Electronic, transport and optical properties in perovskite compound LaGaO$_3$

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Abstract

The perovskite-type oxides ABO$_3$ have a multifunctional application in different area such as promising new anode for rechargeable batteries (Ni/MH), photovoltaic and photochromic, because of their properties variety. In this work, we interested on the calculation of the electronic, optical and transport properties of the lanthanum gallate perovskite oxides compound, using the first-principles calculations based on the density functional theory. We determined the exchange and correlation effects by a Generalized Gradient Approximation of Perdew–Burke–Ernzerhof (GGA-PBE). As results the energy gaps of LaGaO$_3$ compound with GGA-PBE have been found as 3.61 eV, from the transport properties we notice that LaGaO$_3$ is P-type materials with electrical conductivity varied from 0 (Ω.m.s)$^{-1}$ at 0 K to 10 $\times$ 10$^{20}$ (Ω.m.s)$^{-1}$ at 800 K.

1. Introduction

The perovskite materials have a lot of scientific interest because of their large and important applications in different area such as electrochromic [1], energy storage [2, 3], solar cell [4, 5], we can find the same material used in different domains due to their physical and chemical behaviors, such as density of states, Fermi energy, dielectric function and phonon dispersion that have a unique nature. The perovskite-type oxides ABO$_3$ can be synthesized with a wide variety combinations of chemical elements, the A-site can be filled by cations M$^{3+}$ (Fe, La, Gd), M$^{2+}$ (Ca, Sr, Ba) or M$^{+}$ (Na, K), and the B-site can be occupied by M$^{3+}$ (Mn, Fe, Co, Ga), M$^{4+}$ (Ce, Zr, Ti) or M$^{5+}$ (Nb, W). The correlation between these sites gives us different structures, cubic, tetragonal, monoclinic, hexagonal and orthorhombic, it is known that cubic (Pm3m) is the ideal perovskite structure [6]. In this one the A cation is situated at the corner of the cube, while B cation is situated at the centre. This variety of ABO$_3$ combinations give us materials that can be used in various fields such as photovoltaic [7], solid oxide fuel cells (SOFC) [8, 9] and batteries [10, 11]. The LaAlO$_3$, a typical perovskite with variety applications, has allured considerable interest as over layer in conventional thermal barrier coatings [12], as a Promotion of electrochemical performances of LiNi$_{0.5}$Co$_{0.5}$O$_2$, Mn$_{0.5}$O$_2$ cathode [13]. The pure lanthanum aluminate is a material with low ionic conductivity; doping LaAlO$_3$ with cations such as Sr$^{2+}$ and Mg$^{2+}$ results an excellent oxygen ionic conductor. LaAlO$_3$ has sparked renewal interest these last years because of its application in various field such as solid oxide fuel cells (SOFCs) [19], anode for rechargeable batteries [20] and also can be used as a substrate material for the epitaxial growth of high temperature superconducting thin films [21]. The LaGaO$_3$ perovskite oxide is crystallizes in orthorhombic structure with Pnma space group and transforms to rhombohedral symmetry at 145 °C [22], the valence state of La and Ga is retain at (+3) in oxide, so when we doped LaGaO$_3$ [23] with cations that have a lower valence such as Mg or Ca, the concentration of oxygen vacancy can be substantially increased. And it has a band gap of 3.61 eV which is
A width of 4.12 eV is consisting of La contributions from La and Ga states. The conduction band located in the band energy between 5 and 10 eV with we notice that the valence band with a width of 7.7 eV is consisting of O.

The gap of LaGaO3 determined from GGA-PBE is 3.61 eV.

In this work all calculations are based on the density functional theory (DFT), the solution of Kohn–Sham equations are obtained by using Wien2k ab initio simulation program [25]. We determined the exchange and correlation effects by GGA-PBE. The electronic, transport and optical properties have been calculated in stable orthorhombic phase which conforms to Pnma space group. In these calculations we had a 7 × 5 × 7 Monkhorst −Pack set of k-point mesh of Brillouin zone integration generated automatically, the Rmt Kmax value was fixed to 7 (Rmt present the small atomic radius in the unit cell, while Kmax present the size of the largest vector in the plane wave expansion) [26]. The optimization of LaGaO3 lattice parameters is calculated using Tomas Kana package. The transport proprieties are calculated using BoltzTraP code [27]. The hybrid exchange correlation functionals like B3LYP and B3PW allows to achieve much better agreement with the experiment for the band gaps of perovskite materials, than the GGA-PBE exchange-correlation functional [28, 29].

2. Computational methods

In this work all calculations are based on the density functional theory (DFT), the solution of Kohn–Sham equations are obtained by using Wien2k ab initio simulation program [25]. We determined the exchange and correlation effects by GGA-PBE. The electronic, transport and optical properties have been calculated in stable orthorhombic phase which conforms to Pnma space group. In these calculations we had a 7 × 5 × 7 Monkhorst −Pack set of k-point mesh of Brillouin zone integration generated automatically, the Rmt Kmax value was fixed to 7 (Rmt present the small atomic radius in the unit cell, while Kmax present the size of the largest vector in the plane wave expansion) [26]. The optimization of LaGaO3 lattice parameters is calculated using Tomas Kana package. The transport proprieties are calculated using BoltzTraP code [27]. The hybrid exchange correlation functionals like B3LYP and B3PW allows to achieve much better agreement with the experiment for the band gaps of perovskite materials, than the GGA-PBE exchange-correlation functional [28, 29].

3. Results and discussion

LaGaO3 perovskite oxide with Pnma space group have a structure with four atoms of Lanthanum, four atoms of Gallium and twelve of Oxygen. The calculated and experimental lattice parameters are given in table 1. We used the experimental lattice parameters to do the optimization using a package developed by Tomas Kana. As a result of our calculation from the standard DFT calculation we obtained a close to the experimental value of 4.4 eV [24]. However, to our best knowledge the transport properties of orthorhombic structure still have not been reported yet.

Table 1. The present work is calculated using the GGA-PBE method. The experimental and other theoretical lattice constants are listed for comparison.

| Lattice parameters | Present work (Å) | Experiment (Å) [30] | Other theoretical (Å) |
|--------------------|------------------|----------------------|-----------------------|
| a                  | 5.580            | 5.524                | 5.612 [23], 5.477 [23]|
| b                  | 5.554            | 5.492                | 5.557 [23], 5.463 [23]|
| c                  | 7.874            | 7.774                | 7.792 [23], 7.735 [23]|

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We calculated the band structure of lanthanum gallate perovskite (LaGaO3) using GGA-PBE density functional approximations. The results are illustrated in figure 1.

We have chosen the Fermi level (E_F) to be zero at the top of the valence band. As shown in figure 1 the band gap of LaGaO3 determined from GGA-PBE is 3.61 eV.

The total (DOS) and partial (PDOS) density of state of LaGaO3 perovskite compound are shown in figure 2, where we observe that in the entire range La and Ga states hybridize with O, inclusive of the conduction and valence bands, which indicate that La-O and Ga-O bonding are principally covalent. The electron charge was transferred from La and Ga to O due to the large difference between states, revealing the ionic bonding characteristic.

The band energy between −14.5 and −11.5 eV mainly consist of La(5p) and Ga(3d). According to figure 2(b) we notice that the valence band with a width of 7.7 eV is consisting of O(2p), with small but no negligible contributions from La and Ga states. The conduction band located in the band energy between 5 and 10 eV with a width of 4.12 eV is consisting of La (4f).

To connect the electronic structures of a solid to the microscopic physical transitions between bands we use the dielectric function.

To calculate the complex part of this function we used the equation.

\[ \varepsilon(w) = \varepsilon_1(w) + i\varepsilon_2(w) \]  

The \( \varepsilon_2 \) and \( \varepsilon_1 \) are respectively the imaginary and real part of the dielectric function; we can determine the real part from the imaginary part using the Kramer–Kronig relations [31]. We can calculate the imaginary part by:

\[ \varepsilon_{2(\omega)} = \frac{2\Pi e^2}{\Omega \varepsilon_0} \sum_{k,v,r} \left| \tilde{\Psi}_k^{\uparrow \downarrow} | u, r \rangle \tilde{\Psi}_k^{\uparrow \downarrow} \right|^2 \delta (E_{ck} - E_{vk} - h\omega) \]  

\[ \varepsilon_1(\omega) = 1 + \left( \frac{2}{\Pi} \right) \int \frac{d\omega'}{\omega^2 - \omega'^2} \varepsilon_2(\omega') \]  

The c and v are the conduction and valence band, \( \tilde{\Psi}_k^{\uparrow \downarrow} \) and \( \tilde{\Psi}_k^{\uparrow \downarrow} \) are the wave function of valence and conduction band at k point, \( \varepsilon_0 \) is the vacuum dielectric constant, \( \Omega \) is the volume, \( h\omega \) is the energy of the incident phonon, u is the vector defining the polarization of the incident electric field, u r is the momentum operator.
From the real and imaginary part of the dielectric function we can determine all the optical properties such as the absorption $\alpha(\omega)$, reflectivity $R(\omega)$, optical conductivity $\sigma(\omega)$, energy loss $L(\omega)$, refractive index $n(\omega)$ and the extinction coefficient $K(\omega)$.

Figure 1. Band structure of LaGaO$_3$ derived from GGA-PBE functional density.

Figure 2. DOS and PDOS of LaGaO$_3$ derived from various density functional approximation: (a) DOS with GGA-PBE functional; (b) PDOS with GGA-PBE.
The dielectric function and all the optical properties are determined using GGA-PBE functional as shown in figure 3. According to the figure 3 (a) we notice that both the imaginary and real part of the dielectric function increased with energy and attained maximum at 7.8 and 5.1 eV, respectively. This peak is a result of the electron
transition from O(2p) orbitals to La(4f) orbitals and Ga 4s4p orbitals, the real part of dielectric function start to decrease after the sharp peak and attained minimum at 9.8 eV. The absorption coefficient \( \alpha(\omega) \) of a material allows us to determine the penetration’s degree of light into the material before being absorbed. As showing in figure 3(b) we observe that the absorption decreases rapidly when the wavelength \( \lambda \) increases. The max value of the absorption is \( 6.5 \times 10^4 \) cm\(^{-1} \) is obtained at ultraviolet light \( (\lambda = 200 \text{ nm}) \). When we go over \( \lambda = 200 \text{ nm} \), we notice a rapid decrease of the absorption as a function of \( \lambda \), after that we obtain a stable value \( 0.2 \times 10^4 \) cm\(^{-1} \) in the visible and infrared. According to figure 3(d) we notice that the largest energy loss peak occurs at about 12.8 eV, representing the characteristic affiliated with plasma oscillation. The refractive index \( n(\omega) \) is a dimensionless size characteristic of a medium, describing the behavior of light in it, this depends on the measurement wavelength, but also the characteristics of the environment (in particular pressure and temperature). From the figure 3(e), we notice that the refractive index is 2.8 when the wavelength is equal to \( \sim 250 \text{ nm} \) (ultraviolet). In the range of wavelength between 400 and 1000 nm, we observe that the refractive index is conserved at 2.1. The figure 3(f) shows that the reflectivity \( R(\omega) \) decreases with the wavelength, we observe that the highest value of R (0.26) is obtained in ultraviolet at 220 nm. For both approximation the reflectivity decreases as a function of \( \lambda \) and stabilizes at 0.12 in the visible and infrared.

To calculate the transport proprieties we used the semi-classical Boltzmann theory embedded in BoltzTraP code. The band-structure and the crystal structure determined by wien2k are used as an input to run the Boltztrap code, we had as results the electrical conductivity \( (\sigma/\tau) \), Seebeck coefficient \( (S) \), electronic thermal conductivity \( (\kappa_e) \), and electronic power factor \( (P_F) \). The Seebeck coefficient \( (S) \) allows us to indicate if we have a domination of charge carrier, \( S \) with a negative sign represent n-type materials, positive sign p-type materials. According to figure 4(a), we notice that we have a positive sign of \( S \) (p-type) in the entire range of temperature. We can conclude that our compound is a P-type material. The electrical conductivity \( (\sigma) \) of LaGaO\(_3\) is illustrated in figure 4(b) showing that the electrical conductivity increases rapidly by increasing temperature and reach a maximum at 800 K with a value of \( \sim 10 \times 10^{18} \) (\(\Omega\cdot\text{m} \cdot \text{s})^{-1}. P_F = S^2 / \sigma \tau \) represent the power factor, were \( P_F \) is...
proportional to the electrical conductivity \((\sigma / \tau)\) and the square of the Seebeck coefficient \((S^2)\). From the figure 4(d), we observed that the power factor was almost zero at low temperature \((<50 \text{K})\), then we had a rapid increase of power factor when the temperature increases to reach a maximum value \((3.7 \times 10^{11} \text{W/m.k}^2\text{s})\) at 800 K. The thermal conductivity \(K\) of any material depend on the molecular vibrations and the motion of the free electrons. From the figure 4(c), we notice that the electronic thermal conductivity increases with the temperature, so we can say that the molecular vibration increases.

4. Conclusions

In this paper we determined the electronic, optical and transport proprieties of LaGaO\(_3\) perovskite compound using GGA-PBE approximation. The transport proprieties are investigated using BoltzTraP code. According to the electronic band structure calculated with GGA-PBE approximation, we conclude that we have an indirect gap, the value of the band gap determined from GGA-PBE 3.61 eV. From the density of states we notice that we have a covalent and ionic hybridization between La and O and also between Ga and O in the entire range of energy. All optical properties are calculated and illustrated in details, showing that our materiel is a good absorber at ultraviolet, and the reflectivity don’t exceed 20% in the entire range of wavelength. From the transport properties we notice that LaGaO\(_3\) is P-type materials with electrical conductivity varied from \(0 \text{(}\Omega\text{.m)}^{-1}\) at 0 K to \(10 \times 10^{20} \text{(}\Omega\text{.m)}^{-1}\) at 800 K.

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