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Band structure of tetragonal $BaTiO_3$

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Abstract. The electronic structure, total density of states DOS and electronic density in ferroelectric tetragonal crystal $BaTiO_3$ are studied using WIEN2k package. This employs the full potential-linearized augmented plan wave FP-LAPW method in the framework of the density functional theory DFT with the generalized gradient approximation (GGA). The results show an indirect band gap of 2.30 eV at the Γ point in the Brillouin zone. The calculated band structure and density of states of $BaTiO_3$ agree with the previous experimental and theoretical results, as do the charge distribution and the prediction of the nature of the chemical bonding.

PACS. 71.15.Mb Density functional theory, local density approximation, gradient and other corrections

1 Introduction

Barium titanate ($BaTiO_3$) is one of the most important ferroelectric oxides in electronics applications. Barium titanate is well known for its technological applications. It has been widely used in electromechanical actuators and in photo-galvanic devices [1]. As a ceramic material, it is currently used in capacitors and sensors while the optical properties of the single crystal also present a great interest for non-linear optics applications [2,3].

$BaTiO_3$ is the first advance ceramics piezoelectric, and yet, because of its chemical stability and high dielectric constant, has many other applications. The abrupt change of dielectric constant with temperature is the main difficulty for using it as a dielectric material. The ceramic phase has PTC properties which are related to grain properties of ceramics. The ceramics is optically opaque while the single crystal is transparent. This material was the best piezoelectric ceramic until PZT was discovered [2,9].

The electronic structure of $BaTiO_3$ has been the subject of many investigations [5,6,8]. Most of the studies that have been carried out into the electronic structure are experimental and only a few of them are theoretical [4,10].

In the present study, the electronic structure, density of state and electronic density of tetragonal perovskite $BaTiO_3$ in the ferroelectric phase are calculated by the FP-LAPW method with the DFT in GGA in [11,12]. The calculated results are compared with the experimental measurements, the result are in good agreement with experimental results.

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2 The calculation method

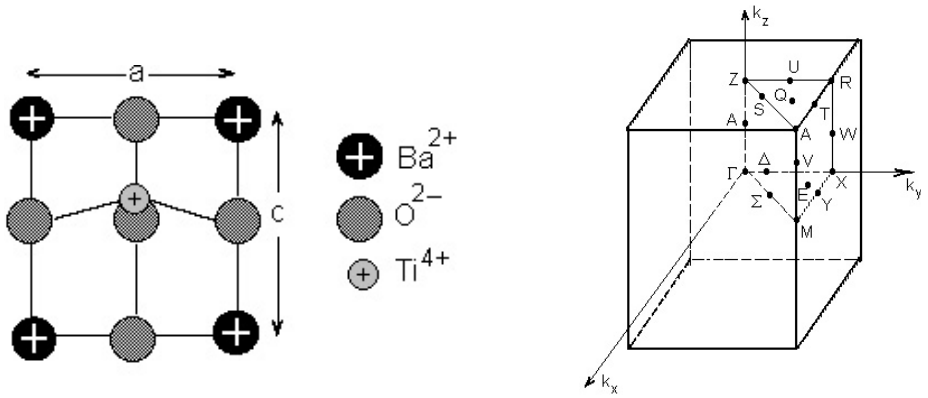
The crystal structure of $BaTiO_3$ in the ferroelectric phase has been studied experimentally using various techniques. The ferroelectric phase is tetragonal and belongs to the space group P4mm. There are five atoms in a unit cell. The experimentally measured lattice constants $a_0 = 3.9945$ Å and $c_0 = 4.0335$ Å, were used in our calculations. The atomic positions in units of a along the X and Y axis and c along the Z axis are as follows: Ba at (0,0,0), Ti at (0.5,0.5,0.514), O_1 at (0.5,0.5,−0.025), O_2 at (0.0,0.5,0.488) and (0.5,0.0,0.488) [4,6]. Figure 1a shows the unit cell and Figure 1b the Brillouin zone of $BaTiO_3$ for this structure. The shifts from the value 0.5 in the atomic coordinates indicate the lack of the inversion symmetry in the tetragonal phase and thus result in the displacement polarization and the ferroelectric behavior. In $BaTiO_3$, the Ti-O bond is stronger than the Ba-O band and as a result the motion of the Ti becomes more important in the ferroelectric transition.

The electronic structure, total density of states (DOS) and electronic density in ferroelectric tetragonal crystal $BaTiO_3$ are studied using the Wien2k package. This employs the FP-LAPW method in the framework of the DFT with the generalized gradient approximation (GGA) for solving the Kohn-Sham equation [11,12].

3 Results

3.1 Electronic structure

The crystal structure of $BaTiO_3$ in the para- and ferroelectric phase has been studied experimentally using



(a) (b)

Fig. 1. (a) The tetragonal unite cell of $BaTiO_3$. (b): Brillouin zone for a tetragonal $BaTiO_3$ structure.

various techniques [4–6,8]. This provides us with the structural parameters needed in our work and also the basis for comparison of the final results. Here in our calculations we used 400 k-points. The value for the convergence parameter taken to be, $Rk_{max} = 7$. This is a parameter in the package that its right choice determines the stability and convergence of the calculations. Under these conditions the values of the others parameters are chosen as follows $G_{max} = 14$, R_{MT}(Ba) = 2 au, R_{MT}(Ti) = 1.95, R_{MT}(O) = 1.5 and the convergence and stability in terms of energy is achieved at the energy tolerance of 0.0001 Ry. The value of the parameter Rk_{max} controls the size of the basis sets in these calculations. The value of Rk_{max} for the systems studied, was chosen to be 7. This gives well converged basis sets consisting of approximately 3092 plane waves. Integrations in reciprocal space were performed using the special points method. We used meshes which represent 400 k-points in the first BZ. This corresponds to 70 special k-points in the irreducible wedge for the tetragonal structure. The calculated electronic band structure of the tetragonal phase of $BaTiO_3$ is shown in Figure 2. The zero of the energy was set at the top of the valence band and the energy scale is in eV. The results indicate that there is some dispersion of the bands around the top of the valance band. This is in agreement with the experimental and theoretical results of the effective mass of the holes around the top of the valence band which shows strong anisotophy [4]. Figure 2 shows that the FP-LAPW method yielded an indirect band gap of 2.30 eV fairly close to experimental valence of 2.8 to 3 eV [16,17]. There are, however, some experimental complications in determining the exact band gap, including the optical absorption edge tails which extend to several tenths of an eV [10].

The electronic structure in Figure 2 was calculated using the experimental lattice constant (a and c). The electronic structures of the valence bands, the band gap, and the low-energy conduction bands determine the most important properties of the material in electronic device applications. The calculated valence bands below the Fermi energy agree well with other first-principle studies [6,10]. Figure 2 shows that the lowest energy states of the conduction bands are at the Γ point. This disagrees slightly with the *ab initio* calculations of Bagayoko *et al.* [4]. Their calculations show that the position of the conduction band minima is slightly away from the Γ point.

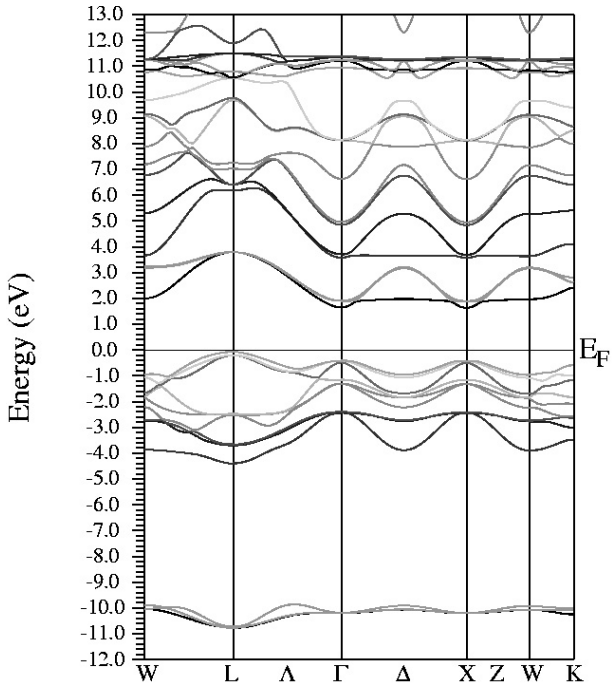


Fig. 2. The calculated electronic band structure of the Ferroelectric tetragonal $BaTiO_3$. The zero of the energy was set at the top of the valence band.

3.2 Density of states

The electron distribution in an energy spectrum is described by the density of states (DOS) and can be measured in photoemission experiments [4]. The total DOS spectrum of tetragonal $BaTiO_3$ is shown in Figure 3, the valence and conduction band edges near the Fermi energy are quite sharp. This is consistent with the experimental finding of a relatively sharp absorption edge in optical

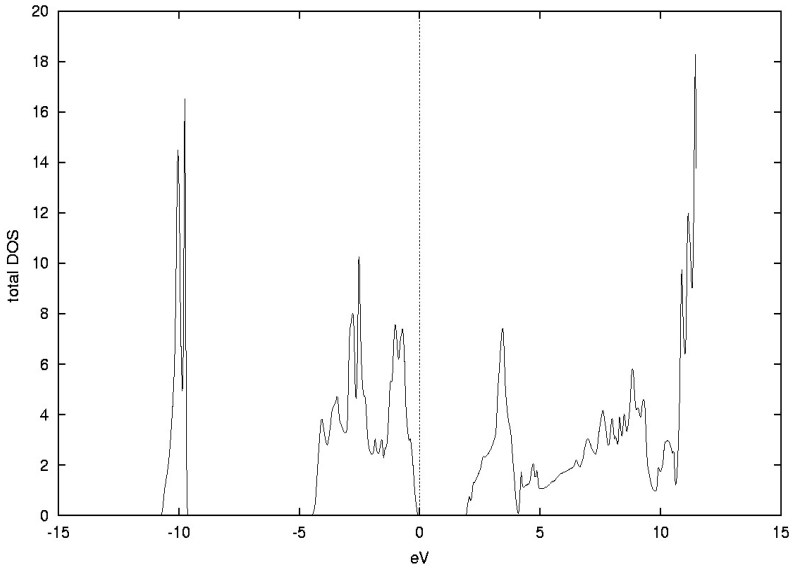
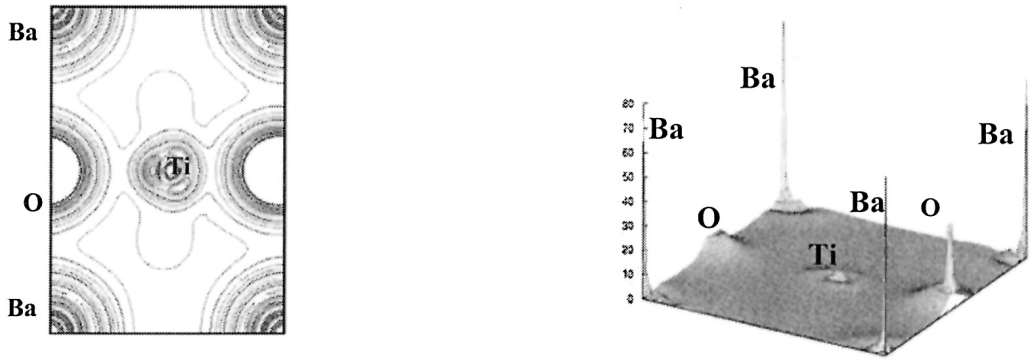


Fig. 3. The total density of states (DOS) for ferroelectric tetragonal $BaTiO_3$.



(a) (b)

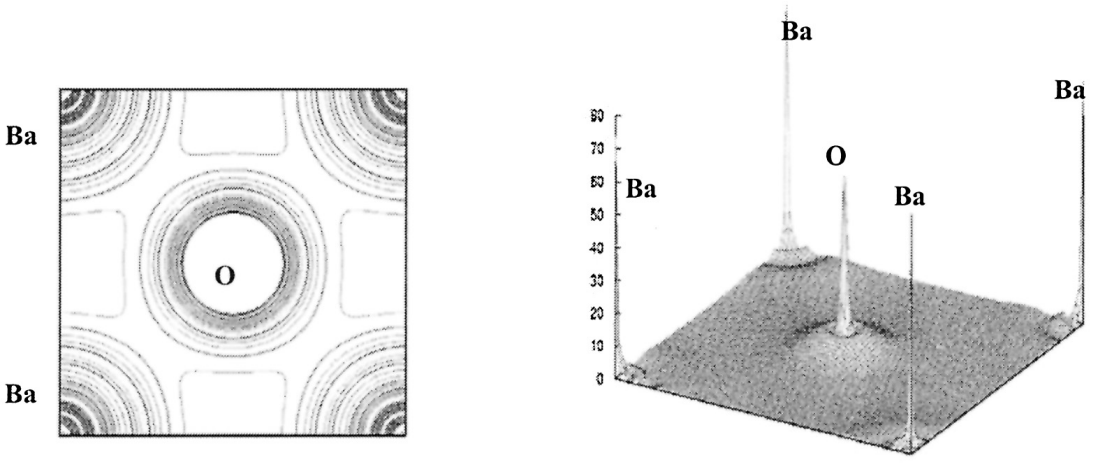
Fig. 4. The electron-density in (110) plane, (b) in three dimension.

measurements of $BaTiO_3$. Another very useful piece of information to examine is the hybridization and charge distribution.

Figure 3 shows the total density of states for the valence and conduction band. In this figure the zero of the energy scale (the top of the valence band) shows the position of the Fermi level. To obtain a measure of the contribution of different atomic states in the band structure and also their possible hybridizations we made a detailed study of the partial density of the states. The study of the partial density of states showed that the hybridization of Ti $3d$ and oxygen $2p$ and their contribution to the states on the valence and conduction band. There is, however, only a very weak hybridization of the Ba P state with the O $2p$ state in the valence band. The major contribution around the conduction band edge is from the Ti $3d$ states with a small component from the O $2p$ states. A direct consequence of the electronic structure of $BaTiO_3$ is that the photo-excitation of the electrons from the top of the valence band to bottom of the conduction band will have the effect of bringing electrons from the oxygen atoms to the titanium atoms. This will lead to a noticeable change of the effective charge of the Ti and O atoms. The modification of the effective atomic charge then changes the local dipoles and the dielectric properties.

3.3 Electronic charge density

To further study the charge distribution and also the nature of the chemical bonding, we calculated the electron charge density for the tetragonal phase of $BaTiO_3$. The effective charge density of tetragonal $BaTiO_3$ was computed using the calculated electron wave function and density The results are shown in Figure 4. Figure 4a shows the charge density in a (110) plane through Ti, Ba, and O1 atoms. In addition to the electron charge density in real



(a) (b)

Fig. 5. (a) The electron-density in (100) plane, (b) in three dimension.

space for the (100) plane that passes through Ti and Ba atoms is shown in Figure 5. From the contours of charge density in Figure 4 it appears that the Ba-O bond is typically ionic, this is because there is not much bonding charge to link the Ba and O atoms and the almost spherically symmetric charge density around these atoms.

The Ti-O bond, however has covalent character, this is quite apparent from the noticeable charge distribution at the middle of the Ti-O bond. The atomic size may be estimated from the charge distribution in Figure 4. In perovskite $BaTiO_3$, the Ba atoms form a backbone of the lattice. The size of the Ba atoms is much larger than that of Ti and O. It is interesting to see that the size of the oxygen atoms is only slightly larger than that of the titanium atoms. Of course, the determination of the atomic size is largely dependent on how one divides up the electron charge in real space. The charge distributions in Figure 4a are consistent with the reported results of reference [4]. The study of Figures 4 and 5 shows that there is the important hybridization between Ti $3d$ and O $2p$ which again emphasizes the large covalent character of their bond.

4 Conclusion

We have made a detailed investigation of the electronic structure and DOS of ferroelectric $BaTiO_3$ in the tetragonal phase using the FP-LAPW method. Our calculations show that the fundamental gap of $BaTiO_3$ is indirect and occurs between the Γ point (the bottom of conduction band) and the L point (the top of the valence band) and our band structure are qualitatively in good agreement with other theoretical results. The calculated value of the fundamental gap is 2.3 eV which shows a some improvement on the previous theoretical calculations and is fairly close to the experimentally reported values 2.8–3 eV. The origin of this discrepancy may be GGA. Our calculations of the total DOS and the study of charge distribution and the nature of the chemical bandings are also in agreement with the previous experimental and theoretical works. We employed a GGA, the FP-LAPW method and a new procedure to calculate the electronic structure, band gap and DOS of $BaTiO_3$ by Wien2k package. Calculations of the optical properties and also further investigation on the improvement of the results are in progress.

References

1. B. Jaffe, W.R. Cook, H. Jaffe, *Piezoelectric ceramic* (Academic, New York, 1971)
2. A.J. Moulson, J.M. Herbert, *Electroceramics* (Chappman and Hall, 1990)
3. R.N. Schwartz, B.A.W. Wechsler, R.A. Mcfarlane, Phys. Rev. B **46**, 3263 (1992)
4. D. Bagayoko, G.L. Zhao, J.D. Fan, J.T. Wang, J. Phys. Cond. Matt. **10**, 5645 (1998)
5. F.M. Michel-Calendini, G. Mesnard, J. Phys. C **6**, 1709 (1973)
6. R. Cohen, H. Krakauer, Ferroelectrics **136**, 65 (1992)
7. R. Cohen, H. Krakauer, Ferroelectrics **150**, 1 (1993)
8. R. Cohen, H. Krakauer, Phys. Rev. B **42**, 6416 (1990)
9. W.D. Kingery, H.K. Bowen, D.R. Uhlman, *An Introduction to ceramics* (John Willey and Sons Inc., 1975)
10. D. Bagayoko, G.L. Zhao, J.D. Fan, J.T. Wang, Proc. Louisiana, Acad. Sci. **60**, 43 (1997)
11. J.P. Perdew, J.A. Chevary, *et al.*, Phys. Rev. B **46**, 6671 (1992)
12. J.P. Perdew, Physica B **172**, 1 (1991)
13. P. Blaha, K. Schwarz, WIEN2k, Vienna university of Technology, Austria (2002)
14. S.H. Wei, H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985)
15. V.V. Nemoshkalenko, V.N. Antonov, *Computational Methods in Solid State Physics* (Gordon and Breach Science Publishers, 1998)
16. M. Cardona, Phys. Rev. A **140**, 651 (1965)
17. H.F. Cheng, J. Appl. Phys. **79**, 7965 (1996)
18. W.Y. ching, J. Am. Ceram. Soc. **73**, 3135 (1990)