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The effects of Ni on structural and electronic properties of $BaTiO_3$ ceramic

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Abstract

The theoretical effects of Ni on structural and electronic properties of $BaTiO_3$ ceramic have been studied using full potential-linearized augmented plane wave (FP-LAPW) method in the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA). The result of electronic structure shows a direct band gap of 2eV at the Γ point in the Brillouin zone. The results of calculation show that the chemical character of the lower valence band is mainly O-2s in nature while the upper valence band is predominantly O-2p in nature with a small admixture of Ti and Ni. The bottom of the conduction band is mainly composed of Ti-3d states with some mixture of Ba-5s state. We find also a notable contribution of O-2p states in the lower part of the conduction band. This points out to the hybridization effect between Ti-3d and O-2p orbital while the basic contribution Ni in conduction band up is e_g. It appears also that the Ba–O bond is typically ionic while the Ti–O bond has a strong covalent character.

Keywords: D. $BaTiO_3$ and titanates; Ni

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1. Introduction

With out a doubt $BaTiO_3$ ceramic is one of the most studied ferroelectric materials. This ceramic shows piezoelectric properties and has chemical and mechanical stability in a wide range of temperature, which facilitates in bulk polycrystals and both epitaxial and polycrystalline thin film [1]. All of these properties make this material very useful in different applications such as dynamic random-access memories, piezoelectric transducer, thermistors and actuators [2,3]. In addition, it has large electro-optic coefficients and high photorefractive sensitivity, which allows this crystal to be used as an optical sensor [4]. Despite the fact that many studies have been done so far on this ferroelectric material our knowledge of its fundamental properties are not satisfactory. Most of the studies carried out up to now are experimental and a few theoretical investigations so far have been done [5–10]. This could be partially explained by difficulties in using computer modeling to reproduce the unusual physical properties of this ceramic material.

Impurities in perovskite crystals play an important role in many physical applications, particularly in what regards optical absorption, resistors, gas sensors and the change of dielectric properties under illumination, the so-called photorefractive effects [5,7,8].

The aim of this research is to study the influence of Ni-doping upon the electronic band structure properties, density of state and density of electronic state of $BaTiO_3$ in cubic phase.

2. Description of the method

For calculation of electronic structure, total density of states (DOS) and electronic density a potential-linearized augmented plane wave (FP-LAPW) method in the framework of the density function theory (DFT) with the generalized gradient approximation (GGA) has been developed.

The basic method is solving the Kohn–Sham equation and this calculation has been performed by solutions self-consistent [11–15]. For calculating the electronic

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structure a supercell consisting of 40 atoms has been used throughout the work. This model is based on the so-called large unit cell (LUC) approach, which has shown high reliability in point defect studies in a number of crystals [16,17]. The information about the computational equations of the total energy of the LUC model is given in Ref. [16]. The LUC of 40 atoms for both cubic and tetragonal phases rearrange in the $BaTiO_3$ structure due to the Ni-impurity is shown in Fig. 1.

In the FP-LAPW method, space is divided into two regions, spherical "muffin-tins" around the nuclei in which radial solutions of Schrodinger equation and their energy derivatives are used as basis functions, and an "interstitial" region (I) between the muffin tins (MT) in which the basis set consists of plane waves. Core states are treated fully relativistically and valence and semi-core states are treated semi-relativistically (i.e. ignoring spin-orbit coupling). In this method the distinction between the valence and core states is made through the value of the energy and −7Ry is taken as the boundary value.

To proceed with the solution of the Kohn–Sham equation in the WIEN2k package [18], the charge density of the atoms is calculated separately and then using the principle of the superposition the total density and thus the eigenvalues and eigenvectors are calculated self-consistently.

3. Results and discussion

In the LUC of 40 atoms for the $BaTiO_3$ structure the nickel replaces on the barium's positions in which located in the center of the LUC structure. As shown in Fig. 2, the vicinity of defect (VOD) is thus composed of 12 oxygens and eight titaniums.

Table 1 shows the number of core states for atoms in supercell are 12 orbital for Ba, five orbital for Ni, four orbital for Ti and one orbital for oxygen atoms.

The number of k-points was 400 and the value of convergence parameter is taken to be, $Rk_{max} = 7$, for which the calculations stabilizes and convergence in terms of the energy is achieved. This gives well-converged basis sets consisting of approximately 3916 plane waves. Under this conditions the values of the other parameters are: $G_{max} = 14$, $R_{MT}(Ba) = 2.2$ au, $R_{MT}(Ni) = 2.2$ au, $R_{MT}(Ti) = 1.9$ au, $R_{MT}(O) = 1.8$ au and lattice constant, $a = 15.14$ au.

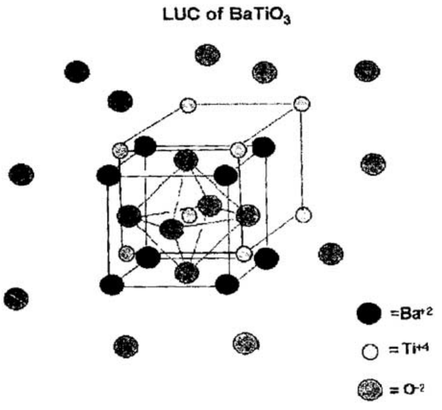

Fig. 1. The large unit cell of $BaTiO_3$.

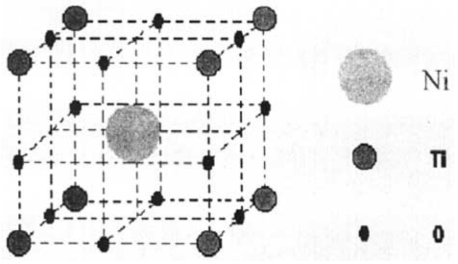

Fig. 2. Vicinity of defect composed of eight titaniums and twelve oxygens. The nickel replaces one of the bariums situated in the central of the LUC.

Table 1
Total schematic of core, semi core and valence states for LUC

Atom	Core	Semicore	Valence
O	1s	2s	2p
Ti	1s, 2s, 2p*, 2p	3s, 3p	4s, 3d
Ni	1s, 2s, 2p*, 2p, 3s	3p	3d, 4s
Ba	1s, 2s, 2p*, 2p, 3s, 3p*, 3p, 3d*, 3d, 4s, 4p*, 4p	5s	5p, 6s

In this table p* indicated that the quantum magnetic number is different as p.

To produce a new electronic densities the combination factor was chosen to be $Q = 0.4$ through the self-consistent cycle. For partial waves in atomic spheres maximum value L is 10 and in non-muffin-tin calculations, maximum value l is 4. The calculated electronic band structure of the 40 LUC is shown in Fig. 3 and it contains 310 energy bands. The zero of the energy was set at the top of the valance band. The energy scale is in eV and the origin of energy was arbitrarily set to be at the maximum valance band. Fig. 3 shows a large dispersion of the bands and the FP-LAPW method is yielded a direct band gap 2 eV at Γ point. This gap is greater than the calculated band gap 1.8eV for pure $BaTiO_3$ in cubic phase. The calculated electronic band structure of cubic phase of $BaTiO_3$ is shown in Fig. 4.

By comparing Figs. 3 and 4 it can be seen that the Ni impurity in $BaTiO_3$ increase electrical resistant and this agrees with experimental results [10]. Therefore, it is suggested that the Ni ion acts as an electronic acceptor in the $BaTiO_3$ lattice. Comparing Figs. 3 and 4 it can be seen that the conduction and valance bands have maximum distance in M point. In Fig. 4, it is clear that both valance and conduction bands are degenerate while in the LUC model they are not separate degenerates. The

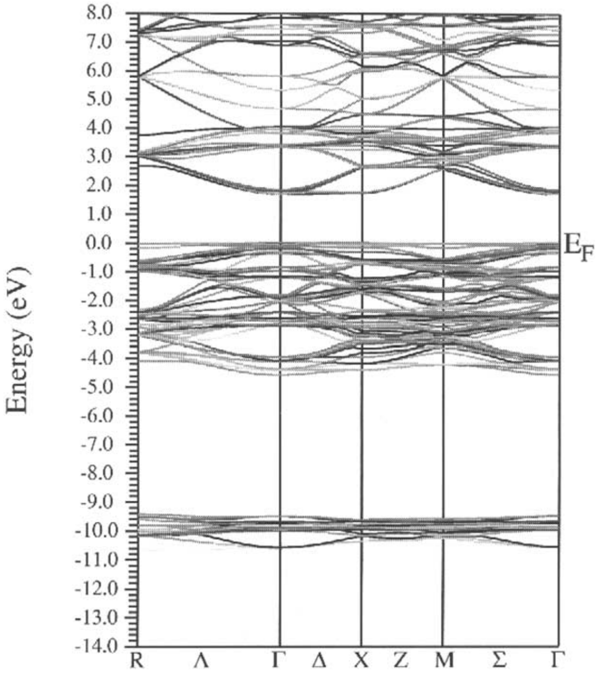

Fig. 3. The calculated electronic band structure of the LUC of 40 atoms. The zero of the energy was set at the top of the valance band.

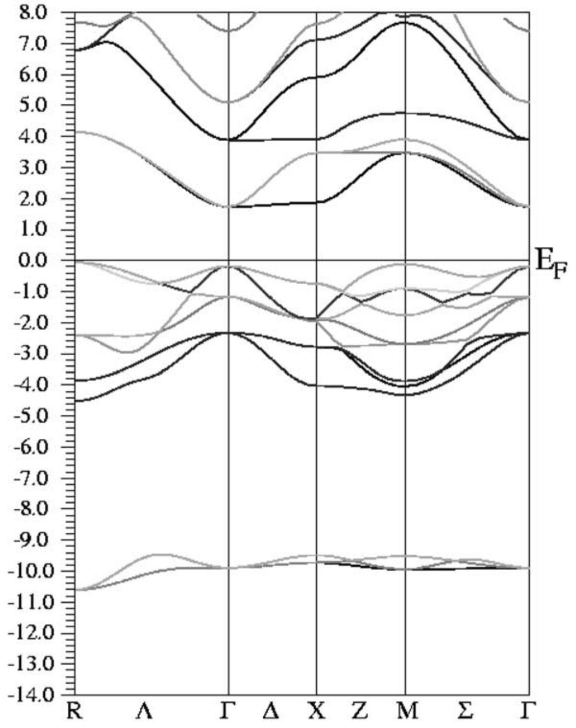

Fig. 4. The calculated electronic band structure for cubic BaTiO$_3$.The zero of the energy was set at top of the valence band.

electron distribution in an energy spectrum is described by the DOS and can be measured in photoemission experiments. The total DOS spectrum of the supercell is between −10 eV and 15 eV as shown in Fig. 5. Since there is no certain boundary between total density under and up Fermi level, so the impurity of Ni can be either on Ba or Ti sites.

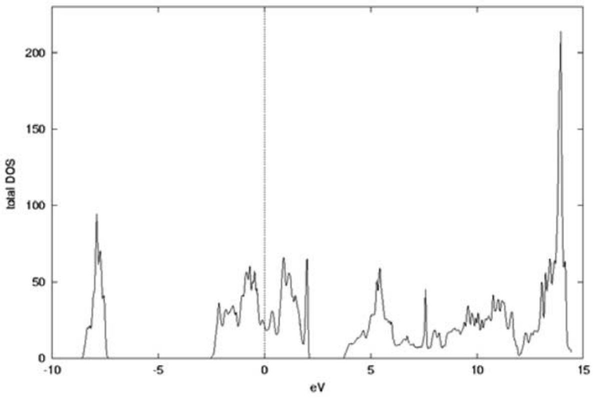

Fig. 5. The total density of states (DOS) for 40 atoms LUC.

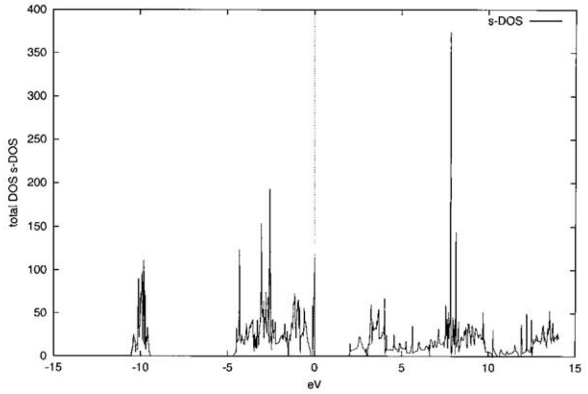

Fig. 6. The total density of state (DOS) orbital S for 40 atom LUC.

Fig. 6 shows the total DOS of S orbital of 40 atoms LUC. The valence band edges near the Fermi energy are quite sharp, while the conduction band edges near the Fermi energy are not.

The partial density of states (PDOS) of the 40 atomic LUC are shown in Fig. 7. The DOS peak at the -7.5eV [Fig. 7(a)] mainly represents the contribution of Ba-5p state in bottom valence and small contribution in top of the valence band. In Fig. 7(b), the PDOS peak at the 11.5 eV mainly represents the contribution of Ba-d state in the conduction band more than the valence band and e_g contribution is more than e_{2g} and the smallest contribution in valence band. The result of the calculation shows that the chemical character of the lower valence band is mainly O-2s while the upper valence band is predominantly O-2p in nature, with a small admixture of Ti and Ni. The bottom of the conduction band is mainly composed of Ti-3d states with some admixture of Ba-5s state. We find also a notable contribution of O-2p states in the lower part of the conduction band. This points out to the hybridization effect between Ti-3d and O-2p orbital while the basic contribution Ni

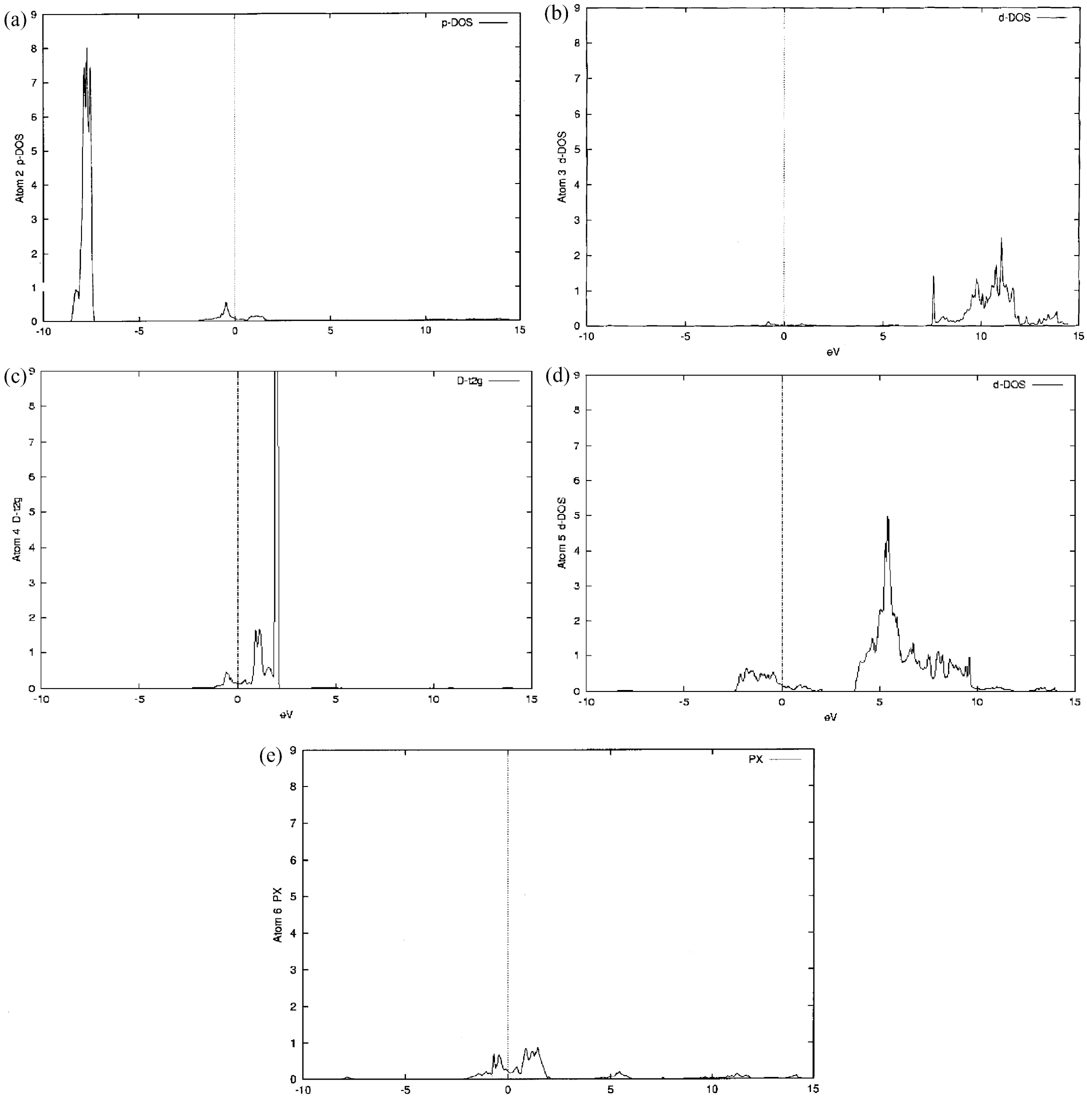

Fig. 7. The partial density of states (PDOS) for 40 atomic LUC: (a) p orbital of Ba atom, (b) d orbital of Ba atom, (c) d orbital of Ni atom, (d) d orbital of Ti atom, and (e) p orbital of O atom.

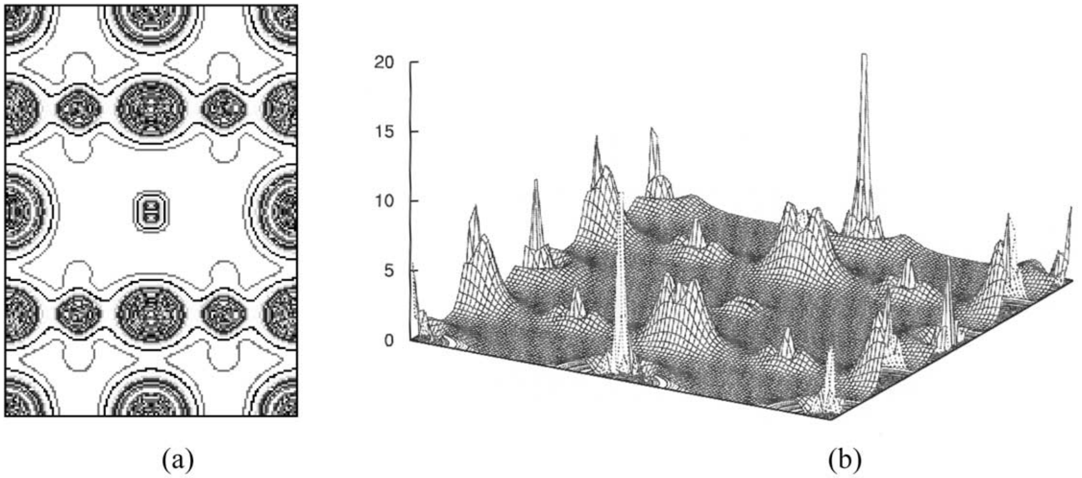

Fig. 8. Electron density distributions for 40 atomic LUC (a) in the (110) plane and (b) in three dimensions.

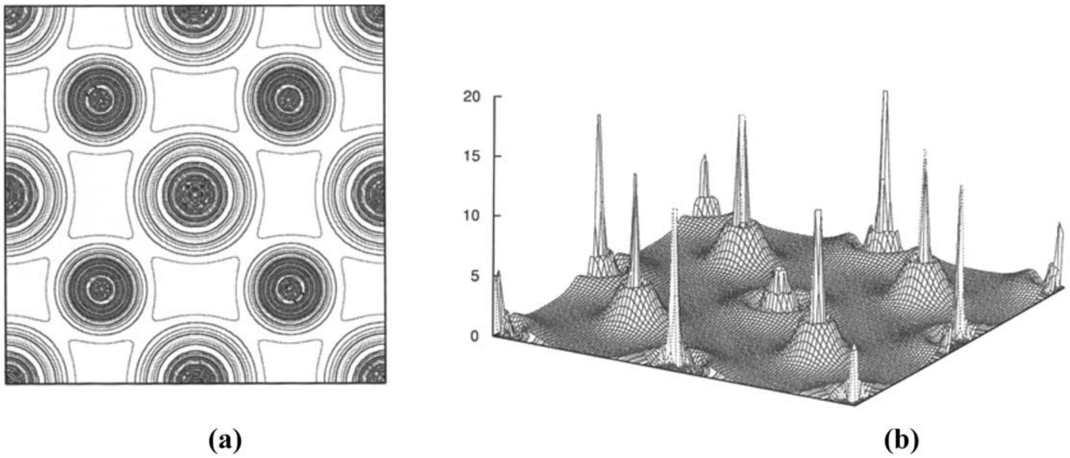

Fig. 9. Electron density distributions for 40 atomic LUC in the (100) plane and (b) in three dimensions.

in conduction band up is e_g. Figs. 8 and 9 show the electron charge density in real space for the 40 atomic LUC is shown in plan (110) and (100). From Fig. 8 it appears that the Ba–O bond is manly ionic while the Ti–O bond has a strong covalent character. In perovskite $BaTiO_3$, the Ba atoms form a backbone of lattice and the size of the Ba atoms in much larger than that of Ti and O. It is interesting to see that the size of the oxygen atoms in only slightly larger than that of the titanium.

4. Conclusions

We have made a detailed investigation of the electronic structure and DOS of BaTiO3 in the cubic phase by addition impurity Ni, using the FP-LAPW method. The calculations show that the band gap of LUC is direct at the Γ point and is equal to 2 eV. The result also shows that the total DOS and the study of charge distribution and the nature of the chemical bonding are also in agreement with the previous experimental and theoretical works.

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