

Semi-empirical calculations of the electronic and atomic structure of polarons and excitons in ABO_3 perovskite crystals

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Abstract

Our quantum chemical calculations performed by means of the intermediate neglect of differential overlap confirm the existence of the self-trapped electrons in $KNbO_3$, $KTaO_3$ and $BaTiO_3$ crystals. The relevant lattice relaxation energies are 0.21, 0.27 and 0.24 eV, whereas the optical absorption energies are 0.78, 0.75 and 0.69 eV, respectively. We suggest theoretical interpretation of the so-called *green* luminescence (2.2–2.3 eV) in ABO_3 perovskite crystals as a result of the recombination of electrons and holes forming the charge-transfer-vibronic-excitons. The calculated luminescence energies for $SrTiO_3$, $BaTiO_3$, $KNbO_3$ and $KTaO_3$ perovskite crystals are in a good agreement with the experimentally observed energies.

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1. Introduction

Ternary ABO_3 ferroelectric perovskites have numerous technological applications [1]. Their properties are influenced by point defects, primarily vacancies. For instance, laser second harmonic generation in $KNbO_3$ is reduced by the blue-light-induced absorption [2]. Despite the fact that such light-induced absorption is well known for many perovskites, the effect was studied only in a few papers. Relatively little is known about in-

trinsic point defects in ABO_3 . A broad absorption band around 2.7 eV has been observed in electron-irradiated $KNbO_3$ crystals and is ascribed tentatively to *F*-type centers (O vacancy with one or two trapped electrons) [3,4]. Transient optical absorption around 1.2 eV has been associated recently [4], in analogy with other perovskites, with a hole polaron (a hole bound to some defect), whereas IR absorption (around 0.8 eV) is associated with an electron polarons [5]. Recently [6,7] we performed semi-empirical calculations for the *F* centers and hole polarons bound to a K vacancy in $KNbO_3$. Based on these calculations, we confirmed preliminary interpretations of above-mentioned absorption bands at 1.2 and 2.7 eV.

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Many ABO_3 perovskites reveal photoluminescence in the visible range. This, so-called green luminescence band peaks around 2.5 eV in $BaTiO_3$ [8] and at 2.2–2.3 eV in $KTaO_3$ and $KNbO_3$ [9]. The origin of this luminescence has been discussed more than once. Suggested mechanisms include donor–acceptor recombination [10], recombination of electron and hole polarons, charge-transfer vibronic excitons (CTVE) [11–13] and transitions in MeO_6 complexes [14]. In this paper, we perform modelling of electron polarons and triplet excitons in ABO_3 perovskites and compare calculated optical energies with relevant experiments.

2. Intermediate neglect of differential overlap method

Ab initio methods are still time consuming for the treatment of the electronic and atomic structure of complex systems, especially those with partly covalent chemical bonding, like perovskites. For a study of relatively complicated cases of perovskite solid solutions, defects and excitons, there is a need to close the gap between accurate but time consuming ab initio methods [15–18] and widely used, simple but not so accurate semi-empirical quantum chemical methods with transferable parameters valid for a wide class of systems. An example of such a method is the intermediate neglect of differential overlap (INDO) [19–21], which is a simplified version of the Hartree–Fock formalism.

In the last decade the INDO method has been successfully used in a study of bulk solids and defects in many oxides [20–26] and semiconductors [27]. This method has been earlier applied to the study of phase transitions and frozen phonons in pure $KNbO_3$ [28], pure and Li doped $KTaO_3$ [29], solid perovskite solutions $KNb_xTa_{1-x}O_3$ [30,31], as well as F centers and hole polarons in $KNbO_3$ [32–34].

The detailed analysis of the development of the INDO parametrization for pure $KNbO_3$ and $KTaO_3$ is given in [28,29] whereas for $BaTiO_3$ and $SrTiO_3$ in [35,36]. The INDO method reproduced very well both available experimental data and results of ab initio LDA-type calculations. In particular, this method reproduces the effect of

ferroelectric instability of $KNbO_3$ due to off-centre displacement of Nb atoms from the regular lattice sites, as well as the relative magnitudes of the relevant energy gains for the [1 0 0], [1 1 0], [1 1 1] Nb displacements. These are consistent with the sequence of the stability of the tetragonal, orthorhombic and rhombohedral phases, respectively, as the crystals temperature decreases. This is a very non-trivial achievement, since the typical energy gain due to the Nb off-centre displacement is only of the order of several mRy per unit cell. In these calculations we use supercells of 135 atoms.

3. Quantum chemical modelling of electron polarons

In our calculations of the electron polarons in $BaTiO_3$ we relaxed six O atoms around the central Ti atom, where the electron polaron is mainly localized, and kept fixed all other atoms, see Fig. 1. (We restricted ourselves to the cubic $BaTiO_3$ phase.) As a result of 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) and relaxation of remaining two nearest O atoms inwards, by 1.1% a_0 along the z -axis. The total energy gain of a system due to lattice relaxation around Ti atom is 0.24 eV, see Fig. 2.

As a result of combined breathing mode and the Jahn–Teller effect, initially threefold degenerate ground state of a system with the symmetry t_{2g} splits into two levels, non-degenerate and twofold degenerate. As a result of asymmetric geometry relaxation a considerable electron density is localized on the Ti $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ atomic orbitals. In fact, about 80% of an extra electron density is localized on the Ti atom, which confirms a model of small-radius electron polaron in $BaTiO_3$. 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 the experimentally detected one [37]. We have calculated also the electron polaron optical absorption energy, using the Δ SCF scheme, and found it to be 0.69 eV. The absorption process corresponds to a charge transfer to the nearest Ti atom. This absorption band has been detected recently experi-

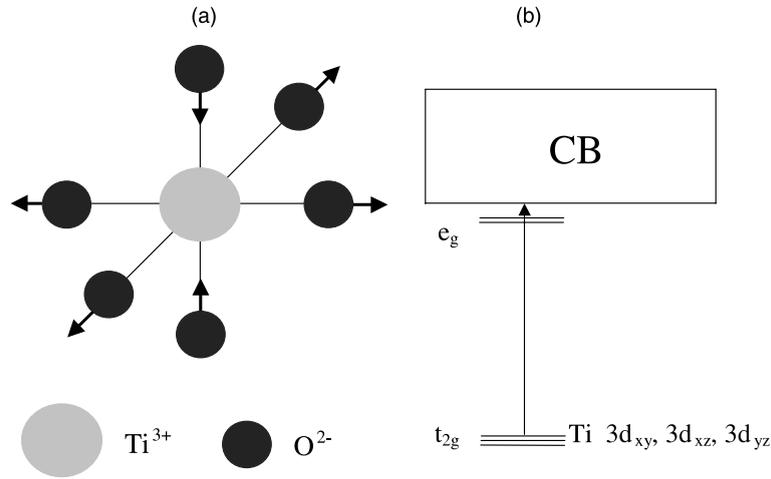


Fig. 1. (a) Asymmetric oxygen relaxation around the central Ti atom where the self-trapped electron in BaTiO₃ is localized. Two O atoms move towards a central Ti atom along the z-axis and the other four O atoms relax outwards in the x–y plane. (b) Positions of 3d states of a central Ti atom in the BaTiO₃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

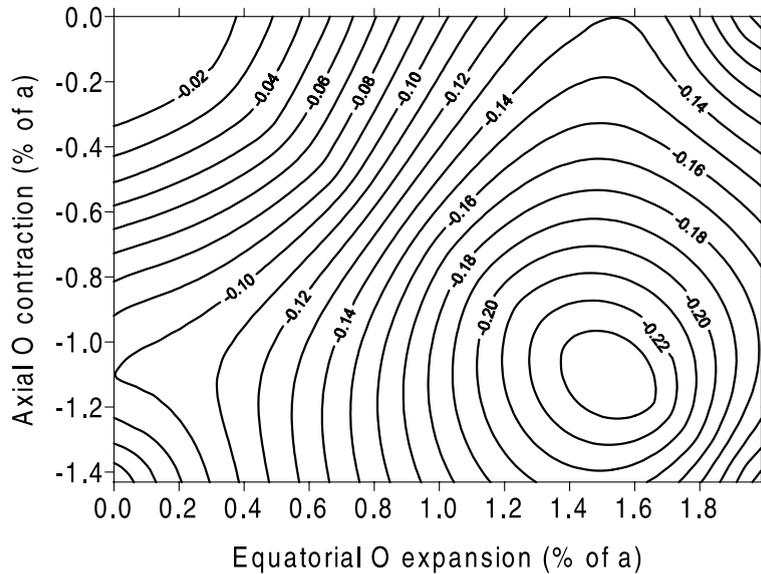


Fig. 2. A contour plot of the lattice energy gain due to outward x–y displacement of four equatorial O atoms and the inward relaxation of two oxygens along the z-axis.

mentally under picosecond laser excitation [38], with absorption energy ≈ 0.6 eV. Our calculated electron polaron energy for BaTiO₃ (0.69 eV) is also close to Nb⁴⁺ polaron absorption band

detected recently around 0.72 eV in strontium barium niobate [39]. This lies also in the same energy range as our previous electron polaron calculations in ABO₃, see Table 1.

Table 1
Optical absorption energies of electron and hole polarons in ABO₃ perovskites as calculated by means of INDO method^a

Crystal	Type of polaron	Absorption energy (eV)	Relax. energy (eV)	
			INDO	LMTO [33]
BaTiO ₃	Electron polaron	0.69	0.24	
KNbO ₃ [9,33]	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 [9]	Electron polaron	0.75	0.27	

^a The relevant lattice relaxation energies is calculated by INDO and ab initio FP-LMTO methods.

4. Calculations of triplet excitons in ABO₃ perovskites

In our previous study [9,40] we modelled the triplet exciton in a cubic phase of KNbO₃ and KTaO₃ perovskites. Our main conclusion is that the triplet exciton consists mainly of three atoms: two Nb atoms (Nb₁ and Nb₂) and O₁ atom between them (in the KNbO₃ case). The main effect is a charge transfer ($\approx 0.5e$) from the O₁ atom onto nearest Nb₁ atom. This increases the vibronic interaction and induces the local lattice instability. This results in a formation of the excited state with a new equilibrium charge transfer and lattice relaxation [12,13]. As a result of modelling, we found that the CTVE consists of a pair of spatially well correlated electron and hole polarons localised mainly on the nearest Nb₁ and O₁ atoms. These

two atoms are displaced from the lattice sites towards each other due to the effective Coulomb attraction. This is accompanied with a strong (a few eV) vibronic energy reduction. These properties are in agreement with semi-phenomenological CTVE model proposed earlier [41,42].

These findings are confirmed by our present calculations for the exciton in a cubic phase of SrTiO₃. The oxygen ion O₁ in SrTiO₃ is displaced by 4.6% a_0 (lattice constant) towards Ti₁ ion. Simultaneously, this Ti₁ ion reveals a displacement of 2.6% a_0 towards the O₁ ion, whereas another Ti₂ ion (which is located on the other side from the oxygen ion O₁ along the CTVE axis) shows a repulsion from the O₁ and is displaced outwards by 4.1% a_0 , see Fig. 3. We obtained that the total energy reduction in CTVE in SrTiO₃ due to the lattice relaxation of O₁, Ti₁ and Ti₂—three main

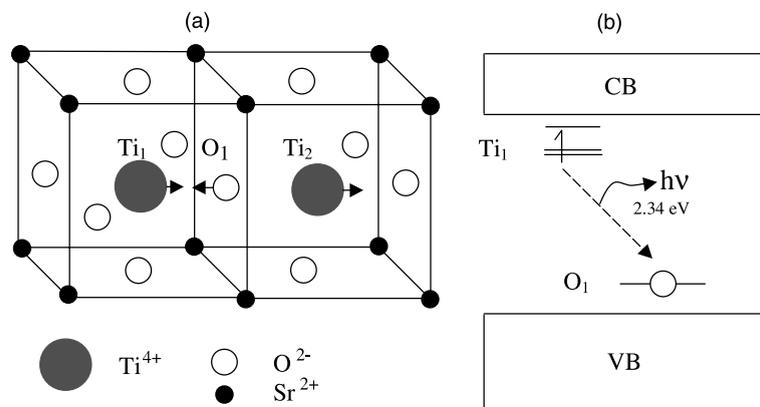


Fig. 3. (a) The INDO-calculated triad atomic structure of a single CTVE in SrTiO₃. The directions of displacement of three active Ti₁–O₁–Ti₂ ions constituting the triad centre are shown. (b) A schematic view of the Ti and O energy levels induced by the CTVE in the band gap and its luminescence.

atoms—is quite appreciable—2.04 eV. The most significant charge transfer ($0.45e$) occurs between O_1 and Ti_1 ions. Results of the INDO calculations for the lattice energy gain— E_{rel} and displacements of three basic atoms involved into an exciton formation for four ABO_3 perovskites are collected in Table 2.

The strong lattice distortion caused by the CTVE induces local energy level in $SrTiO_3$ band gap. Namely, the O_1 energy level with the hole is located 0.7 eV above the VB top, its wave function consist mainly of its $2p_x$ atomic orbitals directed towards the Ti_1 atom. On the other hand, two closely located Ti_1 energy levels (one of them is twofold degenerate) appear at 0.6 eV below the CB. They have t_{2g} symmetry and consist mainly of $3d_{xy}$ atomic orbitals of Ti_1 with admixture of Ti_2 ion atomic orbitals. Table 2 presents the distance of the donor and acceptor one-electron energy levels from the relevant bands for all four perovskites.

In our model the luminescence arises due to the electron transfer from the donor level (close to the CB bottom and formed by the electron polaron) to

the hole level (close to the VB created by the hole polaron). As one can see in Table 3, the luminescence energies calculated using the Δ SCF method are close to the experimentally observed values for all four ABO_3 crystals. The luminescence quenching energy calculated for $KNbO_3$ as typical ABO_3 crystal, is very small, <0.1 eV, which explains why the green luminescence is observed only at very low temperatures.

5. Conclusions

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 [37]. The theoretically calculated electron polaron absorption energy in $BaTiO_3$ (0.69 eV) agrees well with the only experimental estimate of 0.6 eV [38].

Our calculations for a series of perovskite materials— $SrTiO_3$, $BaTiO_3$, $KNbO_3$ and $KTaO_3$ —give a strong support to the green luminescence in these crystals as a result of the recombination of the electrons and holes forming the charge transfer vibronic exciton rather than due to the electron transitions in a MeO_6 complex. Our results also demonstrate that well-parametrised quantum chemical methods are a very efficient tool for the study of optical properties of advanced perovskite materials.

Table 2

Results of charge transfer vibronic exciton calculations for cubic phases of four ABO_3 perovskites performed by means of the INDO method^a

Crystal	E_{rel} (eV)	Δ (% of a_0)	ϵ_d , eV	ϵ_a , eV
$SrTiO_3$	2.04	2.6; -4.6; 4.1	0.6	0.7
$BaTiO_3$	2.20	2.8; -4.7; 4.2	0.65	0.8
$KNbO_3$	2.37	2.9; -4.9; 4.3	0.7	0.9
$KTaO_3$	2.71	3.1; -5.2; 4.5	0.8	1.0

^a E_{rel} is the lattice energy gain, Δ is B_1 , O_1 , B_2 atomic displacements (Fig. 3a) along the (1 0 0) axis (in percent of lattice constant), ϵ_d , ϵ_a are distances from donor (acceptor) levels to the edges of relevant bands.

Table 3

Green luminescence energies in ABO_3 perovskites (in eV) as calculated by means of INDO and detected experimentally

Crystal	Calculated	Experimental
$SrTiO_3$	2.34	2.4 [8]
$BaTiO_3$	2.30	2.5
$KNbO_3$ (cubic phase)	2.17 [9]	2.15
$KNbO_3$ (orthorhombic phase)	2.2	2.15 [9]
$KTaO_3$	2.14 [9]	2.2–2.3 [9]

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