

Analysis of radiation-induced hole localisation in titanates

Arvids Stashans and Henry Pinto

Centro de Investigación en Física de la Materia Condensada, Corporación de Física
Fundamental y Aplicada, Apartado 17-12-637, Quito, Ecuador

Abstract. Hole self-trapping in technologically important BaTiO_3 and SrTiO_3 crystals is studied using a quantum-chemical method developed for periodic systems, e.g., crystals. The computations are carried out in the self-consistent-field manner using the embedded molecular cluster model. The possibility of spontaneous hole self-trapping is estimated by employing an analytical procedure based on the energetical favourability principle. Our results support the self-trapping of radiation-induced hole in BaTiO_3 crystals while such an outcome is not predicted for SrTiO_3 crystals. Computational results are discussed in the light of available experimental data on light-induced absorption spectra measurements in BaTiO_3 crystals.

Keywords: Hole self-trapping, BaTiO_3 , SrTiO_3 .

* Corresponding author: FAX: +593-2-403656, E-mail: sauleskalns@yahoo.com

1. Introduction

Perovskite-type ceramics are now the focus of extensive study due to their unusual magnetic and dielectric properties and a wide range of applications. Additionally, the question if carrier self-trapping can occur in a given material is of fundamental nature. Radiation-induced holes can result in the formation of resonant states within the valence band and rapid hole self-trapping in the lattice. These radiation-created point defects can participate in different charge-transfer processes as well as contribute into material absorption and light-induced absorption changes. This points to the importance of our understanding of the self-trapped holes (STH) and their influence upon different properties of solids.

The existence of a number of hole centres has been established a long time ago in oxide crystals (Spaeth and Koschnick, 1991), where they are trapped at oxygen atoms near a cation vacancy or impurity. The existence of STH in oxide crystals is a matter of long-term debate. The problem is that these defects cannot be monitored by the direct electron paramagnetic resonance (EPR) technique due to the zero nuclear spin on regular O atoms. As far as we know there is only one exception: EPR experiments have revealed STH in fused silica (Griscom, 1989). Additionally, there exist experimental results that indirectly support the existence of stable STH polarons in corundum crystals (Kulis *et al*, 1991).

The purpose of the present work is to examine if hole self-trapping can occur in perfect BaTiO₃ and SrTiO₃ crystals under irradiation and to discuss possible effects of the STH upon the crystals electronic, optical and structural properties.

2. Methodology

Since holes are *charged* intrinsic defects, their simulation by periodic models is not feasible without the inclusion of compensating charges. That is why we have chosen to use the embedded molecular cluster (EMC) model (Kantorovich, 1988) with the cluster consisting of 90 atoms. The EMC model was used within the semi-empirical Hartree-Fock computational scheme (Stefanovich *et al*, 1990), developed especially for periodic systems, e.g., computations in crystals. The method is based on a reliable parametrization scheme (Shluger, 1985), which allows one to reduce the computational time considerably by introducing some numerical parameters. Parametrization of the BaTiO₃ and the SrTiO₃ crystals has been done before (Stashans and Pinto, 2000; Stashans and Sánchez, 2000). Here we shall only note that we reproduced very well the geometry and electronic band structure of both crystals as well as the basic properties (ground states, ionisation potentials, inter-atomic distances) of some Ba- and Sr-containing test molecules.

In studies of complex materials containing point defects our method is sometimes more reliable than the corresponding *ab initio* techniques, especially if one studies large enough systems. Through the semi-empirical parametrization one can eliminate some artificial effects that occur as a result of the one-electron approximation. This was demonstrated, for instance, in the TiO₂ crystal, where our method (Stashans *et al*, 1996) gave a better description of the electronic band structure properties than the Hartree-Fock *ab initio* approach (Fahmi *et al*, 1993).

In order to calculate whether the STH state is energetically preferred to a free-hole state in a given material it is necessary to calculate the so-called self-trapping energy:

$$\Delta E_{\text{ST}} = E_{\text{ST}} - E_{\text{F}}^{(k)} \quad (1)$$

where E_{ST} is the hole energy for the fully relaxed ST state and $E_{\text{F}}^{(k)}$ is the energy of the free-hole state. If ΔE_{ST} is negative, the hole can be trapped spontaneously. The larger the absolute value of negative ST energy, the larger the lifetime of the hole in the ST state rather than in the free-hole state. To realise in practice the calculation of the ST energy, we have used the idea of Gilbert (Gilbert, 1966) who considered hole self-trapping as a hypothetical two-stage procedure. The localisation of a free hole in a local perfect crystal region in the first stage, and the subsequent relaxation of the lattice with accompanying electronic charge redistribution around the defect in the second stage. In the first stage, the hole acquires a positive contribution to its energy due to the loss of kinetic energy in the local state. In the second stage, however, the hole acquires a negative energy due to the atomic displacements around the localised hole. A competition between the positive localisation energy, E_{loc} , and the negative relaxation energy, E_{rel} , results in the actual sign of the ST energy:

$$\Delta E_{\text{ST}} = E_{\text{loc}} + E_{\text{rel}} \quad (2)$$

and allows one to determine the possibility of finding stable hole polarons in a given crystal under irradiation.

Considering the Wannier representation of the localised states and a Fourier transform of the valence band energies (Kantorovich *et al*, 1994) one can obtain the E_{loc} in the following manner:

$$E_{\text{loc}} = \int \epsilon N_j(\epsilon) d\epsilon \quad (3)$$

where $N_j(\epsilon)$ is the density of states of the valence band j normalised to unity and the integration is performed over the whole bandwidth. The E_{rel} is computed as a difference in total energies of the EMC in the relaxed and unrelaxed states.

3. Results and discussion

In both crystals, when a hole was inserted into the molecular cluster, its spin density was found to be localised mainly on one of the O atoms, i.e., it was found that the hole polaron has a one-site spatial configuration.

In order to estimate the relaxation energy term, E_{rel} , we included in the automated geometry optimisation 27 atoms situated around the oxygen, which receives a hole. As a result we obtained E_{rel} equal to 3.85 eV and 2.90 eV for the BaTiO₃ and SrTiO₃ crystals, respectively. We estimated E_{loc} using the equation (3), which gave us 2.36 eV and 2.85 eV for the BaTiO₃ and SrTiO₃ crystals, respectively. Then using the expression (2) we calculated the value of the hole self-trapping energy to be -1.49 eV and -0.05 eV for the BaTiO₃ and SrTiO₃ crystals, respectively. The value of the ΔE_{ST} has to be negative and sufficiently large in order to observe the stable polarons in a given crystal. That is why we can conclude that the spontaneous occurrence of hole polarons in the pure strontium titanate lattice is practically impossible due to the negligible value of the ΔE_{ST} . In the case of the BaTiO₃ lattice, however, one can expect the spontaneous self-trapping of holes under irradiation.

Below we shall analyse the influence of the self-trapped hole upon different properties of the BaTiO₃ crystal. As it was mentioned above, the hole finds itself

localised on one of the O atoms (denoted hereafter as O^-) around which 80% of the hole spin density is found. The defect-surrounding the Ti and O atoms share the remaining 20%. The O^- is situated practically in the middle of the EMC, so any influence of the cluster border effects on the outcome of computations is automatically excluded. The lattice distortion in the defective region indicates that the negatively charged O atoms move inward by approximately 0.10 Å while the positively charged Ba and Ti atoms move outward by approximately 0.06 Å with respect to the defect, respectively. This is in accordance with expectations since the O^- has positive effective charge with respect to the perfect crystalline lattice after receiving a hole. Additionally, we observe small rotations of the STH-surrounding the O atoms by $\approx 1^\circ$ with respect to the vertical axis, which passes through the O^- . In our opinion, these rotations might be attributed to the Jahn-Teller effect (Englman, 1972), which reduces the total energy of the system by asymmetric atomic displacements.

The main contribution to the wave function of the ground state of the STH is due to the $2p_x$ atomic orbital (AO) of the O^- . In order to obtain the excited state of the STH, we acted in the following way: an electron from one of the occupied orbitals in the upper valence band, related to the O^- , was taken and put into the unoccupied ground state of the STH polaron. During this procedure we employed the density matrix of the polaron ground state as an initial guess. Then, according to the Franck-Condon principle, the absorption energy was obtained as a difference of total energies of the EMC for the self-consistent-field (SCF) ground and excited states with a fixed atomic configuration (Δ SCF method). We have found that the hole polaron wave function in the excited state consists mainly of O $2p_z$ AO strongly overlapping with $3d_{z^2}$ and 4s AOs of two nearest Ti atoms situated along the vertical axis. The contribution of these

titanium atoms into the wave function of the excited state increases around 3.5 times compared to the ground-state wave function, which means that the wave function in the excited state is considerably more delocalised compared to the ground state. The calculation of the STH absorption energy by the Δ SCF method gave us the value of 0.5 eV. This magnitude is very close to the experimentally observed value of 0.53 eV found in the light-induced absorption spectra measurements (Song *et al*, 1998) in the undoped BaTiO₃ crystal. To our mind, this might be indirect proof of the existence of a self-trapped hole polaron in barium titanate. They also can act as shallow levels in the sense that thermal ionisation of the STH from such a level to the valence band can occur. This means that these point defects can contribute into the non-linear photoconductivity in the barium titanate (Fridkin and Popov, 1978). The self-trapped holes also were discovered indirectly in barium titanate by the EPR studies (Possenriede *et al*, 1992) where these authors came to the conclusion that a number of nonparamagnetic centres can be attributed to the O⁻ defects. However, the authors state that these point defects are unlikely to contribute to the shallow levels important in the photoconductivity process since they are thermally ionised already near 100 K. Still, it has to be noted that under very intense illumination the number of O⁻ centres could be sufficient to act as shallow levels even at high temperatures.

In summary, it follows from our investigation that hole polarons trapped at *regular oxygen sites* can occur spontaneously in BaTiO₃ crystals since it is energetically favourable with respect to the free-hole state. This outcome is not predicted for SrTiO₃ crystals where the self-trapping energy is practically equal to zero. Thus, this point defect can contribute to the non-linear photoconductivity observed in BaTiO₃. In other

words, in barium titanate, not only can trivalent impurities act as radiation-created hole traps but *regular oxygen atoms* can also do that.

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