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# Quantum chemical modelling of ‘green’ luminescence in self activated perovskite-type oxides

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## Abstract

We discuss the origin of the intrinsic visible band emission of  $ABO_3$  perovskite oxides (so-called ‘green luminescence’) which remains a topic of high interest during the last quarter of the century. We present a theoretical calculation modelling of this emission in the framework of a concept of charge transfer vibronic excitons [Phys. Solid State, 40 (1998) 834], i.e. as a result of radiative recombination of correlated (bound) self-trapped electron and hole polarons in the highly polarizable  $ABO_3$ -type matrix. The Intermediate Neglect of Differential Overlap method combined with the Large Unit Cell periodic defect model was used for quantum chemical calculations and theoretical simulation of the green emission for a series of model  $ABO_3$  perovskites. The ‘green’ luminescence energies for  $PbTiO_3$ ,  $SrTiO_3$ ,  $BaTiO_3$ ,  $KNbO_3$  and  $KTaO_3$  perovskite-type crystals agree well with those experimentally observed earlier.

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## 1. Introduction

Conventionally luminescence of wide-gap materials (e.g. oxides) appears only as a result of the presence of intrinsic defects due to doping by impurities. However, in so-called ‘self-activated phosphors’ luminescence, observed e.g. under photo excitation, can be excited even in high quality pure materials. Such a property is inherent to the  $ABO_3$  perovskite crystal family, which reveals a broad-band emission in the visible spectral region (so called ‘green’ luminescence) peaking at around 2.4 eV for  $SrTiO_3$  [2–4], 2.5 eV in  $BaTiO_3$  [5,6], 2.15 eV in  $KNbO_3$  [7] and 2.2–2.4 eV in  $KTaO_3$  [8,9] and at 2.4 eV in  $PbTiO_3$  [10]. The nature of this wide-band visible luminescence universal for  $ABO_3$  perovskite-type oxides is still a subject under discussion. Its various mechanisms, such as, e.g. donor–

acceptor recombination [11], transitions in  $MeO_6$  complexes [12,13], recombination of electron and hole polarons [14] and charge transfer vibronic exciton (CTVE) [1,15,16] have been proposed. A way to verify these models is to perform numerical calculations and to compare theoretically calculated luminescence energies with the respective reliable experimental data. It should be pointed out specifically that CTVE cannot be treated as a conventional exciton. This quasi-particle consists of a pair of strongly correlated electronic and hole polarons which characterizes the family of highly polarized partly covalent  $ABO_3$  oxides with low-lying TO optical modes and pronounced vibronic effects. Due to the strong electron–phonon interaction, the radiative annihilation of CTVE does not give a narrow emission line, but produces unstructured wide band. In this paper, the modelling of triplet CTVE excitons in  $PbTiO_3$ ,  $SrTiO_3$ ,  $BaTiO_3$ ,  $KNbO_3$  and  $KTaO_3$  crystals including calculation of their luminescence energies is performed by means of the semi-empirical Intermediate Neglect of Differential Overlap (INDO) method. Reliable experimental data on wide-band

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luminescence for  $\text{PbTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{KNbO}_3$  and  $\text{KTAO}_3$  have been taken from publications available.

## 2. Computational method

Ab initio methods are still cumbersome, rather expensive and time-consuming for the treatment of the electronic and spatial structure of complex systems, especially those with relatively high covalence contribution in the chemical bonding, like  $\text{ABO}_3$  perovskites. This is why it is necessary to find a reasonable compromise between accurate but time consuming, ab initio methods [17–22] and widely used simple phenomenological approaches. One possibility is to use the semi-empirical quantum chemical methods, which are parameter-dependent, but parameters used are transferable for chemical constituents given, and are not subject to adjustment for each new compound under study. An example of such a method is the updated INDO method. The INDO has been developed in the 1970s by Pople [23], and modified for ionic/partly covalent solids in the 1990s [24,25]. Since the semi-empirical INDO method is based essentially on the Hartree–Fock formalism, it allows to calculate both the ground and excited states of the system and thereby, also the respective energies for absorption and luminescence optical transitions, which we compare with the respective experimental data. Absorption and luminescence energies are calculated as the difference of total self-consistent energies for the ground and excited states (known as  $\Delta\text{SCF}$  method). As it was demonstrated in Ref. [26], the accuracy of the INDO method is sufficient enough even for the adequate description of tiny energy differences related to the  $\text{ABO}_3$  ferroelectric instability. During recent years the INDO method has been successfully applied to simulations of the impurity centres and defect structures in many oxides [27,28] and perovskite-type materials [26,29–34] including  $\text{KNb}_x\text{Ta}_{1-x}\text{O}_3$  (KTN) solid solutions [35,36]. The relevant INDO parameterisation for  $\text{BaTiO}_3$  is described in Ref. [37], for  $\text{SrTiO}_3$ —in Ref. [38] and for  $\text{PbTiO}_3$ —in Ref. [39]. We use the periodic supercell model, in the form of the large unit cell (LUC) method [40,41], with a primitive unit cell volume extended by a factor of  $3 \times 3 \times 3 = 27$  and thereby containing 135 atoms. The basic idea of the LUC method is the calculation of the electronic structure of the extended (large) unit cell at  $k = 0$  of the narrowed Brillouin zone (NBZ), which is equivalent to usual band calculation at those  $k$  points, which transform to the NBZ centre while extending the unit cell [40–42].

## 3. Results of computer simulations

In order to explain theoretically experimental data dealing with the ‘green luminescence’ in  $\text{ABO}_3$  perovskites [2–8,10–14], as a first step we have calculated the triplet

state of excitons therein. Qualitatively, results are similar for all  $\text{ABO}_3$ , we illustrate now with the case of  $\text{PbTiO}_3$ . Our calculations have demonstrated that the triplet exciton is a triad centre containing one active O atom ( $\text{O}_1$ ) and two Ti atoms located on opposite sites from this O atom (see Fig. 1a). The total energy of the system is lowered by the combination of Coulomb attraction between the electron and hole polarons and the vibronic effect typical for this CTVE [15,16,43]. In order to find the CTVE energy minimum, a self-consistent geometry optimisation for the 135 atom LUC (see Fig. 1a) was performed. According to our calculations, the oxygen ion  $\text{O}_1$  in  $\text{PbTiO}_3$  is displaced by  $4.4\% a_0$  (lattice constant) towards the  $\text{Ti}_1$  ion (Fig. 1a) which is active in the CTVE formation. Simultaneously, this  $\text{Ti}_1$  ion reveals the displacement of  $2.5\% a_0$  towards the  $\text{O}_1$  ion, whereas another  $\text{Ti}_2$  ion (which is located on the other side from the oxygen ion  $\text{O}_1$  along the CTVE-axis) experiences a repulsion from the oxygen  $\text{O}_1$  and is displaced outwards by  $3.9\% a_0$ . We obtained that the total energy gain in CTVE in  $\text{PbTiO}_3$  due to the lattice relaxation of  $\text{O}_1$ ,  $\text{Ti}_1$  and  $\text{Ti}_2$ —three main atoms—from their unrelaxed state is quite appreciable—1.91 eV. The most significant charge transfer occurs between  $\text{O}_1$  and  $\text{Ti}_1$  ions and is equal to  $-0.42 e$ . In fact, these two atoms are bound hole and electron polarons. Our INDO results for CTVE in four  $\text{ABO}_3$  perovskites, along with the results of  $\text{PbTiO}_3$  are collected in Table 1.

The strong lattice distortion caused by the CTVE induces

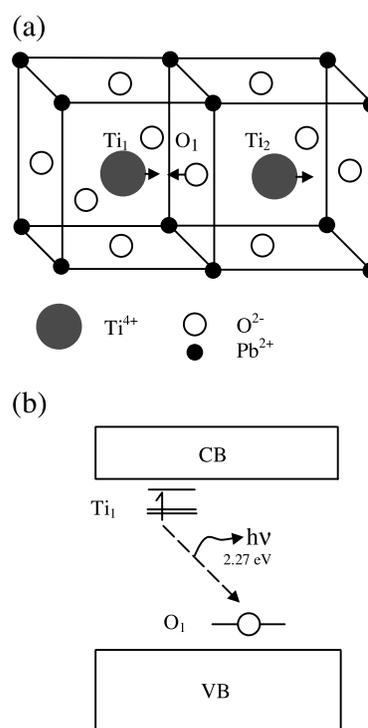


Fig. 1. Schematic view of the CTVE in  $\text{ABO}_3$  perovskites (a) and its luminescence (b).

Table 1  
Results of CTVE calculations for ABO<sub>3</sub> perovskite materials by means of INDO method

ABO <sub>3</sub> Crystal	Relaxation energy due to CTVE formation (eV)	Displ. of Me <sub>1</sub> –O–Me <sub>2</sub> atoms in the CTVE (% of $a_0$ )	The energy level of the electron polaron (eV) below the CB bottom	The energy level of the hole polaron (eV) above the VB top
PbTiO <sub>3</sub>	1.91	2.5; 4.4; 3.9	0.5	0.65
SrTiO <sub>3</sub>	2.04	2.6; 4.6; 4.1	0.6	0.7
BaTiO <sub>3</sub>	2.20	2.8; 4.7; 4.2	0.65	0.8
KNbO <sub>3</sub>	2.37	2.9; 4.9; 4.3	0.7	0.9
KTaO <sub>3</sub>	2.71	3.1; 5.2; 4.5	0.8	1.0

local energy levels in the PbTiO<sub>3</sub> band gap. Namely, the O<sub>1</sub> energy level with a hole is located 0.65 eV above the valence band (VB) top, its wave function consists mainly of its 2p<sub>x</sub> atomic orbitals directed towards the Ti<sub>1</sub> atom. On the other hand, two closely located Ti<sub>1</sub> energy levels (one of them is two-fold degenerate) appear at 0.5 eV below the conduction band (CB). They have t<sub>2g</sub> symmetry and consist mainly of 3d<sub>xy</sub> atomic orbitals of Ti<sub>1</sub> and to a smaller extend Ti<sub>2</sub> ions, with an admixture of atomic orbitals of nearest Ti atoms surrounding the CTVE (Fig. 1b). The luminescence energies calculated using the  $\Delta$ SCF method are in good agreement with the experimentally observed values for all the ABO<sub>3</sub> crystals under examination (see Table 2 and Ref. [44,45]).

#### 4. Conclusions

The quantum-chemical INDO calculations performed for a series of five perovskite-type oxides—PbTiO<sub>3</sub>, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, KNbO<sub>3</sub> and KTaO<sub>3</sub>—justify the interpretation of the universal green luminescence in these self-activated crystals as a result of the radiative recombination of the self-trapped electrons and holes forming the CTVE, rather than of the electron transitions in a MeO<sub>6</sub> complex or donor–acceptor recombination, as was intuitively suggested earlier. Our results also demonstrate that well-parametrised semi-empirical quantum chemical methods could be successfully used for the study of optical properties of modern advanced materials, e.g. oxide perovskites.

We would like to stress that we focused in this paper on the qualitative explanation of the basic mechanisms of the green luminescence in ABO<sub>3</sub> perovskites. In fact the calculated luminescence energies are slightly larger than the experimental values, which could be a result of the optical gap overestimate, typical for Hartree–Fock-type methods. It should be also reminded that LDA calculations typically strongly underestimate the gap. Note that our INDO parametrisation was carefully developed to reproduce a sequence of phase transitions in ABO<sub>3</sub> perovskites due to off-centre displacement of B ions, and relevant phonon properties [26]. This guarantees the correct relaxation energy and thus luminescence energy.

Table 2  
Luminescence energies in PbTiO<sub>3</sub>, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, KNbO<sub>3</sub> and KTaO<sub>3</sub> perovskites

ABO <sub>3</sub> Crystal	Calculated (eV)	Experimental (eV)
PbTiO <sub>3</sub>	2.27	2.4 [10]
SrTiO <sub>3</sub>	2.34	2.4 [3,4]
BaTiO <sub>3</sub>	2.30 [29]	2.5 [5,6]
KNbO <sub>3</sub>	2.17 [44,45]	2.15 [7]
KTaO <sub>3</sub>	2.14 [44,45]	2.2–2.4 [8,9]

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