

First-principle modelling of the ferroelectric switching in BaTiO₃: concurrent switching versus domain wall motion

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Abstract

The ferroelectric switching phenomenon has been investigated on a BaTiO₃ supercell in the tetragonal state using a first-principles density functional theory. The study shows that a consecutive reversal of polarization via switching of adjacent elementary unit cells is energetically more favourable than the single domain switching. The results thus explain the energetic rationality for the domain wall formation in an ideal structure without the presence of any microscopic non-uniformity. The analysis of individual domain wall energy densities suggests that it is not a constant quantity. The coercive field values for switching different domains have been computed, which identifies the nucleation and propagation phases of domain wall motion.

Keywords: density functional theory, linearized augmented plane wave, Berry phase, polarization, ferroelectricity

(Some figures may appear in colour only in the online journal)

1. Introduction

The ferroelectric effect plays a major role in applications such as ferroelectric non-volatile memories [1], positioning systems, medical imaging and therapeutic ultrasound transducers [2]. The performance of those systems is governed by the switching of polarization

due to an external electric field. The switching occurs via nucleation of domains with inverse polarization followed by their growth. The latter is referred to as domain wall motion. The presence of a domain wall significantly influences the response of the ferroelectric materials to the external electric field [3–5]. Haun [6] showed that more than half of the dielectric and piezoelectric response in PZT is contributed by domain wall motion. One of such major ferroelectric effects is the hysteresis energy loss, which is one of the sources of excess heat generated in ferroelectric materials during operation [7, 8].

Domain walls in ferroelectric materials have been studied theoretically mostly using semi-empirical molecular dynamics [9–14]. These models successfully captured both the nucleation of domains and their successive growth in response to the applied electric field. With their molecular dynamic simulations, Shin *et al* [12] proposed a model for nucleation and motion of domain wall. Their study suggested that under the influence of an applied electric field, the ferroelectric switching process occurs by nucleation of a two-dimensional region with inverse polarization followed by its relative propagation in the uniform bulk materials. The model, however, relies on inputs from first-principle studies [15, 16] such as the interatomic potential, domain wall formation energy, spontaneous polarization, and its profile across the wall.

Ab initio study of ferroelectric switching is limited to Landau–Devonshire (LD) [17–19] parametrization that relates computed energy and polarization parameters of ferroelectric and paraelectric state assuming a soft mode phase transition [20–22]. However, the presence of the periodic boundary condition in density functional theory (DFT) implies that such explanation of polarization inversion is a concurrent switching of the body-centred atom between two equivalent positions throughout the entire bulk materials (i.e., single domain switching). Such a phenomena therefore clearly ignores the existence of domain walls with formation and propagation of regions with opposite polarization. Investigations of ferroelectric domain walls within the first-principle study are also mostly limited to calculation of their formation energy [15, 23]. Meyer and Vanderbilt [16], Beckman *et al* [21] further advanced the first-principle modelling of propagation of domain walls and determined the energy barrier associated with the motion of 180° and 90° walls in PbTiO₃. Results of their study are applicable to the growth of established domains, whereas the initiation (nucleation) phase remains overlooked in the model. These gaps motivated us to perform an *ab initio* study of polarization reversal that considers both domain wall nucleation and propagation stages.

Ferroelectric domain walls are considered to be Ising type where the polarization switches, traversing through a zero polarization along a high-symmetry path [24]. This Ising-type switching is considered favourable in ferroelectric materials because of their strong electrostrictive nature. Polarization reversal through any path other than the high-symmetry path would require a very high amount of elastic energy [24] due to a large lattice strain. Nevertheless, several recent studies [16, 25–27] provided the evidence of the Bloch-like and Néel-like rotation of polarization through a curved path.

Here, we perform a theoretical study of Ising-type polarization reversal via 180° domain wall motion in BaTiO₃, which is one of the most well-characterized perovskite compounds. The present study is focused on the material in the tetragonal state, which is the stable structure at room temperature. It should be noted that below room temperature, BaTiO₃ can undergo two more phase transitions: (i) tetragonal to orthorhombic at 5°C and (ii) orthorhombic to rhombohedral below –90°C [28]. The tetragonality of the structure is held constant throughout the calculations, which represents an isolated domain wall located at distant sites from the surface and interfaces [21]. The obtained energy profile suggests that the ferroelectric switching occurs as a result of sequential reversal of polarization in adjacent cells, which is the essence of domain wall formation and motion. The results are applied to the calculation of the coercive fields for initiation and propagation of domain walls in BaTiO₃.

Table 1. Structural parameters for BaTiO₃ in the tetragonal phase obtained theoretically and experimentally.

Structural parameters	Present calculations	Experimental structure [34]	Other DFT calculations [35]
a (Å)	3.93	3.986	3.929
c/a	1.005	1.01	1.01
$\delta z_{\text{Ba}}/c$ (fixed)	0.0	0.0	0.0
$\delta z_{\text{Ti}}/c$	0.009	0.015	0.009
$\delta z_{\text{O}_1}/c$	-0.015	-0.023	-0.013
$\delta z_{\text{O}_2, \text{O}_3}/c$	-0.010	-0.014	-0.009

2. Computational details

The first-principle calculations are carried out within a linear augmented plane wave method using the DFT implemented in WIEN2k package [29]. The local spin density approximation [30–32] has been chosen for the exchange correlation functional, since it was successfully applied previously [16, 21, 33] for studying of ferroelectric materials and their properties. The Brillouin zone for single elementary cell calculations was sampled using $6 \times 6 \times 6$ k -mesh. In the case of supercell calculations, the k -mesh was adjusted accordingly in order to maintain the same k -point density. The radii R_{MT} of muffin tin spheres centered at individual atoms are chosen to be equal 2.3, 1.8 and 1.54 Bohr for Ba, Ti and O, respectively. The product of the minimum R_{MT} radius and the maximum cut-off wave vector in the reciprocal space was kept at the constant value of $R_{\text{MT}}K_{\text{max}} = 7$ throughout all calculations. The energy to separate core and valence electrons was set such that electrons in the following orbitals were treated as valence electrons: Ba—5s 5p 6s, Ti—3s 3p 3d 4s and O—2s 2p.

Self-consistent structural parameters of BaTiO₃ were used in the calculations. The internal degrees of freedom for tetragonal structures were fully relaxed by minimizing the Hellmann–Feynman forces acting on atoms below 0.2 mRy/Bohr. The fully optimized structural parameters are listed in table 1.

The polarization inversion in the single cell was associated with a reaction coordinate ξ , which takes the values of 1 and 0 for the relaxed ferroelectric tetragonal structure and the corresponding centrosymmetric structure, respectively. The structural parameters for an arbitrary transition state ξ were determined by a linear interpolation

$$\delta z(\xi) = \delta z(1) \xi. \quad (1)$$

We assumed that the tetragonality of the lattice remained unchanged during this transition.

Polarization properties were calculated based on the modern theory of polarization [36, 37] in the framework of the Berry phase approach [38]. This capability is implemented in a BerryPI package [39] for WIEN2k in conjunction with WIEN2WANNIER code [40].

3. Results and discussion

3.1. Ferroelectric switching and domain wall motion

Figure 1 shows a potential energy curve that corresponds to the variation of total energy per unit cell as function of the reaction coordinate for a BaTiO₃ single cell. The energy profile is obtained by shifting Ti and O₂ atomic positions between ferroelectric and paraelectric state according to equation (1). The barrier for switching between two equilibrium positions is found

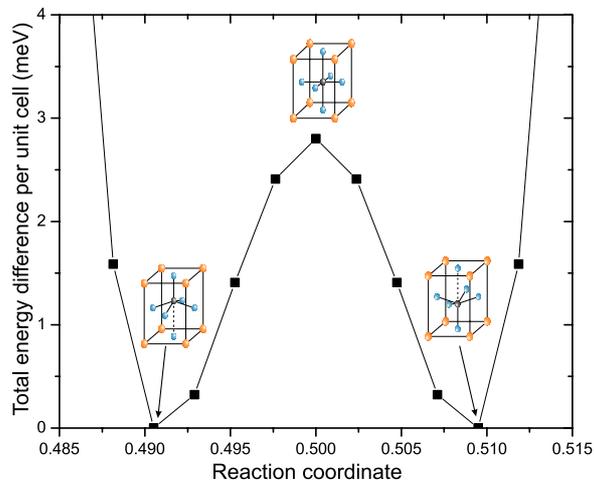


Figure 1. Potential profile associated with polarization inversion for a single unit cell of BaTiO_3 . (Lines are a guide to the eye.)

to be $E_b = 2.8$ meV per unit cell, which represents concurrent (i.e., single domain) switching. Previous theoretical studies [20, 41] indicate that the barrier height is extremely sensitive to the choice of an exchange correlation functional, mismatch of the lattice parameters and the choice of the basis set, which results in a wide range of values reported $E_b = 5\text{--}100$ meV. Therefore, we base further discussion on the relative difference in the barrier height rather than its absolute value.

Figure 1 is a representative of a single domain switching between two opposite ferroelectric states. However, as mentioned earlier, such a switching process disregards the presence domain wall. In order to resolve such a disagreement, we first validate the existence of the domain wall within the framework of our first-principle study. This is performed by comparing the potential energy profile associated with the polarization inversion in a single cell with a supercell model that captures the essence of domain wall motion.

In order to model the ferroelectric switching via a domain wall motion, we choose a supercell that consists of six unit cells as illustrated in figures 2(a)–(d). Although Padilla *et al* [15] was able to capture 180° domain wall energy for BaTiO_3 using only a four-crystallographic unit model, a six unit cell model is chosen for the present study in order to capture a wider region of domain wall motion. It was also previously shown by Meyer and Vanderbilt [16] for PbTiO_3 that such a structure is also large enough to capture the 180° domain wall energy accurately. According to our study, the ferroelectric switching occurs via consecutive switching of polarization in adjacent unit cells as depicted in figures 2(a)–(c), which represent the nucleation and growth of the domain with opposite polarization. The corresponding potential profile is presented in figure 2(e) (solid line).

The potential energy diagram in figure 2(e) was obtained by moving the Ti atom of a particular unit cell from one polarization state to its alternative switching configuration. For the switching of each successive cell, several intermediate structures were chosen by varying the Ti atomic position along the Ising switching path. As a result, the domain walls become Ba centered after the polarization reversal of each individual cell. Structural parameters were allowed to relax at every state in order to obtain their minimum energy configuration. However, constraints were applied to all the Ba atoms and the relevant Ti atom of the cell in which the

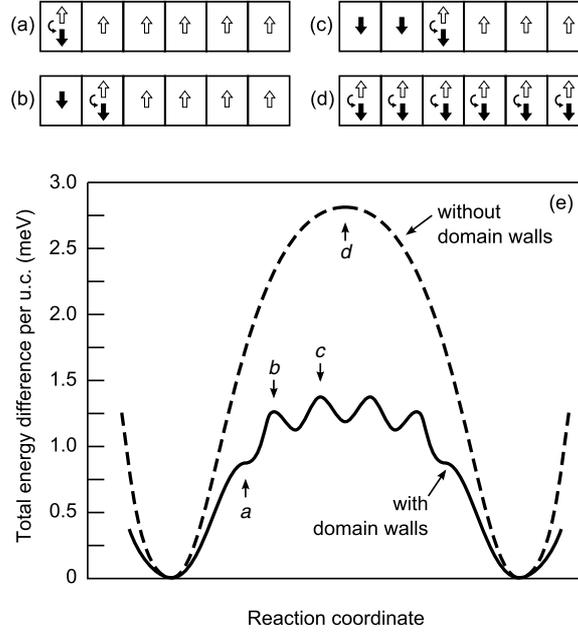


Figure 2. Consecutive (a)–(c) and concurrent (d) processes of polarization inversion in BaTiO₃ supercell. The arrows on panels (a)–(d) illustrate the polarization vector of individual unit cells. The total energy variation per unit cell during the switching process is shown on panel (e) as a function of the reaction coordinate for both scenarios. The energy barriers are linked with the corresponding structural transitions (a)–(d).

domain wall is persisting in order to prevent the collapse of the structure to a single domain. The presence of significantly smaller forces (of the order of 3 mRy/bohr) on the the fixed atoms (all Ba and one Ti) indicate that the applied restriction had negligible effects on the computed energy.

Analysis of the potential profile in figure 2(e) indicates that in contrast to the single cell switching (dashed line), the potential profile for consecutive process (solid line) is non-monotonic with a series of peaks associated with the barriers to be overcome during switching of individual cells. The energy barrier for the initiation of the switching process (figure 2(a)) is about two to three times higher than the barriers that corresponds to the polarization inversion of rest of the structure. Moreover, the barrier height reduces significantly as the size of domain with opposite polarization grows. The resultant barrier for consecutive switching of polarization in the entire supercell is approximately 1.5 meV per unit cell, which is twice as low in comparison to the concurrent process. This clearly favours the formation of domain walls and their successive propagation as a mechanism for ferroelectric switching within the first-principle framework as that process requires much lower energy to be overcome.

3.2. Domain wall energy

The required domain wall energy for switching each individual cell can be expressed as the energy density per unit wall area,

$$J_{dw} = \frac{E_{tot,DW} - E_{tot,SD}}{2A}, \quad (2)$$

where $E_{\text{tot,DW}}$ is the total energy of the supercell in the presence of a domain wall, $E_{\text{tot,SD}}$ is the total energy of the single domain supercell and A is the area of that domain wall. The factor of two accounts for the presence of the second domain wall due to the periodic boundary conditions. Using equation 2, the energy density per unit area of the Ba-centered domain walls are found to be 2.71 mJ m^{-2} , 3.62 mJ m^{-2} and 3.68 mJ m^{-2} , respectively, for polarization reversal of the first (figure 2(a)), second (figure 2(b)) and third (figure 2(c)) cells. Previous first-principles studies [15, 16] of 180° switching in BaTiO_3 observed constant domain wall energy density values that ranged from $6\text{--}7.2 \text{ mJ m}^{-2}$. In contrast, the present study finds that J_{dw} is essentially not a constant value, rather, it changes as the domain wall motion occurs. Our results suggest that the domain wall energy density increases during the domain growth stage, then it reaches almost a constant value as the wall moves to the third cell. It should be noted the values of the domain wall energy density due to their dependence on cell parameters and exchange correlation functional differ significantly from the results obtained by previous studies.

3.3. Coercive field

In this section, we apply results of the domain wall motion study to calculate the coercive field of BaTiO_3 . The coercive field is defined as the field required to balance the polarization between oppositely polarized domains resulting in a vanishing net polarization of the material.

According to the definition of the electric enthalpy, the electric field corresponds to a slope of the total energy density U versus polarization curve [21]. The coercive field is then determined by the maximum slope of $U(P)$ function along the reaction (switching) path

$$\mathcal{E}_c = \left. \frac{dU}{dP} \right|_{\text{max}} . \quad (3)$$

In order to remove small fluctuations in DFT-computed potential energy profile, the obtained data for energy as a function of polarization have been interpolated using a polynomial fitting. The obtained energy profile is shown in figure 3. Using the energy profile, we find that switching of polarization in the first unit cell (figure 2(a)) requires a very high coercive field of 112 MV m^{-1} . However, for polarization reversal in the second and third unit cells (figures 2(b) and (c)), much lower magnitude fields of 35 MV m^{-1} and 25 MV m^{-1} are needed, respectively. It has been shown by Shin *et al* [12] that it is the nucleation of the domain wall that requires a significantly higher coercive field in comparison to the growth stage. Thus, we can identify the polarization inversion of the first unit cell as being in the nucleation stage and the switching of the second and third stages can be represented as the growth of initially nucleated domains.

Finally, it should also be noted that the values of the coercive fields calculated here are still much greater in magnitude in comparison to the earlier results ($\mathcal{E}_{c,\text{nucleation}} \sim 0.46\text{--}1.86 \text{ MV m}^{-1}$) [12] obtained by Shin *et al* [12] and also the experimental results of $\mathcal{E}_c \sim 0.07 \text{ MV m}^{-1}$ for BaTiO_3 [42, 43]. Several factors can contribute to such a discrepancy between the computed coercive field and other results. Amongst them, one important parameter can be the temperature condition of the material being examined [44, 45]. DFT computations are performed at the ground state level at zero temperatures. In contrast, the compared results [12, 42, 43] were obtained with material persisting in the room temperature range. It has been suggested by the literature [44, 45] that the domain-wall-motion-dependant properties (coercive fields) are strongly dependant on the temperature. Another important contribution can come from the domain wall width, which changes inversely with the coercive field [46]. Experimentally, the domain wall width for 180° -type domain wall in BaTiO_3 was found to be ranging from $6\text{--}50 \text{ \AA}$ [47, 48], depending on the contribution from extrinsic factors. However,

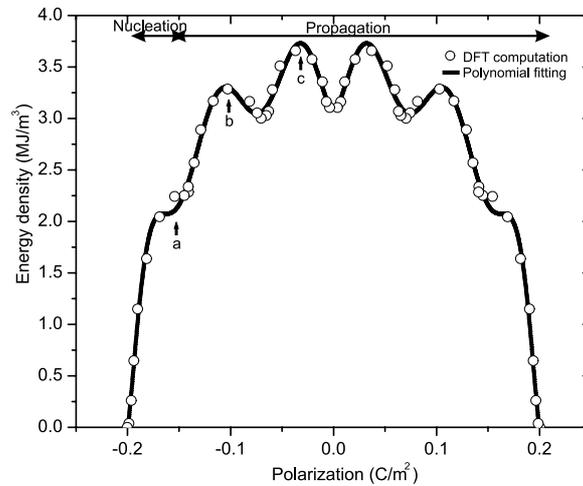


Figure 3. Energy profile as a function of polarization considering nucleation and propagation of domain walls. The labels (a)–(c) refer to the barriers for the consecutive switching of individual cells shown in figure 2(a)–(c).

the polarization profile of the ideal BaTiO₃ structure (figure 3) in the present study suggests a domain wall width of roughly one unit cell. Capturing the large experimentally observed domain wall requires a three-dimensional structure that expands over a very large number of unit cells, which is extremely challenging for *ab initio* methods. Such a large domain wall can, however, be observed using semi-empirical molecular dynamics simulations [12], which rely on first-principle inputs and empirical relationships to obtain the coercive field value. Responsible extrinsic factors such as defect-mediated nucleation of domains [33, 49], surface charge polarization [46], and grain size [50] contribute to discrepancies in the computation of coercive field, which are beyond the limit of first-principle simulations.

4. Conclusions

Using a first-principle potential profile study, we have shown that polarization switching is a non-concurrent process that results in the formation of domain walls. We have also computed the domain wall energy density values at several stages of the polarization inversion process, which suggests that it is essentially not a constant quantity but rather changes as the motion continues. Results of the calculations also show that the initiation of domain wall motion requires overcoming a much higher energetic barrier than the values that correspond to further movement. Also, analysis of our computed coercive field values for different stages of domain wall motion identifies and distinguishes between the nucleation and propagation phases at the microscopic level.

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