Mott-Wannier excitons in the tetragonal BaTiO$_3$ lattice

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ABSTRACT: Structural and electronic properties of excitons in the tetragonal BaTiO$_3$ crystal is studied using a quantum-chemical method developed for crystals. Obtained defect structure corresponds to the so-called Mott-Wannier-type exciton having a considerable distance between the hole and electronic parts of the defect. Performed crystalline lattice relaxation shows displacements of atoms in rather extensive defective region of up to twelve atoms. However, the calculated magnitudes of atomic movements are not large, normally not exceeding 0.08 Å. It is also observed that the self-trapped exciton polarizes the lattice around it. Using the so-called ΔSCF method, the luminescence energy due to the exciton is found to be equal to 0.94 eV.

Key words: BaTiO$_3$; excitons; LUC, structural and electronic properties, luminescence

Introduction

Barium titanate ($BaTiO_3$) is one of the most important perovskite-type crystals. Among a number of important features it has large electro-optic coefficients and high photorefractive sensivity [1]. This material also can be used in self-pumped phase conjugation or holographic storage [2,3] and inexpensive diode lasers [4]. Other important properties are its chemical and mechanical stability in a wide temperature range, which facilitates its fabrication in bulk polycrystals and both epitaxial and polycrystalline thin films [5].

Despite the fact that many studies have been done so far on this ferroelectric material, there is still no sufficient understanding of the nature of many properties and phenomena in the barium titanate. On the other hand, it is well understood that point defects play an important role in many applications of the $BaTiO_3$ crystal. One of the most common defects in non-metallic crystals is the so-called exciton. The triplet exciton is a pair of a hole and an electron, which is produced when photons of energy greater that the energy of the band-gap are absorbed in the crystal. The electron and hole produced in this way are free and may move independently through the crystal, giving rise to photoconductivity. But because an electron and hole have an attractive Coulomb interaction it is possible for stable bound states of the two particles together to be formed, and the photon energy required for this purpose will be less than the band-gap energy. In that case, the re-emission of excitation energy in form of luminescence might occur. It is possible to think of excitons in two different limiting approximations, one due to Frenkel, in which the excitons is considered as tightly bound, and another approximation due to Mott and Wannier, in which the exciton is weakly bound, having an electron-hole interparticle distance large in comparison with an atomic radius.

A long-term investigation of singlet and also triplet excitons has been carried out in cubic-alkali-halide crystals [6-9], which led to the conclusion that intrinsic excitons undergo significant changes between initial photon absorption and the process of exciton radiative annihilation. Free excitons created by exciting radiation undergo transformation into self-trapped excitons in singlet or triplet states. Later on the recombination of electrons and trapped holes causes the appearance of the recombination luminescence of the self-trapped exciton. Some considerable efforts have been done to understand the nature of excitons in corundum (α-Al_2O_3) crystal using the methods of vacuum-ultraviolet spectroscopy as well as intrinsic and extrinsic luminescence excitation by synchrotron radiation [10-12] leading to the observation of luminescence. The adiabatic potential surface for triplet exciton self-trapping has been studied also in the crystalline SiO_2 crystal [13] using the same computer code as we do. This computer code based on the Hartree-Fock formalism has been found to be very reliable in many applications on crystal studies. The computations interpreted in great detail the nature of self-trapped-exciton optical absorption and luminescence in the SiO_2 crystal.

The studies of exitons in the perovskites are very few, due to the complexity of possible spatial configurations of the exciton in these materials and necessity to take into consideration more complex chemical bonding, which includes also a covalent component. However, recently quantum-chemical calculations on self-trapped excitons in $KTaO_3$ and $KNbO_3$ crystals have been performed [14] using again the same computer code. Thus it has been showed repeatedly that the CLUSTERD computer code [15] is adequate for the exciton studies in different oxides. Additionally, we have tested the present method in a number of other applications on titanates. Some examples include studies of hole self-trapping in a pure [16] and defective $BaTiO_3$ crystals [17,18], hole

self-trapping studies in the $SrTiO_3$ cubic lattice [19,20], and defect doping studies in the bulk of $SrTiO_3$ [21-23], $CaTiO_3$ [24], $BaTiO_3$ [25,26], $PbTiO_3$ [27] crystals as well as quantum-chemical computations of defects on the $SrTiO_3$ surfaces [28,29].

The purpose of the present article is to obtain equilibrium geometry and electronic structure of the triplet exciton in the $BaTiO_3$ tetragonal lattice. We also study the lattice distortion due to the exciton and possible luminescence due to the hole-electron pair annihilation.

Brief Outline of the Method

The employed method of periodically repeated large unit cells (LUCs) [13] is designed for the calculation of the total energy and electronic structure of crystals. We preferred to use the LUC model because of its advantage compared to different cluster models, for example, better treatment of the exchange interaction. Additionally, it is important to note that from the viewpoint of simulating the exciton self-trapping the original equivalency of the perfect lattice sites is essential. Just the periodic models meet this condition. A full discussion of the computational relations for calculating the total energy within the framework of the LUC approach is given in numerous works (see [13, 15, 19-29] and Refs. therein) carried out before. Here we shall only state that the method obeys the Hartree-Fock formalism and includes a number of the so-called semi-empirical parameters. The atomic parameter sets are optimized by calculating the following properties and comparing them to the experimental results: (i) the main features of a given crystal (width of the forbidden energy gap, widths of the upper and lower valence bands, lattice constants of the crystal), (ii) the inter-atomic distances and ground states of some selected diatomic molecules, and finally (iii) the ionization

potentials of the host atoms of the crystal. We did the parametrization of the $BaTiO_3$ crystal before [17] where also discussion on the perfect crystal geometry and electronic band structure is made. Within the present work we have exploited a LUC of 135 atoms, i.e., we utilized 27 times (3x3x3) extended primitive unit cell of the barium titanate. As indicated by previous studies [30-32], a four-fold or eight-fold-symmetric extension of the primitive unit cell proves to be completely sufficient to reproduce correctly the electronic band structure of a given crystal.

Structural and Electronic Features of the Exciton

A total spin density analysis is required in order to answer the question of the exciton possible localization/deslocalization configuration. As a result of the spin density analysis for the 135 atomic LUC we have found that 94% of electron is localized on the Ti(11) atom and 87% of hole is localized on the O(8) atom (Fig. 1). The approximate distance between the two centers is about 7.0 Å. This implies that we have the so-called Mott-Wannier-type exciton. The exciton is weakly bound, which is a commonly accepted exciton model for the ionic crystals [30]. We also can state that predominantly electronic part localizes on Ti $3d_{x^2-y^2}$ orbital while the hole part is found to be localized on O $2p_y$ orbital.

The performed geometry optimization leads to rather strong electronic density re-distribution (Table I). It is found that in the central region of the LUC, the hole is localized on the O(8) atom (see Fig. 1). The two-nearest Ti atoms, Ti(5) and Ti(6), situated along the *y*-axis move outward the O(8) atom by 0.08 Å. The O(8) four-nearest Ba atoms also move outward the defect along the <101> direction by about 0.03 Å. Finally, the two titanium-closest O atoms located along the *y*-axis, O(7) and O(9), move

towards the O(8) atom and thus reduce the chemical bond lengths of Ti(5)-O(7) and Ti(6)-O(9). As one can see from the charge analysis (Table I) and considering these particular atomic movements, we have obvious lattice polarization due to the hole presence. This polarization occurs along the y direction and also leads to weakening of the chemical bonding between the oxygen, which receives a hole and its surrounding cations. It is important to state that the polarization axis *does not* coincide with the ferroelectric z-axis. Thus one can see that exciton presence in the ferroelectric tetragonal BaTiO$_3$ phase might reduce ferroelectric polarization in this material and can induce the loss of bulk ferroelectricity in the material.

The analysis of the electronic part of the exciton shows that it is well localized on the Ti(11) atom. Again, due to the vicinity polarization effect we observe the atomic movements along the z-axis as shown in Fig. 1. In the present case the lattice polarization is along the ferroelectric axis. However, its direction is opposite, i.e., the induced local polarization due to the electron trapping at the Ti(11) atoms reduces the total ferroelectric moment. The calculated relaxation energy as a difference between the total energies of relaxed and unrelaxed systems is found to be equal to 4.4 eV.

Luminescence due to the Exciton

Deexcitation of an exciton gives rise to luminescence, which can be observed experimentally. In our study, the luminescence energy was obtained as the difference of total energies for the self-consistent-field ground and excited states for optimized triplet exciton geometry (ΔSCF method). That is, the potential energy curve is calculated for the triplet exciton, and then according to the Frank-Condon principle the luminescence energy is that for the vertical transition from the minimum of the triplet exciton relaxed

state to the SCF singlet state of the exciton for a fixed atomic arrangement. Thus computed luminescence energy was found to be equal to 0.94 eV.

In this connection, some recent results reported for the triplet exciton state in the cubic phase of $BaTiO_3$ crystal [31] should be mentioned. Since the authors use the electronic density matrix in their analysis of electron and hole polaron localization within the crystalline lattice, rather than the spin density matrix, which could give a more precise pattern for the exciton localization, and it is also not clear that the geometry used corresponds to the equilibrium geometry, a direct comparison with the present work is not possible. However, it seems likely that the experimentally observed green luminescence in a number of perovskites is due to singlet excitons in these materials. Since the triplet state of a given excited system normally lies lower than the singlet state, the luminescence energy due to the triplet exciton should be considerably smaller than the band-gap width, which is around 3 eV in $BaTiO_3$, and thus fall within the infrared spectrum.

Conclusions

The developed for crystals quantum-chemical approach has been applied to study the triplet state of exciton in tetragonal $BaTiO_3$ crystal. The geometry of both, hole and electronic parts of the exciton has been found. The model of the so-called Mott-Wannier exciton, which normally occurs in ionic crystals, describes very well our results. The hole and electron parts are well localized on oxygen and titanium atoms, respectively, with inter-particle distance equal to 7.0 Å. The performed atomic displacements and electronic charge density re-distribution point to very strong

polarization in the defective region. The exciton-induced dipole moment is opposite to the existing ferroelectric polarization, thus leading to the loss of bulk ferroelectricity in the material.

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TABLE I

Atomic displacements, Δr, (in Å) and changes in atomic charges, ΔQ, (in e) in the BaTiO$_3$ due to the triplet exciton localization. The atomic numeration coincides with the one in Fig. 1. The direction of the atomic movements is depicted in the figure.

Atom	Δr	ΔQ
Ba (1)	0.03	-0.001
Ba (2)	0.03	-0.001
Ba (3)	0.03	-0.001
Ba (4)	0.03	-0.001
Ti (5)	0.08	-0.135
Ti (6)	0.08	-0.135
O (7)	0.03	+0.138
O (8)	0.00	+0.376
O (9)	0.03	+0.138
Ti (10)	0.04	-0.276
Ti (11)	0.08	-0.055
O (12)	0.04	+0.051

Figure Captions

FIGURE 1. The hole part, O(8) atom, and the electron part, Ti(11) atom, of the exciton and displacements of the neighboring atoms. The positive Ti and Ba atoms move outwards while the negative O atoms move towards the O(8) atom. One can observe the lattice polarization effect along the y axis due to the hole presence. The electron polaron also produces some polarization along the z axis.

Hole

Electronic part

z

y

x

Ba

Ti

O