First-Principles Studies for Electronic Structure and Optical Properties of \( p \)-Type Calcium Doped \( \alpha \)-Ga\( _2\)O\( _3 \)

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Abstract: Gallium oxide (Ga\( _2\)O\( _3 \)) is a promising wide-band-gap semiconductor material for UV optical detectors and high-power transistor applications. The fabrication of \( p \)-type Ga\( _2\)O\( _3 \) is a key problem that hinders its potential for realistic power applications. In this paper, pure \( \alpha \)-Ga\( _2\)O\( _3 \) and Ca-doped \( \alpha \)-Ga\( _2\)O\( _3 \) band structure, the density of states, charge density distribution, and optical properties were determined by a first-principles generalized gradient approximation plane-wave pseudopotential method based on density functional theory. It was found that calcium (Ca) doping decreases the bandgap by introducing deep acceptor energy levels as the intermediate band above the valence band maximum. This intermediate valence band mainly consists of Ca 3p and O 2p orbitals and is adequately high in energy to provide an opportunity for \( p \)-type conductivity. Moreover, Ca doping enhances the absorptivity and reflectivity become low in the visible region. Aside, transparency decreases compared to the pure material. The optical properties were studied and clarified by electrons-photons interband transitions along with the complex dielectric function’s imaginary function.

Keywords: first-principles; density functional theory; pure \( \alpha \)-Ga\( _2\)O\( _3 \); Ca-doped \( \alpha \)-Ga\( _2\)O\( _3 \); electronic structure; optical properties

1. Introduction

Gallium oxides (Ga\( _2\)O\( _3 \)) are entitled to five different polymorphs, namely \( \alpha \), \( \beta \), \( \gamma \), \( \epsilon \), and \( \delta \). Among them, corundum structure \( \alpha \)-Ga\( _2\)O\( _3 \) has emerged as a next-generation power semiconductor material for a sensor, solar-blind UV-photodetectors, photocatalyst, and high-power devices [1–4]. The ultra-wide bandgap semiconductor \( \alpha \)-Ga\( _2\)O\( _3 \) enables high temperature and high voltage device operation such as field-effect transistor (FET) and Schottky barrier diode (SBD). \( \alpha \)-Ga\( _2\)O\( _3 \) is privileged of superior properties such as a smaller electron effective mass, higher breakdown field, and larger Baliga figure of merit [5–7] which have capabilities to go beyond existing technologies to 4H–SiC (3.26 eV) [8] and GaN (3.44 eV) in the power industry [9].

Band structure engineering would open new avenues in device applications [10]. Doping with particular elements in practical applications can boost the material’s electrical and optical properties and maximize the devices’ efficiency. Mostly, \( \alpha \)-Ga\( _2\)O\( _3 \) is privileged with good \( n \)-type doping conductivity due to its deep donor oxygen defect nature [11]. Silicon (Si) and Tin (Sn) are highly studied \( n \)-type shallow donors with a small ionization energy [11,12]. In contrast, high-quality \( p \)-type \( \alpha \)-Ga\( _2\)O\( _3 \) is challenging due to the lack of hole conductivity, low solubility, and activation rate of dopants which largely impede
the formation of the \( p-n \) junction bipolar semiconductor devices [13–16]. Despite several experimental reports on \( \alpha\text{-Ga}_2\text{O}_3 \), its theoretical analysis is relatively small and started to receive attention recently. The theoretically predicted Gr-I and Gr-II metals show \( p \)-type nature by doping on \( \text{Ga}_2\text{O}_3 \) as reported by Tang et al. [17]. In 2019, Dong et al. investigated the magnesium (Mg) element substitute at the gallium site that had proven to be a good \( p \)-type conductivity in \( \alpha\text{-Ga}_2\text{O}_3 \) through first-principles studies [18]. Tang et al. reported that the same alkaline earth metal group, calcium (Ca), plays a deep acceptor element and studied the electronic structures and optical properties of \( p \)-type Ca doped on a \( \beta\text{-Ga}_2\text{O}_3 \) first-principle calculation [17]. There is a lack of in-depth analysis and systematic study of new strong acceptor doping studies for the bipolar \( p-n \) junction of electronic and optical \( \alpha\text{-Ga}_2\text{O}_3 \) devices, which is of high demand for further exploration of potential \( \alpha\text{-Ga}_2\text{O}_3 \) films.

In this research, Gr-IIA alkaline metal Ca doping \( \alpha\text{-Ga}_2\text{O}_3 \) had reported the electronic structure and optical properties by the first-principles studies based on density functional theory (DFT). The work aims to find Ca potential by substituting the Ga site and supporting this theoretical investigation for future experimental work. Ca attributes of small ionization energy quickly release holes and show \( p \)-type conductivity nature. The doping of Ca contributes to a slight reduction in the optical bandgap due to the addition of the impurity band into the valence band (VB). The optical absorption spectra have shown a redshift of the absorption edge towards the visible-infrared region.

2. Computational Details

In this study, all the calculations were performed by using the Cambridge Serial Total Energy Package (CASTEP) code in Materials Studio (MS) 6.1 software based on the DFT [19]. The ultra-soft pseudopotential approach is used for general energy. The electronic wave function is unfolded with plane wave base groups, and ion potential is replaced by ultra-soft pseudopotential [20]. Ultrasoft pseudopotentials technology interacts with ions and electrons with total energy convergence \( 5 \times 10^{-6} \) eV/atom [21]. Cut-off plane-wave energy is set at 380 eV for total-energy, band structure, and spectra calculations. It has been shown that this functional exchange-correlation gives rise to wide-gap semiconductor atomic geometries with strong ionic bonds in excellent accordance with measured values. The exchange-correlation potential is defined by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) function and the local density approximation (LDA) [22]. The LDA utilization in this simulation work was used to compare the parameters, cell volume, and cell angle from the feature of the GGA-PBE. The electronic and optical characterization is then determined based on the structural geometry optimization to make the calculations effective and trackable [18]. The optimization of all calculated structures was done until the Hellmann Feynman force became less than 0.01 eV/Å (1 Å = 0.1 nm). Broyden-Fletcher-Goldfarb-Shanno (BFGS) is a reliable approach to optimize the structure by full relaxation of the lattice constant and internal coordinates [23]. For maximum stress and displacement, the convergence criterion was 0.02 GPa and \( 5 \times 10^{-4} \) Å, respectively. A primitive cell composed of 30 atoms (12 Ga atoms and 18 O atoms) was used to study the electronic structure and optical properties of the Ca doped \( \alpha\text{-Ga}_2\text{O}_3 \). A \( 3 \times 3 \times 2 \) k-point mesh of Monkhorst–Pack methods was used to integrate the Brillouin zone [24]. Ga, O, and Ca valence shell electrons configuration were [Ar] 3d\(^{10}\)4s\(^{2}\)4p\(^{1}\), [He] 2s\(^{2}\)2p\(^{4}\), and [Ar] 4s\(^{2}\), respectively.

3. Results and Discussion

3.1. Geometrical Structures

Firstly, geometry optimization was implemented using the BFGS method [25]. The most stable structure was achieved after the fully relaxed cell parameter and volume by reducing the energy state [20]. The investigated optimized crystal structure of intrinsic \( \alpha\text{-Ga}_2\text{O}_3 \) and Ca-doped \( \alpha\text{-Ga}_2\text{O}_3 \) is shown in Figure 1a,b. The lattice parameters \( a, b, c, \)
and unit cell volume $V$ are increased after Ca doping due to the larger atomic radius of Ca than that of Ga. Meanwhile, the bandgap $E_g$ decreases with Ca doping.

![Crystal Structure](image)

**Figure 1.** The crystal structure of the primitive cell (a) intrinsic $\alpha$-Ga$_2$O$_3$ and (b) Ca-doped $\alpha$-Ga$_2$O$_3$. Ga, O, and Ca atoms are denoted by brown, red, and green colors, respectively.

Figure 1 shows the typical corundum structure of $\alpha$-Ga$_2$O$_3$ with R$_3$c symmetry, and the crystalline cell comprises six Ga$_2$O$_3$ formula units. In the unit cell of $\alpha$-Ga$_2$O$_3$, oxygen anions are almost closely hexagonally packed, and gallium atoms occupy octahedral two-third sites. Every gallium octahedron shares one face and three edges with the other three octahedra sites. The gallium octahedral sites are distorted by the crystal lattice [7]. We investigated and explored the electronic and optical properties of Ca doped $\alpha$-Ga$_2$O$_3$ by substitution of Ga atoms lowest energy preferred sites. Table 1 lists all the optimized lattice parameters, and cell volume of pure and Ca doped $\alpha$-Ga$_2$O$_3$ material as compared to experimental results ($a = b = 4.983$, $c = 13.433$) [26]. The experimental value for $\alpha$-Ga$_2$O$_3$ has a lattice parameter and cell volume closer to that of the LDA calculation. In addition, the error is less than 1.5%, ensuring the reliability of our results. It has been shown that the calculated LDA is more precise and accurate than GGA-PBE according to the experimental reports on the lattice parameter of hexagonally structured $\alpha$-Ga$_2$O$_3$. Therefore, in this study, the electronic structure and optical properties of Ca doped $\alpha$-Ga$_2$O$_3$ were calculated using the DFT-LDA approach.

| Phase                | $a$ (Å)          | $b$ (Å)          | $c$ (Å)          | $V$ (Å$^3$)        |
|----------------------|------------------|------------------|------------------|-------------------|
| Pure Ga$_2$O$_3$     | LDA-CAPZ         | 4.965 (−0.36%)   | 4.965 (−0.36%)   | 13.338 (−0.71%)   | 284.747 (−1.42%)  |
|                      | GGA-PBE          | 5.074 (1.83%)    | 5.074 (1.83%)    | 13.664 (1.72%)    | 304.656 (5.47%)   |
|                      | GGA-PBE (CASTEP) | 5.028 (0.90%)    | 5.028 (0.90%)    | 13.511 (0.58%)    | 295.807 (2.41%)   |
| Ca-Doped Ga$_2$O$_3$ | LDA-CAPZ         | 5.010 (0.54%)    | 5.010 (0.54%)    | 13.520 (0.647%)   | 293.889 (1.74%)   |
|                      | Expt. [26]       | 4.983            | 4.983            | 13.433            | 288.859            |

Table 1. The lattice parameters ($a$, $b$, and $c$) and unit cell volume ($V$) of basic $\alpha$-Ga$_2$O$_3$ and Ca doped $\alpha$-Ga$_2$O$_3$ crystal structure. The values were compared with theoretical and experimental results.

The bond lengths for pure and Ca-doped $\alpha$-Ga$_2$O$_3$ are shown in Table 2. It is shown that the atomic radius of the Ga atom is smaller than that of the Ca atom according to the periodic table. Therefore, the Ga–O bond length is shorter than the Ca–O and O–O bonds in Ca-doped $\alpha$-Ga$_2$O$_3$. This situation is the same as the pure $\alpha$-Ga$_2$O$_3$ where the Ga–O bond length is shorter than O–O bonds. After Ca doping, the overall bond length is larger than before doping due to the concentration of Ca$^{2+}$ ions.
Table 2. The calculated bond length of undoped and Ca-doped α-Ga2O3.

| Type of Bond Length | Pure α-Ga2O3 | Ca-doped α-Ga2O3 |
|---------------------|--------------|------------------|
| Ga–O (Å)            | 1.989        | 1.993            |
| O–O (Å)             | 2.762        | 2.741            |
| Ca–O (Å)            | –            | 2.253            |

3.2. Electronic Structure

3.2.1. Electron Charge Density

The ionic and covalent bonding-based charge density contours of intrinsic α-Ga2O3 and Ca-doped α-Ga2O3 are shown in Figure 2a,b, respectively. The charge density distributions can be used to assess crystal bonding characteristics. In α-Ga2O3, the ionic or covalent structures are a contentious subject and have vital facts to understand the charge transport property [23,24]. The nuclei are bound by the charge density, which is shared between them. It has been shown that certain covalent bonding characters can exist between Ga and O atoms [24]. The electrons are located around the O atoms in the hexagonal phases, and there is no region of bond localization, indicating a predominantly ionic bond.

![Figure 2](image)

**Figure 2.** Distribution of electron density of (a) pure α-Ga2O3 and (b) Ca-doped α-Ga2O3.

In Figure 2b, a major reflection is observed in the distribution of charge density between the doping Ca atom and native atoms. By incorporating Ca, the oxygen atom’s nearest electrons population reduce compared to distant oxygen atoms, as presented in Figure 2b. Consequently, only the closest few electrons of the O atom donate to the Ca atom, leaving holes in the O atom to be p-type. The Ca atom loses all valence electrons while the electron density around the O atoms increases evidently and further decreases in the region between the Ca atom and the nearest O atom. A strong ionic bonding appears between Ca and the nearest neighbor O atoms. Meanwhile, Ca-doped α-Ga2O3 gives the outer shell electrons 4s² and partial 3p⁶ electrons of Ca atoms coupled with O 2p electrons.

3.2.2. Band Structure and Density of States

The first-principal calculations of the electronic band structure of undoped α-Ga2O3 are shown in Figure 3a. The density of states is shown in Figure 4a,c at different energy windows. The bandgap energy is usually determined between the valence band maximum (VBM) and the conduction band minimum (CBM), placed at the Brillouin region’s G point. The Fermi level is situated at 0 eV of the energy scale. The large disparity of theoretically calculated DFT-LDA bandgap (2.950 eV) and experimental band gap (5.3 eV) is due to the ground state DFT results of strong Coulomb correlation and exchange-correlation potential between the excited electrons in the underestimated LDA bandgap [27].
Figure 3. Energy band structure diagram of (a) pure \( \alpha\text{-Ga}_2\text{O}_3 \) and (b) Ca-doped \( \alpha\text{-Ga}_2\text{O}_3 \); Fermi level is set to zero.

Figure 4. The density of states of (a) pure \( \alpha\text{-Ga}_2\text{O}_3 \), (b) Ca-doped \( \alpha\text{-Ga}_2\text{O}_3 \), (c) pure \( \alpha\text{-Ga}_2\text{O}_3 \) (−10 to 10 energy window), and (d) Ca-doped \( \alpha\text{-Ga}_2\text{O}_3 \) (−10 to 10 energy window).
The electronic band structure of pure $\alpha$-Ga$_2$O$_3$, as shown in Figure 3a, is represented by the crystal structure made with the 12 Ga atoms and 18 O atoms of primitive cells. Figure 4a shows the uppermost valence band is a major contribution of O 2p states with a width from about $-0.12$ to $-7.43$ eV and a minor contribution of Ga 3d, 4p, 4s, and O 2s orbitals which are located between $-11.5$ and $-18.5$ eV. CBM consists of Ga 4s orbital states, and lies between 2.32 to 8.46 eV [26]. The valence band’s edge is reasonably flat, and the effective mass at VBM is relatively high. Characteristics of CBM is almost equally dispersed everywhere.

The electronic band structure of Ca-doped $\alpha$-Ga$_2$O$_3$ is shown in Figure 3b, and its corresponding DOS is shown in Figure 4b,d, at different energy values. The acceptor dopant has been introduced above the valence band and intersected with the Fermi level. The Ca-$\alpha$-Ga$_2$O$_3$ has a direct bandgap with the most upper part of the valence band and the lowest part of the G point’s conduction band. It is noticed that the DFT-LDA calculated bandgap of Ca-doped $\alpha$-Ga$_2$O$_3$ is 2.733 eV which is 0.217 eV less than that of pure $\alpha$-Ga$_2$O$_3$. In Ca-doped systems, the Ca 3p state contributes to the VBM, and the CBM is contributed to by Ga-4s and Ca-3p states. Ca creates dopant states near the topmost of VBs and shift the valence band edge at higher energy and reduce the bandgap.

The Ca 4s state shows very narrow bands at $-15.79$ to $-19.02$ in Figure 4b. The impurity levels lead to the excess holes over the upper part of the valence band [27]. The Ca doped cases’ highest occupy degree shifts dramatically downward by 0.12 eV due to the far higher energy of Ca 4s compared to Ga 3s orbitals. At around $-16.1$ to $-18.6$ eV, six bands are mainly composed of O 2s states and at $2.07$ to $6.94$ eV, six bands are mainly composed of O 2p states (Figure 4b). At around $-11.2$ to $-12.9$ eV, 20 bands consist mainly of Ga 3d states.

(Ga$_{1-x}$Ca$_x$)$_2$O$_3$ alloys bandgap energy with the incorporation of Ca impurity is schematically shown in Figure 5. In $\alpha$-Ca$_2$O$_3$, 3.33% of Ca concentrations were produced by replacing one Ga atom with Ca, respectively. Ca substitutes Ga octahedral sites and fully occupied band energy higher than the original valence band of the Ga$_2$O$_3$. This intermediate band originates from the coupling of Ca 3p, which lies below the O 2p band that forms the higher-lying valence bands, as shown in Figure 5. Furthermore, the intermediate valence band shows that a downward movement of the CBM was formed, attributed to the attraction between the Ca intermediate valence band and the CBM of the host. This situation resulted in a decrease in the bandgap of the (Ga$_{1-x}$Ca$_x$)$_2$O$_3$ alloy with the doping of Ca.

![Figure 5](image_url) Figure 5. Schematic representation of the effects of adding Ca on the electronic band structure of $\alpha$-Ga$_2$O$_3$. (Ga$_{1-x}$Ca$_x$)$_2$O$_3$ with $x = 1/30$. All energies are in eV. The bands showed in green represent the intermediate valence band, composed of hybridized Ca 3p and O 2p orbitals.
3.3. Optical Properties

3.3.1. Theoretical Description and Optical Properties

The optical properties of pure \( \alpha \)-Ga\(_2\)O\(_3\) and Ca doped \( \alpha \)-Ga\(_2\)O\(_3\) can be studied based on the dielectric function, absorption coefficient, and reflectivity. The optical transitions are related to inter-band and intra-band transitions in the crystal structure of solid materials. The inter-band transitions mainly contributed to the semiconductor rather than intra-band transitions to semiconducting crystal structure. The dielectric function \( \varepsilon(\omega) \) has a frequency dependence linear electromagnetic interaction response of incident photons with electrons and is separated into the real part \( \varepsilon_1(\omega) \) and imaginary part \( i\varepsilon_2(\omega) \). It is difficult to achieve accurate optical constants due to the underestimation of the bandgap. Hence, the optical property results were corrected by scissors operators according to experimental results. Scissors operators = 5.3 eV–2.950 eV = 2.35 eV, where 2.950 is theoretical DFT-LDA calculated bandgap and 5.3 eV is experimental bandgap \([28]\). The scissors operators used to shift all conduction levels to match the measured value of the bandgap. All-optical properties can be described from the complex dielectric constant in Equation (1) \([29]\):

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

The imaginary dielectric part \( \varepsilon_2(\omega) \) semiconductors are an essential parameter for determining optical properties for different designs of optoelectronic devices. The dielectric function imaginary part \( \varepsilon_2(\omega) \) is associated with the dielectric loss of energy or absorption of light described by the absorption coefficient in the material while the real part \( \varepsilon_1(\omega) \) is associated with the stored energy within the material (degree of polarization). The complex dielectric function imaginary part \( \varepsilon_2(\omega) \) is determined by summing the transitions between occupied and unoccupied electronic states, as reported in Equation (2) \([22]\):

\[
\varepsilon_2(\omega) = \left( \frac{4\pi e^2}{m\omega^2} \right) \sum_{ij} \left( \langle |i|j \rangle^2 f_i(1-f_j) \times \delta(E_{jk} - E_{ik} - \omega) \right) \text{d}^3k
\]  

where \( m \) is the mass of free electrons, \( e \) is the electron charge, \( M \) is the dipole matrix, and \( \omega \) is the frequency of incident photons. \( i \) and \( j \) are the initial and final states, respectively, \( f_i \) denotes the Fermi distribution function and \( i \)-th state with wave function vector \( k \). The dielectric function real part \( \varepsilon_1(\omega) \) can be derived from the imaginary part \( i\varepsilon_2(\omega) \) by the Kramers–Kronig dispersion Equation (3) \([30]\):

\[
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \omega\varepsilon(\omega)\text{d}\omega \left( \frac{\omega^2 - \omega^2}{\omega^2 + \omega^2} \right)
\]  

where \( P \) is the principal value of the integral. The absorption coefficient can be derived from the dielectric function as shown in Equation (4) \([31]\):

\[
\alpha(\omega) = \sqrt{2}(\omega)\left[ \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega) \right]^{1/2}
\]  

3.3.2. Dielectric Function

The dielectric constant is directly proportional to the crystal’s polarizability, representing the deformability of the electronic distribution, and relates the shape of the valence band charge density. Oxygen ions are supposed to contribute to polarizability in such a highly ionic substance as Ga\(_2\)O\(_3\). As was predicted in the current study, a difference of dielectric properties between Ca and \( \alpha \)-Ga\(_2\)O\(_3\) is projected. A considerably larger dielectric constant of \( \alpha \)-Ga\(_2\)O\(_3\) compared to Ca doped \( \alpha \)-Ga\(_2\)O\(_3\) can be drawn to a lightly dense ion package and a large number of Ga atoms coordinated in the \( \alpha \)-Ga\(_2\)O\(_3\) lattice \([7]\).

From Figure \(6\), the calculated imaginary dielectric function of intrinsic \( \alpha \)-Ga\(_2\)O\(_3\) and Ca-\( \alpha \)-Ga\(_2\)O\(_3\) were plotted and compared. The main peaks are 10.12 eV of pure and Ca-doped \( \alpha \)-Ga\(_2\)O\(_3\), respectively, corresponding to the electrons’ transitions from the upper
state O-2p valence band to the lower state Ga-4s conduction band. The Ca-doped α-Ga$_2$O$_3$ peak is smaller than that of intrinsic α-Ga$_2$O$_3$ and is enhanced towards the lower energy site. Moreover, this Ca doping absorption peak at 2.9 eV indicates that the absorption spectra increase from the UV to the visible region, and the average optical transmittance decreases.

![Graph](image)

**Figure 6.** The imaginary part of the complex dielectric function for intrinsic α-Ga$_2$O$_3$ and Ca doped α-Ga$_2$O$_3$.

3.3.3. Absorption and Reflectivity

The absorption spectra of intrinsic α-Ga$_2$O$_3$ and Ca-doped α-Ga$_2$O$_3$ in the range of energy (0 to 40 eV) and wavelength (0–1000 nm) are shown in Figure 7a,b. The presence of a high energy peak at 11.5 eV into the deep ultraviolet region is shown in both cases of α-Ga$_2$O$_3$ and Ca-doped α-Ga$_2$O$_3$. These peaks are associated with the inter-band transition from the valance band O 2p occupied states to the conduction band Ga 4s unoccupied states. From Figure 7a, it is worth noticing that the absorptivity of α-Ga$_2$O$_3$ is in the deep UV spectrum due to its semi-insulating nature. Meanwhile, Ca-doped α-Ga$_2$O$_3$ appears as a sharp new small peak at 2.9 eV which originated from the inter-band transitions of C 3p from the VBM to these CBM that promote $\varepsilon_2$ and enhanced absorption in the visible region.

Figure 7a,b show that the absorption spectra have a redshift with the Ca-doping. This shifting is mainly because of the hole carriers generated after the Ca doping so that the Fermi level enters the valence band, which is realized in the density of the states. The same phenomenon was observed in the absorption spectrum wavelength window in both cases of undoped and Ca doped α-Ga$_2$O$_3$ (Figure 7b). As shown in Figure 7b, the absorption spectra indicate that the transparency decreases with Ca doping due to enhancement of absorbance in the visible region.

Figure 7c,d show the reflection spectra of intrinsic α-Ga$_2$O$_3$ and Ca-doped α-Ga$_2$O$_3$ in the energy and wavelength window regime. For pure α-Ga$_2$O$_3$, a sharp main intense peak appears at 16 eV in the energy range and 70.45 nm in the wavelength range, and it decreases from the deep UV-visible to infrared region. Meanwhile, for the Ca doped α-Ga$_2$O$_3$ system, two major peaks appear at the same position as the pure phase, but reflectivity is lower than that of the pure one. These characters drag material potential towards optoelectronics and bipolar device application.
4. Conclusions

The substitutional Ca doping on the α-Ga₂O₃ electronic, structural, and optical properties was studied through a first-principles calculation based on the DFT. The Ca doping predominantly affects the band structure and optical properties of pure α-Ga₂O₃. The DFT-LDA calculated bandgap of α-Ga₂O₃ is decreased to 2.950 eV after Ca doping and the forbidden bandwidth appeared at the top of the valance band. The results obtained show that Ca-doped α-Ga₂O₃ is an obvious variation of energy band structures and the charge density distribution. The acceptor energy states are composed of Ca 3p and O 2p orbital states. The Ca-doped α-Ga₂O₃ dynamic dielectric function is observed. The most important absorption peak shifted in the visible regime; it realizes p-type α-Ga₂O₃ but not a strong p-type candidate for optoelectronic device application. However, the lack of experimental results about the optical properties of Ca doped α-Ga₂O₃ requires further experimental works to compare with our simulation results.

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