

Quantum chemical study of effects produced by Nb- and La-doping in BaTiO₃

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Abstract. The effects produced in BaTiO₃ due to Nb and La doping have been studied. The investigation has been performed using a quantum chemical method developed for crystals and it is based on the Molecular Orbital theory. The geometry relaxation due to the Nb impurity shows a symmetric character in both phases, cubic and tetragonal, i.e., outward defect-closest barium displacements and inward oxygen displacements. The relaxation energy, as a difference for fully relaxed and unrelaxed systems, is found to be equal to 1.69 eV and 5.44 eV for the cubic and tetragonal phases, respectively. It is found that the extra electron belonging to Nb transfers from the local energy level within the band gap to the conduction band. In the case of the La impurity, the lattice distortion shows a non-symmetric pattern in the cubic phase. Although titaniums move away symmetrically by 0.07 Å, the oxygen displacements are asymmetric along only one crystallographic axis by 0.02 Å. In the tetragonal phase only defect-nearest oxygens move towards the La impurity by 0.06 Å while the titaniums remain motionless. The calculated relaxation energy for this phase is found to be equal to 0.84 eV and 0.52 eV for the cubic and tetragonal phases, respectively. The extra electron in the case of La-doping remains within the band gap.

Introduction

During the past decades BaTiO₃ has been one of the most studied materials. This is basically due to its ferroelectric properties in tetragonal phase and high dielectric constant at ambient temperature. In addition, its chemical and mechanical stability in a wide temperature range facilitates its fabrication in bulk polycrystals in both epitaxial and polycrystalline thin films. These properties make this ceramic material very useful in different applications such as dynamic random-access memories, piezoelectric transducers, optical sensors, thermistors and actuators.

Despite the fact that many studies have been done so far on this material our knowledge of its fundamental properties is not satisfactory. Most of the studies have been carried out experimentally. There are only few theoretical investigations. This could be partially explained by difficulties in using computer modelling to reproduce the unusual physical properties of this ceramic material.

In the present work the effects on different BaTiO₃ properties are studied due to the Nb and La-doping, considering both cubic and tetragonal phases. For this aim we use the advanced quantum-chemical method, which solves the Schrödinger equation for a system of atoms fixed periodically. Within the method we make use of the periodic LUC (Large Unit Cell) model as it is implemented into the CLUSTERD computer code [1]. Some numerical parameters are incorporated into the computational scheme.

Due to its semi-empirical character the computer program is not cumbersome and time consuming in treatment of electronic and spatial structures of complex systems, in particular, with a partially covalent chemical bonding, like oxide crystals. Up to now the method has been successfully employed to investigate several perfect and defective oxides and materials with simpler electronic band structure. It also has an important advantage of precise geometry prediction for crystals containing point defects (See [2-4] and Refs. therein).

The purpose of our research is to study the influence of the Nb and La impurities upon the electronic band structure properties, as well as impurity effects on crystal geometry in both cubic and tetragonal phases.

Brief Description of the Method

BaTiO₃ monocrystal has two crystallographic phases. Above 380 K it has cubic phase and below 380 K it switches to the tetragonal or ferroelectric phase. In order to understand fully the effects of impurity doping, both phases need to be studied.

Our investigation is done using a supercell of 135 atoms within the so-called LUC approach, which has shown high reliability in point defect studies in a number of crystals. The use of a large size supercell has the advantage of making the impurity-impurity interaction negligible. This permits us to study *a single defect* within the periodic model.

The information about the computational equations of the total energy of the LUC model is given in [5]. Here we shall only outline the main ideas of the method. The Fock matrix elements contain a number of numerical parameters, which are chosen in such a way that they reproduce the basic crystal characteristics, i.e., widths of the forbidden energy gap, widths of the upper and lower valence bands, chemical composition of valence and conduction bands and lattice constants for both cubic and tetragonal structures. Later the obtained parameter set is used to study defect doping. The complete description of BaTiO₃ parametrization is given in Refs. 2.

Results and Discussion

The chemical character of the lower valence band of the cubic BaTiO₃ crystal obtained by the LUC computations is mainly O 2s AOs (atomic orbitals), while the upper valence band is predominantly O 2p in nature with a small admixture of Ti 3d AOs. The bottom of the conduction band is composed of Ti 3d states mainly, with a small contribution of Ba 5s states [2]. We observe some change in valence and conduction band compositions when study the tetragonal phase of the crystal.

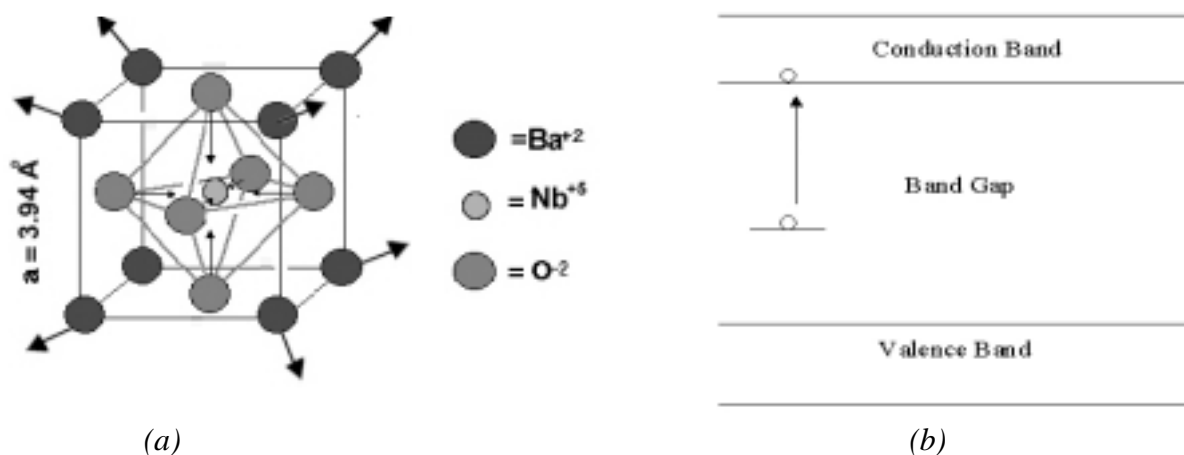


Fig. 1 (a) The relaxation of the lattice due to the niobium impurity for the cubic phase. The eight niobium-closest bariums move outwards while the six niobium-nearest oxygens move towards the impurity. (b) Electron transfer effect observed in BaTiO₃ due to Nb impurity for both cubic and tetragonal phases.

In particular, a considerable amount of Ti 3d AOs is found in the upper valence band and also a notable contribution of O 2p states in the lower part of the conduction band are observed. This points to the hybridisation effect between Ti 3d and O 2p AOs, which accompanies the phase transition: cubic (paraelectric) \rightarrow tetragonal (ferroelectric).

In the case of Nb-doping we replace one of the titanium atoms in the central part of the LUC by Nb impurity (see Fig. 1a). After performing the relaxation of the structure including an automated geometry optimization, the final atomic configuration for the defect vicinity is attained.

In the cubic phase the relaxation of the structure shows outward symmetrical displacements of the barium atoms by 0.09 Å, while the oxygen atoms move toward the impurity by 0.02 Å. These displacements have a symmetric character (See Fig.1a).

In the tetragonal phase the structure relaxation is similar. The barium atoms move outwards the niobium by a distance of 0.09 Å. However, the direction of these displacements is now different from the one found for the cubic phase. These movements are observed only within the x - y plane, while the motion along the z axis is negligible. The same occurs with the neighbouring oxygens, i.e., they move towards the impurity by a distance of 0.01 Å along *only one* axis, x or y , displacements along the z axis are very small. The calculated relaxation energy for this phase is found to be equal to 5.44 eV.

Among the electronic properties of BaTiO₃, it is relevant to mention that due to this kind of doping, an extra electron is imposed to the system by the niobium impurity. This electron instead of occupying the local energy level within the band gap is transferred to the conduction band. This effect is observed for both crystallographic phases (see Fig. 1b). Thus our computations indicate that the extra electron remains at higher energy level. This new effect as well as details concerning charge variation of the surrounding atoms due to the niobium impurity is discussed in details in one of our previous works [6].

In the case of the La doping, the impurity replaces one of the barium atoms located in the middle of the supercell. After performed geometry optimization the calculations yield the structures shown in Fig. 2a and 2b for the cubic and tetragonal lattices, respectively.

In the cubic phase the titanium atoms move away from the impurity by a distance of 0.07 Å. The defect-neighbouring oxygens located in the upper and lower planes with respect to the impurity experience slight movements of about 0.02 Å toward the impurity. These movements are exclusively along the z axis (see Fig. 2a). The calculated relaxation energy for this phase is found to be equal to 0.94 eV.

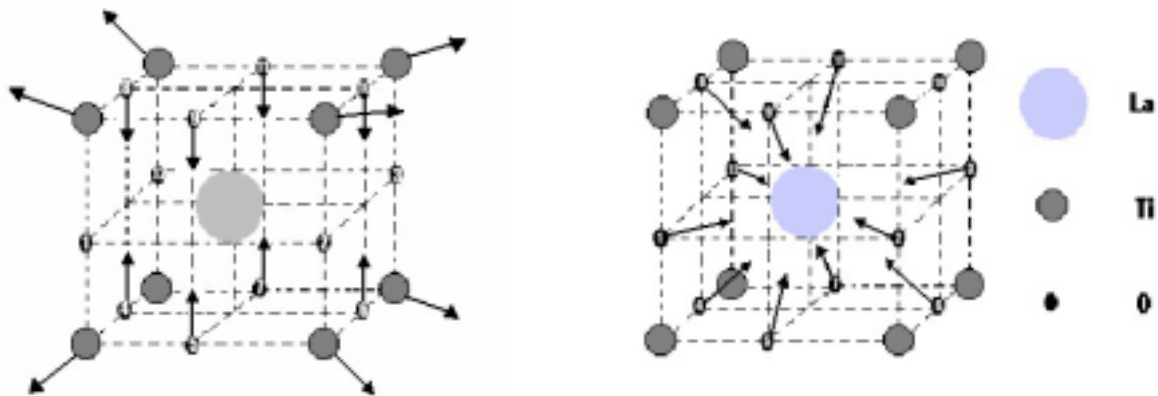


Fig 2. (a) The relaxation of the structure due to the lanthanum impurity doping in the cubic phase. The defect-neighbouring oxygens located in the upper and lower planes with respect to the impurity experience slight movements toward the impurity. These movements are exclusively along the z axis. (b) Lattice distortion due to the lanthanum impurity in the tetragonal phase. The oxygens move toward the impurity. The impurity-surrounding titaniums remain motionless.

In the tetragonal phase the optimization of the structure gives us the movements of the oxygens towards the impurity by a distance of 0.06 Å. The impurity-surrounding titaniums remain motionless in this phase as it is shown in Fig. 2b. The details concerning charge variation of the surrounding atoms due to the lanthanum impurity are described in Refs. 7.

There are remarkable differences in the final geometry between the two phases. However, the atomic displacements are symmetric and show the importance of ionic nature in the chemical bonding of the crystal. The obtained lattice distortion is anticipated due to the Coulomb law. The extra electron imposed on the system by the lanthanum atom remains within the band gap for both phases.

Conclusions

Using the advanced quantum-chemical computer code we have studied Nb- and La-doping in the BaTiO₃ crystal and effects of this doping upon structural and electronic properties of the crystal considering both cubic and tetragonal lattices. As a result we came to the following conclusions.

- There is a difference of 3.75 eV in relaxation energies between cubic and tetragonal lattices for the case of Nb-doping. This might be attributed to the different symmetry and compactness of the crystalline lattice.
- The observed extra electron transfer from the local energy level within the band gap to the conduction band might be attributed to the electrical conductivity augmentation in the niobium-doped material known experimentally [8].
- The absence of titanium movements in the tetragonal phase of the La-doped BaTiO₃ crystal can be explained by the screening effect produced by the surrounding oxygens on the impurity electrostatic charge.
- The localisation of the extra electron within the band gap in the La-doped material is in agreement with the experimental observations [9], which show no increase in the electrical conductivity under these doping conditions.

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