Investigation of LaAlO₃ pervoskite compound for optoelectronic and thermoelectric devices under pressure

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Abstract
The electronic, optical and thermoelectric properties of LaAlO₃ are studied under different pressure ranges (0–40 GPa) by using the full potential linear augmented plane wave method (FP-LAW). Calculations are done by Perdew–Burke–Ernzerhof generalized gradient approximation (PBEsol-GGA) by utilizing Wien 2k code. It was observed that with the increase of pressure band gap increased and the nature of band gap transform from indirect to direct. In Optical properties, optical conductivity, refractive index, absorption coefficient, and dielectric function are calculated at different pressures. Thermoelectric properties have been studied at temperature (150–800 K) and pressure (0–40 GPa) by using Boltz Trap code. At 800 K the values of power factor were 6.831 W K⁻² cm. s and 22.13 W K⁻² cm. s, respectively. Figure of merit was achieved up to 0.6. Results revealed that LaAlO₃ is a suitable candidate for optoelectronic and thermoelectric devices.

1. Introduction
Perovskite oxides are versatile compounds which display diverse metal–insulator transitions, superconductivity, ferroelectricity, piezoelectricity, structural phase transition sequences and thermoelectric properties. Lanthanum Aluminates (LaAlO₃) have potential innovative applications because of its unique properties. LaAlO₃ compound is a favourable candidate due to most significant properties like it has wide band gap 4.6 to 5.6 eV, high dielectric constant [1, 2] and thermal stability [3–6]. Thermal stability increases on annealing of metal oxide–semiconductor field effect transistor (MOSFET). LAO can be utilized as a substrate for high temperature superconducting layers due to best insulating buffer [7]. The wide band gap and transparency of LaAlO₃ is beneficial and used for optical or laser-host applications. Many researchers examined the electronic, optical and thermoelectric properties of perovskite compounds [7–10]. Roosmalen et al analyzed the structure of SrZrO₃ in 1992 [9]. Baudali et al in 2009 computed the structural, electronic, optical and thermal properties of SrTiO₃ [10]. Theoretical work on the optoelectric properties of the LaAlO₃ still not completely investigated under pressure. In literature, by using thermoelectric potential various semimetals, semiconductors, ceramics and Nanocomposites are evaluated. However, thermoelectric properties of BiBO₃, BiAlO₃ and LaAlO₃ are also studied [11]. In the recent past years, the perovskite compounds of different classes such as BaClO₃ [12], BaPaO₃ under different pressures [13], paramagnetic perovskites such as PbTaO₃ [14] and inverse perovskites [15] have been paid considerable attention to investigate the structural, electronic, mechanical and thermodynamic properties. In this study the influence of pressure on electronic, optical and thermoelectric properties of Lanthanum Aluminates (LaAlO₃) are studied. The Best thermoelectric efficiency of materials is evaluated by power-factor (PF) σS² and figure of merit (ZT) [16]. In this work paper, the combination of different strategic
parameters is used to calculate the ZT parameter. The prime idea to achieve this involves the minimization of the lattice contribution towards thermal conductivity. Electronic and optical properties are also calculated.

2. Computational method

The present calculations are performed by solving the Kohn–Sham equations [14] in the frame work of density functional theory (DFT) approach as presented in the WIEN2k code [15, 16]. For the thermoelectric properties BoltsTrap code was used for calculations. The muffin-tin radii for La, Al and O are fixed at 2.1, 1.7 and 1.9 a.u., respectively in these calculations. The cubic structure of LaAlO3 optimized with space group pm-3m (221) by means of Perdew–Burke–Ernzerhof- generalized gradient approximation (PBEsol- GGA) that is used to evaluate structural properties [17, 18]. Atoms are positioned as La present at the corner 1a (0, 0, 0), Al is body centered atom 1b (0.5, 0.5, 0.5), O at the faces 3c (0, 0.5, 0.5), (0.5, 0, 0.5), (0.5, 0.5, 0) in cubic unit cell. By using the 1000 k mesh point are achieved for the determination of structural properties. BoltzTraP code is used to calculate thermoelectric properties [19].

3. Results and discussions

3.1. Electronic properties

Electronic properties of LaAlO3 are discussed at various pressures. It was observed that compression on the system increases the band gap. The electronic band gap is found by the distance between the states of the conduction band (CBM) minima and valance band maxima (VBM). At 0 pressure, the indirect band gap was obtained due to bottom point of conduction band at Γ and uppermost point of valance band at M in Brillion zone as shown in figure 1 (a). By increasing the pressure from 0–40 GPa, electronic band gap increases from 3.46 eV to 3.56 eV and shifts from indirect to direct band gap as demonstrated in figure 1. The Calculated results of LaAlO3 electronic band structure are comparable with the experimental result of Feng et al [20]. The estimated band gaps are in good agreement by previous, theoretical outcomes [21–25]. Lee et al stated that if bond length and power of covalent bond increases then bonding energy decreases hence it has smaller band gap [26]. In figures 1(a)–(d), shown that band gap is increasing by decreasing the bond length at different pressures which is comparable with conclusion of Lee et al The total density of states, (TDOS) and partial density of states (PDOS) of LaAlO3, under the applied pressure are shown in figures 2 and 3.

In PDOS, the La-5p states and O-2p state is coinciding with the fermi level it has been seen that the aluminium atoms don’t affect much in the electronic band configuration. In general, due to the electronegativity of oxides the beginning of the wide band gap occurs [27–29]. Density of states is separated into three regions, lower valance band (LVB), upper valance band (UVB) and third region which is conduction band. In these figures, region of lower valance band is from 0 to −4 eV and of upper valance band starts from −4 to −8 eV. Figure 3(d) shows that in the lower valance band region Al-p show dominant peaks instead the sub state of La and O. The upper valance band shows that La-5p and O-2p are close to the fermi level and display the large contribution in this region. In conduction band the main influence is due to the La-p. The Conduction band is formed due to the unoccupied and partially, occupied states. By increasing the pressure strength, the hybridization enhanced between the La-5p and O-2p states. Electronic bands structure and DOS of LaAlO3 are well matched with the experimental and theoretical data of PbMoO3 and PbTaO3 perovskite compounds.
3.2. Optical properties

The study of optical properties of LaAlO₃ provides useful information regarding their application in the opto-electronic devices. The optical response of the medium is elaborated by the dielectric function ε(ω) = ε₁(ω) + iε₂ at all photon energies.

The electronic band structures are directly linked with the imaginary part ε₂(ω) which shows the occupied and unoccupied states. The real part (ε₁) of the dielectric function tells about the polarizability and the absorption of light by the material, refractive index, optical conductivity, extinction coefficient, reflectivity, absorption coefficient and optical parameter are represented by imaginary part of dielectric constant ε₂(ω). In figure 4(a), it can be seen that the real part of dielectric function attains maximum peaks 5.26, 5.33, 5.55, 5.75 and 5.84 eV at 0, 10, 20, 30, 40 GPa, respectively. From the electronic band structure calculations, the imaginary part ε₂(ω) has been obtained by using following formula [30]:

![Figure 2. Total Density of state (TDOS) of (a) LaAlO₃ (b) La (c) Al and (d) O.](image)

![Figure 3. Partial density of state (PDOS) of (a) La-s (b) La-p (c) Al-s (d) Al-p (e) O-s and (f) O-p atoms in LaAlO₃.](image)
The Kramers-Kronig relation was used to derive the real part of the dielectric function from the imaginary part:

\[
\epsilon_2(\omega) = \frac{\epsilon^2 \hbar}{\pi m^2 \omega^2} \sum_{kk'} \int \left| n_n(k, \omega) \right|^2 \delta [\omega_n(k) - \omega] d^3k
\]  

(1)

The refractive index is directly linked with the photons which are released during electromagnetic interaction and play an important role in the bonding of compound. For the ionic compound, the value of refractive index is less compared to the covalent bounded compound. Covalent bond has a greater number of sharing electrons which are responsible for the release of a large number of photons. In the lower energy region, values of refractive index are almost constant at all given pressures and start increasing after 2.26 eV for 0, 10, 20, 30, and 40 GPa as represented in Figure 4(c). The reflection of photons at different incident angles from the surface of the material shown by peaks of different intensity.

The following equation is used to calculate the refractive index:

\[
\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega^2 - \omega'^2} d\omega
\]  

(2)

Figure 4. (a) Real part of dielectric function (b) Imaginary part of dielectric function (c) Refractive index (d) Reflectivity (e) Extinction Coefficient (f) Absorption Coefficient (g) Optical conductivity.

Refractive index is directly linked with the photons which are released during electromagnetic interaction and play an important role in the bonding of compound. For the ionic compound, the value of refractive index is less compared to the covalent bounded compound. Covalent bond has a greater number of sharing electrons which are responsible for the release of a large number of photons. In the lower energy region, values of refractive index are almost constant at all given pressures and start increasing after 2.26 eV for 0, 10, 20, 30, and 40 GPa as represented in Figure 4(c). The reflection of photons at different incident angles from the surface of the material shown by peaks of different intensity.

The following equation is used to calculate the refractive index:

\[
n(\omega) = \left( \frac{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)}{2} + \epsilon_2(\omega) \right)^{1/2}
\]  

(3)

The optical reflectivity related with the real part of the dielectric function, at the point where the reflectivity goes to decrease, and the real part gives -ve value. The reflectivity starts at 36.3% of its maximum value, then it oscillates to 0.33 at 8.38 eV for LaAlO₃ as shown in Figure 4(d). The extinction coefficient k(\omega) and the imaginary part of dielectric function (\epsilon_2) show the similar trend. The photon energy peak values of extinction coefficient were 1.66, 1.69, 1.72, 1.74, 1.54 at 0, 10, 20, 30, 40 GPa, respectively as shown in Figure 4(e). The approximations involved in the results of these parameters can cause a small difference in peak intensity.
The following formulas are used to calculate the values of reflectivity $R(\omega)$ and extinction coefficient $k(\omega)$

$$k(\omega) = \frac{\alpha \lambda}{4\pi}$$

$$R(\omega) = \frac{[\alpha(\omega) - 1]^2 + k^2(\omega)}{[\alpha(\omega) + 1]^2 + k^2(\omega)}$$

Absorption spectrum give light harvesting ability of material as shown in figure 4(f) [31]. The absorption coefficient and optical conductivity are calculated by the following formula [32]:

$$I(\omega) = \frac{4\pi}{\lambda} \left( \frac{\varepsilon_1^2(\omega) + \varepsilon_2(\omega)}{2} + \varepsilon_0(\omega) \right)^{1/2}$$

$$\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega)$$

where $\lambda$, $\omega$, $\varepsilon_1$, and $\varepsilon_2$ basically represents the wavelength, imaginary and real part of dielectric constant and angular frequency of the incident light. The highest peaks of absorption are obtained at 4–12 eV. The absorption coefficient and extinction coefficient are proportional to each other through the relation $\alpha = 4\pi k / \lambda$. The optical conductivity peaks show the strong absorption of phonon energy in the range of 3.5 to 10 eV in ultraviolet region as shown in figure 4(g). Within these energy ranges compound is optically active, and all the UV frequencies are absorbed in this energy region.

### 3.3. Thermoelectric properties

Thermoelectric behaviour of LAO was investigated at ambient pressure because LAO band gap displays an increasing trend with applied pressure. The transport behaviour has been investigated by using BoltzTraP code [32, 33]. The variation of Seebeck coefficient, electrical conductivity, thermal conductivity, power factor ($S^2 \sigma$) and figure of merit ($\rho S^2 T/K$) are shown in figure 5. Effect of temperature on different transport coefficients are studied at different pressures. The figure 5(a) shows the relation of electrical conductivity and temperature. It is observed that by increasing temperature, the electrical conductivity increases which shows the semiconductor behaviour of the compound [34]. At 40 GPa the increase in temperature causes a linear increase in electrical conductivity, due to the thermal excitation of electrons in the valence band. The calculated electrical conductivity was found $0.5488 \times 10^{20} (\omega \cdot m \cdot s)^{-1}$ at room temperature (RT). Electrical conductivity increases from $0.858 \times 10^{20} (\omega \cdot m \cdot s)^{-1}$ at 800 K. The Seebeck coefficient (thermoelectric power) $S$, for LAO is plotted in figure 5(b). Seebeck coefficient at all pressure is positive which show that the sample has p-type semiconductor like behaviour. The seebeck S increases rapidly with increasing temperature. At 40 GPa, the large variations have been observed but below this pressure the variations in seebeck coefficient is small. In the pressure range 10–30 GPa, the average value of $S$ was found 70 ($\mu$ V/K). This is a direct consequence of the indirect to direct band gap transition, as discussed above. This material is a promising candidate for thermoelectric devices due to higher values of $S$ [35]. At 40 GPa and 150 K the minimum value of Seebeck is 52.70 ($\mu$ V/K) and maximum value is 160.55 ($\mu$ V/K) that is linearly increased. Figure 5(c) displays the variation of thermal conductivity with temperature. Thermal conductivity is constant at all pressures, but it slightly decreases at 40 GPa. The thermal conductivity increased with increasing temperature due to the excitation of the charge carriers. From 0–30 GPa, thermal conductivity (K) increases linearly and become constant at 650–800 K. The maximum value of thermal conductivity at 800 K and 40 GPa is $30.462 \times 10^{14}$ W m$^{-1}$ K$^{-1}$. K.s which shows that it is a good heat conductor. This type of material is used in faster cooling rate [36]. The LaAlO$_3$ compound is helpful to prepare homogeneous sample [37]. Low values of thermal conduction are applicable for thermal insulation [38, 39].

One more important factor that have thermal effect is $ZT$ that tells about the thermal efficiency, calculated from the relation $ZT = \sigma S^2 K / T$ (where the symbols have their usual meanings) [40] shown in figure 5(d). The maximum value of $ZT$ is 0.58 at 40 GPa. At this pressure, $ZT$ has higher values, so LAO well applicable for thermoelectric applications. [41]. As the material have maximum value of $ZT$, the material becomes much more efficient in converting the heat energy into useful electrical energy [42]. The value of $ZT$ increases with temperature, at 500 K it become constant for 10–30 GPa. The $ZT$ values of LAO increases with increases of temperature in the measured temperature range 150–800 K. The high value of $ZT$ is obtained at 40 GPa that is 0.6 at 800 K. LAO can be used for the thermoelectric devices [35]. By increasing temperature, the value of power factor (PF) increases, and maximum value is achieved at 800 K as shown in figure 5(e). Power factor is an accumulated effect of Seebeck coefficient and electrical conductivity. PF also increase linearly within the temperature range 400 to 800 K and has comparable results with the BiAlO$_3$ compound [43]. The value of PF at 500 K for 0 GPa and 40 GPa is $5.5 \times 10^{11} \ W \cdot K^{-2} \cdot cm \cdot s$ and $11.06 \times 10^{11} \ W \cdot K^{-2} \cdot cm \cdot s$, respectively. The highest value is obtained at
800 K and at 40 GPa which is $22.136 \times 10^{11}$ W K$^{-2}$.cm.s. This type of material shows the capability to have potential applications in thermoelectric industry operating at high temperature [40].

4. Conclusion

In this work, electronic, optical and thermoelectric properties of LaAlO$_3$ have been calculated by using WEIN2K software under different pressure range. By increasing pressure, the size of band gap increased, and the nature of band gap shifts from indirect to direct. DOS and electronic band structure showed that LaAlO$_3$ is semiconductor in nature. The Calculated optical properties such as the dielectric function increases by increasing the band gap with pressure. Thermoelectric properties have been studied by using BoltzTrap code at 150–800 K. At 800 K the value of power factor for 0 and 40 GPa was calculated 6.831 (W/K$^2$. cm. s) and 22.13 (W/K$^2$. cm. s), respectively. Results revealed that LAO is a suitable candidate for optoelectronic and thermoelectric devices.

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