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LETTER TO THE EDITOR

Quantum chemical modelling of electron polarons and 'green' luminescence in $PbTiO_3$ perovskite crystals

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Abstract

In an extension of our previous study on the electron polarons and excitons in $KNbO_3$, $KTaO_3$ and $BaTiO_3$ (Kotomin E A, Eglitis R I and Borstel G 2000 *J. Phys.: Condens. Matter* **12** L557; Eglitis R I, Kotomin E A and Borstel G 2002 *J. Phys.: Condens. Matter* **14** 3735) by the semiempirical Hartree–Fock method we present here results for free electron polarons in the $PbTiO_3$ perovskite crystal. We discuss the origin of the intrinsic visible band emission of $PbTiO_3$ perovskite oxides (so-called 'green luminescence') which has remained a topic of high interest during the last quarter of a century. We present a theoretical calculation modelling this emission in the framework of a concept of charge transfer vibronic excitons, i.e. as a result of radiative recombination of correlated (bound) self-trapped electron and hole polarons in the highly polarizable $PbTiO_3$-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 $PbTiO_3$ perovskite. The calculated 'green' luminescence energy for $PbTiO_3$ perovskite-type crystals agrees well with experimental measurements presented in this letter.

The existence of small radius polarons in ionic solids was predicted theoretically by Landau in 1933 [3–5]. Strict experimental (ESR) proof of self-trapped holes has been given in alkali halides by Känzig in 1957 [5]. Since then it had been believed for a long time that electron self-trapping is not possible energetically in ionic solids because a lot of energy is necessary to localize an electron on a single cation, which is the first stage of the trapping process. This

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energy loss is not compensated by the energy gain due to crystal polarization at the second stage of the self-trapping. The first ESR evidence appeared in 1993 [6] for the *electron* self-trapping in $PbCl_2$ crystals, and one year later for that in $LiNbO_3$ perovskite crystals [7]. Lastly, very recently, the existence of self-trapped electrons in $BaTiO_3$ was discussed [8–10]. A number of theoretical and experimental studies of hole polarons in $BaTiO_3$ have been performed in recent years [11–15].

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 $SrTiO_3$ [16], 2.5 eV in $BaTiO_3$ [17], 2.15 eV in $KNbO_3$ [18] and 2.2–2.4 eV in $KTaO_3$ [19, 20] and at 2.38 eV in $PbTiO_3$ single crystals, as specially examined and reported in this letter. 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 [21], transitions in MeO_6 complexes [22, 23], recombination of electron and hole polarons [24] and charge transfer vibronic exciton (CTVE) [25–28] 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 consist of a pair of strongly correlated electronic and hole polarons which is characteristic for 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 an unstructured wide band. In this letter, the modelling of triplet CTVE excitons in $PbTiO_3$ crystals including calculation of their luminescence energies is performed by means of the semi-empirical intermediate neglect of differential overlap (INDO) method. Because of technological problems, only preliminary photoluminescence properties of polycrystalline powder $PbTiO_3$ have been reported [29] up to now. In this letter, we perform respective photoluminescence spectra measurements for single-crystalline $PbTiO_3$ specimens, and compare results with the relevant INDO calculations.

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 ABO_3 perovskites. This is why it is necessary to find a reasonable compromise between accurate but time consuming, *ab initio* methods [30–35] 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. INDO was developed in the 1970s by Pople [36], and modified for ionic/partly covalent solids in the 1990s [37, 38]. Since the semi-empirical INDO method is based essentially on the Hartree–Fock formalism, it allows us 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 the ΔSCF method). As demonstrated in [39], the accuracy of the INDO method is sufficient even for the adequate description of tiny energy differences related to the 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 [40–42] and perovskite-type materials [39, 43–47] including $KNb_xTa_{1-x}O_3$ (KTN) solid solutions [48, 49]. The relevant INDO parametrization for $PbTiO_3$ is described in [50]. We use the periodic supercell model, in the form of the large unit cell (LUC) method [51, 52], 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 $\boldsymbol{k} = \boldsymbol{0}$ of the narrowed Brillouin zone (NBZ), which is equivalent to usual band calculation at those $\boldsymbol{k}$ points which transform to the NBZ centre while extending the unit cell [51–53].

$PbTiO_3$ single crystals have been grown by H Hesse (Chochralsky grown) at the University of Osnabrück. Single-domain experimental specimens were fabricated as polished parallelipeds oriented along the [100] principal axes of tetragonal C_{4v} structure. Emission photoluminescence spectra were recorded with a SPEX single-grating spectrometer and corrected for the cooled photomultiplier response (RCA GaAs C31034). An AXBO 450 high pressure Xe lamp with a SPEX Minimate as the variable bandpass filter was used as the excitation source. Emission was measured in the reflection geometry with a nonpolarized light. Specimens were suspended in the vacuum and attached at the tip of a Leybold optical, He controlled, closed cycle cryostat system.

All $PbTiO_3$ single crystals used revealed nearly the same structure of the emission spectrum under inter-band (VB $\rightarrow$ CB) photoexcitation ($h\nu > 2.8$ eV). Figure 1 presents the emission spectrum under excitation at 350 nm as taken at 10 K. The emission intensity is only a bit weaker as compared to $SrTiO_3$. This allows us to suggest that the weakness of the visible emission reported earlier [29] was due to powder $PbTiO_3$ samples. From figure 1 it is seen that the broad band emission spectrum can be resolved into two Gaussians with maxima at ~450 nm (2.75 eV) and at ~542 nm (2.28 eV). It should be mentioned that only in a few crystalline specimens of not very good quality could we find hints of the presence of another emission band centred at 650 nm, which was reported in powder $PbTiO_3$ [16] and attributed there to optical transitions from the CB bottom to the Pb^{2+} levels. For this reason, we believe that the intensity of this band strongly depends on specimen quality and it arises due to impurities and defects. Figure 1 shows that the two mentioned emission bands obviously dominate in the emission spectrum, while the component centred at 650 nm, even if exists, is very weak in the crystalline $PbTiO_3$. As a result, when considering only reliable, systematically reproducible experimental data, we used two Gaussian bands to fit the actual wide visible emission. Taking into account the results and interpretation of [29], we believe that the emission band at 450 nm belongs to spectrally unresolved or broadened optical transitions of free excitons. Another emission at 542 nm is the 'green luminescence' universal for ABO_3 perovskite oxides and we attributed it to the self-trapped exitonic emission (CTVE) under discussion.

Recently, we performed calculations for electron polarons in $KNbO_3$, $KTaO_3$ and $BaTiO_3$ perovskite crystals [1, 2], and found that the energy gain due to electron self-trapping is 0.21, 0.27 and 0.24 eV, respectively [1, 2]. The relevant electron polaron absorption energies in $KNbO_3$, $KTaO_3$ and $BaTiO_3$—0.78, 0.75 and 0.69 eV [1, 2]—agree well with the only experimental estimate of 0.6 eV for $BaTiO_3$ [54]. In the present work, we modelled the electron polaron in $PbTiO_3$. In our numerical simulations we used the $3 \times 3 \times 3$ extended cubic $PbTiO_3$ with the LUC containing 135 atoms. In order to find the energy minimum of the system, we allowed six nearest oxygen atoms in the octahedron around a central Ti atom to relax (figure 2(a)). All other Ti and Pb atoms, as well as remaining O atoms, were kept fixed at their perfect lattice sites. According to our INDO calculations (figure 2(b)), the ground state is initially threefold degenerate (t_{2g}). This degeneracy is lifted as a result of combined breathing mode and Jahn–Teller (JT) effects: outward displacement of four nearest equatorial O atoms by 1.46% a_0 and relaxation of the two oxygens inwards along the z direction by

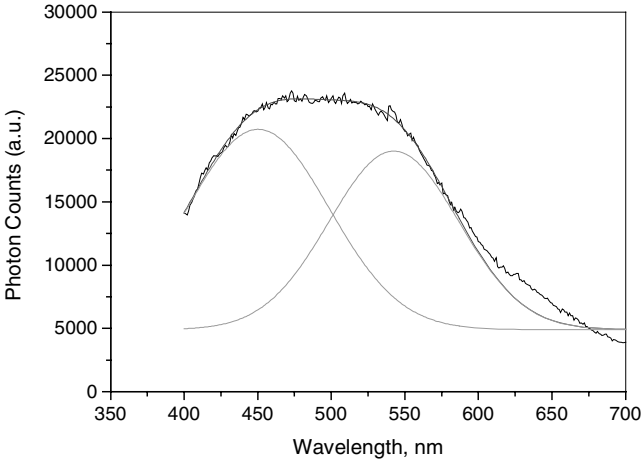

Figure 1. Emission spectrum of $PbTiO_3$ under photo-excitation at 350 nm measured at $T = 10$ K, with a Gaussian fit into two components.

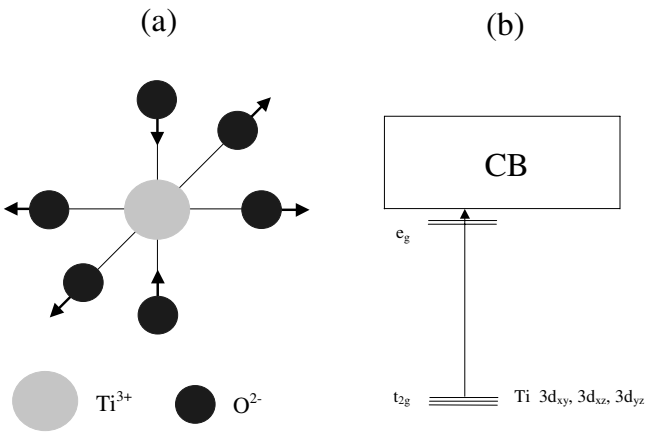

Figure 2. (a) Sketch of the asymmetric O atom relaxations around an electron localized on the central Ti atom in the self-trapped electron. (b) Local energy states within the gap.

1.04% a_0 (figure 3). The total energy gain is 0.22 eV. A similar JT electron polaron was observed recently experimentally in $BaTiO_3$ [8, 9].

As a result, a considerable electron density is localized on the central Ti atom producing three narrowly spaced energy levels in the bandgap. They consist mainly of the xy, xz and yz Ti 3d atomic orbitals (split t_{2g} energy level in an isolated ion); another two empty levels are located close to the conduction band bottom. The electron polaron absorption energy calculated by means of ΔSCF is 0.73 eV. The absorption process corresponds to a charge transfer to the nearest Ti atom.

In order to explain theoretically experimental data dealing with the 'green luminescence' in $PbTiO_3$ perovskites, as a first step we have calculated the triplet state of excitons therein. Our calculations have demonstrated that the triplet exciton is a triad centre containing one active O atom (O_1) and two Ti atoms located on opposite sites from this O atom (see figure 4(a)). The total energy of the system is lowered by the combination of Coulomb attraction between

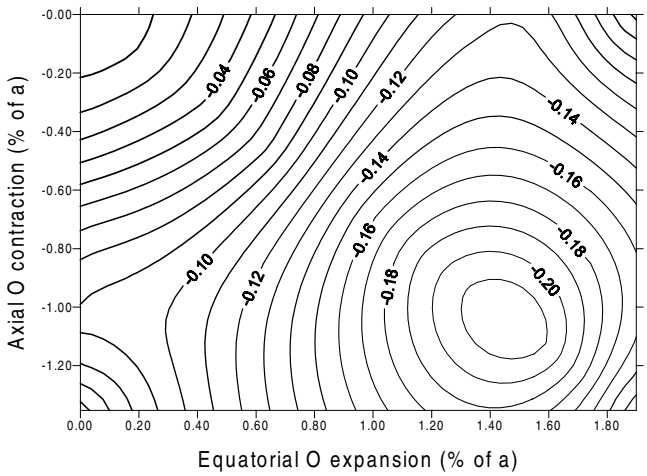

Figure 3. A two-dimensional contour plot of the lattice energy gain due to outward x–y displacement of four equatorial O atoms and the inward relaxation of two oxygens along the z-axis.

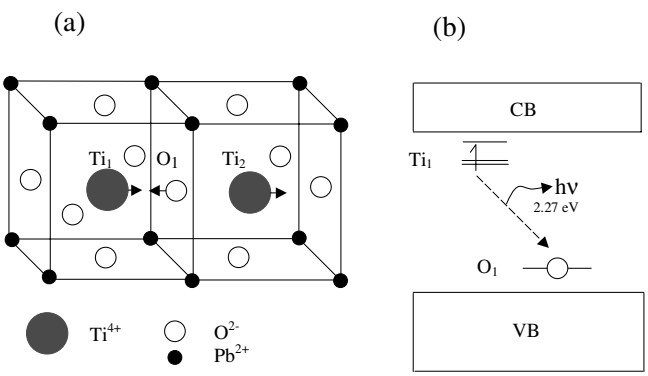

Figure 4. Schematic view of the CTVE in $PbTiO_3$ perovskites (a) and its luminescence (b).

the electron and hole polarons and the vibronic effect typical for this CTVE [26–28]. In order to find the CTVE energy minimum, a self-consistent geometry optimization for the 135-atom LUC (see figure 4(a)) was performed. According to our calculations, the oxygen ion O_1 in $PbTiO_3$ is displaced by 4.4% a_0 (lattice constant) towards the Ti_1 ion (figure 4(a)) which is active in the CTVE formation. Simultaneously, this Ti_1 ion reveals the displacement of 2.5% a_0 towards the O_1 ion, whereas another Ti_2 ion (which is located on the other side from the oxygen ion O_1 along the CTVE-axis) experiences a repulsion from the oxygen O_1 and is displaced outwards by 3.9% a_0. We obtained that the total energy gain in CTVE in $PbTiO_3$ due to the lattice relaxation of O_1, Ti_1 and Ti_2—the three main atoms—from their unrelaxed state is quite appreciable, −1.91 eV. The most significant charge transfer occurs between O_1 and Ti_1 ions and is equal to −0.42 e. In fact, these two atoms are bound hole and electron polarons.

The strong lattice distortion caused by the CTVE induces local energy levels in the $PbTiO_3$ bandgap. Namely, the O_1 energy level with a hole is located 0.65 eV above the valence band (VB) top; its wavefunction consists 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 0.5 eV below the conduction band (CB). They have t_{2g} symmetry and consist mainly of $3d_{xy}$ atomic orbitals of Ti_1 and to a smaller extent Ti_2 ions, with an admixture of atomic orbitals of nearest Ti atoms surrounding the CTVE (figure 4(b)). The luminescence energy calculated using the ΔSCF method -2.27 eV is in good agreement with the experimentally observed value -2.38 eV for the $PbTiO_3$ crystals under examination.

Our quantum chemical INDO calculations gave additional evidence for the existence of electron polarons in $PbTiO_3$ crystals. The theoretically calculated electron polaron absorption energy in $PbTiO_3$ (0.73 eV) is close to our previous results for the electron polarons in $BaTiO_3$ (0.69 eV), $KNbO_3$ (0.78 eV) and $KTaO_3$ (0.75 eV) [1, 2] and agrees well with the only experimental estimate of 0.6 eV for $BaTiO_3$ [54].

The quantum chemical INDO calculations performed for a $PbTiO_3$ perovskite-type oxide justify the interpretation of the universal 'green' luminescence in the $PbTiO_3$ crystals as a result of the radiative recombination of the self-trapped electrons and holes forming the CTVE, rather than due to the electron transitions in a MeO_6 complex or donor–acceptor recombination, as was intuitively suggested earlier. Our results also demonstrate that well-parametrized semi-empirical quantum chemical methods could be successfully used for the study of optical properties of modern advanced materials, e.g. oxide perovskites.

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