Using different DFT implementations for studying structural, electronic and electrical properties of tetragonal $BaTiO_3$ and $PbTiO_3$

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Abstract

Structural, electronic, and electrical properties of tetragonal barium titanate ($BaTiO_3$) and lead titanate ($PbTiO_3$) single crystals have been investigated using first principle calculations. We use density functional theory (DFT) as implemented in Quantum Espresso. In our calculations, we consider several DFT implementations (plane waves vs localized basis sets, all electron vs pseudo potential calculations, etc.) in order to figure out which one gives the best results for structural, electronic and electrical properties of these two ferroelectric oxide materials. The results we obtained, for both materials at room temperature, of equilibrium lattice constants, equilibrium unit cell volume, electronic band structure, density of states (DOS), gap energy and dielectric constants are in good agreement with previous experimental and theoretical findings. Furthermore, the spontaneous polarizations of both materials are calculated using the modern theory of polarization. Our calculated values of these polarizations agree well with the corresponding measured values.

Keywords

Barium titanate, Lead titanate, Density functional theory, Tetragonal phase, Lattice parameters, Electronic band structure, Density of states, Gap energy, Spontaneous polarization, Exchange-correlation.

Introduction

Ferroelectricity is a characteristic of certain materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. Barium titanate and lead titanate are perovskite type materials, which are known for their various properties : high dielectric constant, ferroelectric behavior below the Curie point, spontaneous polarization and non-linear optical coefficients.

The origin of ferroelectricity in $BaTiO_3$ and $PbTiO_3$ derives from the displacement of ions relative to each other [1]. $BaTiO_3$ and $PbTiO_3$ are two of the interesting and more studied perovskites possessing a ferroelectric phase at room temperature. Structural, electronic and electrical computations, for these two materials, are performed by using density functional theory as implemented in Quantum Espresso.

Methods and Procedures

1- Fundamentals of DFT theory:

- **Schrödinger equation:** $H\Psi(r_i, R_I) = E\Psi(r_i, R_I)$
- **Hamiltonian:** $H = T_n + T_e + V_{en} + W_{ee} + V_{nn}$
- **Born-Oppenheimer Approximation:** $H = T_e + V_{en} + W_{ee} + V_{nn}$
- **Energy of an electronic system:** $E(\rho(\vec{r})) = F_{HF} + \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r}$
- **Energy of the system:** $E_0 = \min(E(\rho(\vec{r})))$
- **Kohn-Sham equations:** $\left(-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right)\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r})$
- **Exchange-correlation functional:**

$$E_{xc}^{LDA} = \int \rho(\vec{r})\varepsilon_{xc}\rho(\vec{r})d\vec{r} \quad \text{and} \quad E_{xc}^{GGA} = \int f(\rho(\vec{r}), \nabla\rho(\vec{r}))d\vec{r}$$

2- Quantum Espresso commands: vc-relax, scf, nscf, bands, dos.

3- XCrysDen for viewing the output results like optimized structure, band structure, and density of states.

4- Calculation of the polarization.

Conclusions

In the present work, we studied how the choice of exchange-correlation functional influences both the structural and electrical properties of tetragonal $BaTiO_3$ and $PbTiO_3$. In our calculations, we consider functionals for describing the exchange-correlation energy . As expected, small under- or over-estimations of lattice parameters and spontaneous polarizations were observed for BLYP, PBE and LDA approximations. The results are presented for optimized lattice parameters, density of states, gap energy, and spontaneous polarization. Our calculated values for various magnitudes show a good agreement with experimental data.

References

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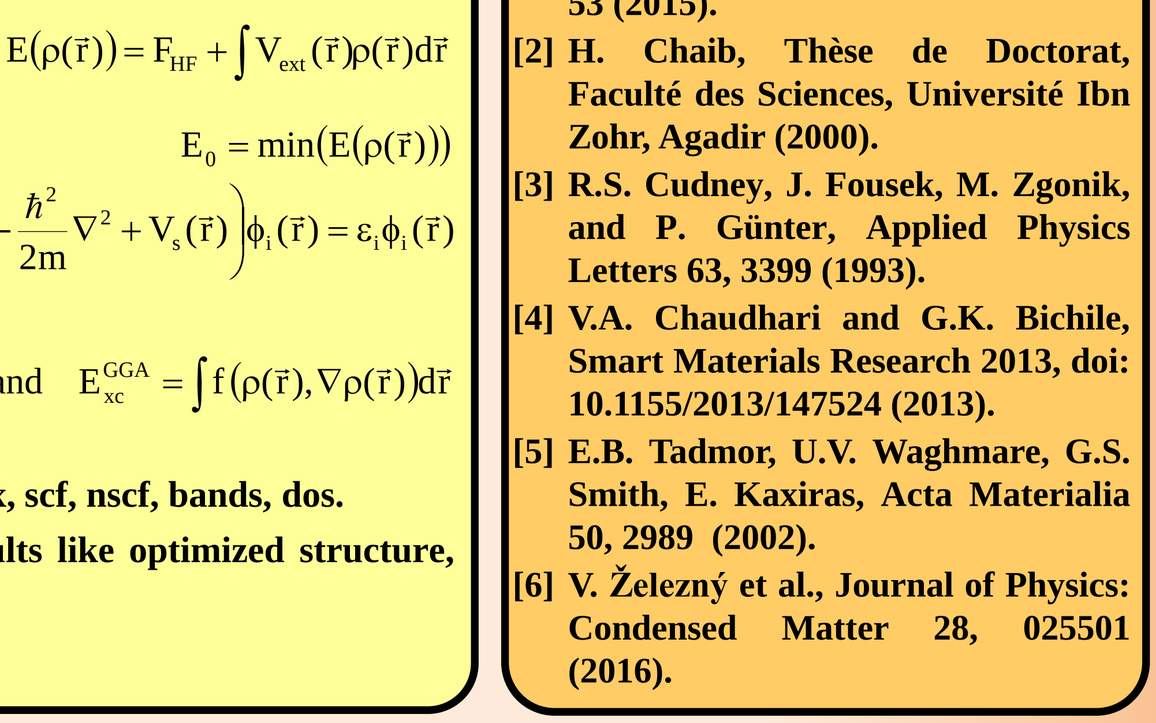
Data and Results

The calculations are performed, for barium titanate and lead titanate in their tetragonal phase, by using Quantum Espresso. In these calculations several exchange-correlation functionals are considered. The results of the optimized lattice parameters and spontaneous polarization are reported in the table below. The figures in the right represent the energy of both materials as function of their lattice parameter a as well as the DOS as function of the energy. The calculated values of the gap energy, for $BaTiO_3$ and $PbTiO_3$ respectively, are 4.8 and 7.3, while their measured ones are 3.7 [1] and 3.88 [6].

$BaTiO_3$	BLYP	PBE	LDA	Measurement
a(A°)	4.086	4.029	4.026	3.992 [2]
c(A°)	4.099	4.162	4.042	4.035 [2]
P(C/m^2)	0.278	0.279	0.278	0.278 [3]
$PbTiO_3$	PBESOL	PBE	LDA	Measurement
a(A°)	3.894	3.939	3.856	3.996 [4]
c(A°)	4.058	4.097	4.010	4.152 [4]
P(C/m^2)	0.803	0.803	0.802	0.730 [5]