

# Structural and Electronic Properties of La-doped CaTiO<sub>3</sub> Crystal

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**ABSTRACT:** There is experimental and computational evidence that some important properties such as electrical conductivity and ferroelectricity in the CaTiO<sub>3</sub> crystal change according to the dopant states. Using an INDO quantum-chemical computational method modified for crystal calculations we explore the stability of the La-doped CaTiO<sub>3</sub> crystal in both phases, cubic and orthorhombic. The calculations are carried out by means of the supercell model based on the LUC (Large Unit Cell) approach as it is implemented into the CLUSTERD computer code. The equilibrium geometry for impurity is found together with the crystalline lattice distortions. Atomic displacements and relaxation energies are analyzed in a comparative manner for the two crystallographic phases. A new effect of electron transfer from the local one-electron energy level within the band-gap to the conduction band is observed.

**Key words:** CaTiO<sub>3</sub>; periodic LUC model; impurity-doping; structural and electronic properties

## Introduction

Numerous scientific studies have been carried out on the perovskite-type titanates since the discovery of ferroelectricity in the  $\text{BaTiO}_3$  crystal in the 40's. There are myriads of applications in which titanates are the key materials. Therefore, the knowledge of changes of the electronic, structural and optical properties due to the doped states in these ceramic materials is very essential and it is one of the most important subjects of present-day research. Huge efforts have been done so far by both experimental and computational groups to study titanates with perovskite structures such as  $\text{CaTiO}_3$  [1, 2],  $\text{SrTiO}_3$  [3, 4] and  $\text{BaTiO}_3$  [5, 6]. However, a theoretical basis of carrier generation and behavior in these materials has not been definitely elucidated yet. Recently, we have achieved some interesting and encouraging results in titanate calculations. The examples include study of self-trapped [7] and acceptor-impurity trapped [8, 9] hole polarons in  $\text{BaTiO}_3$ , the computation of point defects in  $\text{SrTiO}_3$  [10] including La-doping in the superconducting phase of this material [11].

$\text{CaTiO}_3$  shows an unstable cubic structure, which exists at very high temperatures. The closer packed orthorhombic phase is found to be more stable, which has been shown in our previous study [12]. This is due to the fact that the ionic radius of a Ca ion is smaller than that of Sr and Ba ions. As a result, atomic rearrangement occurs leading to the orthorhombic structure. Because of its rather complicated geometry, only few studies have so far been reported on the electronic structure of this material [2, 13]. However, this crystal has some important applications. The most known examples are as follows:  $\text{CaTiO}_3$  is one of the important constituents for the disposal of high level radioactive waste materials [14, 15], it is also utilized in the construction of field

devices and sensors for the study of the rheology of the interior mantles of the Earth [16].

The importance of this material was shown in recent experimental work done on carrier generation mechanisms in Y- and Nb-doped  $\text{CaTiO}_3$  monocrystals [2, 13]. These measurements pointed out a drastic increase of the electrical conductivity if the impurity concentration is sufficiently high. Furthermore, two broad bands were observed above the Fermi level using inverse photoemission spectroscopy and X-ray absorption spectroscopy [17] measurements. These experimental results have been later explained by computational quantum-chemical studies of Nb-doped  $\text{CaTiO}_3$  [12]. La is one of the common impurities in calcium titanate crystals. Therefore, we have performed for the first time a quantum-chemical study to get reliable answers on physical properties of La-doped  $\text{CaTiO}_3$  crystal.

The objective of this work is to study the equilibrium geometry of a La impurity in  $\text{CaTiO}_3$  cubic and orthorhombic lattices as well as the lattice distortion due to the impurity doping. The study of electronic properties is done in a comparative manner for the cubic lattice *versus* the orthorhombic one. The article is organized as follows: In the second section, the computational method is outlined giving a short description of the periodic LUC (Large Unit Cell) model. The third and fourth sections deal with results concerning lattice distortion in the cubic and tetragonal phases of the material due to the La presence and also contain some data on the perfect crystal computations. The fifth section gives results of the extra electron influence upon the band structure properties. Finally, our conclusions are given in the last section.

## Computational Details

A quantum-chemical semi-empirical INDO method developed especially for crystals is used in the present work. The method is based on the Molecular Orbital (MO) theory [18]. This quantum-chemical computational scheme has been used with great success recently, especially exploiting the so-called LUC model [19]. The model is capable of simulating real crystals, because it takes into account the property of periodicity and can incorporate point defects. The method as it is implemented into the CLUSTERD computer code [20] is very reliable in treating periodic systems. Due to its semi-empirical character and a specific parameterization scheme [21] the computer program is not cumbersome and time consuming in the treatment of the electronic and spatial structure of complex systems. Thus, it is especially useful in the treatment of crystals with mixed ionic-covalent chemical bonding, like  $\text{CaTiO}_3$ . Up to now a number of crystals using this methodology have been studied, the examples include materials such as  $\text{SiO}_2$  [19],  $\alpha\text{-Al}_2\text{O}_3$  [22-25],  $\text{TiO}_2$  [26-29] and  $\text{WO}_3$  [30].

Within the method each MO is constructed as a linear combination of atomic orbitals (LCAO) [18] in order to express the wave function of the system. Each energy value is calculated by the Hartree-Fock Self-Consistent-Field (SCF) method and the total energy of the system is obtained including the system periodicity and symmetry. The most convenient and accurate way to study periodic systems containing point defects is the periodic LUC model. The basic idea of the LUC is in computing the electronic structure of the unit cell extended in a special manner at  $\mathbf{k}=0$  in the reduced Brillouin zone (BZ). This is equivalent to a band structure calculation at those  $\mathbf{k}$  points,

which transform to the BZ center on extending the unit cell [19]. The total energy of the crystal is written in the following way:

$$E_{\text{LUC}} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}^{00}} + \frac{1}{2} \sum_{A \in \text{LUC}} E_C^A + \sum_j^{\text{occ}} \varepsilon_j(0) + \frac{1}{2} \sum_{\mu, \nu \in \text{LUC}} \rho_{\mu, \nu}(0) Q_{\mu \nu} \quad (1)$$

Here  $\varepsilon_j(\mathbf{k})$  are the eigenvalues of Fock's matrix, occ is the number of occupied electronic states in the system,  $\rho_{\mu \nu}(\mathbf{k})$  are the density-matrix elements in the basis of Bloch's combinations of atomic orbitals (AOs),

$$E_C^A = Z_A \sum_{l \neq 0} \sum_{B \in \text{LUC}} \left[ \frac{Z_B}{R_{AB}^{0l}} - \sum_{\mu \in B} \rho_{\mu \mu}(0) (v^{A0})_{\mu \mu}^{ll} \right], \quad (2)$$

$$Q_{\mu \nu} = T_{\mu \mu}^{00} - \sum_{A \in \text{LUC}} Z_A (v^{A0})_{\mu \mu}^{00} + \sum_{l \neq 0} H_{\mu \mu}^{0l}, \text{ if } \mu = \nu \quad (3)$$

$$Q_{\mu \nu} = \sum_l H_{\mu \nu}^{0l}, \text{ if } \mu \neq \nu \quad (4)$$

where  $T_{\mu \mu}^{00}$  are the matrix elements of the kinetic energy operator,  $(v^{A0})_{\mu \mu}^{ll}$  are those of the electron-core interaction operator,  $R_{AB}^{0l}$  is the distance between the cores of atoms A and B,  $Z_A$  and  $Z_B$  are charges of these cores.

The total energy equation (1) is obtained after the introduction of the so-called "cut-off" function

$$\omega(r_{\mu \nu}) = \frac{P_{\mu \nu}^{0l}}{\rho_{\mu \nu}(0)}, \quad (5)$$

The use of the "cut-off" function is possible due to the fast decrease of the overlap integral  $S_{\mu \nu}^{0l}$  with the inter-atomic distance  $r_{\mu \nu}$ . We can also note that the Coulomb interaction is treated very precisely in the LUC model thanks to the theory of special  $\mathbf{k}$  points. The Coulomb lattice sums are calculated using the Ewald method [31].

## Cubic Phase of Pure and La-doped CaTiO<sub>3</sub> Crystals

The primitive unit cell of the CaTiO<sub>3</sub> lattice contains 5 atoms. We have extended it to a system of 80 atoms conserving the symmetry properties of the pure crystal, i.e., equivalent to a 16 times (4x2x2) symmetric extension. We treat the LUC of 80 atoms as a primitive unit cell, which leads us to the so-called supercell model. In order to find the wave function of the system, the following basis set was utilized: 2s and 2p for the O atom, 3d, 4s and 4p for the Ti atom, 4s and 3p for the Ca atom and finally, 6s, 6p and 5d for the La donor atom. So we restricted ourselves to the so-called valence basis set. The previously derived [12] numerical parameters are shown in Table I. In Table II we present some properties of the La atom and the LaO molecule reproduced earlier [11] using our semi-empirical basis set.

The band structure properties of a pure crystal were found to be in a very good agreement with the experimental data [13, 17]. The lower valence band (LVB) mainly is composed of O 2s AOs. The upper valence band (UVB) is composed of O 2p AOs. Finally, we obtain very narrow sub-band of Ca 3p AOs situated just between the two valence bands described above. The lower part of the conduction band (CB) has mainly Ti 3d in nature with some admixture of Ca 4s states. Some admixture of Ti 3d AOs in the UVB and O 2p AOs in the CB is also observed. In general, the cubic structure is not stable and is observed only above approximately 1533 K [34]. During our periodic quantum-chemical parameterization we managed to reproduce completely the geometry of this crystal for both crystalline lattices [12].

The La-doping procedure was done replacing one La atom for one of the Ca atoms in a central region of the supercell. We can note that this atomic substitution adds one extra electron (remember that Ca has two valence electrons, while La has three valence electrons) into the system. Due to the impurity insertion, which is a considerable perturbation for the otherwise perfect crystalline lattice, one can anticipate atomic displacements, which would reduce the total energy of the system. Different kinds of atomic relaxation were considered, which included both symmetric and asymmetric atomic displacements. Additionally, an automated geometry optimization procedure [35] was utilized. As a result we have obtained the following lattice distortion. The twelve La-neighboring O atoms move towards the impurity by 0.21 Å along the  $\langle 110 \rangle$  directions. This corresponds to the reduction of the initial inter-atomic distance (equal to 2.68 Å) by 7.84%. This geometry relaxation gives us 4.04 eV contribution into the total relaxation energy, which is equal to 4.78 eV. The eight La-closest Ti atoms move outwards from the impurity along the  $\langle 111 \rangle$  directions by 0.03 Å. This corresponds to the augmentation of the initial inter-atomic distance between the La and Ti atoms (equal to 3.29 Å) by 0.99%. The contribution into the total relaxation energy of this atomic movement is equal to 0.14 eV or 2.96%. Finally, we have considered movements of the four impurity-nearest Ca atoms that are situated initially at 3.78 Å from the defect. The obtained magnitude of displacement for the Ca atoms is 0.13 Å along the  $\langle 100 \rangle$  directions. This corresponds to the augmentation of the La-Ca distance by 3.50%. The latter atomic displacements give us 0.60 eV contribution into the total relaxation energy, which is 12.50% of its total magnitude. The initial geometry configuration for the defect-surrounding region and the directions of atomic displacements are shown in the



Figure 1, where the first two orders of defect-nearest atoms can be observed. Table III shows all contributions into the lattice relaxation energy.

We have attempted to change atomic positions in different asymmetric ways but did not succeed in reducing the system's total energy. Obviously, only symmetric types of atomic displacements occur in the cubic lattice of the La-doped  $\text{CaTiO}_3$  crystal. We note that, in general, atomic movements are in accordance to the Coulomb's law since the La atom has a larger positive charge with respect to the Ca atom for which it substitutes ( $q_{\text{La}} = 2.37 e$ ,  $q_{\text{Ca}} = 1.88 e$ ). Therefore, the negative O atoms move inwards whereas the positive Ti and Ca atoms move outwards the impurity. This result is also in accordance with a number of recent works [7-12] on impurity doping studies.

Comparing the present results with our previous work [9], we can observe that in the cubic phase of La-doped  $\text{CaTiO}_3$  we have obtained larger relaxation energy (4.78 eV) than in the case of similar Nb-doping computations (3.83 eV). In our mind, this effect can be understood by the following fact: The impurity size ( $\text{La}^{57}$ ) in our present work is considerably larger (approximately two times) than in the previous case ( $\text{Nb}^{41}$ ). Therefore, La introduction produces stronger effect of lattice distortion. This is the only explanation since the variation of electrical charge is practically identical ( $Q_{\text{Nb}} - Q_{\text{Ti}} = 0.91 e$  and  $Q_{\text{La}} - Q_{\text{Ca}} = 0.91 e$ ) in both cases. We can also note that Nb atom finds itself in the vicinity of six O atoms while the La atom is situated in the middle of twelve O atoms. Since just oxygens give the predominant contribution into the relaxation energy one can expect larger magnitude of the relaxation energy for La-doping in otherwise the same crystalline lattice.

## **Orthorhombic Phase of Pure and La-doped $\text{CaTiO}_3$ Crystals**

A similar procedure was applied to the orthorhombic phase. A crystallographic system consisting of 80 atoms was explored by analyzing the electronic band structure. This supercell size was obtained by extending 4-times (2x2x1) the primitive unit cell of 20 atoms. The analysis of energetic bands shows similarities with the corresponding bands of the cubic phase. However, a considerably higher admixture of Ti 3d AOs in the UVB and O 2p AOs in the CB is observed. This points out the hybridization between Ti 3d and O 2p states, which is normal due to the phase transition from cubic to orthorhombic. In general, our results on electronic band structure are in very good agreement with the available experimental data [13, 17].

Finally, we would like to note that during our periodic quantum-chemical parameterization we managed to reproduce completely the geometry of both crystalline lattices. The obtained lattice parameters  $a = 3.78 \text{ \AA}$  for the cubic and  $a = 5.28 \text{ \AA}$ ,  $b = 5.35 \text{ \AA}$ ,  $c = 7.51 \text{ \AA}$  for the orthorhombic lattices, respectively, are very close to the experimental data [36] equal to  $a = 3.84 \text{ \AA}$  for the cubic and  $a = 5.37 \text{ \AA}$ ,  $b = 5.44 \text{ \AA}$ ,  $c = 7.64 \text{ \AA}$  for the orthorhombic lattices, respectively.

The atomic relaxation in the orthorhombic phase for the La-doped crystal was done in a similar manner as in the cubic phase. We substituted one of the Ca atoms situated in the middle of the 80-atomic supercell by a La atom. Different kinds of lattice distortion were considered. As a result we came to the conclusion that only two types of atomic displacements have non-negligible contribution into the relaxation energy. Firstly, the nine La-closest O atoms move toward the impurity by  $0.05 \text{ \AA}$ , which is 1.85 % of the initial distance, equal approximately to  $2.62 \text{ \AA}$ . We have to note that these movements are along the directions  $\langle 111 \rangle$  and  $\langle 011 \rangle$  depending on atom. This

geometry relaxation produces a 1.44 eV contribution into the total relaxation energy, which is equal to 2.01 eV. Secondly, the eight La-closest Ti atoms move outwards the impurity by 0.02 Å. This corresponds to the enlargement of the La–Ti distance by 0.62 % of the initial distance equal to 3.25 Å. The displacements of Ti atoms are along the  $\langle 011 \rangle$  and  $\langle 111 \rangle$  directions. Both types of atomic relaxation occur in accordance to Coulomb's law, i.e., the negative O atoms move towards the positively charged La atom and the positive Ti atoms move outwards from the impurity. These atomic displacements are shown in the two-dimensional sketch of Figure 2 whereas the information about the corresponding relaxation energies for each type of movement is summarized in Table IV.

The total relaxation energy value obtained for this phase (2.01 eV) is considerably smaller than the corresponding magnitude in our previous work (15.04 eV [12]). In our mind, it is due to the fact that only two atomic spheres have been considered in the present work (the third impurity-nearest sphere of Ca atoms plays an important role in the orthorhombic phase of the Nb-doped  $\text{CaTiO}_3$ ).

### **Influence of the Extra Electron upon the Electronic Band Structure**

The effect of the La atom upon the  $\text{CaTiO}_3$  electronic band structure is without doubt very different for the two crystalline lattices. In the case of the cubic lattice, we find a local one-electron energy level between the top of the UVB and the CB, which is mainly composed of La 6s AO. During the geometry optimization this level tends to fall into the UVB and some hybridization with O 2p AOs occurs.

In the case of the orthorhombic crystal, we observe that the electron jumps from this local energy level to the bottom of the CB. The 4s AOs of the Ca atoms situated in the third defect-surrounding sphere mainly receive this extra electron. Additionally, part of this electron is transferred to the 3d AOs of the Ti atoms from the second sphere (see Figure 2). In other words, the fact that the electron jumps from the local energy level within the band-gap to the CB is connected with the symmetry of the crystal lattice since we do not observe this phenomenon in the cubic structure. In general, this phenomenon of the extra electron jump to the CB is not completely understood. Since the local energy level within the band-gap is situated about 1 eV from the bottom of the conduction band, energy is required for this electron transfer process. In our opinion, the energy accumulated in the crystal due to the lattice relaxation, which occurs after the defect insertion, could be partially used for the transfer process. The mechanism of electron transfer might occur by tunneling if one considers the La-nearest atomic sphere composed of negative O atoms as a potential barrier for a negative electron. The present observations are similar to our studies of the Nb-doped CaTiO<sub>3</sub> crystal [12].

The consequence of the electron transfer effect is the occurrence of free electrons in the CB, which increases the electrical conductivity. This effect is indeed observed in a number of experimental works such as Y- and Nb-doping studies of CaTiO<sub>3</sub> crystals [2, 17] and La-doping [37] investigations, where an increase of enthalpy, entropy and other thermodynamic variables have been observed, if the concentration of La impurity is considerable.

## Conclusions

Using a quantum-chemical method developed for crystal computations we have studied La-doping in both cubic and orthorhombic lattices of the  $\text{CaTiO}_3$  crystal. Our studies reveal for the first time lattice distortion due to presence of the impurity. The obtained atomic displacements are symmetrical in both the cubic and orthorhombic structures. However, there is a considerable difference in the crystalline lattice response to the type (La or Nb) of introduced impurity. Due to the different vicinity of the defect the obtained relaxation energy for La-doping is larger for the cubic phase while in the case of Nb-doping the magnitude is considerably larger for the orthorhombic phase.

A transfer of the extra electron from the local energy level within the band-gap to the CB is obtained. This result together with a number of other studies, including the experimental ones of Nb and Y doping in  $\text{CaTiO}_3$  crystal, point out the augmentation of the electrical conductivity of impurity-doped crystal. In our mind, the electron transfer to the conduction band occurs due to the tunneling effect.

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**TABLE I (a)****Semi-empirical parameter sets for Ca, Ti, O and La atoms.**

Atom	AO	$\zeta$ (a.u.)	$E_{\text{neg}}$ (eV)	$-\beta$ (eV)	$P^0$ ( $e$ )
Ca	4s	1.48	14.0	0.4	0.15
	3p	2.80	42.5	3.0	2.00
Ti	4s	1.40	3.7	0.5	0.65
	4p	1.00	-15.0	0.5	0.04
	3d	1.93	7.2	9.0	0.55
O	2s	2.27	4.5	16.0	1.974
	2p	1.86	-12.6	16.0	1.96
La	6s	1.0	11.3	0.4	0.40
	6p	1.0	2.0	0.4	0.01
	5d	1.97	11.0	6.3	0.08

**TABLE I (b)****Two-center parameters  $\alpha_{\mu B}$  (a.u.<sup>-1</sup>), where  $\mu \in A$ .**

A	B			
	Ca	Ti	O	La
Ca	0.15	0.55	0.18	0.00
Ti	0.07	0.13	0.10	0.00
O	0.57	0.37	0.15	0.53
La	0.00	0.02	0.03	0.01

**TABLE II**

**Calculated properties of the La atom and the LaO molecule in comparison to available experimental data.\***

Property	Calculated results	Experimental data
La atom 1st IP (eV)	5.64	5.61
La atom 2nd IP (eV)	11.59	11.43
LaO molecule ground state configuration	$^2\Sigma^+$	$^2\Sigma^+$
LaO molecule inter-atomic distance (Å)	1.825	1.825

\*The experimental data are taken from Ref. 31 for the La atom and from Ref. 32 for the LaO molecule.

**TABLE****III**

**Contributions into the relaxation energy by the O atoms  $E_O$ , the Ti atoms  $E_{Ti}$ , and the Ca atoms  $E_{Ca}$  in the cubic phase of La-doped  $\text{CaTiO}_3$ .**

Type of relaxation	Partial relaxation energy, eV	Contribution of the partial relaxation energy, %
$E_O$	4.04	84.54
$E_{Ti}$	0.14	2.96

$E_{Ca}$	0.60	12.50
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**TABLE IV**

**Contributions into the relaxation energy by the O atoms  $E_O$ , the Ti atoms  $E_{Ti}$ , and the Ca atoms  $E_{Ca}$  in the orthorhombic phase of La-doped  $CaTiO_3$ .**

Type of relaxation	Partial relaxation energy, eV	Contribution of the partial relaxation energy, %
$E_O$	1.44	71.64
$E_{Ti}$	0.57	28.36



## Figure Captions

**FIGURE 1.** Initial spatial atomic configuration for the  $\text{CaTiO}_3$  cubic phase. Only the defective region around the La impurity is included. The indicated symmetrical displacements of atoms produce the minimal energy configuration.

**FIGURE 2.** A schematic diagram of the La-closest atoms in the orthorhombic  $\text{CaTiO}_3$  crystal. The impurity has nine neighboring O atoms at the average distance of 2.62 Å, which is showed as a first sphere of atoms. The next-neighboring Ti atoms are situated at the average distance of 3.25 Å. They are eight in number and are showed in the second atomic sphere. Only the indicated movements produce a non-negligible atomic relaxation.



