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Quantum chemical modelling of "green" luminescence in ABO_3 perovskites

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Abstract. The origin of the intrinsic excitonic ("green") luminescence in ABO_3 perovskites remains a hot topic over the last quarter of a century. We suggest as a theoretical interpretation for the "green" luminescence in these crystals, the recombination of electron and hole polarons forming a charge transfer vibronic exciton. In order to check quantitatively the proposed model, we performed quantum chemical calculations using the Intermediate Neglect of Differential Overlap (INDO) method combined with the periodic defect model. The luminescence energies calculated for four perovskite crystals are found to be in good agreement with experimental data.

PACS. 71.15.Ap Basis sets (plane-wave, APS, LCAO, etc.) and related methodology (scattering methods, ASA, linearized methods) – 71.35.-y Excitons and related phenomena – 77.84.Dy Niobates, titanates, tantalates, PZT ceramics, etc.

Introduction

Many ABO_3 perovskites reveal the characteristic excitonic luminescence in the visible range (the so-called "green" luminescence) peaking at 2.4 eV in $SrTiO_3$ [1,2] 2.5 eV in $BaTiO_3$ [3,4], 2.2 eV in $KNbO_3$ [5] and 2.3 eV in $KTaO_3$ [6]. The origin of this luminescence has been discussed more than once [7–12]. In order to check the proposed theoretical models, it is essential to perform numerical calculations and compare theoretically calculated luminescence energies with the relevant experimental data. In this paper, we present the results of quantum chemical modelling of triplet excitons in four ABO_3 perovskites – $SrTiO_3$, $BaTiO_3$, $KNbO_3$ and $KTaO_3$ – and suggest a mechanism for their luminescence.

Computational method

Theoretical calculations of the electronic and spatial structure of complex systems, especially those with partially covalent chemical bonding, like perovskites, could be effectively performed using semi-empirical quantum chemical methods. In this paper we employ the Intermediate Neglect of the Differential Overlap (INDO) method. The INDO method was developed in the 70's by Pople [13], widely used in organic chemistry, and modified for ionic/partly covalent solids in the 90's [14,15]. Since the semi-empirical INDO method is essentially based on the Hartree-Fock formalism, it allows the calculation of the excited states of the system, and hence also the relevant absorption and luminescence energies.

It was demonstrated that the accuracy of the INDO method is sufficient for the adequate description of tiny energy differences related to the ferroelectric instability, as well as basic phonon frequencies for different ferroelectric phases [16]. During the last five years the INDO method has been successfully applied to the simulation of defects in many oxides [17–19] and perovskites [16,20–24], as well as $KNb_xTa_{1-x}O_3$ (KTN) solid solutions [25,26]. The relevant INDO parameterisation for $KNbO_3$, $KTaO_3$, $BaTiO_3$ and $SrTiO_3$ is developed in references [16,20,27,28]. To avoid the well-known problem of the boundary conditions in a cluster model, we use the periodic large unit cell model, with a primitive ABO_3 unit cell volume extended by a factor of $3 \times 3 \times 3 = 27$ and thereby containing 135 atoms.

Calculations of triplet excitons in ABO_3 perovskites

In our previous study [29] we modelled the triplet exciton in a cubic phase of $KNbO_3$ and $KTaO_3$ perovskites. We obtained the electron/spin density distribution as a result

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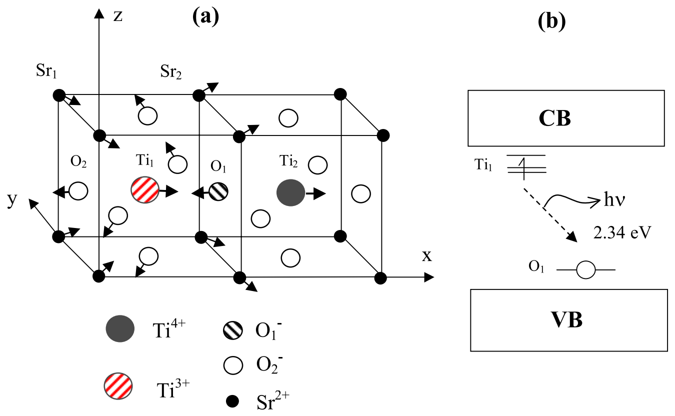

Fig. 1. Schematic view of the structure of charge transfer vibronic exciton in ABO_3 perovskites in a cubic phase (a) and its luminescence (b). Arrows indicate the directions of atomic displacements. Overall 16 atoms are allowed to relax to the total energy minimum.

Table 1. Results of charge transfer vibronic exciton calculations for the cubic phases of $SrTiO_3$, $BaTiO_3$, $KNbO_3$ and $KTaO_3$ perovskites performed by means of the INDO method. $E_{\rm rel}$ is the lattice energy gain, Δ is the B_1, O_1 and B_2 atomic displacement respectively (Fig. 1a) along the (100) axis (in per cent of lattice constant), ε_d and ε_a are distances from the donor (acceptor) levels to the edges of the relevant bands.

Crystal	$E_{\rm rel}$ (eV)	Δ(% of a_o)	ε_d, eV	ε_a, eV
$SrTiO_3$	2.0	2.6; −4.6; 4.1	0.6	0.7
$BaTiO_3$	2.2	2.8; −4.7; 4.2	0.6	0.8
$KNbO_3$	2.4	2.9; −4.9; 4.3	0.7	0.9
$KTaO_3$	2.7	3.1; −5.2; 4.5	0.8	1.0

Table 2. Green luminescence energies in ABO_3 perovskites (in eV) as calculated by means of the INDO method and measured experimentally.

Crystal	Calculated	Experimental
$SrTiO_3$	2.3	2.4 [1,2]
$BaTiO_3$	2.3	2.5 [3,4]
$KNbO_3$ (cubic phase)	2.2 [29]	
$KNbO_3$ (orthorhombic phase)	2.2	2.2 [5]
$KTaO_3$	2.2 [29]	2.3 [6]

of the self-consistent geometry optimisation. Our main conclusion was that the triplet exciton consists mainly of three atoms (the *triad* center shown in Fig. 1a): two B (= Ti, Ta) atoms (B_1 and B_2) and O_1 atom between them. The main effect is a charge transfer ($\cong 0.5\,e$) from the O_1 atom onto the nearest B_1 atom. This increases the vibronic interaction and induces a local lattice instability. This results in the formation of an excited state with a new equilibrium charge transfer and lattice relaxation [8,9,30]. As a result of the modelling, we found that a charge transfer vibronic exciton (CTVE) is formed, consisting of a pair of spatially well correlated electron and hole polarons mainly localised on the nearest B_1 and O_1 atoms. These two atoms are displaced from the lattice sites towards each other due to the effective Coulomb attraction (the electron and hole polarons in fact form a *bipolaron*). This is accompanied by a strong (a few eV) vibronic energy reduction.

The findings are confirmed by our present calculations for the exciton in a cubic phase of $SrTiO_3$. The oxygen ion O_1 in $SrTiO_3$ is displaced by 4.6% a_o (lattice constant) towards the Ti_1 ion (Fig. 1a). Simultaneously, the Ti_1 ion reveals a displacement of 2.6% a_o towards the O_1 ion, whereas another Ti_2 ion (which is located on the other side of the oxygen ion O_1 along the CTVE-axis) shows a repulsion from the O_1, and is displaced outwards by 4.1% a_o. We calculated that the total energy reduction in CTVE in $SrTiO_3$, due to the lattice relaxation of O_1, Ti_1 and Ti_2 – three main atoms, is quite appreciable – 2.04 eV. The most significant charge transfer (0.45 e) occurs between O_1 and Ti_1 ions. Results of the INDO calculations for the lattice energy gain, $E_{\rm rel}$, and displacements of three basic atoms involved in the exciton formation (B_1, O_1, B_2) for four ABO_3 perovskites, are collected in Table 1.

The strong lattice distortion caused by the CTVE induces local energy levels in the $SrTiO_3$ band gap (Fig. 1b). Namely, the O_1 energy level with a hole is located 0.7 eV above the VB maximum, and the wave function mainly consists of its $2p_x$ atomic orbitals which are directed towards the Ti_1 atom. On the other hand, two closely located Ti_1 energy levels (one of them is two-fold degenerate) appear at 0.6 eV below the CB edge. 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 1 presents the distances of the donor and acceptor one- electron energy levels from the relevant bands for all four perovskites. Based on these energies, one could expect that the relevant *thermal* ionisation energies for electron polarons would be quite small, of the order of 0.2 eV, *i.e.* excitonic luminescence should be easily observable only at low temperatures, which is in agreement with experiments.

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) (Fig. 1b). As one can see in Table 2, the luminescence energies calculated using the ΔSCF method are close to the experimentally observed values for all four ABO_3 crystals.

It is possible that the results are unreliable due to the condition that the atomic displacement are restricted to only the three atoms forming the exciton. To verify this, we re-calculated the triplet exciton in the $SrTiO_3$ cubic phase taking into account the relaxation of as many as 13 atoms surrounding the exciton (8 Sr atoms NN for Ti_1, O_2 and 4 other O atoms NN to Ti_1). Their displacements are shown schematically in Figure 1a and the optimised coordinates are summarised in Table 3. The O_2 atom is displaced outwards, and the Ti_1 inwards, along the (100) axis due to their Coulombic repulsion, as well as four other

Table 3. Optimised atomic structure of the triplet exciton in the $SrTiO_3$ cubic phase (see Fig. 1a). Coordinates are in units of lattice parameter.

Atom	x	y	z
1. Ti_1	0.52600	0.50000	0.50000
2. O_1	0.95400	0.50000	0.50000
3. Ti_2	1.54100	0.50000	0.50000
4. O_2	−0.0013	0.50000	0.50000
5. O_2	0.4997	0.50000	1.0013
6. O_2	0.4997	1.0013	0.50000
7. O_2	0.4997	−0.0013	0.50000
8. O_2	0.4997	0.50000	−0.0013
9. Sr_2	1.0019	1.0008	1.0008
10. Sr_2	1.0019	−0.0008	1.0008
11. Sr_2	1.0019	1.0008	−0.0008
12. Sr_2	1.0019	−0.0008	−0.0008
13. Sr_1	0.0015	0.0006	0.9994
14. Sr_1	0.0015	0.9994	0.9994
15. Sr_1	0.0015	0.9994	0.0006
16. Sr_1	0.0015	0.0006	0.0006

NN O atoms. On the other hand, four Sr_1 atoms are attracted to the Ti_1 due to its additional negative charge and four Sr_2 atoms are repeled from the O_1 atom due to its additional positive charge. However, the main result is that all the displacements of the 13 atoms are quite small and give an additional energy gain of only 0.1 eV, in fact negligible compared with the 2 eV lattice energy gain caused by the displacement of the three basic atoms forming the excition – $Ti_{1,2}$ and O_1.

The above described calculations were performed for the cubic crystalline phases stable at high temperatures. However, as was mentioned, the excitonic luminescence is observed at low temperatures, often below the phase transition point. In order to study how this could affect the luminescence energies, we calculated the triplet exciton in the $KNbO_3$ orthorhombic phase which is stable over a broad temperature interval. The reason for studying $KNbO_3$ is that its geometry in all phases is well studied experimentally [16] (unlike $SrTiO_3$). Note that some time ago we performed the INDO comparative study of absorption energies for F – type centers (O vacancy with one and two electrons) in cubic and orthorhombic phases of ferroelectric $KNbO_3$ crystals [21,24]. We found that the F center absorption in a cubic phase is characterised by two energies; 2.73 eV and 2.97 eV, which are close to three absorption energies of the orthorhombic phase (with two different C_s and C_{2v} symmetries of the O lattice sites) – 2.72, 3.04 and 3.11 eV respectively [21].

In the exciton calculations, we used the geometry of the orthorhombic crystalline phase, obtained in our previous paper [16], and re-calculated the coordinates of the three basic atoms forming the exciton (Fig. 2). We found that the O_1 atom moves by 0.201 Å towards the Nb_1 atom, which is displaced by 0.122 Å in the opposite direction. The Nb_2 atom is shifted by 0.179 Å in the same direction as the Nb_1 atom. These displacements of the three atoms are accompanied by a lattice relaxation energy of 2.48 eV, quite close to that found in the cubic $KNbO_3$ phase (2.37 eV [29]). Also, the luminescence energies calculated earlier for the cubic phase (2.17 eV [29]), and now in the orthorhombic phase (2.20 eV), turn out to be very close, and in agreement with the recent experimental data on the green luminescence in $KNbO_3$ [5] (2.15 eV). This demonstrates that the green luminescence energy, practically, does not depend on the actual crystalline phase of a perovskite crystal. This is the more so, since we are interested mostly in a *qualitative* understanding of the luminescence mechanism.

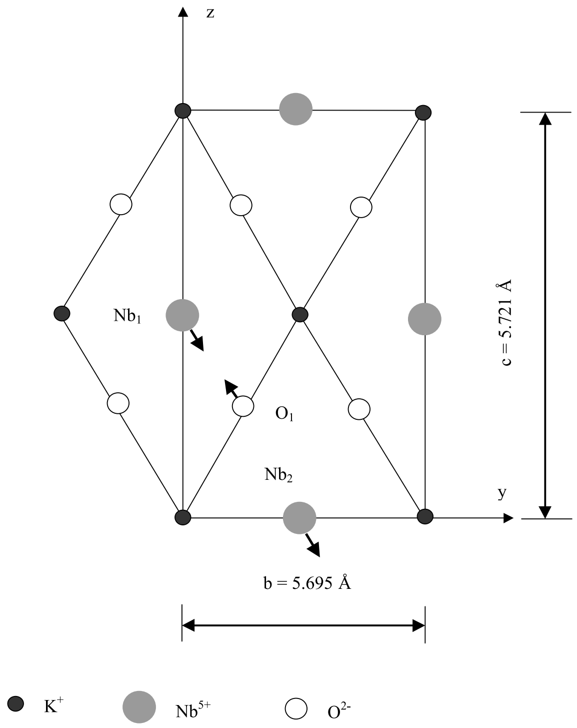

Fig. 2. Sketch of the atomic structure of the $KNbO_3$ exciton in the orthorhombic phase.

Conclusions

Our calculations for a series of four perovskite crystals – $SrTiO_3$, $BaTiO_3$, $KNbO_3$ and $KTaO_3$ – give strong support to the proposal that the “green” luminescence in these crystals is a result of the recombination of the electron and hole polarons forming the charge transfer vibronic exciton. Small thermal ionisation energies for the electron polarons and low energy barrier from the exciton energy curve to the ground state curve are responsible for its observed quenching at low temperatures. We have shown that luminescence energies are not practically dependent on the particular ferroelectric phase since tiny ferroelectric atomic displacements are much smaller than the atomic relaxation of several atoms forming the charge transfer vibronic exciton. Results of independent triplet exciton calculations for four perovskites show surprising similarity in basic parameters (atomic relaxations, lattice energy gains, luminescence energies). Our results also demonstrate that well-parameterised quantum chemical methods are a very efficient tool for the study of optical properties of advanced optical materials.

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