

# Hole polarons in pure BaTiO<sub>3</sub> studied by computer modeling

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**ABSTRACT:** Self-trapped hole polarons in technologically important perovskite-type ceramic of BaTiO<sub>3</sub> have been modeling by means of the quantum-chemical method modified for crystal calculations. The computations are carried out in the SCF manner using the embedded molecular cluster model. The spatial configuration of a hole polaron, displacements of defect-surrounding atoms, wave functions of the polaron ground and excited states are obtained and analyzed. The probability of spontaneous hole self-trapping is estimated in the perfect lattice of BaTiO<sub>3</sub> crystal by calculating the value of hole self-trapping energy as a difference of the atomic relaxation energy and the hole localization energy. This value is found to be negative, -1.49 eV, which demonstrates the preference of the self-trapped polaron state. The calculated polaron absorption energy, 0.5 eV, is discussed in light of the available experimental data.

**Key words:** Perovskites; BaTiO<sub>3</sub>; hole polarons; self-trapping; optical properties

# 1. Introduction

Perovskite-type ceramics are now the focus of extensive study due to their important properties and wide range of applications. Because of its large electro-optic coefficients and high photorefractive sensitivity [1], BaTiO<sub>3</sub> is of special interest. This material also exhibits ferroelectric and piezoelectric properties and therefore finds increasing processibility as an active element in micro-electronic devices. Additionally, BaTiO<sub>3</sub> is a promising material for self-pumped phase conjugation or holographic storage [2, 3] and cheap diode lasers [4].

Although the barium titanate has simple cubic (paraelectric phase) and tetragonal (ferroelectric phase) structures, the literature mainly offers a variety of experimental reports while there have been only few theoretical studies [5-8] of this important crystal. That could be partially explained by difficulties in using computer modeling to reproduce unusual behavior of this ceramic material.

One of the interesting features of the material is the non-linear photoconductivity [9], and it is known that primarily this effect is due to the presence of holes. This is the reason why absorption, light-induced absorption changes, photo and dark conductivities and another light-induced charge-transfer processes have been of intense experimental investigation [10-14]. In order to explain the effect of non-linear dependence of photoconductivity on light intensity, different models have been proposed recently [15-17]. They are based on the presence of shallow one-electron local energy levels within the forbidden energy gap, which act as traps. The authors of these investigations do not explain clearly the origin of these shallow levels, although it is supposed that they

originate from the presence of trivalent impurities like Fe, Co, Rh, etc. As it follows from our calculations some of these local energy levels might be attributed to the presence of self-trapped holes, called here as hole polarons, which can be trapped at *regular O sites* and can occur spontaneously in the BaTiO<sub>3</sub> crystal under the radiation. Despite that the polarons are significantly involved in all relevant light-induced charge-transfer reactions in BaTiO<sub>3</sub>, to our knowledge no attempts had been done so far to study the self-trapping possibilities of a hole in the pure barium titanate lattice. If this self-trapping take place spontaneously then hole polarons could contribute significantly to our understanding of non-linear photoconductivity phenomenon.

The question if carrier self-trapping can occur in a given perfect crystal is of the fundamental nature. First predicted theoretically by Landau in 1933, the hole self-trapping was confirmed experimentally in 1955 by Känzig [18]. He established that self-trapped holes (STH) in pure alkali halides have the structure of  $X_2^-$  (where  $X^-$  denotes a halogen ion) quasi-molecules and are oriented along the  $\langle 110 \rangle$  axes in the face-centered cubic crystals. In recognition of his discovery they are called  $V_K$  centers. Since then the hole polarons have been found in many ionic solids, including alkaline earth fluorides and crystals with KMgF<sub>3</sub> and PbFCl crystallographic structures, as well as rare-gas crystals [19-23]. These point defects are also well established theoretically [24, 25]. However, the existence of STH in oxide crystals is a matter of long-time debate. The problem is that they can not be monitored by the direct electron paramagnetic resonance (EPR) technique due to the zero nuclear spin on regular O atoms. As far as we know there is only one exception: EPR experiments have revealed STH in fused

silica ( $\text{SiO}_2$ ) [26]. Additionally, there exist indirect experimental results, which support the existence of stable STH in corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) crystal [27].

The purpose of the present article is to answer the question if hole self-trapping can occur in the pure  $\text{BaTiO}_3$  crystal and to discuss possible effects of STH upon the crystal electronic and structural properties. The article is organized as follows. In the second section, the computational method is outlined giving short description of the semi-empirical parametrization scheme. The third and fourth sections deal with results of STH presence in the crystal while the fifth section contains results of the STH excited state and absorption energy calculations. Finally, our conclusions are given in the last section.

## **2. Computational details and parametrization**

An advanced version of the Intermediate Neglect of Differential Overlap (INDO) method, modified for crystal calculations (CLUSTERD computer code [28]) was used in our calculations. The method has been found to be very useful in the treatment of the electronic and spatial structure of a number of perfect and defective crystals. It is based on Molecular Orbital (MO) theory [29] and a specific parametrization scheme [30]. Two different models are implemented into the code. The periodic Large Unit Cell (LUC) model [31] calculates both the electronic band structure and the total energy of the perfect crystal via MO as a linear combination of Atomic Orbitals (AO's). The Embedded Molecular Cluster (EMC) model [32] also is based on a strict treatment of the total energy of the whole crystal, accounting for the perturbation (polarization) that

the remaining crystal has on the EMC region, thus leading to the so-called *quantum cluster* approach. This advantage of the EMC model is especially important in the case of charged defect calculations as it was in the present work. Here we have utilized both models. The LUC model was necessary to exploit in perfect crystal calculations and the parametrization procedure. The EMC was used in the studies of hole polarons.

In general, the method reproduces very well spatial and electronic structure of crystals under study. This has been proved for some 30 crystals, including oxide crystals. The power of the method originates from the specific parametrization scheme, which was developed in such a way that it takes into account very precisely crystalline peculiarities.

A full account of the LUC framework is given in Refs. 28 and 31 while the parametrization scheme is described in details in Ref. 30. Here we shall only note that the parameter set contains the following five numerical parameters for each atomic orbital: (i) the orbital exponent  $\zeta$  which enters the radial part of the Slater-type AO; (ii) the  $m$ th AO populations  $P_{mm}^{(0)A}$ ; (iii) the  $m$ th AO electronegativity  $E_{\text{neg}}^A(m)$ ; (iv) the resonant integral parameter  $\beta_{AB}$ ; and finally, (v) the parameter  $\alpha_{mB}$  characterizing the non-point nature of the atomic core B and additionally the diffuseness of the  $m$ th AO belonging to the atom A. The numerical parameters approximate some one- and two-center integrals [30] in the Hartree-Fock theory thus reducing remarkably the computational time and making available the investigation of complex systems. This is the reason why advanced semi-empirical codes are still important in the Computational Physics and the existing *ab initio* techniques are still not so widely applied in the modeling of defect properties in solids.

We have used 8-times (2x2x2) extended LUC to parametrize the BaTiO<sub>3</sub> crystal. The reduced Brillouin zone (BZ) corresponding to the LUC is thus eight times smaller than the BZ constructed from the primitive unit cell and each  $k$ -point in the reduced BZ corresponds to a family of eight points of the full BZ. Therefore, the 8-times extended LUC describes reliably the band structure of the perfect barium titanate, since it simulates eight  $k$ -points in the full BZ. The INDO parameter sets for O and Ti atoms were taken from Refs. 28 and 33, respectively. The parameter set for the Ba atom was optimized by reproducing the following data: the main features of the barium titanate crystal (width of the forbidden energy gap, widths of the upper and lower valence bands, density of states (DOS) of the valence bands, cubic lattice constant of the crystal) and the first two ionization potentials for the Ba atom.

We reproduced quite well the ionization potentials for the Ba atom (Table I) and the main electronic and spatial properties of the BaTiO<sub>3</sub> crystal (Table II and Figure 1). The obtained lattice constant  $a = 4.01 \text{ \AA}$  matches exactly the corresponding experimental value. The widths and compositions of the valence bands are in a good agreement with the X-ray photoelectron spectra results [35]. As it follows from the Figure 1b the lower valence band is composed mainly of O 2s states while the upper valence band predominantly is O 2p in nature. A small admixture of the Ti 4s states was found in the lower valence band and considerably higher degree of admixture of the Ti 3d states was present in the upper valence band as it is shown in the Figure 1c. In addition, the subband of Ba 5p states was found to be located just below the upper valence band. We considered essential to include the Ba 5p states as the basis AO's within the valence basis set since their overlap with AO's of the other atoms is not

negligible. We have to note that the obtained DOS and the composition of the valence bands are in a good agreement with the experimental data and another computations [35]. The only discrepancy between the INDO calculated electronic band structure results and the experimental data was observed to be for the value of the forbidden energy gap width. There are two reasons for this disagreement. First, the omission of long-range correlation effects (only the short-range correlation corrections are accounted through the use of semi-empirical parameters). Second, the fact that the Hartree-Fock approximation involves the self-consistent determination of only the filled molecular orbitals while the conduction band states are not self-consistent. Long-range correlation between valence electrons is known to raise the upper valence band and to lower the bottom of the conduction band leading to a reduction of the bandgap width for the oxide crystals by approximately 2-4 eV [37, 38]. This estimated quantity is reasonably close to our "error" of 2.44 eV. It has to be stressed once more that within the current method one should keep the forbidden energy gap considerably larger than the known experimental value in order to reproduce *correctly* the electronic band structure of the system under study. Thereby optimized parameters are given in Tables III and IV. We have to note that the utilized computer program has been proved to be very reliable in a number of applications, including defect studies in such complex oxides as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [37, 39, 40], TiO<sub>2</sub> [41, 42] and WO<sub>3</sub> [43]. It also has been used before very successfully to study STH or hole polarons in a number of alkali halide crystals, MgO,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>.

### 3. Estimation of a hole polaron self-trapping energy

A hole polaron is a *charged* intrinsic defect and its simulation by periodic models is problematic without the inclusion of some compensating charge [44]. Therefore, we chose to use the EMC model [32] with the cluster consisting of 40 atoms. The size of the  $[\text{Ba}_8\text{Ti}_8\text{O}_{24}]^0$  cluster was considered to be sufficient because of a small contribution of the covalent character on the chemical bonding in the  $\text{BaTiO}_3$ , i.e., a small effect of exchange interaction term which usually requires to use extended system in order to study point defect properties. Also, by exploiting the 40-atom molecular cluster we preserved the symmetry of the crystal, which was important to reproduce reliably electronic band structure of the defective region and to calculate the absorption energy of the hole polaron.

In order to estimate hole polaron self-trapping energy one has to return to the idea of Gilbert [45]. He considered polaron self-trapping as a hypothetical two stage procedure: (i) localization of a free hole in a local perfect crystal region, and (ii) subsequent relaxation of the crystalline lattice with accompanying electronic density redistribution in the defective region until the polaron state is formed. In the first stage, the hole acquires a positive contribution to its energy due to the loss of the kinetic energy in the local state. In the second stage, the hole acquires a negative energy due to the crystal relaxation around the localized polaron. A competition between the positive localization energy,  $E_{\text{loc}}$ , and the negative relaxation energy,  $E_{\text{rel}}$ , is decisive to make a final conclusion about the possibility of finding stable hole polarons in a given crystal. If  $E_{\text{loc}} + E_{\text{rel}} < 0$ , then the formation of stable hole polarons is energetically favorable in a



given crystal. If  $E_{\text{loc}} + E_{\text{rel}} > 0$ , the self-trapping does not occur. To be exact we have to name two more contributions to the energy balance of the polaron. These are the loss in the polarization energy associated with the mobile hole,  $E_{\text{pol}}^1$ , which involves only electronic polarization, i.e., displaced shells and secondly, the polarization energy,  $E_{\text{pol}}^2$ , associated with the rest of the lattice outside the defective region.  $E_{\text{pol}}^2$  includes both atomic and electronic polarization terms. It was estimated in a number of works [37, 46] that  $E_{\text{pol}}^1$  and  $E_{\text{pol}}^2$  do not differ much in the absolute value but have the opposite signs, so one can neglect these two terms in the first approximation.

When a hole was inserted into the molecular cluster, its spin density was found to be localized mainly on one of the O atoms, i.e., the polaron has one-site spatial configuration. For a one-site Wannier-type localized state of the hole one can use Fowler estimate [47] as  $E_{\text{loc}}$  being equal to the half width of the upper valence band. However, this approximation is valid only for very diffuse and smooth energy bands, which is not our case because we have considerable admixture of Ti 3d states in the O 2p valence band. In other words, the "center of gravity" of the O 2p band is not located at the exact middle of the band. Considering the Wannier representation of localized states and Fourier transform of the valence band energies (see Ref. 46 for more details) one can obtain the "center of gravity" of the corresponding occupied valence band in the following manner:

$$\varepsilon^{(w)} = \int \varepsilon N_j(\varepsilon) d\varepsilon , \quad (1)$$

where  $N_j(\varepsilon)$  is the density of states (DOS) of the valence band  $j$  normalized to unity and the integration is performed over the whole bandwidth. Using this approach we obtained the value of 2.36 eV as a hole localization energy  $E_{loc}$ .

In order to estimate the relaxation energy term,  $E_{rel}$ , we allowed to make displacements to 18 atoms situated around the oxygen, which receives a hole.  $E_{rel}$  was calculated as a difference of total energies of the molecular cluster in the relaxed and unrelaxed states, giving the value of 3.85 eV. Then using the simple equation:

$$\Delta E_{ST} = E_{loc} + E_{rel} , \quad (2)$$

we obtained -1.49 eV as a value of the hole self-trapping energy. Since  $\Delta E_{ST} < 0$ , self-trapping is favored with respect to a free delocalized hole in the valence band and we predict the spontaneous occurrence of hole polarons in the perfect barium titanate cubic lattice.

To check our results we have additionally estimated the value of  $E_{loc}$  using the Kantorovich theory [46, 48], which introduces an intermediate state L on the hole self-trapping path, considering this state L as the self-trapped hole in the unrelaxed crystal. This idea gives one an opportunity to take into account both free and localized states of the hole within the same perfect crystal computation [46]. The application of this method gave us 2.64 eV for the  $E_{loc}$  and subsequently -1.21 eV as the value of  $\Delta E_{ST}$ .

#### 4. Lattice distortion due to the hole polaron

As it was mentioned above the hole finds itself localized on O(1) atom (see Figure 2) where around 80% of the hole spin density is found while the remaining 20%

are shared by the defect-surrounding Ti and O atoms. The O(1) atom is situated practically in the middle of the molecular cluster, so any influence of the cluster border effects on the outcome of computations is excluded. The automated geometry optimization was carried out using the downhill simplex method in multidimensions [49]. During the geometry optimization, the 18 defect-nearest atoms were allowed to move from their regular lattice sites. As a result it was found that only seven atoms change their positions by noticeable magnitude while the relaxation of the remaining atoms can be neglected. As it follows from Table V and Figure 2, the O atoms of the defective region move towards while positively charged Ba and Ti atoms move outwards the O(1) atom. This is in an accordance with the expectations since the O(1) atom has the positive effective charge with respect to the perfect crystalline lattice after receiving the hole. Additionally, one can observe from the Figure 2b small rotation of the polaron-surrounding O atoms by  $\approx 1^\circ$  with respect to the vertical z-axes, which passes through the O(1) atom. The effect of atomic rotation in the region around the point defect was observed also in another polaron studies [50]. In our mind it might be attributed to the Jahn-Teller effect [51], which reduces the total energy of the system by asymmetric atomic displacements. In general, these displacements depend on the point group symmetry of the defect under study. Finally, we can note that the absolute magnitudes of atomic movements are rather small which points out to the rigid lattice of the BaTiO<sub>3</sub> crystal and predominant ionic nature of the chemical bonding in the crystal in agreement with the known experimental data. This might be also attributed to the close packed cubic structure, where the atoms do not have a sufficient space to move.

## 5. Calculation of the polaron absorption energy

The main contribution to the wave function  $\phi_h$  of the ground state of the hole polaron is due to the  $2p_x$  AO of O(1) atom, which receives the hole as it is shown in the Table VI. In order to obtain the excited state of the polaron, we acted in the following way: an electron from one of the occupied states in the upper valence band, related to the O(1) atom was taken and put into the unoccupied ground state of the hole polaron. During this procedure we employed the density matrix of the polaron ground state as an initial guess. Then according to the Frank-Condon principle the absorption energy was obtained as a difference of total energies of  $[\text{Ba}_8\text{Ti}_8\text{O}_{24}]^+$  cluster for the SCF ground and excited states with a fixed atomic configuration ( $\Delta\text{SCF}$  method). We found that the hole polaron wave function  $\phi_{h^*}$  in the excited state consists mainly of O  $2p_z$  AO strongly overlapping with  $3d_{z^2}$  and  $4s$  AOs of two nearest Ti atoms, Ti(6) and Ti(7), (see Table VI and Figure 2). The contribution of these titaniums into the  $\phi_{h^*}$  increases around 3.5 times compared to the ground-state wave function  $\phi_h$ , which means that the wave function in the excited state is considerably more delocalized as in the ground state.

The calculation of polaron absorption energy by  $\Delta\text{SCF}$  method gave us the value of 0.5 eV. This magnitude is very close to the experimentally observed value of 0.53 eV found in the light-induced absorption spectra measurements [17] in the undoped  $\text{BaTiO}_3$  crystal. In our mind, this might be not pure coincidence but indirect prove of self-trapped hole polaron existence in the barium titanate.

## 6. Conclusions

We have presented a theoretical study of the STH polaron in pure BaTiO<sub>3</sub> crystal. Using the INDO version of Hartree-Fock theory modified for crystal calculations we attempted for the first time to investigate possibilities of a hole self-trapping in this material. The outcome of our calculations indicates that there is a large probability of finding stable hole polarons in the BaTiO<sub>3</sub> crystal localized on a single O atom. The estimation of the hole polaron self-trapping energy gave us the value of -1.49 eV.

In our mind, the presence of hole polarons localized on regular O atoms might contribute significantly into our understanding of non-linear photoconductivity phenomenon in the barium titanate. We do not oppose to the existence of impurity-trapped hole polarons in this material considered so far in the scientific publications. But, as it follows from our investigation, hole polarons trapped at *regular oxygen sites* can occur spontaneously in this material since it is energetically favorable with respect to the delocalized hole state. Thus this point defects *can contribute* into the non-linear photoconductivity. In other words, not only trivalent impurities can act as polaron traps but also *regular oxygen atoms* can do that. Our explanation of the fact that no experimental reports have been made so far on the existing of hole polarons in the pure BaTiO<sub>3</sub> crystal is that the experimental confirmation by the direct EPR measurements is complicated by the zero nuclear spin on regular O atoms. Finally, we would like to note that the indirect prove of self-trapped hole polaron existence in the BaTiO<sub>3</sub> crystal follows from the light-induced absorption spectra measurements [17]. In these studies

the observed polaron absorption energy in undoped BaTiO<sub>3</sub> crystal was found to be equal to 0.53 eV which is very close to our estimate of 0.5 eV.

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**TABLE I.** Calculated Ba ionization potentials (in eV) in comparison to the experimental data [34].

	INDO results	Exp. data
1st IP	5.69	5.21
2nd IP	11.97	10.001

**TABLE II.** Basic properties of the BaTiO<sub>3</sub> crystal obtained by the quantum-chemical method in comparison to the available experimental results:  $\Delta E_g$ , width of the forbidden energy gap (in eV);  $E_{v1}$ , upper valence band width (in eV);  $E_{v2}$ , lower valence band width (in eV);  $a$ , lattice constant (in Å);  $q(\text{Ba})$ ,  $q(\text{Ti})$  and  $q(\text{O})$ , charges on Ba, Ti and O atoms, respectively, (in  $e$ ).

Property	INDO results	Exp. data <sup>a</sup>
$\Delta E_g$	5.4 <sup>b</sup>	2.96
$E_{v1}$	5.7	4.8
$E_{v2}$	3.2	2.8
$a$	4.01	4.01

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q(Ba)	1.73
q(Ti)	2.65
q(O)	-1.46

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<sup>a</sup> The experimental values of  $\Delta E_g$ ,  $E_{v1}$  and  $E_{v2}$  are taken from Ref. 35; the experimental value of lattice constant  $a$  is taken from Ref. 36.

<sup>b</sup> Calculated as a difference between the HOMO and LUMO, i.e., only short-range correlation effects have been taken into account through the parametrization.

**TABLE III.** Semi-empirical parameter sets used in the present work:  $\zeta$  (au),  $E_{\text{neg}}$  (eV),  $P^0$  (e) and  $\beta$  (eV).

Atom	AO	$\zeta$	$E_{\text{neg}}$	$P^0$	$\beta$
Ba	6s	1.65	11.34	0.2	-0.4
	5p	2.8	30.6	2.0	-4.0
Ti	4s	1.4	1.4	0.65	-0.5
	4p	1.1	-10.0	0.04	-0.5
	3d	1.93	-2.9	0.62	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0

**TABLE IV.** Semi-empirical two-center parameters  $\alpha_{mB}$  ( $\text{au}^{-1}$ ) optimized during the calculations;  $m$ th AO belongs to the atom A, where  $A \neq B$ .

A	B		
	Ba	Ti	O
Ba	0.20	0.52	0.33
Ti	0.11	0.13	0.10
O	0.52	0.36	0.15

**TABLE V.** Atomic coordinates, displacements,  $\Delta r$ , (in Å) and rotational angles,  $\alpha$ , (in degrees) in the polaron-surrounding defective region obtained by the automated geometry optimization. A "+" sign denotes displacements of the atoms towards the O(1) while a "-" sign means displacements in the opposite direction. Note that the origin (0.0, 0.0, 0.0) is occupied by a Ba atom. The atomic numeration corresponds to the one in the FIGURE 2.

Atom	Coordinate	Perfect crystal	Defective crystal	$\alpha$	$\Delta r$
O(2)	x	0.000	0.108	1.47	+0.132
	y	2.005	2.053		
	z	2.005	2.061		
O(3)	x	4.010	3.997	0.52	+0.044
	y	2.005	1.984		
	z	2.005	2.045		
O(4)	x	0.000	0.132		+0.160
	y	2.005	2.025		
	z	6.015	5.922		
O(5)	x	2.005	2.041	1.09	+0.040
	y	4.010	3.993		
	z	2.005	2.013		
Ti(6)	x	2.005	1.996		-0.124
	y	2.005	1.988		
	z	2.005	1.880		
Ti(7)	x	2.005	2.000		-0.036
	y	2.005	1.988		
	z	6.015	6.055		
Ba(8)	x	0.000	-0.016		-0.040
	y	0.000	-0.025		

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$z$	4.010	3.981
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**TABLE VI.** Wave functions expressed in the AO's coefficients for the ground  $\phi_h$  and excited  $\phi_h^*$  states of the hole polaron.

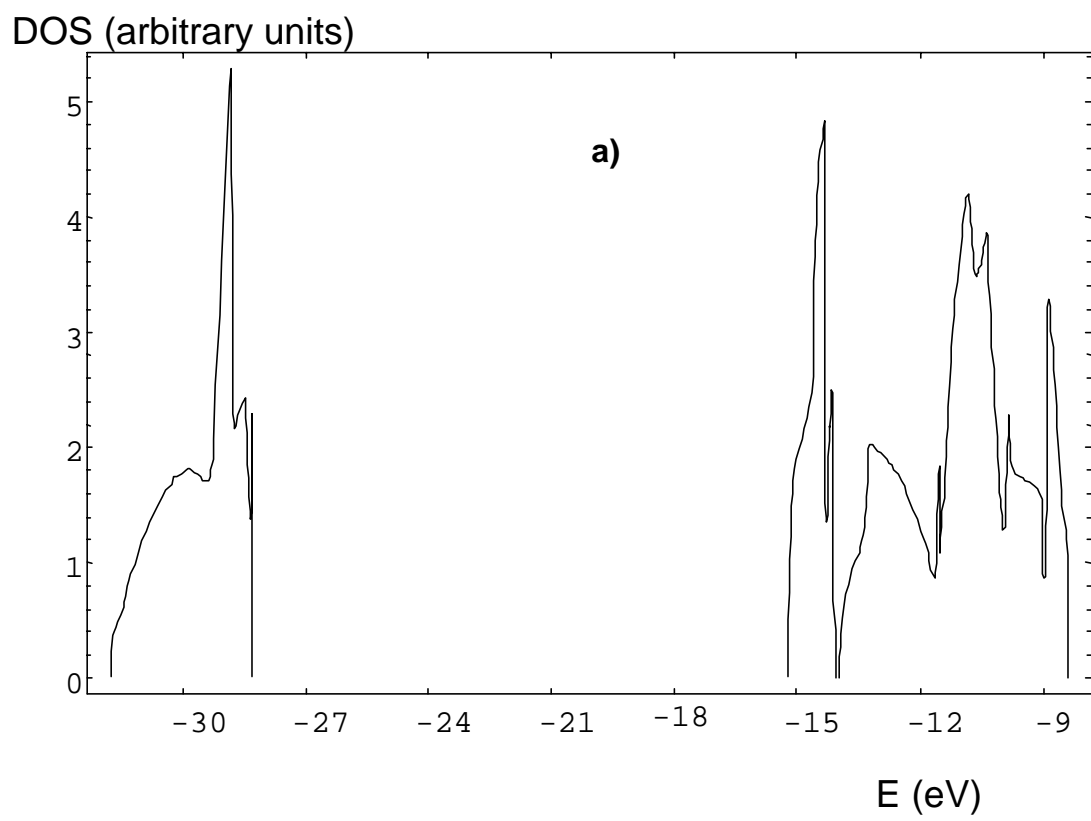
	Atom	AO	AO coefficients
$\phi_h$	O(1)	2p <sub>x</sub>	0.81655
	Ti(6)	4p <sub>x</sub>	0.19603
	Ti(7)	4p <sub>x</sub>	0.22317
$\phi_h^*$	O(1)	2p <sub>z</sub>	-0.66146
	Ti(6)	4s	0.24354
	Ti(7)	3d <sub>z<sup>2</sup></sub>	-0.32794
		4s	-0.40766

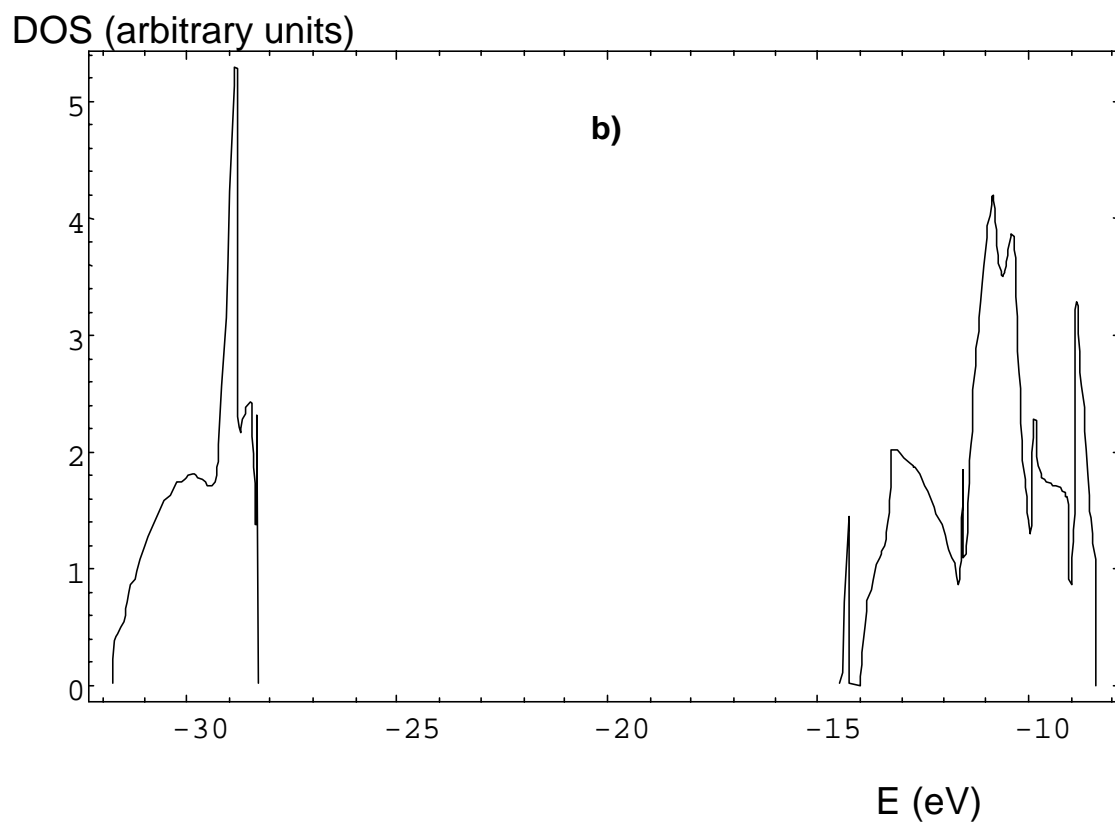
## FIGURE CAPTIONS

**FIGURE 1.** The DOS for the upper and lower valence bands of the BaTiO<sub>3</sub> cubic lattice obtained by the LUC computations: a) total DOS; b) DOS for the O 2s and 2p states; c) DOS for the Ba 5p, 6s and Ti 3d, 4s and 4p states.

**FIGURE 2.** Atomic displacements in the [Ba<sub>8</sub>Ti<sub>8</sub>O<sub>24</sub>]<sup>+</sup> cluster around the polaron: a) the arrows show Ti atoms moving away from the polaron; b) rotation of the O atoms situated in the defective region.







DOS (arbitrary units)

