The Electronic and Ferroelectric Properties in Strontium and Zirconium Doped BaTiO$_3$ from First-Principles Calculations

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Abstract—The structure, electronic and ferroelectric properties of BSZT were investigated based on first-principles calculations. The result of relaxation structure and two-dimensional charge density indicates that the tetragonal crystalline structure is distorted after Sr and Zr doping. The double-well curve fits well with the phenomenological Landau-Devonshire theory. Moreover, the smaller Zr ion displacement leads to a lower spontaneous polarization of BSZT than the original BaTiO$_3$. The hybridization between the 3d states of Ti and the 2p states of O, and the hybridization between the 4d states of Zr and the 2p states of O are observed in the density of states, which is the reason for the ferroelectricity of BSZT materials.

1. Introduction

Barium titanate with general ABO$_3$ formula have been described as a promising material category in recent decades. Barium titanate materials have excellent properties such as piezoelectricity, ferroelectricity, high dielectric constant and thermoelectricity[1–3]. Pure BaTiO$_3$ shows a smaller piezoelectric response, the largest leakage current, a lower Curie temperature ($T_c$), and a smaller breakdown strength. In order to develop the dielectric, ferroelectric and piezoelectric properties of BaTiO$_3$ ceramics, efforts have been made in various directions, including substitution of heterovalent ions by solid solution formation and field engineering, but with limited success [4,5]. The current analysis strategy is realized by simulating a new system and replacing Ba$^{2+}$ or Ti$^{4+}$ with alternative ions with comparable ion sizes. For example, the Nb shows a significant effect on the dielectric properties of BaTiO$_3$ [6]. Benlahrache et al. [7,8] found that the microstructure of barium titanate changed significantly and the dielectric constant increased by adding NaNbO$_3$. With the increase of Sr content, the Curie temperature of (Ba,Sr) TiO$_3$ (BST) ceramics decreases linearly [9]. Ciomaga et al. found that Zr with different substitution concentrations has a strong impact on the properties of BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) ceramics. [10]. Alshoaibi et al. discussed the influence of Y atom doping Ba and Ti of BaTiO$_3$ on the electronic structure and optical properties of the system. The results show that Y doping can significantly improve the dielectric properties of BaTiO$_3$ [11]. However, as far as we know, there is no theoretical study on the ferroelectric properties of BSZT materials.

In this work, we have studied the properties of BSZT ferroelectric materials using first principles calculations. The substitution effect of Ba and Ti by strontium and zirconium into BaTiO$_3$ on the structure, electronic and ferroelectric properties were discussed.

2. Computation details

We performed the first-principles calculations based on the density functional theory (DFT) with
generalized gradient approximation (GGA), as implemented Vienna Ab-initio Simulation Package (VASP) [12,13]. Select a $2 \times 2 \times 2$ super cell, which contains 40 atoms, belongs to the P4$_{mm}$ space group, and the initial lattice constant $a = b = 3.9905$, $c = 4.023$. Cut-off energy was set to 600 eV. The pseudopotentials were constructed according to the electronic configuration of Ba 5s$^2$5p$^6$6s$^2$ states, Sr 4s$^2$4p$^6$ states, Ti 3s$^2$3p$^6$3d$^2$4s$^2$ states, Zr 4s$^2$4p$^6$4d$^2$5s$^2$ states and O 2s$^2$2p$^4$ states. Monkhorst-Pack k-point $5 \times 5 \times 5$ was used for geometry optimization and electronic structure calculations. Using GGA + U methods, the Hubbard energy exchange correlation potentials of the 3d orbitals of Ti atoms and the 4d orbitals of Zr atoms were corrected by $U = 10$ eV and $U = 6$ eV, respectively. The convergence standard of the interaction force between atoms is 0.01 eV/Å, and the convergence standard of the system energy is $1 \times 10^{-8}$ eV/Å. The spontaneous polarization calculation adopts the standard Berry-phase method.

3. Results and discussion

3.1. Electron charge density

Figure 1 shows the crystal structures of the ferroelectric and paraelectric phases of BSZT after relaxation and the two-dimensional charge density. One-eighth of Ba$^{2+}$ and Ti$^{4+}$ were replaced by Sr$^{2+}$ and Zr$^{4+}$. The positive relaxation of Ti and Zr along the c axis in the ferroelectric phase deviates from the octahedral center compared to the paraelectric phase. From fig.1(c), it can be found that the electronic charge density of Ti ion overlaps with upper oxygen ions (O3) and the right oxygen ions (O1) in the same plane to form a covalent bond. The absence of hybridization of Ti1 and O4 exhibits ionic bonding. Zr and the surrounding O ions have similar chemical bond characteristics.

![Optimized structure of (a) ferroelectric and (b) paraelectric BSZT. Two-dimensional charge density of (c) ferroelectric and (d) paraelectric BSZT.](image)

3.2. Double-well potential

In order to further explore the influence of Ti and Zr ion shifts on the ferroelectric properties of BSZT, we used the modern polarization theory to calculate the spontaneous polarization of BSZT. The spontaneous polarization of ferroelectrics is defined as the polarization change when the paraelectric phase transforms into the ferroelectric phase.

Figure 2 shows the variation of energy difference with polarization function of BSZT. The phenomenological Landau-Ginsburg-Devonshire theory is used to fit the energy polarization curve as follows,

$$\Delta G = \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^2 + \frac{1}{6} \gamma P^6$$
Where $\alpha$, $\beta$ and $\gamma$ are coefficient constants, and $P$ is the polarization of each unit cell.

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\text{Fig. 2. Double-well potential of BSZT versus polarization}
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For BSZT, the potential curve fitted well with the LGD model. In Fig.2, the symmetry point of the minimum on both sides represents two stable polarization states of equal magnitude and opposite directions. Paraelectric corresponds to $P=0$ in the figure, which has no Ti displacement as shown in Fig. 1(b, d). We calculated the polarization value of BSZT is 18.07 $\mu\text{C/cm}^2$, which is a decrease compared to undoped BaTiO$_3$. The reduction of spontaneous polarization indicates that the ferroelectric performance of BSZT is weaker than that of undoped BaTiO$_3$.

### 3.3. Band structure and density of states

Fig.3(a, b) illustrates the band structure of BSZT, which is calculated in the Brillouin region with and without Hubbard energy adjustment in the direction of high symmetry. The calculated BSZT band gap without Hubbard correction is 1.92 eV, which is much lower than the original BaTiO$_3$ bandgap value which is attributed to the limitations of GGA functional. Taking into account the Hubbard potential adjustment, the band gap is increased to 3.14 eV, but it is still slightly smaller than the 3.2 eV band gap of pristine BaTiO$_3$.

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\text{Fig. 3. Calculated band structure of BSZT (a) without and (b) considering Hubbard adjustment.}
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Fig. 4 shows the density of states (DOS) and partial density of states (PDOS) of BSZT ferroelectrics without and with Hubbard adjustment. In the fig. 4(a), the energy band of $\sim$34 eV is composed of 3p state of Ti atom. The energy band at $\sim$26 eV is composed of 6s state of Ba atom. The energy band from $\sim$17 eV to $\sim$15 eV is mainly composed of the 2s state of O atom. From $\sim$11 eV to $\sim$10 eV, it is mainly composed of 5p state of Ba atom. In the Fig.4 (c, d), the 3d state of Ti atom at the conduction band is improved by Hubbard potential correction. The valence band of $\sim$5 to 0 eV is mainly composed of 2p
states of O atom and 3p and 3d states of Ti atom. The conduction band of 2 eV to 8 eV mainly comes from the 3d state of Ti atom and the 2p state of O atom. It is proved that the strong hybridization between 3d orbital of Ti and 2p orbital of O, Zr 4p and O 2p states is the source of ferroelectricity of BSZT material.

![Calculated density of states of BSZT](image)

4. Conclusion

According to first-principles calculations, we have investigated the structural, electronic and ferroelectric properties of the (BaSr)(ZrTi) material. The double-well curves fit well with the LGD model. The squeezing of Sr ions on the oxygen octahedra and the smaller displacement of Zr ions lead to the reduced spontaneous polarization, revealing the weaker ferroelectricity of BSZT compared to pristine BaTiO3. After adding Hubbard energy adjustment, the band gap of BSZT is 3.14 eV, slightly lower than 3.2 eV of original BaTiO3. The result of density of states demonstrates that the ferroelectricity of BSZT material originates from the hybridization between the 3d states of Ti and the 2p states of O, and the hybridization between the 4d states of Zr and the 2p states of O.

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