

Quantum chemical modelling of electron polarons and charge-transfer vibronic excitons in BaTiO₃ perovskite crystals

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Abstract

As an extension of our previous study on the electron polarons and excitons in KNbO₃ and KTaO₃ [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 BaTiO₃ perovskite crystal. Our INDO calculations confirm the existence of self-trapped electrons in BaTiO₃. 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 Ti³⁺ 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 BaTiO₃ 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 BaTiO₃ 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 PbCl_2 crystals, and one year later for that in LiNbO_3 perovskite crystals [8]. Lastly, very recently, the existence of self-trapped electrons in BaTiO_3 was discussed [9]. A number of theoretical and experimental studies of hole polarons in 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 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 ABO_3 perovskites reveal photoluminescence in the visible range. This ‘green’ luminescence band peaks around 2.5 eV in BaTiO_3 [15] and at 2.2–2.3 eV in KTaO_3 and 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 MeO_6 complexes [18]. In this paper, we perform modelling of the self-trapped electrons, triplet excitons in 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 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 BaTiO_3 is described in [34]. To avoid the problem of cluster boundary conditions, we use here the periodic supercell model, with a primitive 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 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 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

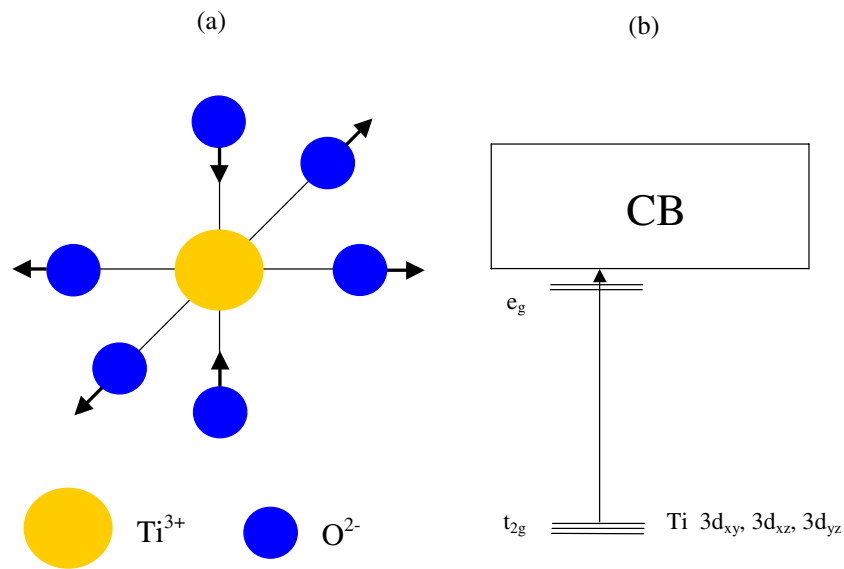


Figure 1. (a) Asymmetric oxygen relaxation around the central Ti atom where the self-trapped electron is localized. Two O atoms move towards a central Ti atom along the z -axis and the other four O atoms relax outwards in the x - y plane. (b) Positions of 3d states of a central Ti atom in the BaTiO₃ band gap.

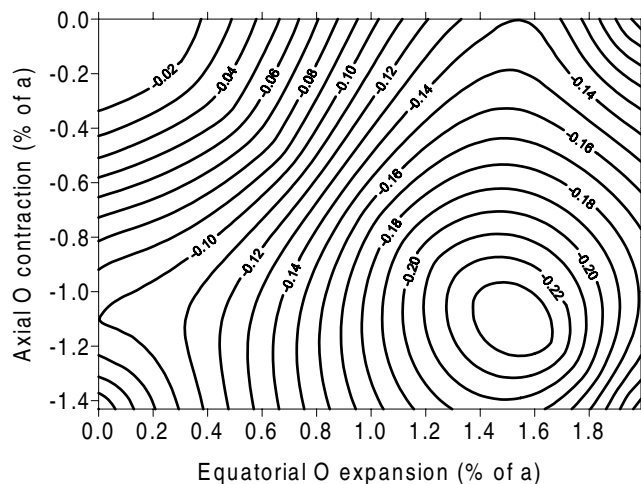


Figure 2. 2D A contour plot of the lattice energy gain due to outward x - y displacement of four equatorial O atoms and the inward relaxation of two oxygens along the z -axis.

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 BaTiO₃.

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 ABO₃ 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 ₃ , KNbO ₃ and KTaO ₃				
Crystal	Type of polaron	Absorption energy (eV)	Relaxation energy	
			INDO	LMTO [30]
BaTiO ₃ (This paper)	Electron polaron	0.69	0.24	
KNbO ₃ [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 ₃ [1]	Electron polaron	0.75	0.27	

degenerate. Due to this asymmetric atomic relaxation, a considerable electron density is localized on the Ti 3d_{xy}, 3d_{xz} and 3d_{yz} 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 BaTiO₃ 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_g symmetry are located close to the CB bottom. The calculated t_{2g} ground-state symmetry agrees well with that detected experimentally [9]. Using the Δ 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 BaTiO₃ is also close to the Nb⁴⁺ 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 ABO₃: 0.78 eV for KNbO₃ and 0.75 eV for KTaO₃ (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 BaTiO₃ 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 KNbO₃ and KTaO₃ 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 O₁ atom and two Ti_{1,2} atoms located on its two opposite sides. We obtained that the total energy gain for a single self-localized CTVE in BaTiO₃ is 2.2 eV. This indicates a strong vibronic coupling. The accompanying lattice relaxation is quite large. That is, the oxygen ion O₁ has a displacement of 4.7% a₀ towards the Ti₁ ion (figure 3(a)). Simultaneously, the above-mentioned Ti₁ reveals a displacement of 2.8% a₀ towards O₁, whereas Ti₂ has a repulsion from the O₁ by 4.2% a₀. 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 O₁ ion onto the Ti₁ ion. Note that the charge transfer between the O₁ ion and the second Ti ion Ti₂ is considerably smaller, only $\approx 0.1 e$.

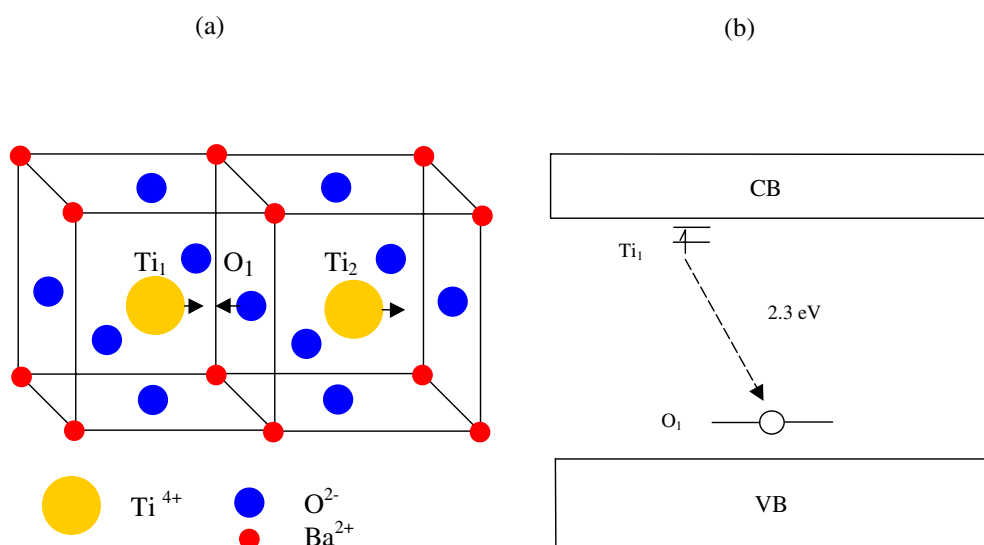


Figure 3. (a) The INDO-calculated triad atomic structure of a single CTVE in BaTiO₃. The directions of displacement of three active Ti₁–O₁–Ti₂ ions constituting the triad centre are shown. (b) A schematic view of the Ti and O energy levels induced by the CTVE in the band gap and its luminescence.

This means also that in the CTVE the electronic polaron is localized mainly on a single Ti₁ 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 BaTiO₃ band gap. The energy level of the electron polaron shared by the two Ti ions in BaTiO₃ 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 Ti₁ 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 O₁ 2p_x atomic orbital directed towards the Ti₁ ion. The luminescence energy calculated using the Δ 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 KTaO₃ (2.14 eV) and KNbO₃ (2.17 eV) [39], as well as to the experimental value of 2.4 eV observed for SrTiO₃ [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 KTaO₃ and KNbO₃ [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 O₂ in the intermediate chains reveal 0.33% shifts which are parallel to the O₁ ions in the CTVE chains

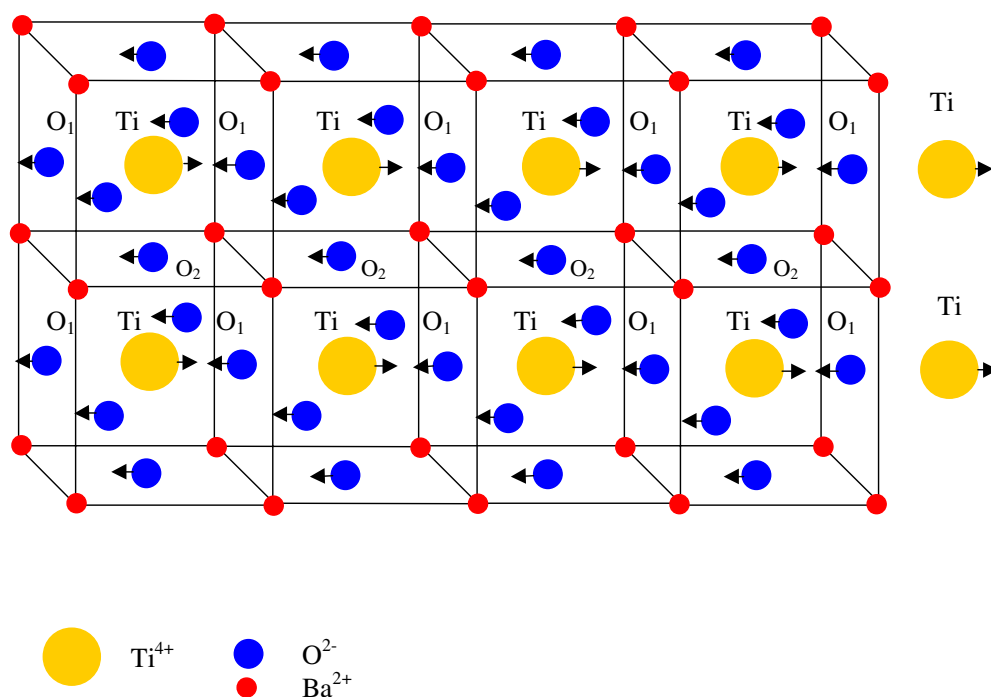


Figure 4. A sketch of the structure of the CTVE phase.

(figure 4). The CTVE–CTVE correlation energy (the energy gain per the electron–hole pair due to the CTVE–CTVE interaction) in BaTiO_3 turns out to be quite considerable, 0.35 eV. Experimental manifestations of this CTVE phase in 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 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 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 KNbO_3 (0.78 eV) and KTaO_3 (0.75 eV).

Our INDO calculations gave strong support to the explanation of ‘green’ luminescence in 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 MeO_6 complex, as had been suggested intuitively earlier [17].

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