 5s\(^1\) for Mo, [Ne] 3s\(^2\) 3p\(^3\) for Al, [He] 2s\(^2\) 2p\(^1\) for B, [He] 2s\(^2\) 2p\(^2\) for C, [He] 2s\(^2\) 2p\(^3\) for N and [He] 2s\(^2\) 2p\(^4\) atoms. To determine a suitable k-points and cutoff energy, single point energy calculations were performed for different k-points at fixed kinetic energy cutoffs for each compounds. On the other hand, a total energy calculation at fixed k-points for each compounds (determined above) while the k-points was varied. We show the convergence of the total energy difference with respect to the k-points sampling (a) and total energy difference versus the cutoff energies (b) indicated in figure 1. In MoAlX compounds, the converged k-points sampling in the Brillouin zone was set to \(24 \times 6 \times 25\) based on the Monkhorst-Pack method \cite{23} whereas, a suitable cutoff energy of 1000 eV was employed to represent the electronic wave function (figure 1(b)) during geometry optimization, the smearing width was set to 0.001 eV for accurate magnetic moments with a maximum force of 0.01 eV \(\text{Å}\), displacement of 0.0005 \(\text{Å}\), convergence tolerance of \(5.0 \times 10^{-6}\) eV per atom and the maximum stress of 0.02 GPa were used for MoAlX compounds.

3. Results and discussion

3.1. Structural stability

Figure 2 indicates the crystal structure of MoAlX (X = B, C, N and O) unit cell. MoAlX undertakes an orthorhombic crystal phase with the space group of Cmcm \cite{10, 17}. The equilibrium lattice constants, volume (\(\text{Å}^3\)), bulk modulus (GPa), density (g cm\(^{-3}\)), heats of formation (KeV/atom), magnetic moment (\(\mu_B/\text{atom}\)), elastic constants (\(C_{ij}\)) of MoAlX and available experimental-theoretical lattice constants of MoAlB are listed in table 1. We note that MoAlB has comparable lattice constants with experimental and theoretical data. Therefore, our first principle calculations are reliable.

![Figure 1](image-url)
The density of a compound plays a significant role in determining a material's use in lightweight applications such as the aerospace industry. Furthermore, we have calculated the density of the MoAlX compounds as

$$\rho = \frac{M_W \times N}{Vol \times A_0}$$

(1)

where $Vol$ is the volume of the unit cell, $M_W$ is the average molecular weight of the elements in the unit cell, $N$ is the total number of atoms and $A_0$ is the Avogadro’s number ($6.022 \times 10^{23}$). The densities of MoAlB, MoAlC, MoAlN and MoAlO (6.41 g cm$^{-3}$, 6.38 g cm$^{-3}$, 6.71 g cm$^{-3}$ and 6.44 g cm$^{-3}$) are higher than L12 NiAl (6.14 g cm$^{-3}$) [24] usually used for aerospace industry. Therefore, these particular materials may be limited in this application above.

The heats of formation $\Delta H_f$ determine the energetic stability of a material during the formation of its elements and is defined here as

$$\Delta H_f = \left[ \frac{E(\text{MoAlX}) - (aE_{Mo}^f + bE_{Al}^f + cE_{X}^f)}{a + b + c} \right]$$

(2)

where $E(\text{MoAlX})$ denotes the total energy of the structures whereas, $E_{X}^f$ are the energies of each individual metal species in their ground states where $X = B, C, N$ and O, $a$, $b$ and $c$ are the number of atoms for individual metals and non-metals [24, 25]. The heats of formation that is positive describes the thermodynamic instability whilst negative heats formation indicates energetically stable materials. It is clear that all the MoAlX compounds have negative heats of formation and therefore, are thermodynamically stable with possible experimental
Furthermore, these compounds possess zero and theoretical study of ref deformation. The MoAlB and MoAlC compounds shows that orthorhombic compounds possess nine independent elastic constants along compression resistance along (3.2. Mechanical and elastic properties

The mechanical properties of a solid describe the essential information regarding the elastic behavior of materials. To achieve a possible experimental synthesis, the mechanical stability of MoAlX (X = B, C, N and O) compounds are analyzed through the elastic properties. Specifically, the independent elastic constants are calculated to describe the mechanical resistance in a crystal when external stresses are applied. The calculation of elastic constants is done by applying a small strain to the unit cell to determine the total energy variation \[ E[100] \]

\[ \frac{\Delta E}{V_0} = \frac{1}{2} \sum_{i,j=1}^{9} C_{ij} \varepsilon_i \varepsilon_j \]  

(3) 

Where \( \Delta E \) is the total energy difference between the deformed and initial unit cell, \( V_0 \) is the original cell volume, \( C_{ij} \) (\( i,j = 1 \) to 9) are the elastic constants and \( \varepsilon_i \) or \( \varepsilon_j \) is the strain. Due to symmetric conditions, orthorhombic compounds possess nine independent elastic constants \( (C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55} \text{ and } C_{66}) \) and were calculated based on stress–strain method [24]. The calculated elastic constants are listed in table 2. According to Born–Huang conditions [28], orthorhombic compounds needs to fulfil the mechanical stability criteria below:

\[
\begin{align*}
(G_{11} + C_{22} - 2G_{12}) > 0, & \quad (G_{11} + C_{33} - 2G_{13}) > 0, & \quad (G_{22} + C_{33} - 2G_{23}) > 0, \\
C_{11} > 0, & \quad C_{22} > 0, & \quad C_{44} > 0, & \quad C_{55} > 0, & \quad C_{66} > 0, \\
(C_{11} + C_{22}C_{33} + 2C_{44} + 2C_{55} + 2C_{23}) > 0.
\end{align*}
\]

(4)

The elastic constants in MoAlB are positive and satisfy the mechanical stability criteria in accord with the theoretical study of ref [10]. Therefore, MoAlB can be synthesized experimentally (confirms the heat of formation results in table 1) as opposed to MoAlC, MoAlN and MoAlO compounds that are mechanically unstable due to negative \( C_{66}, C_{13}, C_{44} \) and \( C_{55} \). The elastic constants \( C_{11} \) and \( C_{33} \) are essential to describe linear compression resistance along \([100]\) and \([001]\) directions [29] whereas, \( C_{11} \) and \( C_{12} \) describe the compressibility in materials. In MoAlB, we note that \( C_{11} \) is smaller than \( C_{33} \) and larger than \( C_{22} \), therefore good bonding strength/compressibility is expected in \([100]\) direction more than \([001]\) with anisotropic behavior. On the other hand, MoAlC and MoAlN indicate that \( C_{11} \) is larger than \( C_{22} \) and \( C_{33} \). This indicates that MoAlX (X = C and N) possess relatively weak bonding strength with mechanically isotropic conduct. Moreover, we note that MoAlX compounds have \( C_{11} > C_{12} \) and therefore are less compressible. The elastic constant \( C_{44} \) indicates the resistance to shear deformation where stress is applied to the \((100)\) plane of a compound. In MoAlB compound, it is clear that \( C_{44} \) is greater as opposed to MoAlC, MoAlN and MoAlO. Therefore, MoAlB is more resistant to shear deformation. The MoAlB and MoAlC compounds shows that \( C_{44} \) is higher than \( C_{66} \), indicating that the shear along the \((100)\) plane is difficult relative to the shear along the \((001)\) plane. On the other hand, MoAlN and MoAlO indicate \( C_{44} \) lower than \( C_{66} \) and therefore, the shear along \((100)\) is relatively simple as opposed to shear along \((001)\). From the \( C_{ij} \) results, we computed the bulk modulus \( B \) and shear modulus \( G \), Young’s modulus \( E \), Poisson’s ratio \( \nu \) and hardness \( H \) of the orthorhombic compounds using Voigt- Reuss- Hill (VRH) method [30, 31] with the equations below:

| Compounds | MoAlB Present | MoAlB theor | MoAlC | MoAlN | MoAlO |
|-----------|---------------|-------------|-------|-------|-------|
| \( C_{11} \) | 366.65 | 347 [11] | 450.48 | 538.32 | 305.91 |
| \( C_{12} \) | 141.76 | 142 [11] | 117.13 | 102.34 | 94.21 |
| \( C_{13} \) | 146.66 | 145 [11] | 5.08 | −32.19 | 51.59 |
| \( C_{22} \) | 321.38 | 325 [11] | 240.15 | 219.69 | 306.14 |
| \( C_{23} \) | 125.39 | 120 [11] | 139.40 | 157.56 | 181.82 |
| \( C_{33} \) | 411.32 | 403 [11] | 307.62 | 224.25 | 225.72 |
| \( C_{44} \) | 194.33 | 191 [11] | 75.18 | 65.74 | −166.45 |
| \( C_{55} \) | 161.78 | 160 [11] | 86.08 | 89.11 | −19.50 |
| \( C_{66} \) | 168.10 | 170 [11] | −980.28 | 73.25 | 82.77 |
Table 3. The calculated Bulk modulus (B), Shear modulus (G), Young’s modulus (E), Cauchy pressure (C12-C44) in GPa Poisson’s ratio (\(\nu\)), Vickers hardness (HV) and machinability index (\(\mu_M\)) for MoAlX. The Voigt, Reuss and Hill are the approximation respectively.

| Compounds | MoAlB | MoAlC | MoAlN | MoAlO |
|-----------|-------|-------|-------|-------|
| \(B_v(\text{GPa})\) | 214.11 | 169.05 | 159.74 | 165.89 |
| \(B_g(\text{GPa})\) | 211.78 | 166.89 | 144.49 | 154.44 |
| \(B_h(\text{GPa})\) | 212.78 | 167.97 | 152.12 | 160.17 |
| \(G_v(\text{GPa})\) | 150.35 | -114.70 | 95.92 | 15.38 |
| \(G_g(\text{GPa})\) | 142.29 | 104.17 | 56.64 | -416.81 |
| \(G_h(\text{GPa})\) | 146.32 | 5.26 | 76.28 | -201.72 |
| \(E_v(\text{GPa})\) | 357.15 | 15.95 | 196.08 | 1043 |
| \(B_v/G_h\) | 1.45 | -31.93 | 1.99 | -0.79 |
| \(\nu\) | 0.22 | 0.51 | 0.29 | 1.59 |
| \(C_{12}-C_{44}\) | -52.57 | 41.96 | 36.6 | 260.66 |
| \(H_v\) | 20.45 | - | 9.03 | - |
| \(B_v/C_{44}\) | 1.09 | 2.23 | 2.31 | -0.96 |
| \(A_1\) | 1.60 | 0.40 | 0.32 | -1.94 |
| \(A_2\) | 1.34 | 1.38 | 2.77 | -0.46 |
| \(A_3\) | 1.66 | -8.59 | -0.92 | 0.78 |
| \(A_u\) | 0.29 | -10.49 | 3.57 | -5.09 |

\[ B_v = \left( \frac{B_v + B_h}{2} \right) \]

\[ B_h = \left( \frac{B_v + B_R}{2} \right) \]

\[ B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})} \]

\[ G_V = \frac{1}{15}(G_{11} + C_{22} + C_{33} - G_{12} - G_{13} - C_{23}) \]

\[ + \frac{1}{5}(C_{44} + C_{55} + C_{66}) \]

\[ G_R = \left( \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})} \right) \]

\[ E_v = \left( \frac{9B_hG_h}{3B_h + G_h} \right) \]

\[ \nu = \left( \frac{3B_h + 2G_h}{2(3B_h + G_h)} \right) \]

\[ H_v = 0.92K^{0.13}G^{0.708} \]

where \(S_i\) corresponds to elastic compliances and their values are obtained from an inversion of the elastic constant matrix, \(S = C^{-1}\). The Vickers hardness described by Tian et al [32] is represented as \(HV\), where \(K = G_{12}/B_{12}\). The bulk modulus \(B_{12}\), shear modulus \(G\), Young’s modulus \(E\), in GPa, a ratio of the bulk to shear, Cauchy pressure \((C_{12}-C_{44})\), Poisson’s ratio, Vickers hardness \((HV)\) and elastic anisotropic factor \((A)\) of MoAlX compounds are shown in Table 3. The calculated bulk modulus \(B_h\) of MoAlB \((212.78\text{ GPa})\) is in accord with the previous theoretical data of MoAlB \((209\text{ GPa})\) [11] whereas, the bulk modulus of MoAlC, MoAlN and MoAlO are 167.97 GPa, 152.12 GPa and 160.17 GPa. Furthermore, \(B_h\) indicates a measure of resistance to volume change when pressure is applied with MoAlB having higher \(B_h\) compared to others and therefore, more resistant to volume change. The shear modulus is closely related to the resistance of the material to plastic deformation [34]. The higher the shear modulus \(G\), the stronger is the resistance to reversible deformation on
shear stress, whilst Young’s modulus $E$ indicates how stiff the material is under external stress [35]. We note that the calculated $G$ and $E$ of MoAlB (146.32 GPa and 357.15 GPa) are in good agreement with previous theoretical data of MoAlB ($G = 144$ GPa) [11]. In addition, this compound is more resistant to reversible deformation and possesses stiff characteristics. Pugh’s ratio [33, 36, 37] represents the ductile/brittle nature of a material. If the value of $B/G$ is higher than 1.75, the material is ductile otherwise it would be brittle. In this case, the $B/G$ values of MoAlB (1.45), MoAlC (−31.93), MoAlO (−0.79) compounds are all brittle compared to the MoAlN (1.99) that is ductile respectively. This is consistent with the previous theoretical results of MoAlB (1.45) [11]. The brittle MoAlX materials can be improved by doping or pressure increase [38]. The Cauchy pressure $C' = C_{12} - C_{44}$ also shows the ductile/brittle nature of a compound. A negative Cauchy pressure suggests brittleness while a positive one implies ductility in a material [39, 40]. It is seen that the Cauchy pressure of MoAlB is negative whilst, MoAlN is positive indicating brittleness and ductility behavior consistent with the $B/G$ ratio above. Whereas, MoAlC and MoAlO have negative Cauchy pressure contradicting the results of B/G ratio. Moreover, another parameter to identify if the material is brittle/ductile is the Poisson’s ratio ($\nu$). For metals, ceramics and polymers with $\nu > 0.25$ are expected to be ductile otherwise brittle. Our MoAlB (0.22) and MoAlN (0.29) results indicate that $\nu < 0.25$ and $\nu > 0.25$, therefore are brittle and ductile in accord to the B/G ratio and Cauchy pressure. Industrial machinability includes the cutting of materials, nature of cutting, cutting fluids and geometry at low cost. Machinability is calculated using the equation below [29, 41]:

$$\mu_B = \left( \frac{B}{C_{44}} \right)$$

(14)

Machinability can be used as a measure of plasticity and lubrication in a material [42–45], from equation (15) above, we can say that the larger the value of $B/C_{44}$ indicates great lubricating properties, high plasticity and less friction in the material. The $B/C_{44}$ values of MoAlB (1.09), MoAlC (2.23), MoAlN (2.31) and MoAlO (−0.96) are in the range of −0.96 to 2.31. The MoAlN possess relatively good lubricating properties and high plasticity under machinery as opposed to other compounds due to larger $B/C_{44}$. To further analyze the plastic and elastic properties of the MoAlX compounds, Vickers hardness ($H_V$) was calculated in table 3. It was observed that the hardness values range from 9.03 GPa to 20.45 GPa. The computed MoAlB (20.45 GPa) agrees well with other borides including MoB (23 GPa MoB$_x$ (21 GPa-27 GPa)) [18] but nearly twice the value compared to the experimental MoAlB (11.4 GPa-13.6 GPa) by Sankalp et al [7] and theoretical MoAlB (12.7 GPa) by Li et al [10]. This may be due to the different use of plane-wave energy cutoff energy and k-points. In this manuscript, we applied a deep plane-wave energy cutoff of 1000 eV and the k-points of 24 x 6 x 25 as opposed to 400 eV [11]. Therefore, MoAlB is considered to be a hard material compared to other MoAlX (X = C, N and O) compounds. Elastic anisotropy is linked with micro-cracks in materials and is essential in engineering applications [46, 47].

The shear anisotropic factor ($A_1, A_2$ and $A_3$) corresponds to a measure of the degree of anisotropy defined below

$$A_1 = \left( \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \right)$$

(15)

for shear anisotropy ($A_i$) in {100} plane between (011) and (010),

$$A_2 = \left( \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \right)$$

(16)

shear anisotropy ($A_j$) in {010} plane between (011) and (001) and

$$A_3 = \left( \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \right)$$

(17)

shear anisotropy ($A_k$) in {001} plane between (110) and (100)

$$A^U = \frac{5G_U}{G_R} + \frac{B_U}{B_R} - 6 \geq 0$$

(18)

Materials with $A_1, A_2, A_3 > 1$ or $A_1, A_2, A_3 < 1$ are anisotropic whereas, $A^U = A_1 = A_2 = A_3 = 1$ indicates isotropic behavior [48, 49]. The computed $A^U$ values of the MoAlX (X = B, C, N and O) compounds are found in table 3. The shear anisotropic factors of MoAlB are ($A_1 = 1.60, A_2 = 1.34$ and $A_3 = 1.66$), MoAlC ($A_1 = 0.40, A_2 = 1.34$ and $A_3 = −8.59$), MoAlN ($A_1 = 0.32, A_2 = 2.77$ and $A_3 = −0.92$) and MoAlO ($A_1 = −1.94, A_2 = −0.46$ and $A_3 = 0.78$). The shear anisotropic factors of MoAlB are in agreement with the previous theoretical MoAlB ($A_1 = 1.67, A_2 = 1.33$ and $A_3 = 1.75$) [12]. We note that all the investigated MoAlX compounds have an anisotropic behavior due to $1 < A^U < 1$.

3.3. Electronic and magnetic properties

In this section, we describe both the electronic and magnetic properties of the MoAlX (X = B, C, N and O) to gain a deeper understanding of the nature of bonding in these materials. The computed magnetic moments are indicated in table 1. We find that all the thermodynamically stable MoAlX have zero or negligible magnetic
moments. Therefore, these compounds are non-magnetic. Electronic properties assume an essential part in justifying the stability and magnetic moment of materials [50]. The calculated density of states and band structures for the MoAlX compounds are shown in figures 3 and 4. We find an overlap in MoAlX states in the vicinity of the Fermi energy ($E_f$) level without a bandgap between the valence-conduction bands, indicating that they possess a metallic behavior. This attributes to the major contribution of Mo-d states and partial B-p states at the $E_f$ level with Al-contribution being negligible in MoAlB, MoAlC, MoAlN and MoAlO compounds. This observation is in agreement with the previous study of MAX compounds [10, 51, 52]. The DOS profiles of MoAlX shows a strong hybridization between Mo-d and B-p, C-p, N-p and O-p states predicting covalent bonds.

Figure 3. Total and partial density of states (TDOS and PDOS) of MoAlB (a), MoAlC (b), MoAlN (c) and MoAlO (d) compounds. The Fermi energy is represented by the dash lines.

Figure 4. Total and partial density of states (TDOS and PDOS) of MoAlB (a), MoAlC (b), MoAlN (c) and MoAlO (d) compounds. The Fermi energy is represented by the dash lines.
in Mo-B, Mo-C, Mo-N and Mo-O respectively. Moreover, the spin-up and down states in MoAlX are symmetric with no net spin polarization shown in figure 3. This symmetric balance in the spin-up and down states cancel the magnetic moments associated with the electron spin, this confirms the zero or negligible magnetic moments in these compounds (table 1).

3.4. Electron charge density distribution
In this section, we discuss the bonding behavior of MoAlX (X = B, C, N and O) compounds through their electron charge density differences [53, 54] plots calculated here. Figure 5 indicates the electron density difference distribution for all the four MoAlX compounds. The color scales found on the charge density maps show the total electron density in these compounds. The high charge densities (electron access) are represented by blue color and the red color indicates low charge densities (electron deficiency). We note that in MoAlX compounds, the charge accumulation is mainly observed around both nearest-neighbor of B-Mo, C-Mo, N-Mo, O-Mo, B-B, C-C, N-N, O-O, Al-Al and B-Al bonds with covalent hybridization formed between them. This is in agreement with the DOS results. Comparing the charge density maps of MoAlB, MoAlC, MoAlN and MoAlO compounds, it is observed that the B, C, N and O atoms have high electron density as opposed to Mo and Al. Furthermore, Mo and Al atoms are electron deficient in all MoAlX compounds. It is seen that MoAlB possess a spherical charge distribution showing a relatively ionic contribution to the bonding whereas, an oblate charge distribution is prominent in MoAlX (X = C, N and O) suggesting directional or covalent bonding in C-Mo, N-Mo, B-B, B-Al, Mo-Al, Mo-Mo and Al-Al. This is in accord with the observation of Naher et al [29].

3.5. Optical properties
Optical properties present vital information in the design and examination of optoelectronic and photovoltaic applications such as detectors, light sources and solar panels [55]. Moreover, these properties can be described using optical parameters such as dielectric function, conductivity, reflectivity, absorbance, refractive index and loss function. Dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) is one of the important parameters that can derive all other properties mentioned above, where \( \varepsilon_1(\omega) \) is the real part and \( i\varepsilon_2(\omega) \) is the imaginary part defined as:

\[
i\varepsilon_2(\omega) = \frac{2\varepsilon^2\pi}{\Omega\varepsilon_0} \sum_{k, \nu, \epsilon} \left| \langle \varphi_{E_k}^{\nu} | \hat{u} | \varphi_{E_k}^{\epsilon} \rangle \right|^2 \varepsilon_k \varepsilon_k^* \delta(\varepsilon_k - \varepsilon_k^* - \varepsilon)
\]  

where \( (\omega) \) is the frequency of light, \( \Omega \) is the unit cell volume, \( e \) is the charge of an electron, \( \hat{u} \) vector defines the polarization of the incident electric field, \( \varphi_{E_k}^{\nu} \) and \( \varphi_{E_k}^{\epsilon} \) represent the valence and conduction bands wave function at \( k \). Kramers-Kronig relation is applied on the imaginary part of the dielectric function to derive the real part \( \varepsilon_1(\omega) \). The imaginary part consists of the intra and inter-bands transition respectively, where the Intra-band transitions play a vital role in low energy infrared part of the spectra. On the other hand, the inter-band term relies on the electronic properties of a material [29, 56].
This parameter $\varepsilon(\omega)$ describes the material’s response to the incident electromagnetic wave of light. Since MoAlX ($X = B, C, N$ and $O$) compounds are elastically anisotropic, a direction dependence can be suggested from the optical parameters. We present the optical properties for MoAlX compounds in figures 6(a)–(i). In MoAlX compounds, a polarization direction $(100)$ of the incident electric field was used throughout. The electronic properties showed that all MoAlX compounds are metallic and therefore a Drude damping correction is crucial\cite{57,58}. All the optical constants of MoAlX compounds have been calculated with a Drude damping of 0.05 eV and a plasma frequency of 3 eV\cite{10}. The dielectric parameter of MoAlX compounds are found in figures 6(a)–(b), the real and imaginary parts, (c and d) Conductivity (real and imaginary parts), (e and f) Refractive index $\eta(\omega)$ and $K(\omega)$, (g) Absorbance $\alpha(\omega)$, (h) Loss function $L(\omega)$ and (i) Reflectivity $R(\omega)$.

![Figure 6. Optical properties of MoAlX (X = B, C, N and O) compounds are (a and b) dielectric functions $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ for real and imaginary parts, (c and d) Conductivity (real and imaginary parts), (e and f) Refractive index $\eta(\omega)$ and $K(\omega)$, (g) Absorbance $\alpha(\omega)$, (h) Loss function $L(\omega)$ and (i) Reflectivity $R(\omega)$.](image-url)
refractive index is large with a high ability to absorb radiation. In addition, the refractive index decrease with an increase in energy (0–50 eV). This observations agree with the studies by Naher et al [29]. Moreover, high refractive index materials play a vital role in light-emitting display devices due to their excellent optoelectronic properties. Absorbance is an optical parameter to describe the optimum solar energy conversion. Figure 6(g) shows the absorption spectra of MoAlX as a function of the photon energy. We observe two peaks at 10 eV and 37 eV in MoAlX compounds. The calculated peak of MoAlB located at 10 eV is in accord with the previous theoretical data of MoAlB (9.4 eV) [10]. It is noted that the absorption spectra starts at zero photon energy due to their metallic characters and increases sharply to the first broad peaks of 250000−350000 cm−1 at 10 eV. Then it decreases to approach zero at 35 eV and increase to the second-highest sharp peaks of 250000−500000 cm−1 at 37 eV. Therefore, the photon energy range of 0–35 eV suggests a reasonable absorbing feature to ultraviolet radiation in MoAlX. The electron energy loss function $L(\omega)$ guides the effective Coulomb interaction in a solid and also describes the optical spectra of a material. Figure 6(h) presents the electron energy loss curves of MoAlX with the highest peak commonly known as the plasma frequency [55] that represents the plasma resonance. This resonance attributes to the collective charge excitation when an electron traverse a solid. In MoAlX compounds, we note that the plasma frequency peaks of $L(\omega)$ are located at 21–24 eV respectively. The calculated plasma frequency peak for MoAlB (21 eV) in agreement with the previous theoretical data MoAlB (20.4 eV) of Li et al [10] and therefore confirms the reliability of our models. These sharp peaks in the loss function correspond to the reduction of absorption in figure 6(g). If the incident light energy is greater than the plasma frequency peaks, MoAlX compounds are expected to be transparent and undergo transition from metallic to dielectric response. These observations are in accord with the theoretical studies of Li et al [10] and Naher et al [29].

Figure 6(i) presents the reflectivity spectra for all MoAlX compounds as a function of photon energy. In MoAlX compounds, the reflectivity spectra start from zero frequency at about 0.99, decreases to reach the first minimum between 0–15 eV and then decreases with increasing photon energy approaching zero. Therefore, MoAlX possesses high reflectivity in the energy range up to ~15 eV and is in accord with the previous study of the calculated MoAlB (~19 eV) compound [10]. Therefore, these MoAlX compounds have the potential to be used in reflective solar coating applications.

4. Conclusion

Density functional theory calculations have been executed to study the structural, mechanical, electronic and optical properties of the MoAlX (X = B, C, N and O) compounds. The calculated lattice parameters of MoAlB are in accord with the available experimental and theoretical values and therefore, confirming the accuracy of our model. The heats of formation for all the compounds were observed to be negative, indicating thermodynamic stability. The electronic structures of MoAlX show metallic behavior with low DOS visible at the Fermi energy level indicating structural stability, confirming the heats of formation results. The charge density difference plots show a spherical charge distribution with ionic bonding in MoAlB whereas in MoAlX (X = C, N and O) compounds, an oblate charge distribution is observed indicating covalent bonding. The optical properties are examined. MoAlX possesses high reflectivity in the energy range up to ~15 eV and their plasma frequencies are 21–24 eV. In addition, MoAlX compounds are highly conductive at a low energy range with an expected metallic to dielectric transition, if the incident light has a frequency greater than 21–24 eV. Furthermore, MoAlX compounds can be used in engineering and optoelectronic applications attributing to good structural, electronic and optical properties respectively. We are optimistic that this study will inspire researchers to investigate these interesting materials in further detail in future, both theoretically and experimentally.

Acknowledgments

All the calculations have been performed in University of South Africa (UNISA) using the high performance computing facilities.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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