Electronic and optical behaviour of lanthanum doped CaTiO₃ perovskite

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Abstract

To improve the efficiency of perovskite based solar cells, doping of heavier elements in Perovskite materials (ABX₃) can modulate its electronic and optical properties significantly. Thus it is important to understand the possible microscopic origin of the band gap modification and optical enhancement after heavier element doping using first-principles studies. Here we investigate the effect of La doping, while substituting the Ca atom, on the electronic and optical properties in CaTiO₃ perovskite material using generalized gradient approximation within density functional theory. We observe a decrease in lattice constants and bond lengths in LaxCa1−xTiO₃, mainly due to re-distribution of electronic charge density between La and Oxygen, as confirmed by charge density contour. We further notice a widening of electronic band gap and an upward shift of Fermi level into the conduction band, thus characterizing LaxCa1−xTiO₃ as an n-type material. DOS diagram attributes this shift mainly due to the appearance of La p-DOS and d-DOS and their repulsion with N p-DOS, when La enters into the host lattice at Ca site. Investigation of optical properties upon La Doping in CaTiO₃ exhibits further shifting of polarization and refractive index to lower values as compared to its pure counterpart, due to dominating semiconducting behavior and hence one observes a blue shift in absorption and reflection spectrum accordingly. Energy loss function is found to be consistent with absorption and extinction coefficient measured in case of LaxCa1−xTiO₃. All these results are found to be consistent with the existing experimental and first-principles studies.

1. Introduction

Calcium Titanium Oxide (CaTiO₃) mineral is considered as an origin of term Perovskites after its discovery by a Russian mineralogist Count Lev Aleksevich Von Perovski [1]. The class of Perovskites, whose general formula is ABO₃, evinces excellent physiochemical properties for example; ferroelectricity and dielectric properties, ionic-conduction properties [2], superconductivity [3] and insulator-metal transition [4]. Since A and B being two cations of different sizes bonded with X anion (mostly Oxygen atoms), the cations A belong to alkaline earth metal group (Ca, Mg, Sr etc) and are slightly bigger in size than the other cations B of transition metal’s group. CaTiO₃ exhibit various phases at different temperatures. If CaTiO₃ is synthesized below 1107 °C, it is orthorhombic and transforms into tetragonal phase upon temperature increase up to 1227 °C. While its cubic phase is reported for temperatures above 1300 °C [5]. The reported negative temperature coefficient (NTC) of CaTiO₃ makes it ideal for resistor element [5].

The cubic form of CaTiO₃, Perovskite is ideal for device applications such as capacitors [6] wireless communications [7, 8], displays [9], random access memories [10], piezoelectric, tunable microwave devices [7, 11], transducers and sensors [7, 12] due to its distinctive simple structure and properties (dielectric, ferroelectric).
These properties of CaTiO₃ type of Perovskites are further influenced strongly by the presence of lattice defects at cation A or B sites, nature of material (bulk or nanostructures), particle size and morphology including exposed surface area [13–16]. These aspects are often explored by using density functional theory (DFT), which provides not only the physical insight about various phenomena but also serves as an important tool to predict the un-explored materials and their properties in advance. Wang et al[17] had explored the effect of surfaces on the optical and dielectric properties of CaTiO₃ using first-principles calculations, following the similar type of work done by Cockayne et al[18] and Gillet et al[19] predicted the cubic phase of this material with no flipping of phases, when the pressure was raised up to 26 GPa. Keeping in view the difficulty to study phase transitions under high pressure and temperature, Saad et al[20] evaluated the effect of higher pressures on the structural, elastic constant and electronic properties of CaTiO₃ using ab-initio calculations. For its bulk crystals, different values of the electronic band gap are reported such as 3.4 eV, 3.86 eV and 3.97 eV [14]. Wang et al[21] found the optical band gap of 3.95 eV for CaTiO₃ thin layers of width ~100 μm. Later on the carrier generation and compensation mechanisms were analyzed by measuring the electrical and optical properties of Yttrium and Neodymium doped CaTiO₃ [22, 23]. It was observe that the conductivity first decreased and then increased with dopant concentration at high temperatures. In addition, all the doped samples exhibited p-type conductivity at higher temperatures and metallic behavior at low temperatures. Remarkable increment in conductivity shifted the optical absorption to the infrared region. Moreover, the x-ray absorption spectroscopy measurements and inverse photoemission spectroscopy indicated the presence of two bands above Fermi level [24] and the explanation of these results were provided by first-principles studies of Nb–doped CaTiO₃ [25] later on.

La offers significant modifications in structural, electronic and optical properties of perovskites [26]. Here the effect of different doping concentration on the electronic and optical properties of CaTiO₃ is ignored primarily due to two reasons. First of all, it has been observed experimentally that the solubility of Lanthanum in perovskite materials such as lead titanate (PbTiO₃), lead zirconate (PbZrO₃), lithium tantalate (LiTaO₃), barium titanate (BaTiO₃) and niobate (LiNbO₃) [26] is critically lower [27, 28], which limits higher dopant concentration (even 5%–10%), thereby adding further un-clarity in understanding the role of Lanthanum on structural and optical modifications of perovskites and oxides [29–31].

To date, there is no report available to explore the effect of Lanthanum (La) as a dopant on the structural, electronic and optical study of CaTiO₃.

First we explore the micro-structural origin of La doping in CaTiO₃ lattice using first principles studies. Since the physical properties (structural, electronic and optical properties) of the material under study vary significantly upon doping. We find La occupies Ca place in host lattice and hence the bond length decreases. This gives rise to an increase in indirect band gap after La doping. It is important to mention here that the calculated band gaps for pure and La doped systems are of indirect nature. The Fermi level is appeared to be shifted upward gives rise to an increase in indirect band gap after La doping. It is important to mention here that the calculated values of the electronic band gap are reported such as 3.4 eV, 3.86 eV and 3.97 eV [14]. Wang et al[21] found the optical band gap of 3.95 eV for CaTiO₃ thin layers of width ~100 μm. Later on the carrier generation and compensation mechanisms were analyzed by measuring the electrical and optical properties of Yttrium and Neodymium doped CaTiO₃ [22, 23]. It was observe that the conductivity first decreased and then increased with dopant concentration at high temperatures. In addition, all the doped samples exhibited p-type conductivity at higher temperatures and metallic behavior at low temperatures. Remarkable increment in conductivity shifted the optical absorption to the infrared region. Moreover, the x-ray absorption spectroscopy measurements and inverse photoemission spectroscopy indicated the presence of two bands above Fermi level [24] and the explanation of these results were provided by first-principles studies of Nb–doped CaTiO₃ [25] later on.

2. Computational details

Kohn–Sham equations are worked out to investigate the structural, electronic and optical properties of La doped CaTiO₃ using robust techniques of plane-wave basis set along with pseudopotentials approach within the context of density functional theory (DFT). Electron–exchange correlation effects are approximated via generalized gradient approximation performed by Perdew–Burke Erzenhoff (GGA-PBE) and electron-ion interactions with Ultrasoft pseudopotential (USP)[32, 33]. Pseudopotential approach, as implemented in CASTEP, furnishes efficient and faster calculations due to the non priori nature of atomic orbital’s shape approximation at the start. USP offers frozen core approximation hierarchy and hence relatively smaller numbers of Fourier components are needed to approximate electron-ion interactions. This save computational time while maintain reasonable accuracy [34].

CaTiO₃ is an n-type chemically stable semiconductor with wide band gap of 3.6 eV [35, 36]. It belongs to the space group pm-3m, with Ca ions placed at the corners (1/2,1/2,1/2), Ti at the body center (0,0,0) and Oxygen at face center (1/2,0,0; 0,1/2,0; 0,0,1/2). A Super cell of $2 \times 2 \times 1$ dimension was used to investigate the La doping effect in CaTiO₃, as shown in figure 1. The first row elements and transition metals turn out to be suitable dopants in Perovskites [37]. The Pseudo-atomic configurations for La, O, Ti and Ca are $5d^{1}6s^{2}$, $2s^{2}2p^{4}$, $3d^{2}$ $4s^{2}$, $4s^{2}$ respectively.

Electronic wave functions are expanded by using plane wave basis set with optimized cut-off energy ($E_{cut}$) of 300 eV. In addition, the Brillouin zone integration is carried out via Monkhorst pack grid of $2 \times 2 \times 1$ k-points.
Geometry optimization was performed via single point energy calculations to obtain ground state energy structure. In geometry optimization step, the atomic positions and lattice parameters were iteratively refined in a mixed space of cell internal parameters and cell degrees of freedom. This iterative process was continued until the forces per atoms were found less than 0.03 eVÅ\(^{-1}\) and the energy convergence threshold as \(1.0 \times 10^{-5}\) eV atom\(^{-1}\). Then the optimized structure was exploited to calculate the electronic and optical properties of CaTiO\(_3\) before and after La doping. Comparative analysis of both the systems (doped and undoped systems) is presented and discussed in next section.

### 3. Results and discussion

#### 3.1. Geometry optimization

In order to estimate the structural, electronic and optical properties of Pure and doped CaTiO\(_3\), geometry optimizations are executed on each supercell to reduce external stresses. This gives rise to relaxed CaTiO\(_3\) crystal lattices and energy versus volume optimization plot resulted in equilibrium lattice parameters in both cases. The calculated lattice parameters (\(a=b=c\)) in case of CaTiO\(_3\) system are 3.931 Å which are in good agreement with the other experimental lattice parameters of 3.897 Å\(^3\) and 3.895 Å\(^3\)\(^\)\(^\)\(^\)\(^\) [38], [39]. In addition the calculated lattice parameters are slightly overestimated in contrast with those lattice constants (3.89 Å) [20] calculated by FP-LAPW method as implanted in wien2k, by using GGA method and are close to the other first principles studies 3.937 Å\(^3\) [13]. The minute deviation of our results with the experiments [32, 33] and theory [13, 20] ensures the validity and accuracy of our calculations. In table 1, lattice parameters before and after La doping in CaTiO\(_3\) are enlisted.

Furthermore, When Ca is replaced by La atom, the bond lengths between (La–Ca) is calculated to be 3.892 Å, which is less than that of the bond length (3.931 Å) [40] between (Ca–Ca) in pure structure as given in table 1. It should be noted that the experimentally calculated bond length between two Ca atoms is 3.89 Å. It is less than the bond length calculated herein using GGA approximation [38]. (Ca–Ca) bond length calculated with the other DFT calculations [38] is 3.90 Å, rather close to our findings. Shortening of bond lengths illustrate the stronger interaction among La, Ca and O atoms after doping as compared to the pure CaTiO\(_3\). Table 1 also shows longer bond length in case of La–Ti atoms (3.439 Å) than Ca–Ti bond length (3.387Å\(^3\)) and hence weaker interaction between La and Ti is evident. In addition, we have calculated La and O bond length is 2.760 Å less than the Ca and O bond length (2.765 Å). The experimental bond lengths between Ca and O were reported as 2.75 Å [39] and 2.76 Å [41].

In addition, nature of bonding among different atoms and bond lengths are confirmed by electronic charge density plot as shown in figure 2. Pure CaTiO\(_3\) shows spherical charge distribution between Ca (light green) and oxygen (red) atom, with covalent bond formed between two atoms.

We have observed pure ionic nature of Ca–Ti bond as evident from spherical shape of the charge density cloud (figure 2(a)), in accordance with the already existing literature [20]. Also the nature of Ti–O bond changes from almost spherical shape to the oval one upon La (Light blue) doping as shown in figure 2(b). So La (light blue) doping, after substitution at Ca site, induces strong hybridization between La and oxygen atoms in this case, and hence the bond length appeared to be shorter (figure 2). This is due to the reason that O-atom having...
| Bond Lengths (Å) for Pure and La-doped CaTiO$_3$ | Present Study | Others |
|-----------------------------------------------|---------------|--------|
| Lattice parameters (Å) for Pure CaTiO$_3$ | 3.931 (pure) 3.892 (doped) | 3.897$^{38}$, 3.895$^{39}$ 3.89$^{40}$ |
| Lattice parameters (Å) for La-doped CaTiO$_3$, $a=b=c$ | 3.931 (doped) 3.892 (doped) | 3.90$^{13}$ 2.750$^{20}$ |
| Bond Lengths (Å) for Pure CaTiO$_3$, $a=b=c$ | 3.387 (Ca–O) 3.37$^{40}$ (Ca–O) 2.76$^{20}$ (La–O) 2.75$^{20}$ (La–O) | —— —— —— —— |
| Bond Lengths (Å) for La-doped CaTiO$_3$, $a=b=c$ | 3.439 (La–O) 2.760 (La–O) | —— —— |

Table 1. Lattice parameter and bond lengths for Pure and La-doped CaTiO$_3$. 

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higher electronegativity than La atom attracts La valence electrons more towards itself and hence the nature of bond might shift from pure covalent to a dominant ionic. This is also possible as La-d electrons are more delocalized as compared to Ca-s electrons [20].

3.2. Electronic properties of La-doped CaTiO₃
Electronic response of a material is envisioned by the electronic band structure and density of state (DOS) properties [42]. Electronic band structure offers insight of possible energy domain, which an electron may or may not have. In case of semiconductor occupied states are represented by valence band and forbidden energy gap possesses no electrons. Conduction band is usually empty in semiconductor material, but a smaller value of band gap or addition of dopant can result in shift of electron to this band [43, 44]. CaTiO₃ being a wide band gap Semiconductor encounters large separation between top of valence band maximum (VBM) and bottom of conduction band minimum (CBM) and hence absorb energy only in ultraviolet range. Electronic band structures of pure and La doped CaTiO₃ in high symmetry directions are calculated and shown in figure 3.

Figure 3(a) representing that the maximum of valance band is at R point and minima of conduction band is at G point. The topology of CaTiO₃ bang gap closely resembles to that reported by S Tariq et al [20]. As shown in figure 3, the Fermi level of LaTiO₃ is set to 0 eV [45]. The difference between these two points is 1.84 eV. As these two points are not on same k-point, so the band gap of CaTiO₃ is of indirect nature. This value of band gap (1.84 eV) is about 50% smaller than the experimental values of 3.5 eV [46]. Moreover, in first-principles calculation performed by Saad Tariq et al using full potential linear augmented plane wave method (FP-LAPW) using GGA approximation, the band gap of CaTiO₃ has been reported to be 2.003 eV [20].
Severe underestimation of band gap in our case is one of the main limitations of DFT theory [45]. Unlike direct band gap, where the band edges are aligned, indirect band gap contains un-aligned band edges (with different energy and momentum values), that is why the electron cannot make direct transition to the conduction band at optical excitations. Thus the radiative recombination is only possible if there is an emission of phonons at first, leading to a considerable momentum and energy losses. So both the phonon and photon emissions are involved in indirect band gap materials.

Doping of La at Ca site in CaTiO$_3$ redistributes the electronic band structure as shown in figure 3(b), where the top of valence band lies at M point and the minimum of conduction band is located at G point. Hence, we get wider indirect band gap of 2.12 eV after La doping in CaTiO$_3$. Figure 3(b) demonstrates the pinning of Fermi level (FL at 0 eV) positioned into the conduction band. This is in good agreement with the previous work of titanate series (SrTiO$_3$, CaTiO$_3$ and BaTiO$_3$), where the CB minimum shifted to lower energies upon doping of heavier element of higher atomic number at A cation site [47]. In addition, increase in band gap can be linked with the structure (lattice parameters and bond lengths). Lattice parameters in case of La doped CaTiO$_3$ are reduced in contrast with pure CaTiO$_3$, thus giving rise to an increase in band gap. As we see that the high symmetry points M and G move away from the Fermi level by enhancing the electronic band gap, therefore we consider the breaking of weak covalent bond between Ti and Ca might be responsible for further conversion of indirect band gap into the direct one, as observed in [20].

Now we investigate the widening of band gap and shifting of Fermi level via explaining the electronic band structure and its composition for pure and La doped CaTiO$_3$-DOS using the concept of partial, elemental and total DOS in both cases as shown in figures 4(a)–(f). It furnishes important understanding about the states availability corresponding to each energy level.

Figure 4(a) demonstrates the partial density of states (PDOS) before and after doping, whereas the Figures 4(b) to (e) illustrate the atomic DOS of Ca, Ti, O and La respectively. PDOS of CaTiO$_3$ show dominant contribution from p-DOS at the top of valence band (figure 4(a)), which is modified significantly after La doping, where the bottom of valence band (−8 eV to −12). It is observed that the bottom of valence band contains major contribution from s-DOS after La doping in CaTiO$_3$ with relatively less dominant part played by p-DOS. Furthermore, the top of conduction band is composed of d-DOS with weaker density of p-DOS in case of pure CaTiO$_3$. La doping offers significant p-orbitals located in between 0–7 eV, while d-DOS are far higher in concentration as compared to its p-DOS counterpart. In order to understand the exact elemental composition at different location of PDOS, we have represented the elemental contribution before and after doping in CaTiO$_3$ in subsequent figures 4(b)–(e).
Figure 4(f) gives the comparative analysis of total density of states (TDOS) of pure and La doped CaTiO3. TDOS diagram for pure CaTiO3, ranges from −5 eV to −13 eV. The topology of TDOS expresses the top of valence band having width of 5 eV, whereas the top of the conduction band has a width of about 13 eV. Top of conduction band attributes major contribution from O-p-DOS with a negligible contribution of Ti-d DOS (figure 2(d)). Ca-p-DOS also show significant contribution, than those of O-p DOS, at the top of valence band (figure 2(b)). This trend is in good agreement with the previous reported results [48].

Whereas the top of conduction band (0 to ~8.3 eV) is composed of mainly Ca-p DOS and Ti-d DOS (figures 4(b) and (c). In this region, the contribution of Ca-s DOS and Ti-s DOS is relatively small. Now TDOS in case of La doped CaTiO3 offer more wider region with higher electronic states per unit energy. DOS are redistributed significantly after La doping in CaTiO3. Greater energy gap between the valence band and minimum conduction band is apparent from the TDOS diagram. TDOS diagram shows the shifting of valence band to much lower energies. Now the valence band has significant contribution from La p and d-DOS, along with minor part played by La-s DOS. It is evident from figures 4(d), that the O-p DOS are shifted to higher energies after La doping possibly due to O-p and La-d DOS repulsion. This result in shifting of Fermi level into the conduction band, making La doped CaTiO3 as n-type material. Appearance of conduction band is significantly modified due to La, whose p and d-DOS lie into the Fermi level (figure 4(e)). In addition, the numbers of electronic states available to be occupied are comprehensively enhanced. Thus we assert that the shifting of Fermi level into the conduction band is a result of O-p DOS displacement to conduction band due to their repulsion with La p-d DOS. Depending upon the significant modifications in electronic band structure, La doped CaTiO3 can be considered as a potential material for photoelectric applications.

3.3. Optical properties

As pure CaTiO3 belong typically to a family of semiconductors, thus it is imperative to modify its physical properties via doping with specific element at specific site. Here we analyze the effect of La doping in CaTiO3. In order to elaborate the response of doped perovskite materials in contrast with the pure materials, we calculate their optical properties such as energy loss function, absorption coefficient, complex dielectric constant, complex refractive index and reflectivity. First of all we calculate the optical properties of pure CaTiO3 and then compare with those of La-doped one as shown in figure 5. Optical properties mentioned above are frequency dependent and are interrelated. Hence one can calculate any desired quantity from any already known optical property. Maxwell equations provide solid foundation to extract all these properties, initially calculating complex dielectric function first. Complex dielectric constant (\(\varepsilon = \varepsilon_1 + i\varepsilon_2\)) explain the interaction of material to varying electric fields. It consists of two parts, \(\varepsilon_1\) and \(\varepsilon_2\), the real part of dielectric function (DF), is a measure of polarization induced in pure and doped CaTiO3, as a function of externally applied electric field as shown in figure 5(a). Imaginary part of DF (\(\varepsilon_2\)) elucidates the dissipation of energy within the materials as given in figure 5(b) and is related to the absorption. Both the components of DF are dependent upon the energy. \(\varepsilon_2\) can be obtained from the electronic band structure directly and \(\varepsilon_1\) by using Kramer–Kroning dispersion relation.

Figure 5(a) expresses the larger value of \(\varepsilon_1\) for pure CaTiO3 at 0 eV as compared to that of La doped CaTiO3. Decrease in real part of DF in case of La doped CaTiO3 is attributed to more metallic character of pure CaTiO3, which shifts to semiconducting behavior upon La incorporation into the host lattice. As the energy of incident radiations increases, \(\varepsilon_1\) which corresponds to the polarization of material approaches to its maximum value. More semiconducting behavior requires more incident energy to get maximum polarization. Therefore, one observes \(\varepsilon_1\) getting its peak value at lower energy in case of pure CaTiO3 in contrast with its doped counterpart. High frequency dielectric function of orthorhombic CaTiO3 has a value of 6.25, whereas its cubic phase (present study) has its value close to 6 at 0 eV [49].

Meanwhile, as the imaginary part of DF (\(\varepsilon_2\)) increases, energy contribution to polarization decreases and approaches to its minimum value corresponding to highest value of \(\varepsilon_2\) which is around 4.8 eV for pure structure and 6 eV for La doped CaTiO3.

Absorption spectra for La doped CaTiO3 shows a blue shift in absorption edge (located at 2.12 eV) as compared to its pure structure, where the CaTiO3 starts absorbing electromagnetic radiations at around 1.84 eV, which is underestimated due to the lower value of band gap observed in these calculations. Absorption coefficient approaches to its maximum value at about 28 eV for CaTiO3 and it shifts to more higher value of approximately 42 eV for La doped CaTiO3. Multiple absorption peaks may belong to the electronic transition between Ti-d to Ca-d and La-d states. This shifting of absorption edge to higher energies is an indication of band gap enhancement. Energy loss function (ELF) characterizes the amount of energy lost within the materials, when electromagnetic radiations are incident upon it. We consider in this case the electrons are not attached to their lattice positions but perform plasma oscillations. Maximum value of ELF corresponds to these oscillations [50].

ELF approaches to its maximum values at around 10 eV for La doped CaTiO3, where the real part of DF is minimum. It is the main characteristic of semiconductors. Ellipsometry measurement of Low-energy electron
energy loss function (EELS spectrum) of polycrystalline CaTiO$_3$, in the range of 0 eV to 62 eV, [49] suggested the lowest possible transition at 6.0 eV. This peak was attributed to the band gap transition. In addition to this lowest energy peak, other EELS peaks were reported at 14.4 eV, 23.4 eV, 35.2 eV and 47.3 eV. In this study, EELS spectrum has multiple peaks at 6 eV, 8 eV, 11 eV, 14.5 eV, 20 eV, 29 eV, 37 eV and 39.3 eV. These peaks above 20 eV represent transition from bottom of valence band to CB, namely from O-2p to Ti-3d states [49].

Reflectivity (figure 5(e)) can be best explained using the concept of complex refractive index (N), which has two parts such as refractive index (n) and extinction coefficient (k). Refractive index measures the transparency of material, whereas the extinction coefficient describes the attenuation of electromagnetic wave while traversing CaTiO$_3$. At photon energy of 0 eV, the refractive index (n) is maximum (2.46) for pure CaTiO$_3$ with respect to no absorption, but Ueda et al found refractive index slightly smaller than our results i.e. 2.25 eV [49]. The CaTiO$_3$ is transparent at this value and peaks its values at 2.7 eV until the material start absorbing. As long as the absorption increases, the refractive index decreases and hence the transparency of material decreases. Then beyond 30 eV, it almost remains unity after plasma oscillation takes place, which demonstrate the insulator-like behavior. For La doped CaTiO$_3$, the refractive index (n) decreases to a value of 1.8 at 0 eV due to decrease in real part of DF. Extinction coefficient (k) is in good agreement with the absorption in pure CaTiO$_3$ and is shifted to higher energy in case of La doped CaTiO$_3$, in agreement with its absorption spectrum. Reflectivity of pure CaTiO$_3$ is higher as compared to its La doped counterpart, and achieves its maxima and minima corresponding to refractive index of the relevant pure and doped cases. The reflectivity La doped structure decreases significantly to almost 50% in contrast with its pure counterpart, whereas the peaks provide threshold values for possible indirect band optical transition from valence band to the conduction band mainly due to O-2p and Ti-3d states transitions [48].

4. Conclusion

The conclusions of this study are summarized as follows.

This study explains the effects of Lanthanum doping on the optical, electronic, and structural properties of CaTiO$_3$. This all is done with the help of 1st principles calculation, which is based on density functional theory (DFT). The examined structural properties after La-dopant were found to be consistent with the experimental results. Electronic band gap was widened, and Fermi level shifted into the conduction band in case of La-doped system, in contrast with the pure structure. Hence, an n-type degenerate semiconducting behavior was predicted in case of La$_x$Ca$_{1-x}$TiO$_3$, due to Fermi level shifting into the conduction band. These effects were well explained using the concept of density of states (TDOS and PDOS both). After doping, Oxygen p-DOS states at the bottom
of conduction band and top of valance band changes significantly. TDOS also confirmed the shifting of Fermi level into the conduction band in case of La$_2$Ca$_{1-x}$TiO$_3$. At the end, a detailed comparison of optical properties such as complex dielectric function, absorption, spectrum, reflectivity, refractive index and energy loss function is made between pure and La-doped system. Real part of DF (ε$_1$) and refractive index (n) showed a decrease at 0 eV after La doping, where the absorption coefficient shifted to higher energies after doping due to enhanced energy band gap. Energy Loss function and extinction coefficient was found to be consistent with the absorption spectrum.

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