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# Quantum chemical modelling of electron polarons and charge-transfer vibronic excitons in BaTiO<sub>3</sub> perovskite crystals

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## Abstract

As an extension of our previous study on the electron polarons and excitons in KNbO<sub>3</sub> and KTaO<sub>3</sub> [1, 2], we present here results of semi-empirical intermediate-neglect-of-differential-overlap (INDO) calculations for free electron polarons, single-triplet excitons and the excitonic phase in BaTiO<sub>3</sub> perovskite crystal. Our INDO calculations confirm the existence of self-trapped electrons in BaTiO<sub>3</sub>. The corresponding lattice relaxation energy is 0.24 eV and the optical absorption energy 0.69 eV. An electron in the ground state occupies the  $t_{2g}$  orbital of the Ti<sup>3+</sup> ion. Its orbital degeneracy is lifted by a combination of the breathing and Jahn–Teller modes when four nearest equatorial O atoms are displaced by 1.53%  $a_0$  outwards in the  $x$ – $y$  plane and another two nearest oxygens shift 1.1% inwards, along the  $z$ -axis. Our INDO calculations show that creation of charge-transfer vibronic exciton (CTVE) in BaTiO<sub>3</sub> crystal is accompanied by a strong lattice distortion; the relevant energy gain due to CTVE formation is 2.2 eV. Moreover, our INDO calculations predict the existence of a new crystalline phase—that of CTVEs in BaTiO<sub>3</sub> where strongly correlated CTVEs are located in each unit cell of a crystal.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The theoretical prediction by Landau in 1933 of the existence of small-radius polarons in ionic solids was the starting point for worldwide intensive theoretical and experimental investigation of polarons in ionic materials [3–6]. However, it was a quarter of a century later that a strict

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experimental (ESR) proof of self-trapped holes was given for alkali halides by Känzig [3, 4]. The first ESR evidence appeared in 1993 [7] for the *electron* self-trapping in  $\text{PbCl}_2$  crystals, and one year later for that in  $\text{LiNbO}_3$  perovskite crystals [8]. Lastly, very recently, the existence of self-trapped electrons in  $\text{BaTiO}_3$  was discussed [9]. A number of theoretical and experimental studies of hole polarons in  $\text{BaTiO}_3$  were performed in recent years [10–14]. At the same time, to our knowledge, there exist only two studies dealing with the *electron* polaron in  $\text{BaTiO}_3$  [13, 14], one of the topics of our present study. *Ab initio* cluster calculations [14] suggest that this is a small-radius Jahn–Teller (JT) polaron.

Many  $\text{ABO}_3$  perovskites reveal photoluminescence in the visible range. This ‘green’ luminescence band peaks around 2.5 eV in  $\text{BaTiO}_3$  [15] and at 2.2–2.3 eV in  $\text{KTaO}_3$  and  $\text{KNbO}_3$  [1]. The origin of this luminescence has been discussed more than once. Suggested mechanisms include donor–acceptor recombination [16], recombination of electron and hole polarons, charge-transfer vibronic excitons (CTVEs) [17] and transitions in  $\text{MeO}_6$  complexes [18]. In this paper, we perform modelling of the self-trapped electrons, triplet excitons in  $\text{BaTiO}_3$ , and compare calculated luminescence energies with experiment.

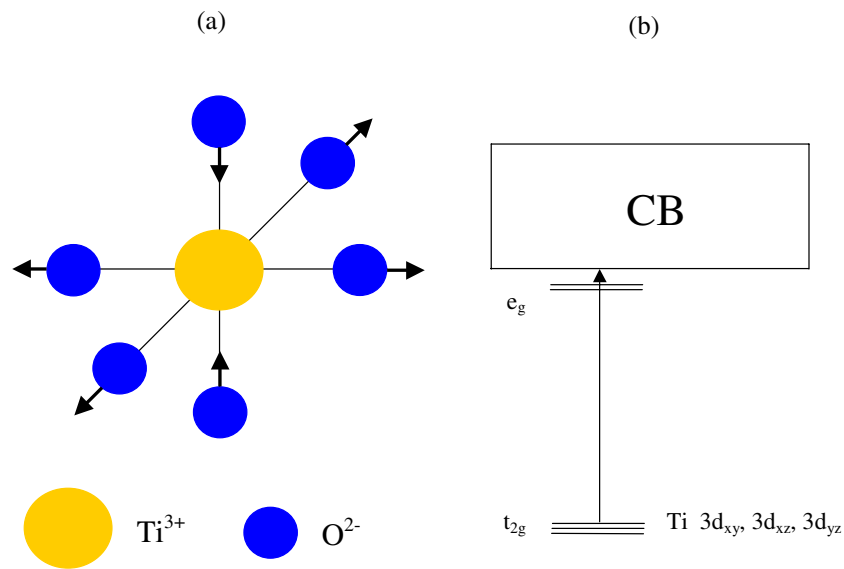
## 2. Computation method

*Ab initio* methods are still cumbersome and time-consuming in the treatment of the electronic and spatial structure of complex systems, especially those with partially covalent chemical bonding, like perovskites. In order to be able to study point defects and polarons in the relatively complicated perovskite structures, there is a need to close the gap between accurate but time-consuming *ab initio* methods [19–21] and widely used, simple but not so reliable parameter-dependent phenomenological approaches. An example of such a method is the widely used intermediate neglect of differential overlap (INDO) developed in the 1970s by Pople [22], and modified for ionic/partly covalent solids in the 1990s [23, 24]. This method is based essentially on the Hartree–Fock formalism. It was demonstrated that the accuracy of the INDO method is sufficient even for adequate description of tiny energy differences related to the ferroelectric instability in  $\text{ABO}_3$  perovskites [25]. During the last five years the INDO method has been successfully applied in the simulation of defects in many oxides [26, 27] and perovskites [25, 28–33]. The relevant INDO parametrization for  $\text{BaTiO}_3$  is described in [34]. To avoid the problem of cluster boundary conditions, we use here the periodic supercell model, with a primitive  $\text{BaTiO}_3$  unit cell extended by a factor of  $3 \times 3 \times 3 = 27$  and thereby containing 135 atoms.

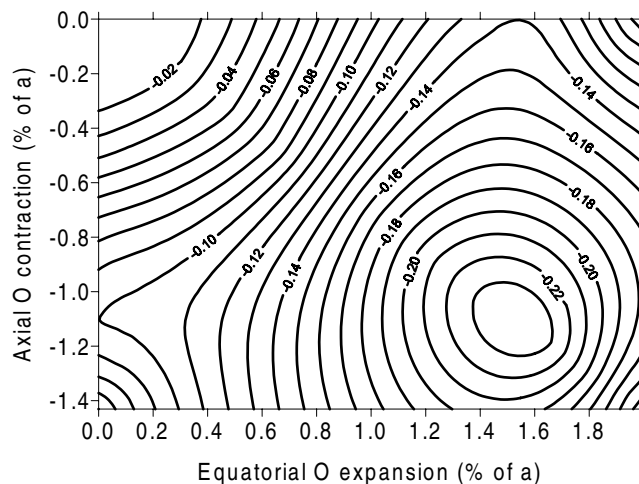
## 3. Computer modelling of the electron polaron in $\text{BaTiO}_3$

In our calculations we relaxed six O atoms around the central Ti atom, where the electron polaron is mainly localized (figure 1), and kept all other atoms fixed. We restrict ourselves to the cubic  $\text{BaTiO}_3$  phase. After geometry optimization, we found that the energy minimum of the system corresponds to outward displacement of four nearest equatorial O atoms by 1.53%  $a_0$  (lattice constant) in the  $x$ – $y$  plane, and relaxation by 1.1%  $a_0$  of the remaining two nearest O atoms inwards along the  $z$ -axis. The total energy gain of a system due to relaxation of six O atoms around the Ti atom is 0.24 eV; see figure 2.

We found that the relaxation of more distant neighbouring atoms barely increases the relaxation energy. For example, each of eight next-nearest-neighbouring Ba atoms shifts only by 0.1%  $a_0$  towards the central Ti atom along the  $x$ - and  $y$ -axes, and by 0.2%  $a_0$  in the  $z$ -direction, which results in a Ba-atom final displacement of  $\approx 0.25\%$   $a_0$  along the cube diagonal towards the Ti atom. The additional energy gain due to relaxation of the eight Ba atoms is



**Figure 1.** (a) Asymmetric oxygen relaxation around the central Ti atom where the self-trapped electron is localized. Two O atoms move towards a central Ti atom along the  $z$ -axis and the other four O atoms relax outwards in the  $x$ - $y$  plane. (b) Positions of 3d states of a central Ti atom in the BaTiO<sub>3</sub> band gap.



**Figure 2.** 2D A contour plot of the lattice energy gain due to outward  $x$ - $y$  displacement of four equatorial O atoms and the inward relaxation of two oxygens along the  $z$ -axis.

only 0.02 eV, which is considerably less than the above-mentioned relaxation energy of the six O ions involved in the electron polaron formation (0.24 eV). This allows us to conclude that the incorporation of the relaxation of only six O atoms nearest to the central Ti atom is sufficient for the description of the basic physics of electron polaron formation in BaTiO<sub>3</sub>.

As a result of the combined breathing mode and JT effect, the initially threefold-degenerate ground state of a system with symmetry  $t_{2g}$  splits into two levels, nondegenerate and twofold

**Table 1.** Optical absorption energies of electron and hole polarons in ABO<sub>3</sub> perovskites as calculated by means of the INDO method. Results for lattice relaxation energies are compared with *ab initio* FP-LMTO calculations.

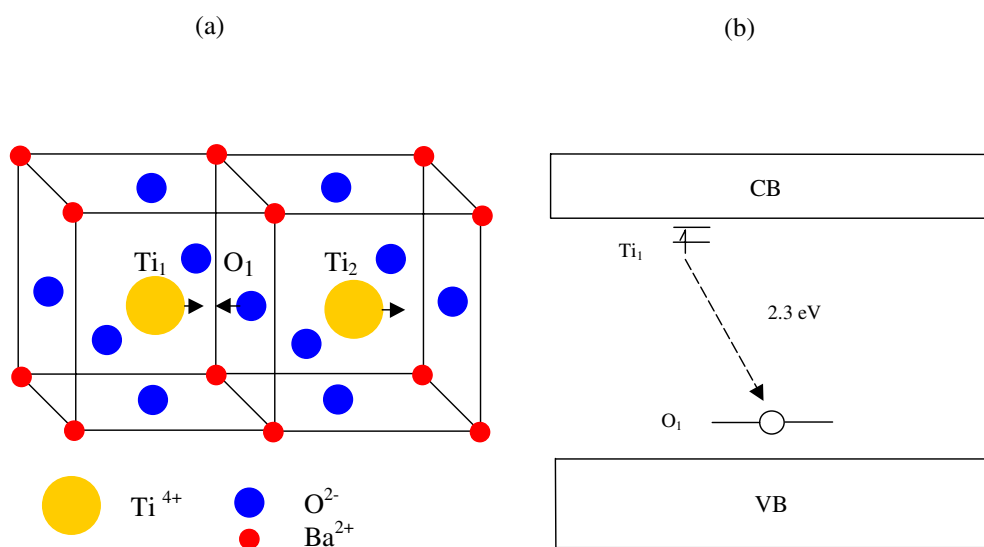
Polaron absorption and relaxation energies in BaTiO <sub>3</sub> , KNbO <sub>3</sub> and KTaO <sub>3</sub>				
Crystal	Type of polaron	Absorption energy (eV)	Relaxation energy	
			INDO	LMTO [30]
BaTiO <sub>3</sub> (This paper)	Electron polaron	0.69	0.24	
KNbO <sub>3</sub> [1, 30]	Electron polaron	0.78	0.21	
	One-site hole polaron	0.90	0.40	0.12
	Two-site hole polaron	0.95	0.53	0.18
KTaO <sub>3</sub> [1]	Electron polaron	0.75	0.27	

degenerate. Due to this asymmetric atomic relaxation, a considerable electron density is localized on the Ti 3d<sub>xy</sub>, 3d<sub>xz</sub> and 3d<sub>yz</sub> atomic orbitals. In fact, about 80% of the extra electron density is localized on the Ti atom, which confirms the model of a small-radius electron polaron in BaTiO<sub>3</sub> suggested in [14]. The polaron ground-state energy level lies 0.7 eV below the conduction band (CB) bottom. This means that the polaron thermal ionization energy could be several tenths of an electron volt, and thus the electronic polaron is stable only at low temperatures.

Another two empty levels with e<sub>g</sub> symmetry are located close to the CB bottom. The calculated t<sub>2g</sub> ground-state symmetry agrees well with that detected experimentally [9]. Using the  $\Delta$ SCF scheme, we have also calculated the electron polaron optical absorption energy to be 0.69 eV. This polaron absorption corresponds to the charge transfer onto the nearest Ti atom. The 0.6 eV absorption band has indeed been detected recently under picosecond laser excitation [35]. Note that our calculated electron polaron energy for BaTiO<sub>3</sub> is also close to the Nb<sup>4+</sup> polaron absorption energy of 0.72 eV observed in strontium barium niobate [36]. This also lies in the same energy range as our previous electron polaron calculations for ABO<sub>3</sub>: 0.78 eV for KNbO<sub>3</sub> and 0.75 eV for KTaO<sub>3</sub> (table 1 and [1]).

#### 4. Computer modelling of single excitons and the excitonic phase

As the next step, we performed calculations for the CTVE [37, 38] in BaTiO<sub>3</sub> crystal. The aim of these calculations was to evaluate the bonding energy of the CTVE, as well as the accompanying lattice distortion and the equilibrium charge transfer. Our INDO calculations are similar to the previous KNbO<sub>3</sub> and KTaO<sub>3</sub> studies [1, 2]. The CTVE is a triplet exciton formed by the vibronic attraction of two close electron and hole polarons. It has a triad structure shown in figure 3(a): the CTVE consists of an active O<sub>1</sub> atom and two Ti<sub>1,2</sub> atoms located on its two opposite sides. We obtained that the total energy gain for a single self-localized CTVE in BaTiO<sub>3</sub> is 2.2 eV. This indicates a strong vibronic coupling. The accompanying lattice relaxation is quite large. That is, the oxygen ion O<sub>1</sub> has a displacement of 4.7% a<sub>0</sub> towards the Ti<sub>1</sub> ion (figure 3(a)). Simultaneously, the above-mentioned Ti<sub>1</sub> reveals a displacement of 2.8% a<sub>0</sub> towards O<sub>1</sub>, whereas Ti<sub>2</sub> has a repulsion from the O<sub>1</sub> by 4.2% a<sub>0</sub>. The strong lattice relaxation inside the CTVE triad is accompanied by an essential charge transfer. The most significant effect is  $\approx 0.5 e$  transfer from the O<sub>1</sub> ion onto the Ti<sub>1</sub> ion. Note that the charge transfer between the O<sub>1</sub> ion and the second Ti ion Ti<sub>2</sub> is considerably smaller, only  $\approx 0.1 e$ .



**Figure 3.** (a) The INDO-calculated triad atomic structure of a single CTVE in BaTiO<sub>3</sub>. The directions of displacement of three active Ti<sub>1</sub>–O<sub>1</sub>–Ti<sub>2</sub> ions constituting the triad centre are shown. (b) A schematic view of the Ti and O energy levels induced by the CTVE in the band gap and its luminescence.

This means also that in the CTVE the electronic polaron is localized mainly on a single Ti<sub>1</sub> ion, which is in qualitative agreement with the results of the previous section.

Due to the above-discussed strong lattice distortion and significant charge redistribution inside the CTVE, local energy levels are induced in the BaTiO<sub>3</sub> band gap. The energy level of the electron polaron shared by the two Ti ions in BaTiO<sub>3</sub> lies 0.65 eV below the bottom of the CB, whereas the energy level of the hole polaron localized on the oxygen ion lies 0.8 eV above the top of the valence band (figure 3(b)). The Ti<sub>1</sub> ion makes the predominant contribution to the molecular orbital of the electron polaron state within the CTVE.

The hole polaron wavefunction consists mainly of the O<sub>1</sub> 2p<sub>x</sub> atomic orbital directed towards the Ti<sub>1</sub> ion. The luminescence energy calculated using the  $\Delta$ SCF method is 2.3 eV, close to the value 2.5 eV observed experimentally [15]. This is also close to the luminescence energy obtained in our previous INDO calculations for KTaO<sub>3</sub> (2.14 eV) and KNbO<sub>3</sub> (2.17 eV) [39], as well as to the experimental value of 2.4 eV observed for SrTiO<sub>3</sub> [40,41].

As the last step, we performed calculations of a new CTVE crystalline *phase* predicted from phenomenological models [37,42] and confirmed recently by us for KTaO<sub>3</sub> and KNbO<sub>3</sub> [2,43]. Such a CTVE phase consists of the strongly correlated CTVEs which occupy *each* unit cell of the crystal (figure 4). That is, the CTVE phase corresponds to a new state of crystal which is characterized by a new equilibrium charge transfer as well as a new set of equilibrium lattice displacements. On the basis of our INDO calculations, the optimized triplet CTVE phase was obtained as a ferroelectric phase with *parallel-displaced* small electron–hole polaron pairs localized on O–Ti ions (figure 4). The total energy reduction for each such O–Ti pair was 1.84 eV. The equilibrium displacements of the O–Ti ions in each electron–hole pair are directed towards each other and rather large: 4.07%  $a_0$  for the Ti ion and 5.03%  $a_0$  for the O ion. This strong lattice distortion is accompanied by 0.8  $e$  self-consistent charge transfer from the O to the Ti ion, in each pair of O–Ti ions of the CTVE phase. Oxygen ions O<sub>2</sub> in the intermediate chains reveal 0.33% shifts which are parallel to the O<sub>1</sub> ions in the CTVE chains

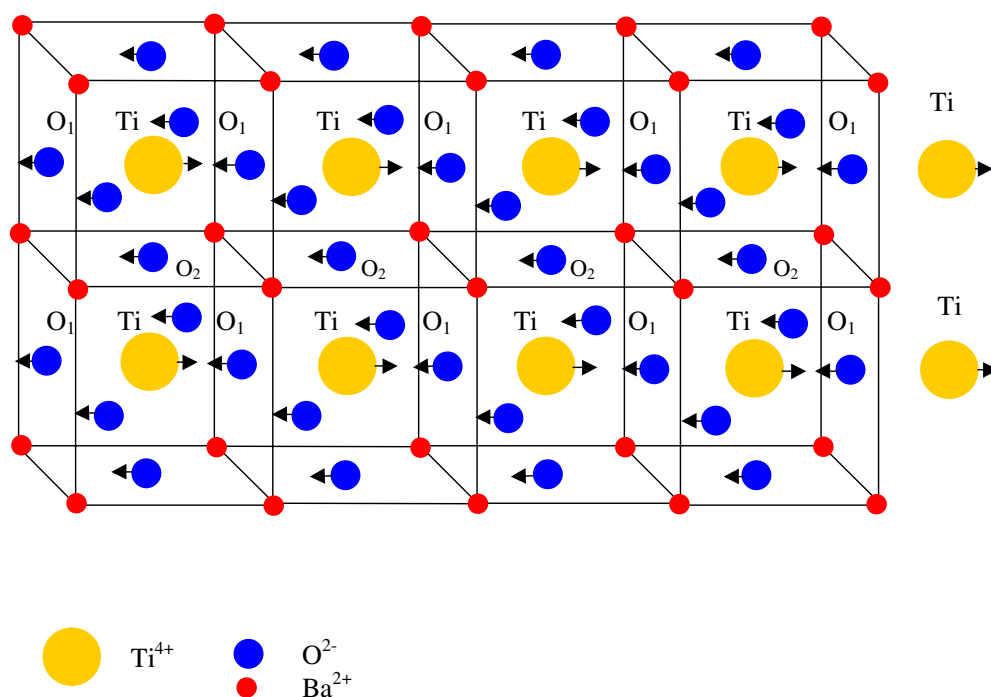


Figure 4. A sketch of the structure of the CTVE phase.

(figure 4). The CTVE–CTVE correlation energy (the energy gain per the electron–hole pair due to the CTVE–CTVE interaction) in  $\text{BaTiO}_3$  turns out to be quite considerable, 0.35 eV. Experimental manifestations of this CTVE phase in  $\text{ABO}_3$  perovskites are discussed in [2].

## 5. Conclusions

Summing up, our quantum chemical INDO calculations gave additional evidence for the existence of electron polarons in  $\text{BaTiO}_3$  crystals which are expected to be stable at low temperatures. The calculated  $t_{2g}$  ground-state symmetry for the electron polaron is in agreement with experimental observations [9]. The theoretically calculated electron polaron absorption energy in  $\text{BaTiO}_3$  (0.69 eV) agrees well with the only experimental estimate of 0.6 eV [35]. It is also close to our previous results for the electron polarons in  $\text{KNbO}_3$  (0.78 eV) and  $\text{KTaO}_3$  (0.75 eV).

Our INDO calculations gave strong support to the explanation of ‘green’ luminescence in  $\text{BaTiO}_3$  crystal as a result of radiative recombination of the electron and hole polarons forming the *charge-transfer vibronic exciton*, rather than due to the electron transitions in the  $\text{MeO}_6$  complex, as had been suggested intuitively earlier [17].

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