A first principles study of the phonon anharmonicity, electronic structure and optical characteristics of LaAlO$_3$

Bahaa Ilyas$^1$ and Badal Elias$^2$

$^1$University of Duhok, Kurdistan Region-Iraq
$^2$University of Duhok, Kurdistan Region-Iraq

Email: bahaestring@gmail.com
bahaa.ilyas@uod.ac

Abstract: The way elementary excitations work together with their couplings and interact as condensed matter systems is very important when designing optimum energy-conversion devices. We investigated the electronic structure of LaAlO$_3$, and we show that the bandgap insulator of LaAlO$_3$ obtained theoretically by the hybrid functional HSE06 is an indirect 5.649eV that show a very good agreement with experimental data. The lattice constant is obtained exactly as experiment. In thermos-electric materials, the concept of conversion-efficiency (heat to electricity) is improved instantly by suppressing the phonon quasi-particles propagations that are responsible for draft macroscopic thermal transport. The material presented here for thermo-electric conversion-efficiency of cubic perovskite LaAlO$_3$, show that it has an ultralow thermal-conductivity, while the formalism to its strong phonon scattering interactions resides mostly unclear. From the bases of Ab-initio simulations, the 4-dimensional phonon-dispersion surfaces of the cubic perovskite LaAlO$_3$, have been mapped and we found that the origins of the ionic potential an-harmonicity being responsible for the unique behaviour and properties of LaAlO$_3$. It is investigated that these phonon scattering arise solely from the LaAlO$_3$ unstable electronic-structure, with its orbital interactions resulting to lattice instability similar to the ferroelectric instabilities. Our results show a microscopic insight bonding electronic-structure and phonon anharmonicity in LaAlO$_3$, and provides some new picture the way interactions happen between phonon–electron and phonon–phonon this lead to understand the concept of ultralow thermal-conductivity. Ab-initio calculations was performed on cubic perovskite LaAlO$_3$ to obtain the phonon density of states (DOS) from 50 K to 5000 K, we find that the anharmonic behaviour starts around temperature limits of 500 K. The computed optical spectra were obtained using both the Beth Slapter Equation BSE and compared with the perturbed method using HSE06, optical spectra show that the inter-band transition occur precisely from the O-valence bands to the La-conduction bands throughout the low energy area. The energy-loss spectrum, optical conductivity and reflectivity and the refractive index are computed from first principles by using HSE06 hybrid functional. The optical band gap of material shows about 6.21 eV, which agrees with some cited experimental measurements

Keywords: LaAlO$_3$, Phonon anharmonicity, Electronic Structure, Optical properties.

1 Introduction

Many of the special characteristics of Lanthanum Aluminate (LaAlO$_3$) in its cubic perovskite form is owed to its uniquely large band gap [1]. LaAlO$_3$ exhibits a wide variety of structural, electronic, optical, phonon, thermal and other unique properties under certain applied conditions. The La-based oxides’ geometry holds an important part to their thermodynamic
character and specific chemical formation. A paper by Woodward and Lufaso [2] provide a fair explanation to how cubic perovskites such as LaAlO$_3$ can go under phase transition when subjected to some limits of pressure and temperature. LaAlO$_3$ perovskite experience a phase transition of $Pm3m$ to $R3c$ when subjected to the studies limits of pressure and temperature. This work provides a precise calculations of the cubic perovskite Lanthanum Aluminate LaAlO$_3$ crystal structure, using $Ab$-$initio$ examination of the structural, electronic, optical, phonon and thermodynamic properties under both high Temperature and pressure ranges.

Performing certain variations considering pressure and temperature is important to reveal changes that occur to the lattice constant, which in its turn stabilizes under moderate pressure and temperature. The mechanical characteristics show the range of practical application of LaAlO$_3$. Fundamental properties, such as the equations of stats, specific heat capacities, Debye-temperature, optical and phonon related properties. The knowledge of elastic moduli is critical to figure the practical applications of the mechanical character of the crystal, some might be the sound velocities, internal strain, thermo-elastic stress. These also offer important information regarding the measure of anisotropy factor that is known to relate to the tendency of either ductility and brittleness and in the case of LaAlO$_3$, brittleness is a key feature of the crystal. The specific heat capacity of a crystal is an important thermal property that indicates the materials heat retention. The obtained microscopic thermodynamic properties are a reflection of the microscopic dynamics of atoms. Due to its unique dielectric properties, LaAlO$_3$ is also widely used in the superconducting microwave devices [3,4]. At the present time, LaAlO$_3$ is the subject of study due to its new identity as a promising candidate as a field transistor and that is because of its high gate oxide especially when mixed with SrTiO$_3$, where both mixed offer an excellent candidate to alongside silicon-dioxide SiO$_2$ or Silicon itself Si [1 0 0] Where a single crystalline of LaAlO$_3$ has a large dielectric constant with a huge optical band-gap of about 6.3 eV [5] and stable thermodynamics as it would be shown in the last section of this work. Moreover, the conduction and valence band character of the LaAlO$_3$ is carefully analyzed and it is briefly described. Interactions of phonon quasiparticles holding orbital degrees of freedom could result to unusual bulk thermodynamic and transport phenomena, such as superconductivity, multiferroicity, charge-density waves, or soft-mode phase transitions. Such couplings are of a particular interest in thermoelectrics, quasi-two-dimensional layered systems, and topological insulators. Thermoelectric devices that are of great interest for generational applications, might require tuning of the quasiparticle transport to achieve a relatively low lattice thermal conductivity and still maintaining a high electrical conductivity [6, 7]. There exist variety of methods to suppress and calm contributions of lattice-vibrations or phonons to the thermal conductivity, such including, leveraging the anisotropic layered-structures, the use of a large unit cells with high optical phonon branches, alloying, scattering acoustic phonons owing to the rattling atoms, or coupling to electronic instabilities [8-16]. Phonons (lattice vibrations) are responsible for most of the sum of the entropy of materials at their modest temperatures or pressures. Phonon entropy can be obtained with a selected set of phonon frequencies in harmonic approximation, but such results are occasionally inaccurate for estimating the thermodynamics of phase stability at elevated temperatures or induced pressures limit [17]. Variations in phonon frequencies under pressure and temperature are of unique importance for calculating the thermodynamic functions [18], understanding this behavior under high-pressure is still emerging. Such studies require phonon spectra at high temperatures and pressures, for which there are few or no experimental data. The thermal properties of Lanthanum Aluminate LaAlO$_3$ are of great importance for LaAlO$_3$-based electronic devices, nanomechanics, thermoelectrics, and photovoltaics [19-28]. In General, a portion of the nonharmonic behavior of crystals is expected to originate from the quasiharmonic thermal-softening or its frequency-reduction of phonons, as the phonon entropy increases, the material starts expanding against its own bulk modulus. The anharmonicity resulting from phonon-phonon interactions causes even more phonon softening, which can account for most of the entropy at high pressures and temperatures. The anharmonic phonon-phonon interactions could also results in shortening the lifetimes of phonons, which may cause expanding of the phonon spectrum and subtle a finite
phonon mean-free-path thermal transport. Lattice dynamics of LaAlO$_3$ has attracted attention owing to its unique dielectric properties, LaAlO$_3$ is also widely used in the superconducting microwave devices [3,4]. At the present time, LaAlO$_3$ offer an excellent candidate to alongside silicon-dioxide SiO$_2$ or silicon itself [1 0 0] where a single crystalline of LaAlO$_3$ has a large dielectric constant with a huge optical band-gap of about 6.3 eV [5] and stable thermodynamics. Improving our knowledge of the phonon dynamics is very important to obtain precise thermoelectric efficiency. The cubic perovskite LaAlO$_3$ is particularly interesting with its $zT = \sigma S^2 T / \kappa$ reaching values above the unity, where $T, S, \sigma, and \kappa$ are the temperature, Seebeck coefficient, electrical, and thermal conductivities, respectively. Thanks to the low lattice thermal conductivities $\kappa$ in the single crystal. Many factors are held accountable for this low $\kappa_{\text{lat}}$, ranging from heavy atomic masses, soft bonds, and to the strong anharmonicity at high pressures and temperatures, which is reflected in the proximity to the lattice instability. The half-filled resonant $p$ band and the nonlinear Al polarizability induce a relatively strong anharmonicity at a long-range interatomic potential [29-38]. Such interactions along the crystallographic directions [100] may cause the transverse-optic (TO) phonon branch that dip to low energy at the zone centre. The strong anharmonicity causes this zone-centre TO phonon to stiffen as $T$ increases in the cubic paraelectric phase in a clear quasi-harmonic lattice [38] but in general agreement with the soft-mode picture of the ferroelectric transition [39].

Although the studies mentioned above assessed and accurately described the lattice dynamics of LaAlO$_3$, but to our knowledge there no study of phonons in LaAlO$_3$ at the studied temperatures and pressures limit, which are important for assessing phonon anharmonicity at higher pressures and temperatures, which is also owed to the character of thermal conductivity at all temperatures. In this work, we explain the origin of the complex TO spectral function, by performing systematic first-principles simulations of the temperature-dependent phonon self-energy. Our results establish that, the TO mode in LaAlO$_3$ is more paraelectric oriented. We try to explain how these results arise from a resonance in the phonon self-energy, which is more pronounced in LaAlO$_3$, owing to a better nest in dispersion. We found that the thermal changes in phonon frequencies were a factor of 7 larger than expected from the quasiharmonic model, indicating a large effect from phonon anharmonicity. The thermal broadening of features in the phonon spectrum also indicates anharmonicity.

## 2 Methods and Modeling

First-principles calculations were performed in the framework of density functional theory (DFT). Using the Projector Augmented PAW method, which was developed by Blöchl (1994) [40]. The basis wave functions were calculated within the ATOMPAW code [41]. The details of the PAW method have already been given several times in the literature [42, 43, 44]. The accuracy of our obtained phonon calculations was carefully evaluated through the use of a powerful Exchange and correlation functionals, throughout this work the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional [45] with the scalar-relativistic BY3LP Pseudopotentials is carried out, in order to get as realistic as possible to predict correct values of the band gap since HSE06 gave a very satisfactory band gap estimation.

Hybrid density functional, which includes a certain amount of Hartree-Fock (HF) exchange, has further improved upon the BY3LP results. This improvement originates from the inclusion of non-dynamic correlations that effectively delocalize the BY3LP exchange hole. Nowadays, the new hybrid density functional of HSE06 is particularly successful in describing the band gap and the ground-state properties of a whole range of materials, which recovers the correct behaviour HSE06 is a screened Coulomb hybrid functional by separating the short-range and long-range HF exchange, which offers highly efficient computations on extended periodic systems. In HSE06, the XC energy is described as follows [45]:

$$E_{\text{XC}}^{\text{HSE06}} = E_{\text{X}}^{\text{HF,SR}} + E_{\text{X}}^{\text{PBE,SR}} + E_{\text{X}}^{\text{PBE,LR}} + E_{\text{C}}^{\text{PBE}}$$  \hspace{1cm} (1)
where $E_X^{HF,SR}$, $E_X^{PBE,SR}$, $E_X^{PBE,LR}$, and $E_C^{PBE}$ represent the short-range HF exchange, short-range Perdew–Burke–Ernzerhof (PBE) exchange, long-range PBE exchange, and PBE correlation terms, respectively. The data obtained through the HSE06 functional is presented as our main results as implemented in the open-source ABINIT code package [46]. The plane-wave cut-off energy achieved convergence at about 435.4 eV. On the other hand, the k-point sampling was dense and the $8 \times 8 \times 8 = 512$ (2048 atoms) Monkhorst and Pack [47] mesh grid was used sampling of the first Brillouin zone when implementing the Hybrid functional HSE06, this sampling was chosen carefully due to the timing and the processing power. However, tests showed that the $24 \times 24 \times 24 = 13824$ was optimum when using the hybrid functional HSE06, tests of high grid number reaching $48 \times 48 \times 48 = 110592$ does not lead to any more sufficient difference in converging the electron energy. The states $La$: $5d^16s^2$, $Al$: $2s^22p^4$, $O$: $3s^23p^4$ were treated as valence states. Setting the parameters in this form, lead to well converged calculations. In order to get well-relaxed crystal structure, the first step in any theoretical $AB$-initio study is to optimize geometry at equilibrium. The structural optimization was conducted using the Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS) [48], which is more efficient for structural optimization than viscous damping, when the number of degrees of freedom needed to optimize is lesser than ten. Recovering the optimized crystal structure requires optimization of each of the internal atomic coordinates, the lattice parameters, and the minimization of forces on each atom. These forces are obtained by Hellmann Feynman theorem [49].

3 Results

3.1 Structure and Stability

The Studied LaAlO$_3$ is a cubic $Pm\overline{3}m$ structure with the unit cell is shown in (Figure 1). To determine the lattice parameters at equilibrium, about 200 values of volumes around the expected equilibrium result are used to estimate the relaxed volume with respect to the ions and shapes, the obtained lattice parameter $a$ values are in a great precision with the experimental values, all the presented calculations are performed under zero temperature, also the drown experimental data were obtained at room temperature [50, 51, 52]. The lattice parameter is $a = b = c$ is 3.715 Å, the use of the hybrid HSE06 estimates the equilibrium volume of LaAlO$_3$ exactly Figure 2 shows a comparison of the estimated volume and its compared experimental analogue.
Figure 1 HSE06 compared with experimental data of the total energy as a function of Volume of the LaAlO$_3$

Figure 2 Electron density map of the volume of LaAlO$_3$
3.2 Electronic Properties

The band structures along high symmetry lines are very useful for examining the main character of electronic properties. Single crystal cubic Perovskite LaAlO$_3$ has a Dirac-cone structure with the high order symmetry directions $R$, $G$, $\Gamma$, $K$, and $R$, in the first Brillouin zone (BZ) and at the K-points, which can be seen Figure 3, the linear-energy bands are forming the parabolic mesh in the increase of the state energy. Furthermore, the $\sigma$ bands, which arise partially from the sp$^2$ bonding, are due forming the $\Gamma$ point at the deeper energy.

The Fermi level is positioned at the Dirac valence cone such that the free holes exist in between the Dirac valence point and the Fermi level ($E_F = 0$).

LaAlO$_3$ has a completely empty $d$-shell, so that the valence states consist of the oxygen $p$ levels at the top of the valence band is greatly flattened, especially between the $R$ and $M$ points with a difference in the energy limited only to 0.04 eV in SrTiO$_3$. In most compounds, the

The band-structure of LaAlO$_3$ in the BZ is examined within HSE06. Our calculations show that an indirect bandgap $\Gamma$-$R$ holding a value of 5.649 eV separates the valence bands from the conduction bands of the cubic perovskite LaAlO$_3$. The valence bands start with a lower limit at -7.78. and end with the Fermi level ($E_F = 0$). We estimate the optical bandgap to be 6.21 eV, which agrees with the experimental value at 6.3 eV [5].

Table 1 Calculated band gaps $E_g$(eV) of LaAlO$_3$ at equilibrium.

| LaAlO$_3$ | R-R  | $\Gamma$-$\Gamma$ | M-M  | G-G  | $\Gamma$-$R$ | exp.  |
|-----------|------|------------------|------|------|--------------|-------|
| HSE06     | 6.849| 6.130            | 7.298| 6.565| 5.649        | 5.6   |
| GW        |      |                  |      |      |              | 5.300 |
| LDA       | 4.523| 3.311            | 3.941| 3.546| 3.051        |       |
| BY3LP     | 6.045| 5.156            | 6.180| 6.405| 4.882        |       |

![Figure 3](image-url) Electronic Band-Structure Energy Dispersion curves along high symmetry Directions of LaAlO3 inside the Brillouin Zone within BY3LP and HSE06 Functionals
The conduction-band is relatively more dissipative than the valence-band. La-atoms are located at the centre of the cubic site affecting the valence bands and forcing them to widen. The conduction-band holds its lowest state at $La d - orbital$, followed by the $Al s - orbital$ at the $\Gamma - point$. In Table 2, we list the calculated direct and indirect band gaps. A comparison of the obtained equilibrium values of the band gap is examined under GGA, LDA, By3LP and HSE06 are given in Table 2, with available experimental band gap measurements of about $5.6 \text{ eV}$. The results computed within LDA tend to underestimate this value by $40\%$, running the calculations under GW-approximation and changing to a $k$-point mesh of $8 \times 8 \times 8 = 512$ within the BZ, gives an approximation of $5.3 \text{ eV}$. While BY3LP underestimated the gap’s value by about $14\%$. The results obtained with HSE06 gave the value of $5.649 \text{ eV}$. The significant splitting of the spin up and down energy bands is revealed near ($E_F = 0$); furthermore, the largest energy spacing reaches $0.5 \text{ eV}$. eigenvalue close to R point constitutes the absolute maximum of the valence band. Generally, a big improvement of the estimated band transition energies. In the HSE06 functional, the Mean Absolute Error (MAE) gave about $0.42 \text{ eV}$, the Mean Error (ME) has the exact value as the MAE and the negative sign, which represents an improvement by roughly a factor of three compared to the BY3LP that has MEA of $1.48 \text{ eV}$. For that we could that the error of predicted and experimental value depends on the type of the material.

### 3.3 Lattice Dynamics

When phonon frequencies are determined, most of the thermodynamic properties can be obtained using statistical physics without further approximations. To decompose the Helmholtz free energy $F$ at temperature $T$ into two additive contributions [52, 53]

$$ F(V_p,T) = E_c(V) + F_{vib}(V,T) $$

where $E_c$ is the total static free-energy per unit cell at $0 \text{ K}$, and $F_{vib}$ is the vibrational Helmholtz free energy contribution given by

$$ F_{vib}(V,T) = k_BT \int_0^\infty \ln \left\{ \frac{\hbar \omega}{2k_BT} \right\} g(\omega,V) d\omega $$

where $k_B$ is Boltzmann constant and $g(\omega,V)$ is the phonon mode density. The term quasiharmonic-approximation is given from the approach that for a particular volume, $F_{vib}(V,T)$ can be calculated under the regular harmonic approximation, and that anharmonic effects are to be included solely through the volume-dependence on the phonon frequencies.

The phonon eigen-energies were computed through density functional perturbation theory DFPT [54, 55]. The free energy was calculated as

$$ F(T,V) = E_0(V) + \int \frac{\omega}{2} + k_BT \ln(1 - e^{\frac{\omega}{k_BT}}) g(\omega) d\omega $$

The quasi-harmonic approximation (QHA) calculations were obtained by minimizing the free energy $F(T,V)$ of Eq. (4) with respect to the volume of the supercell. Ground-state energies $E_0(V)$ were calculated separately and self-consistently for each volume, and the DOS $g(\omega)$ were calculated with the specific lattice parameter, $a_0$, that produced the minimized volume.

The Helmholtz free energy is the key in the calculation, and once its determined as a function of the volume and temperature, many thermodynamic quantities can be obtained from it, such as entropy $S = -(\partial F/\partial T)_V$, enthalpy $H = F + TS$ and so on.

The algorithm implemented to compute phonon dispersions was by introducing a generalized force constant $\Psi^{a,\beta}_{i,j}(P,Q)$ as

$$ \Psi^{l,k}_{a,\beta}(P,Q) = \omega^{l,k}_{a,\beta}(P,Q) + \phi^{l,k}_{a,\beta}(Q) $$

where

$$ \phi^{l,k}_{a,\beta}(Q) = \frac{1}{N} \frac{4\pi e^2 [Z(j) \cdot \hat{q}]_{\alpha}[Z(j) \cdot \hat{q}]_{\beta}}{V_p \hat{q} \cdot \hat{e}_{\infty} \cdot \hat{q}} $$
The evaluation of the dynamical matrix is

\[
D^{ijk}_{\alpha\beta}(q) = \exp[iq \cdot [r(k) - r(j)]] \sum_{Q} \frac{\psi^{ijk}_{\alpha\beta}(p, Q)}{\sqrt{m_j m_k}} \exp[iq \cdot [R(Q) - R(P)]]
\]

The crystal LaAlO$_3$ is put under a relative pressure limits of (0, 8, 10-13 GPa] and temperature [0K to 6000K]. Now, temperature and pressure limits are set to meet the phase shift of LaAlO$_3$, and that pressure after 11 GPa breaks the lattice structure and changes it from Cubic $Pm\overline{3}m$ to rhombohedral $R\overline{3}c$. Specific heat capacity $C_V$. At around temperatures ($T > 2000K$), tends to approach the Petit-Dulong-limit [38] with a value of \((124.62\ J\cdot mol^{-1}\cdot K^{-1})\), a behavior that is common with solids materials. At intimate low temperatures, the vibrational excitations rose purely from acoustic vibrations; $C_V$ is proportional to the third power of temperature $T^3$. At 0Gpa pressure and ambient room temperature, $C_V$ is slightly lower than the Petit-Dulong-limit. Generally, for a given temperature, $C_V$ decreases as pressure increases. Figures 4 shows also the variation of enthalpy, free energy and entropy with temperature over a range of 0-6000K under pressure and it shows a great comparison with experiment [56-59].

![Graph showing calculated Helmholtz free energy, entropy, and constant volume heat capacity for LaAlO$_3$ under pressure and temperature](image)
The entropy and enthalpy show a direct temperature dependence. Entropy’s dependence on temperature reveal signs of bending since ions are forced to polarize while approaching one another. The results of the heat capacity $C_v$ and its temperature dependence results out of the acoustic contributions at the crystal level. The dynamical structure factor was computed from the first principles phonon dispersions and polarization vectors $(\epsilon_{ds})$ as follows [59, 60]:

$$S(Q, E) \propto \sum_s \sum_\tau \frac{1}{E_s} \sum_d \frac{b_d}{\sqrt{M_d}} e^{(-W_d+iQr_d)(Q \cdot \epsilon_{ds})^2} \times (n_s + 1) \delta(E - E_s) \delta(Q - q - \tau),$$

(8)

where $\tau, s, and d$ represent the reciprocal lattice vector, branch index, and atom index in the unit cell, respectively, and $b_d, r_d,$ and $M_d$ are the coherent neutron scattering length, position, and atomic mass for atom $d$. The Debye-Waller factor $W_d$ was calculated assuming the atomic mean-square displacements are isotropic and using their values from the simulation as described in the work of [59, 60, 61].
Figure 5 First-principles simulations reveal the strong dispersion anisotropy and softening with temperature of the optic phonons of LaAlO$_3$ under 0, 4, 6, 10 and 13 GPa.
The result was convoluted with a four-dimensional Gaussian instrument resolution function for $R(Q,E)$. A constant $Q$ resolution of comparable width as the bin sizes of $S(Q,E)$ integration and a known energy-dependent energy resolution were used.

Using Ab initio calculations, one can obtain the ground state energy, electronic wave function, energy-gradient, and properties of periodic systems. Hartree–Fock or Kohn–Sham Hamiltonians can be used. Using HSE06 to calculate the Interatomic Force Constants IFCs can take long period of time and is often expensive, the calculations were obtained using parallel computing with cluster of (4 PC’s with a CPU of 3.5GHz) the calculations took about 200Hr to complete each simulation run.

**Figure 6** Phonon dispersion and DOS of LaAlO$_3$ at 50K, 500K, 1000K, 1500K, 3000K and 5000K
The phonon DOS and dispersions were calculated using renormalized harmonic force constants starting at 50K to 5000K, from the temperature-dependent effective potential (TDEP) methodology. The total and atom-projected (partial) phonon DOS computed for LaAlO$_3$ using tetrahedron integration are shown in Figure 7. The phonon dispersions of LaAlO$_3$ are shown in Figures 5 and 6. First-principles steady phonon calculations show that, at their respective relaxed lattice parameters, LaAlO$_3$ has a single potential-well with a minimum at the center of the crystal configurational positions. This is in good agreement with the experimental observation that stoichiometric LaAlO$_3$ is indeed paraelectric down to 500 K which in comparison with LABO or Al$_2$O$_3$ is slight more instable ferroelectric. The calculated phonon

Figure 7 The total and partial phonon DOS obtained from first-principles calculations of LaAlO$_3$ at 50K, 500K, 1000K, 3000K and 5000K.
dispersion curves and corresponding one-phonon DOS for LaAlO₃ along the high-symmetry directions are illustrated in Figures 5, 6, 7 which suggests that the dispersion curves and corresponding density of states resemble each other for LaAlO₃. The calculated phonon dispersion curves do not contain soft modes at any direction at 50K, which confirms the stability of the compound.

The DOS curves show various number of peaks, which is owned to the portions at the top of these dispersions. Where the lowest peak is located between 0.15 and 0.25 meV and is dominated by the top of the transverse — acoustic (TA) branches, the other two are mixtures of longitudinal acoustic (LA), TO, and longitudinal optical branches.

A cutoff of the phonon-spectrum occurs at 0.04 eV. Figure 7 shows that the phonon DOS go through a systematic decrease in phonon energy thermal softening, and thermal linewidth broadening with increasing temperature. The DOS curves contain several distinct features resulting from Van Hove-singularities. At 500 K, two transverse acoustic modes between 0.0 and 0.05 eV give several peaks near 0.12 meV and the shoulder 0.15 meV, the modes in between 0.05eV and 0.09eV holds 2 TO and and 1 LA modes. The higher-energy feature around 0.15 meV is from transverse and longitudinal optical modes. The high-energy optical modes centered around 0.2 meV show the largest thermal shift of approximately between the range 50 to 5000 K starting at 500K.

Observing Figures 5, 6, 7, at high temperatures there are more down-conversion processes, but an even greater change in up-conversion processes. Figure 7 shows how the strong down-conversion peaks at low temperatures grow approximately linearly with temperature, following the thermal population of phonon modes involved in the interactions. Near the peak at 0.02 eV, one up-conversion band centered at 0.02 eV is also strong. This band comprises scattering channels in which one O-dominated mode is combined with an Al-dominated mode to form a higher frequency La-dominated mode, i.e., O → Al — La. At the low energy side, there is another band below 0.01 meV from two types of up-conversion processes. One is from Ag-dominated modes alone, i.e., Al → La — O. The other involves two O-dominated modes, i.e., Ag → O — O, owing to the increased number of higher energy O-dominated modes that can participate in these processes at higher temperatures.

To understand the temperature dependence of thermal conductivity, one needs to taking into account both the changes in propagation the velocities of the quasiparticles, and the changes in the scattering rates given by Eq(9). In the relaxation time approximation, the phonon gas thermal conductivity is given by

$$K_{lat} = \frac{1}{3} \sum_{\omega_s} C_q v_q^2 \tau_{qs}$$

where $C_q$ is heat capacity, $v_q$ group velocity, and $\tau_{qs}$ is scattering rate of the phonon modes representing the wave-vector $q$ and the branch index $s$. The temperature effects on group velocities is strong in LaAlO₃. This dependence reflects in its turn a strong temperature dependence of interatomic force constants, associated with the bonding.

The scattering rates is obtained from the given perturbation theory [62] and the first order terms of the cubic Interatomic Force Constants (IFCs):

$$\tau_{qs}^{-1} = 2\Gamma_{qs} = \frac{36\pi}{\hbar^2} \sum_{q_1, q_2, s_1, s_2} |V(q_1, q_2, s_1, s_2)|^2$$

$$\times (n_1 + n_2 + 1) \{\delta(\omega_1 + \omega_2 - \omega_{qs}) - \delta(\omega_1 + \omega_2 + \omega_{qs})\}$$

$$+ (n_1 + n_2) \{\delta(\omega_1 - \omega_2 - \omega_{qs}) - \delta(\omega_1 - \omega_2 + \omega_{qs})\}$$

with $n_1 = n(\omega_{q_1 s_1}, T) \propto T$ the Bose occupation (similarly $n_2$), where $\omega$ is the phonon frequency.

The behavior of LaAlO₃ Supplementary Figure 8 including the corresponding IFCs, yields a suppression in the thermal-conductivity and show an increase in Grüneisen parameter of the lowest-energy TO branch at the Γ points, as shown in Figure 8. The large 3rd order force constant $\Psi^{\alpha, \beta, \gamma}_{0,1,1}$, combined with the large population, augmented $|V(q, q_1, q_2, s_1, s_2)|$ in
Eq. (11), therefore is increases the scattering rates as Eq. (10), which leads in most cases to a striking suppression in the thermal-conductivity.

It’s worth noting that also this kind of distortion corresponds or matches structural evolution of the unit cell from \(Pm\overline{3}m\) to \(R3c\) upon cooling, and thus indicates the role of anharmonicity in bonding the structural phase transition. The distortion overlaps strongly with the zone-centre optical phonon mode, TO at \(\Gamma\). On the other hand, the LO at \(\Gamma\) mode is rather insensitive.

The strong TO anharmonic behavior is revealed in the distortion-potential for the centre of the zone TO vibration, 

\[
V(q_1, q_2, s_1, s_2) = \frac{1}{6} \left( \frac{\hbar^3}{8\omega_3\omega_2\omega N} \right) \times \sum_{l,l',k,k',\alpha,\beta,\gamma} \Psi_{0,l,l',\alpha,\beta,\gamma} \epsilon_{\alpha} (k|qs) \epsilon_{\beta} (k'|q_1s_1) \epsilon_{\gamma} (k''|q_2s_2) 
\]

where \(\epsilon(k|qs)\) is the eigenvector, \(R\) is the atomic equilibrium position, and \(M_k\) is the atomic mass. From the first-principles cubic IFCs, \(K_{lat}\), was computed. Our analysis of the 3\(^{rd}\) order of the force constants (FC) and the contributions it plays in thermal transport shows how anharmonicity arises from nonlinear restoring forces, owing to the asymmetric changes of the electronic structure of the movements of La atoms inside the lattice.

The cubic IFCs \(\Psi_{0,l,l',\alpha,\beta,\gamma}\) correspond to the 3\(^{rd}\) derivatives of the potential with respect to the displacements \((\alpha, \beta, \gamma)\) of the triplets of atoms \((i,j,k)\). Through a systematic study of \(\Psi_{0,l,l',\alpha,\beta,\gamma}\), we could identify the non-degenerate triplets with largest 3\(^{rd}\) order FC.
3.4 Optical Properties

Beth-Slapter Equation BSE and GW-approximation were carried out with the added scissors shift of the conduction states to calculate the single-particle states at a fixed geometry, the substitution of only one component of the dielectric tensor for a symmetric LaAlO$_3$ gives rise to the characteristics of the linear optical properties of the compound under study. The real part is presented by $Re(\epsilon)$ or $\varepsilon_1(\omega)$ and the imaginary part by $Im(\epsilon)$ or $\varepsilon_2(\omega)$. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ is calculated using the derived expression given in [63, 64]:

\[
\varepsilon_2(\omega) = \frac{8}{2\pi\omega^2} \sum_{mn'} \int_{BZ} |P_{mn'}(k)|^2 \frac{dS_k}{\omega \omega_{mn'}(k)}
\]

where $P_{mn'}(k)$ is the dipole matrix element in-between states $n$ and $n'$, $S_k$ is the surface energy with constant value, $\omega_{mn'}(k)$ is the energy difference in-between the two states. The real part of the dielectric function is then obtained from the imaginary part by deriving it from the $\kappa$. The imaginary part of the dielectric function is then obtained from the imaginary part by deriving it from the $\kappa$.

The characteristics of the linear optical properties of the compound under study. The real part is limited zero frequency and reaches its maximum value, then it starts to decreases after hitting an gap the larger

An inverse relation exists between the band gap and $\varepsilon_1(0)$, the smaller the value of the energy gap the larger $\varepsilon_1(0)$ value. The Penn model [63] explains the case based on the expression $\varepsilon_1(0) \approx 1 + \hbar \omega_p/2$). The $\varepsilon_1(\omega)$ for the studied compound starts increasing from the limited zero frequency and reaches its maximum value, then it starts to decreases after hitting an incline, and at a certain energy range it goes to zero. The refractive index of optical materials is known for its importance, especially its use in optical devices. Figure 9 inspects the refractive indices variations for LaAlO$_3$ as a function of the incident photon energy. The refractive index tends to have the same pattern of variation as that of $\varepsilon_1(\omega)$. However, the extinction coefficient $k(\omega)$ on the other hand experiences the same pattern as $\varepsilon_2(\omega)$. The reflectivity $R(\omega)$ for the studied compounds is frequency dependent.
Figure 9 The Real, Re(ε) and Imaginary Im(ε) parts of dielectric function, refractive index n(ω) and extinction coefficient k(ω), energy loss function L(ω), reflectivity R(ω), the inter and intra bands and Total Chi for LaAlO₃ withing BSE and HSE06.
What brings up consideration is the fact that maximum reflectivity points occur at negative points of $\varepsilon_1(\omega)$. At the later mentioned values of $\varepsilon_1(\omega)$, the material experiences a metallic behavior in their nature [1]. Generally, reflectivity increases as the metallicity behavior of the compound increases, reaching its maximum range at the lowest negative value of $\varepsilon_2(\omega)$ of 20eV. The reflectivity starts at 50% of its maximum value, then it oscillates to maximum of 1.4. The electron loss energy function $L(\omega)$, plays an important role in describing the loss of energy due to fast moving electrons through the crystal lattice of our material. The plot presents a sharp peak located at about 20eV. This peak clearly shows how screening affects the plasma frequency $\omega_p$. There are also peaks of optical conductivity spectrum, which is assigned to the charge transfer between interbands. A detailed information of the large spectral conductivity weighted change at low frequency is important for analysis of the interaction of localized d-orbital electrons and the delocalized split-up between bands in lanthanum compounds. Figure 9 displays our calculated interband and intraband valence to conduction absorption spectrum and the corresponding transitions between single-particle energy levels, the broadening allows most the transitions to be resolved, however, as such a resolution is not yet accessible. A number of types of the complex dielectric functions $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, provide sufficient information to obtain the optical properties. The imaginary part $\varepsilon_2(\omega)$ was calculated from the momentum matrix elements. Moreover, the real part is obtained from the Kramer-Kronig relationship. Contributions to $\varepsilon(\omega)$ are namely, transitions of intra-band and inter-band. The interband part can furthermore split into a direct and an indirect part, both of the intraband $\text{intra}(2\omega)$ and $\text{intra}(1\omega)$ starts from zero and continues to achieve maximum at 2.0eV and a negative maxima at 3.0eV, on the other hand the intrabands $\text{inter}(2\omega)$ and $\text{inter}(1\omega)$ starts from zero and continues to achieve maximum at around 4.0eV and a negative maxima at 5.0eV.

3. Conclusion

In conclusion, we have studied the Structural, electronic, phonon, thermal and the optical properties of perovskite LaAlO3 using Ab-initio calculations. The structural changes under non-hydrostatic conditions depend on the degrees of freedom within the LaAlO$_3$ structure. we found that the $Pm\bar{3}m$ phase is energetically stable under the studied temperature and pressure limits. The material goes through the $Pm\bar{3}m$ to $R\bar{3}C$ phase shift upon cooling. An indirect bandgap $\Gamma$-$R$ of 5.649eV separates the valence from the conduction bands, it seems that using HSE06 and greatly enhanced the estimation of the band gap. The value of 6.21 eV is in agreement with recent ultraviolet spectroscopic measurements. The thermal properties were computed by using the IFC’s and using the hybrid functional HSE06, the phonon structure indicates anharmonicity upon the studied pressure and temperature. The anharmonicity lattice dynamics of the Perovskite thermoelectric LaAlO$_3$ were investigated with first-principles calculations, our calculations of the phonon DOS of LaAlO$_3$ from 50 to 5000K showed significant thermal-softening and an amount of thermal-broadening. The effect of pressure on the phonons and volume on phonon frequencies, the quasi-harmonic contribution to the non-harmonicity was obtained. We present studies of the optical properties of LaAlO$_3$ using the BSE and HSE06 calculations. Our calculated dielectric-function was shown to agree well with the available experimental measurements. It is clear to note that the difference between the direct band gap and the optical band gap is due to the limitation of the selection-rules in the interband and intraband transitions.
References

[1] Luo X and Wang B 2008 Journal of Applied Physics 104 073518
[2] Lufaso M W and Woodward P M 2001 Acta Crystallographica Section B Structural Science 57 725–738
[3] Dilorio M S, Yoshizumi S, Maung M, Yang K Y, Zhang J and Fan N Q 1991 Nature 354 513–515
[4] Lee A E, Platt C E, Burch J F, Simon R W, Goral J P and Al-Jassim M M 1990 Applied Physics Letters 57 2019–2021
[5] Lim S G, Kriventsov S, Jackson T N, Haeni J H, Schlom D G, Balbashov A M, Uecker R, Reiche P, Freeouf J L and Lucovsky G 2002 Journal of Applied Physics 91 4500–4505
[6] Snyder G J and Toberer E S 2008 Nature Materials 7 105–114
[7] Minnich A J, Dresselhaus M S, Ren Z F and Chen G 2009 Energy & Environmental Science 2 466
[8] Poudel B, Hao Q, Ma Y, Lan Y, Minnich A, Yu B, Yan X, Wang D, Muto A, Vashaee D, Chen X, Liu J, Dresselhaus M S, Chen G and Ren Z 2008 Science 320 634–638
[9] Biswas K, He J, Blum I D, Wu C I, Hogan T P, Seidman D N, Dravid V P and Kanatzidis M G 2012 Nature 489 414–418
[10] Keppens V, Mandrus D, Sales B C, Chakoumakos B C, Dai P, Coldea R, Maple M B, Gajewski D A, Freeman E J and Bennington S 1998 Nature 395 876–878
[11] Koza M M, Johnson M R, Viennois R, Mutka H, Girard L and Ravot D 2008 Nature Materials 7 805–810
[12] Christensen M, Abrahamsen A B, Christensen N B, Juranyi F, Andersen N H, Lefmann K, Andreasson J, Bahl C R H and Iversen B B 2008 Nature Materials 7 811–815
[13] Ma J, Delaire O, May A F, Carlton C E, McGuire M A, VanBebber L H, Abernathy D L, Ehlers G, Hong T, Huq A, Tian W, Keppens V M, Shao-Horn Y and Sales B C 2013 Nature Nanotechnology 8 445–451
[14] Voneshen D J, Refson K, Borissenko E, Krisch M, Bosak A, Piovano A, Cemal E, Enderle M, Gutmann M J, Hoesch M, Roger M, Gannon L, Boothroyd A T, Uthayakumar S, Porter D G and Goff J P 2013 Nature Materials 12 1028–1032
[15] Chiritescu C, Cahill D G, Nguyen N, Johnson D, Bodapati A, Keblinski P and Zschack P 2007 Science 315 351–353
[16] Rhyee J S, Lee K H, Lee S M, Cho E, Kim S I, Lee E, Kwon Y S, Shim J H and Kotliar G 2009 Nature 459 965–968
[17] Fultz B 2010 Progress in Materials Science 55 247–352
[18] Palumbo M, Burton B, e Silva A C, Fultz B, Grabowski B, Grimvall G, Hallstedt B, Hellman O, Lindahl B, Schneider A, Turchi P E A and Xiong W 2013 physica status solidi (b) 251 14–32
[19] Green M A, Zhao J, Wang A, Reece P J and Gal M 2001 Nature 412 805–808
[20] Hochbaum A I, Chen R, Delgado R D, Liang W, Garnett E C, Najarian M, Majumdar A and Yang P 2008 Nature 451 163–167
[21] Cui Y, Zhong Z, Wang D, Wang W U and Lieber C M 2003 Nano Letters 3 149–152
[22] Graetz J, Ahn C C, Yazami R and Fultz B 2003 Electrochemical and Solid-State Letters 6 A194
[23] Boukai A I, Bunimovich Y, Tahir-Kheli J, Yu J K, III W A G and Heath J R 2008 Nature 451 168–171
[24] Hirschman K D, Tsybeskov L, Duttagupta S P and Fauchet P M 1996 Nature 384 338–341
[25] Kelzenberg M D, Boettcher S W, Petykiewicz J A, Turner-Evans D B, Putnam M C, Warren E L, Spurgeon J M, Briggs R M, Lewis N S and Atwater H A 2010 Nature Materials 9 239–244
[26] Tian B, Zheng X, Kempa T J, Fang Y, Yu N, Yu G, Huang J and Lieber C M 2007 Nature 449 885–889
[27] Petersen K 1978 IEEE Transactions on Electron Devices 25 1241–1250
[28] Suda J, Kamishima O, Kawamura J, Hattori T and Sato T 2009 Journal of Physics: Conference Series 150 052249
[29] Abrashev M V, Litvinchuk A P, Iliev M N, Popov V N, Ivanov V G, Chakalov R A and Thomsen C 1999 Physical Review B 59 4146–4153
[30] Boschker H, Richter C, Fillis-Tsirakis E, Schneider C W and Mannhart J 2015 Scientific Reports 5
[31] Lucovsky G and White R M 1973 Physical Review B 8 660–667
[32] Littlewood P B 1980 Journal of Physics C: Solid State Physics 13 4875–4892
[33] Bussmann-Holder A, Bilz H and Vogl R 1983 Springer Tracts in Modern Physics (Springer Berlin Heidelberg) pp 51–98
[34] Rabe K M and Joannopoulos J D 1985 Physical Review B 32 2302–2314
[35] Delaire O, Ma J, Marty K, May A F, McGuire M A, Du M H, Singh D J, Podlesnyak A, Ehlers G, Lumsden M D and Sales B C 2011 Nature Materials 10 614–619
[36] Cochran W 1960 Advances in Physics 9 387–423
[37] Dulong P L and Petit A T 1819 Recherches sur quelques points importants de la theorie de la Chaleur
[38] Heyd J, Scuseria G E and Ernzerhof M 2003 The Journal of Chemical Physics 118 8207–8215
[39] Paier J, Marsman M, Hummer K, Kresse G, Gerber I C and Angyán J G 2006 The Journal of Chemical Physics 125 249901
[40] McNellis E R, Meyer J and Reuter K 2009 Physical Review B 80
[41] Krukau A V, Vydrov O A, Izmaylov A F and Scuseria G E 2006 The Journal of Chemical Physics 125, 224106
[42] Monkhorst H J and Pack J D 1976 Physical Review B 13 5188–5192
[43] Battiti R and Masulli F 1990 International Neural Network Conference (Springer Netherlands) pp 757–760
[44] Kittel C 2005 Introduction to solid state physics 8th ed (Wiley)
[45] Gontze X and Lee C 1997 Physical Review B 55 10355–10368
[46] Togo A, Oba F and Tanaka I 2008 Physical Review B 78
[55] Pettifor D G 1992 *Materials Science and Technology* **8** 345–349
[56] Guan P and Ma X N 2003 *Inventiones mathematicae* **151** 553–577
[57] Anderson O L 1963 *Journal of Physics and Chemistry of Solids* **24** 909–917
[58] Schnelle W, Fischer R and Gmelin E 2001 *Journal of Physics D: Applied Physics* **34** 846–851
[59] Ishibashi S and Terakura K 2008 *Journal of the Physical Society of Japan* **77** 104706
[60] Squires G L 2009 *Introduction to the Theory of Thermal Neutron Scattering* (Cambridge University Press)
[61] Ehlers G, Podlesnyak A A, Niedziela J L, Iverson E B and Sokol P E 2011 *Review of Scientific Instruments* **82** 085108
[62] Tremel W and Hoffmann R 1987 *Inorganic Chemistry* **26** 118–127
[63] Penn D R 1962 *Physical Review* **128** 2093–2097
[64] Xu B, Li X, Sun J and Yi L 2008 *The European Physical Journal B* **66** 483–487