Cell Volume Effect on the Ferroelectric Stability of Perovskite Oxides PbTiO$_3$ and BaTiO$_3$ from First Principle Calculation

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Electronic structure of ferroelectric PbTiO$_3$ and BaTiO$_3$ is calculated by the full potential linearized augmented plane wave method. The total energy as a function of the displacement of Ti-cation is obtained for PbTiO$_3$ and BaTiO$_3$ at different cell volumes. At experimental cell volume Ti-displacement lowers the total energy and the ferroelectricity is stable. When the cell volume is reduced to 90%   total energy is increased with Ti-displacement and ferroelectricity will disappear. The cell volume effect is also confirmed by comparison of the density of states of Ti and O at different cell volumes.

Keywords   density functional theory ferroelectrics phase transition

Introduction

To understand the difference between the behavior of different ABO$_3$ oxides such as BaTiO$_3$ and SrTiO$_3$ Weyrich proposed a cell volume effect.[1] It was then used in explanation of the properties of strontium barium titanate solid solution.[2] For a given ABO$_3$ ferroelectric it was known that the properties changed with pressure in particular the phase transition temperature decreased when the pressure was increased.[3] It is then expected that at a high enough pressure ferroelectricity will disappear even at the lowest temperatures. A qualitative explanation to this effect was given from the soft model [3] but first principles calculation still seems not available.

In order to get an insight into the microscopic mechanism of the cell volume effect of BaTiO$_3$ and PbTiO$_3$ we focus on their total energy and electronic structure simulated by the accurate full potential linearized augmented plane wave FLAPW method. The total energy is calculated as a function of the displacement of Ti-cation and the density of states DOS of Ti and O at different cell volumes. It is shown that the ferroelectricity of BaTiO$_3$ and PbTiO$_3$ will disappear if the cell volume is reduced to 90%. The reason is that at reduced cell volume displacement of Ti-cation will increase the total energy and weaken the hybridization between Ti d and O p.

Calculation

The calculations presented in this work are performed within the generalized gradient approximation GGA [4] to density functional theory using the FLAPW method. In this method no shape approximation on either potential or the electronic charge density is made. We use WIEN97[5] implementation of the method which allows the inclusion of local orbits in the basis improving upon linearization and making a possible consistent treatment of semicore and valence states in one energy window hence ensuring proper orthogonality. In the FPLAPW method the unit cell is divided into two parts   I non-overlapping atomic spheres centered at the atomic sites and II an interstitial region. The FPLAPW method expands the potential in the following form

$$V r = \sum_{lm} V_{lm} r Y_{lm} \hat{r} \qquad \text{inside sphere} \qquad 1$$

$$V r = \sum_{K} V_K e^{iKr} \qquad \text{outside sphere} \qquad 2$$

where $Y_{lm} \hat{r}$ is a linear combination of radial functions times spherical harmonics.

In the cubic phase of BaTiO$_3$ and PbTiO$_3$ the lattice parameter we used is $a = 0.40$ nm. The atomic coordinates are Ba or Pb   0 0 0   Ti 0.5 0.5 0.5   O 1   0 0.5 0.5   0 0.5 0.5   O 2   0.5 0.5 0 . The atomic sphere radii R_i 2.0 1.8 and 1.5 are used for Ba or Pb   Ti O respectively in the calculations. Pb Ba 5d 6s 6p Ti 3s 3p 3d 4s and O 2s and 2p orbitals are treated as valence orbitals. There is no pseudopential approximation core states of atoms were calculated self-consistently in the crystal potential and are treated fully relativistically. The convergence parameter $Rk_{max} R_{mt} * K_{max}$ where K_{max} is the plane wave cutoff and R_{mt} is the smallest one of all atomic sphere radii which controls the size of the basis sets in these calculations is set to be 8.0. This gives well-converged basis

sets consisting of approximately 4719 plane waves.

The calculations are iterated to self-consistency with the specified energy convergence criterion 0.00001 Ryd. Integrations in reciprocal space are performed using special points method. We used $5 \times 5 \times 5$ meshes which represent 125 k-points in the first Brillouin zone. This makes our calculation with a good precision.

Results and discussion

The paraelectric-ferroelectric phase transition in both BaTiO$_3$ and PbTiO$_3$ is from cubic $m3m$ point group to tetragonal $4mm$ point group, whereby the Ti-atom deviates from the oxygen octahedra center and results in a static displacement along ⟨001⟩ direction. In order to understand the cell volume effect on the ferroelectric instability of BaTiO$_3$ and PbTiO$_3$, we calculated the electronic properties of BaTiO$_3$ and PbTiO$_3$ for different displacement of the Ti atom in the ⟨001⟩ direction. Fig. 1 shows the total energy as a function of the Ti atom displacement for different cell volumes of BaTiO$_3$. At the experimental equilibrium volume V_0 ($a = 0.402$ nm), the total energy profile has a double well. For a 10% volume reduction (about $a = 0.381$ nm), the tendency to ferroelectricity no longer exists. Thus the ferroelectric state of BaTiO$_3$ will disappear at a high pressure. Fig. 2 shows that of PbTiO$_3$. Compared with Fig. 1, PbTiO$_3$ has a similar behavior to BaTiO$_3$. While, the energy difference $E_{\Delta z=0} - E_{\min}$ of PbTiO$_3$ is larger than that of BaTiO$_3$, thus the ferroelectricity of PbTiO$_3$ is stronger than that of BaTiO$_3$.
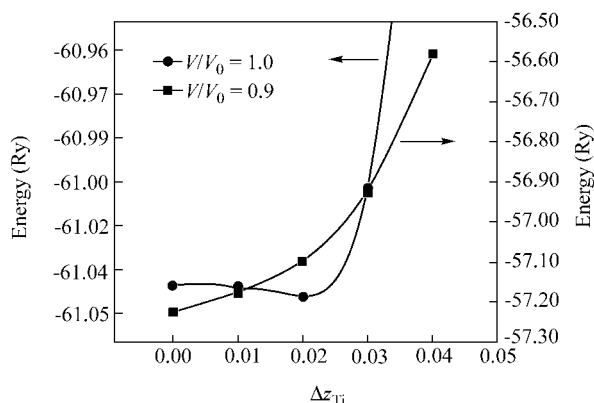

Fig. 1 Total energy (E/Ry $+ 18438$) $\times 100$ of cubic BaTiO$_3$ as a function of the displacement Δz of the Ti atom in the ⟨001⟩ direction for different volume.

From the total energy analysis, it can be seen that the cell volume of PbTiO$_3$ and BaTiO$_3$ is very important to their ferroelectricity. The lattice constants of PbTiO$_3$ and BaTiO$_3$ for a 10% volume reduction (at which the ferroelectric transition no longer exists) are respectively 0.387 and 0.386 nm. For having a ferroelectric transition, the lattice constants of PbTiO$_3$ and BaTiO$_3$ are respectively 0.399 and 0.400 nm.
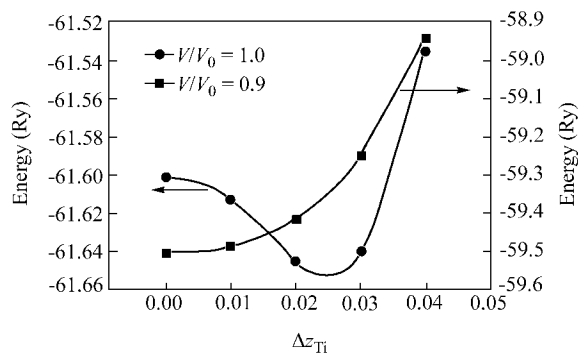

Fig. 2 Total energy (E/Ry $+ 44015$) $\times 100$ of cubic PbTiO$_3$ as a function of the displacement Δz of the Ti atom in the ⟨001⟩ direction for different volume.

Fig. 3 shows the DOS of Ti d and that of O 2 p of PbTiO$_3$ at $\Delta z = 0.02$ for $V/V_0 = 1.0$. Fig. 4 shows the DOS of Ti d and that of O 2 p of the same crystal at $\Delta z = 0.02$ for $V/V_0 = 0.9$. Comparing Fig. 3 with Fig. 4, it can be seen that the DOS of Ti d and O 2 p at different volumes are similar, but the DOS of Ti d and O 2
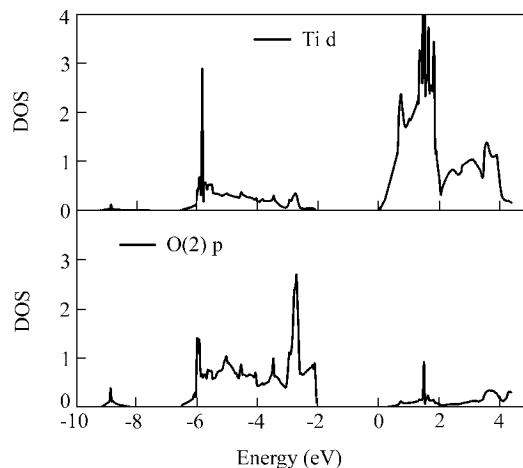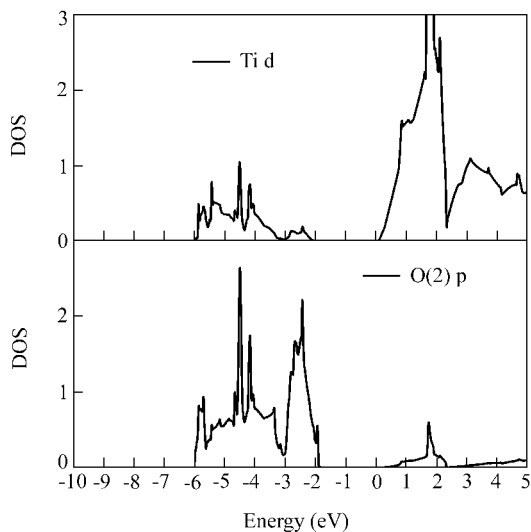

Fig. 3 Density of states of Ti d and O 2 p in PbTiO$_3$ at $\Delta z = 0.02$ Ti for $V/V_0 = 1.0$.
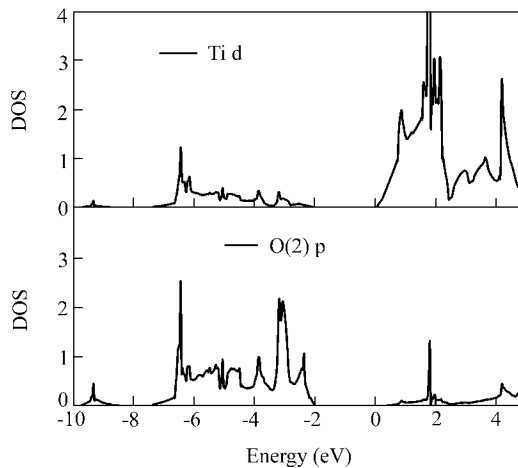
Fig. 4 Density of states of Ti d and O 2 p in PbTiO$_3$ at $\Delta z = 0.02$ Ti for $V/V_0 = 0.9$.

p for $V/V_0 = 1.0$ are much higher than that for $V/V_0 = 0.9$. It can be seen that for $V/V_0 = 0.9$ Ti d and O 2 p do hybridize to some extent but the hybridization is weaker comparing with that for $V/V_0 = 1.0$. Since hybridization between Ti 3d and O 2p is essential for ferroelectricity in $BaTiO_3$ and $PbTiO_3$ the weakening of hybridization implies that the ferroelectricity will decrease and eventually disappear at reduced cell volume. It is consistent with the conclusion from the analysis of total energy.

Fig. 5 shows the DOS of Ti d and that of O 2 p of $BaTiO_3$ at $\Delta z = 0.02$ for $V/V_0 = 1.0$. Fig. 6 shows the DOS of Ti d and that of O 2 p of the same crystal at $\Delta z = 0.02$ for $V/V_0 = 0.9$. From Figs. 5 and 6 it can be seen that the DOS in $BaTiO_3$ are similar to those in $PbTiO_3$ and the hybridization is weakened for reduced cell volume. In other words ferroelectricity will be weaker when the cell is shrunken consistent with the variation tendency of the total energy.

Fig. 5 Density of states of Ti d and O 2 p in $BaTiO_3$ at $\Delta z = 0.02$ Ti for $V/V_0 = 1.0$.

In ferroelectrics there are two kinds of force the short range repulsive force and the long range Coulomb force. The long range Coulomb force is favor to stable ferroelectricity while the short range repulsive force suppresses ferroelectricity. As well known in $ATiO_3$ perovskite ferroelectrics the hybridization between O 2p and Ti 3d is essential condition for stability of ferroelectricity. This hybridization makes the energy of ferroelectric system lower. It is this hybridization that suppresses the short range repul-

sive force and makes ferroelectricity could exist. As result from our calculation the reduction of cell volume in $BaTiO_3$ and $PbTiO_3$ makes atom Ti have smaller active range and makes the short range repulsive force always larger than the long Coulomb force. Thus the ferroelectricity can not be stable and no longer exist.
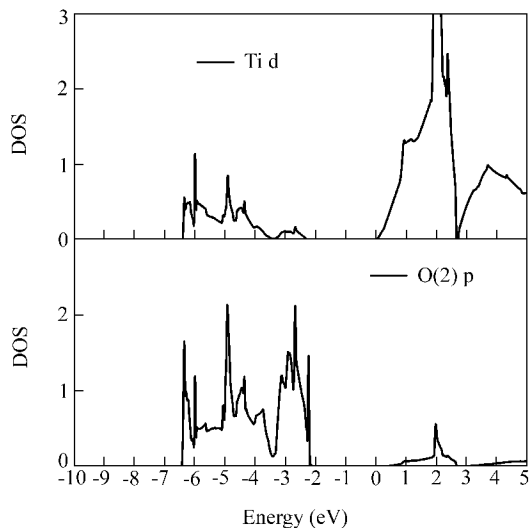
Fig. 6 Density of states of Ti d and O 2 p in $BaTiO_3$ at $\Delta z = 0.02$ Ti for $V/V_0 = 0.9$.

In conclusion both in $BaTiO_3$ and $PbTiO_3$ when the cell volume is reduced the Ti-displacement will result in an increase rather than a decrease of the total energy and the hybridization of Ti d and O p will be weakened. These factors are responsible for the weakening and disappearance of ferroelectricity induced by the cell volume reduction.

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