90° Ferroelectric Domains in PbTiO$_3$: Experimental Observation and Molecular Dynamics Simulations

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We report observation of 90° ferroelectric domain structures in transmission electron microscopy (TEM) of epitaxially-grown films of PbTiO$_3$. Using molecular dynamics (MD) simulations based on first-principles effective Hamiltonian of bulk PbTiO$_3$, we corroborate the occurrence of such domains showing that it arises as metastable states only in cooling simulations (as the temperature is lowered) and establish characteristic stability of 90° domain structures in PbTiO$_3$. In contrast, such domains do not manifest in similar simulations of BaTiO$_3$. Through a detailed analysis based on energetics and comparison between PbTiO$_3$ and BaTiO$_3$, we find that 90° domain structures are energetically favorable only in the former, and the origin of their stability lies in the polarization-strain coupling. Our analysis suggests that they may form in BaTiO$_3$ due to special boundary condition and/or defect-related inhomogeneities.

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I. INTRODUCTION

Ferroelectric transitions in perovskite oxides, such as BaTiO$_3$, are fluctuation driven first-order phase transitions, and hence a state with spatially fluctuating order parameter can readily form as a result of certain mechanical and electric boundary conditions. A common example of such a state is the one with domains of ferroelectric polarization with different symmetry equivalent orientations of order parameter that are separated by domain walls. Indeed, many properties of perovskite ferroelectrics depend on such domain structure, and it is being increasingly relevant at nano-scale. Naturally, the properties of a domain wall or an interface between adjacent ferroelectric domains depend on (a) symmetries and structural details of ferroelectric phases and (b) microscopic couplings responsible for the ferroelectric phase transition.

Perovskite oxides such as BaTiO$_3$ and PbTiO$_3$ are representative ferroelectric materials, although are quite different from each other in terms of their phase transitions. While PbTiO$_3$ undergoes a single strongly first order phase transition from cubic to tetragonal structure as temperature is lowered, BaTiO$_3$ exhibits a sequence of three relatively weaker first-order phase transitions. A paraelectric phase of BaTiO$_3$ with cubic structure transforms into a tetragonal ferroelectric phase at a Curie temperature, 393 K. Further cooling produces sudden changes from a tetragonal phase to an orthorhombic phase at 278 K and from an orthorhombic phase to a rhombohedral phase at 203 K. On the other hand, PbTiO$_3$ exhibits a phase transition from a paraelectric cubic phase to a ferroelectric tetragonal phase at $T_C = 763$ K and remains tetragonal down to 0 K.

While the domain structures in ferroelectrics have been revealed experimentally, detailed in situ experimental analysis of the domains and domain walls is quite challenging and the temperature dependence of dynamics of domain structure is not well understood. In the case of PbTiO$_3$, experimental studies of domains are further more difficult as the sample needs to be heated over its high transition temperature $T_C = 763$ K and such heating leads to evaporation of Pb ions changing the composition of the sample.

Ferroelectric phase transitions in perovskite oxides in bulk and thin film have been investigated by computer simulations such as phase-field method, Monte Carlo simulations, and molecular dynamics (MD) simulations. Recently, Nishimatsu et al. have developed a fast and versatile MD simulator of ferroelectrics based on first-principles effective Hamiltonian, which can be used in systematic studies of bulk as well as thin films. They have studied BaTiO$_3$ bulk and thin-film capacitors and obtained results showing good agreement with experiments. Their MD simulations of BaTiO$_3$ under periodic boundary condition (PBC) for bulk did not show any domain structures, as there is no depolarization field in the PBC of bulk. Simulations of thin-film of BaTiO$_3$ only show 180° domain structures, though 90° domain structures are widely seen in experiments. One of the advantages of MD simulations compared to Monte Carlo simulations is its ability to simulate...
time-dependent dynamical phenomena, e.g. MD simulation can be used to study the evolution of ferroelectric domains as a function of time during heating-up and cooling-down simulations.

In this paper, we report heating-up and cooling-down molecular-dynamics (MD) simulations of bulk PbTiO$_3$ to understand our observation of 90° domain structures in epitaxially-grown sample of PbTiO$_3$. In Sec. II we present experimental details for the sample preparation and we show a transmission electron microscope (TEM) image of 90° domain structure in PbTiO$_3$ film. We briefly explain the first-principles effective Hamiltonian and details of MD simulations in Sec. III and we present our results and analysis of heating-up and cooling-down MD simulations in Sec. IV. We finally summarize our work and conclusions in Sec. V.

II. EXPERIMENTAL DETAILS AND OBSERVATIONS

A. Sample preparation and Methods of TEM

An epitaxial PbTiO$_3$ thick film, with film thicknesses of about 1200 nm, was grown on the SrRuO$_3$/SrTiO$_3$ substrate at 873 K by pulsed metal organic chemical vapor deposition (pulsed-MOCVD) method. SrRuO$_3$ was deposited on (100) SrTiO$_3$ by rf-magnetron sputtering method. The detail of film preparation technique is described elsewhere$^{31,32}$. The TEM specimens were prepared with focused ion beam (FIB) micro-sampling technique. Damage layers, introduced during FIB microfabrication, were removed by low-energy Ar ion milling at 0.3 kV. JEM-2000EXII was used for TEM observations. TEM observations were performed at room temperature.

B. Observed TEM image

In Fig. 1, we show a bright field TEM image of a PbTiO$_3$ thick film, taken with the incident electron beam parallel to the [100] axis of the PbTiO$_3$. The inset in the image is the corresponding selected-area electron diffraction pattern. This bright-field TEM image is taken with the scattering vector $g_{011}$ excited. Here, $a$- and $c$-domains are those with polarization along $a$ and $c$ axes of the PbTiO$_3$ parallel and perpendicular to the substrate, respectively. This domain configuration is typical and very commonly seen for tetragonal PbTiO$_3$ films. The domain size is about 50-200 nm. Such 90° domain configurations, similar to that in Fig. 1, have been also observed in BaTiO$_3$. Boundaries between $a$- and $c$-domains are seen as black lines, as the TEM sample is slightly tilted. From this image, we can not discuss the width of domain walls between $a$- and $c$-domain. High-resolution TEM observation has revealed that the width of 90° domain walls is 1.0 ± 0.3 nm$^{33}$. This end, high-resolution TEM observation was conducted in order to reveal the width of domain walls between $a$- and $c$-domain. Fig. 2 shows the high-resolution TEM image of PbTiO$_3$ film, indicating that the width of domain walls is corresponding to 1 or 2 unit cells.

Before our computational study, it should be worth mentioning that 90° domains have been often observed in both BaTiO$_3$ and PbTiO$_3$, and are both ferroelectric and ferroelastic in nature. Typically, 90° domains are formed in epitaxial ferroelectric and ferroelastic films in order to relax the strain resulting from lattice mismatch with the substrate at and below $T_C$. They nucleate at misfit dislocations formed above $T_C$. Their growth is accompanied with the introduction of the additional dislocation perpendicular to the misfit dislocations and the dissociation of the dislocations into two pairs of partial dislocations around an anti-phase boundary$^{23}$.

III. MOLECULAR DYNAMICS SIMULATIONS

A. Effective Hamiltonian

Heating-up and cooling-down molecular-dynamics (MD) simulations are performed using first-principles effective Hamiltonian$^{28-30,36,37}$. 

![Fig. 1: A bright-field TEM image of a PbTiO$_3$ thick film taken with an electron incident parallel to the [100] of PbTiO$_3$. Scripts a and c in this figure denote a-domain and c-domain, respectively.](image-url)
FIG. 2: A high-resolution TEM image of a PbTiO$_3$ thick film taken with an electron incident parallel to the [100] of PbTiO$_3$. The 90° domain boundary is shown by the chain line.

$$H^{\text{eff}} = \frac{M^*_\text{dipole}}{2} \sum_{R,c} \hat{u}_c^2(R) + \frac{M^*_\text{acoustic}}{2} \sum_{R,c} \hat{v}_c^2(R)$$

$$+ V^{\text{self}}(\{u\}) + V^{\text{dip}}(\{u\}) + V^{\text{short}}(\{u\})$$

$$+ V^{\text{elas}, \text{homo}}(\eta_1, \ldots, \eta_6) + V^{\text{elas}, \text{inho}}(\{w\})$$

$$+ V^{\text{coup}, \text{homo}}(\{u\}, \eta_1, \ldots, \eta_6) + V^{\text{coup}, \text{inho}}(\{u\}, \{w\}),$$

(1)

where $u = u(R)$ and $w = w(R)$ are, respectively, the local dipolar displacement vector and the local acoustic displacement vector of the unit cell at $R$ in a simulation supercell. $\alpha = x, y, z$ is the Cartesian directions. Braces $\{\}$ denote a set of $u$ or $w$ in the supercell. $\eta_1, \ldots, \eta_6$ are the homogeneous strain components. $M^*_\text{dipole}$ and $M^*_\text{acoustic}$ are the effective masses for $u$ and $w$, respectively.

The new parameters can be easily derived from the previous ones. We list values of all the parameters used in our simulations and how they are related to the previous work in Table I.

**TABLE I:** The parameters of first-principles effective Hamiltonian for PbTiO$_3$ used in our simulations are given in the second column and how these parameters are related with the parameters in the previous work are shown in the third column.

| parameter | value | relation |
|-----------|-------|----------|
| $a_0$ [Å] | 3.969 | $a_0$ |
| $B_{11}$ [eV] | 117.1 | $C_{11}$ |
| $B_{12}$ [eV] | 51.6 | $C_{12}$ |
| $B_{44}$ [eV] | 137.0 | $C_{44}$ |
| $B_{1xx}$ [eV Å$^2$] | $-114.02$ | $2(g_0 + g_0)$ |
| $B_{1yy}$ [eV Å$^2$] | $-13.67$ | $2g_0$ |
| $B_{1zz}$ [eV Å$^2$] | $-22.67$ | $g_2$ |
| $\alpha$ [eV Å$^4$] | 27.83 | $B + C$ |
| $\gamma$ [eV Å$^4$] | $-34.48$ | $-2C$ |
| $k_1$ [eV Å$^6$] | $-42.42$ | $D$ |
| $k_2$ [eV Å$^6$] | 0 | $\eta$ |
| $k_3$ [eV Å$^6$] | 0 | $\eta$ |
| $k_4$ [eV Å$^8$] | 156.43 | $E$ |
| $m^*$ [amu] | 100.0 | $Z^*$ |
| $Z^*$ [e] | 10.02 | $Z^*$ |
| $\epsilon_{\infty}$ | 8.24 | $\epsilon_{\infty}$ |
| $\kappa_2$ [eV Å$^2$] | 1.170 | $A$ |
| $j_1$ [eV Å$^2$] | $-1.355$ | $2a_T$ |
| $j_2$ [eV Å$^2$] | 4.986 | $2a_L$ |
| $j_3$ [eV Å$^2$] | 0.222 | $b_1 + b_{11}$ |
| $j_4$ [eV Å$^2$] | $-0.018$ | $2b_{22}$ |
| $j_5$ [eV Å$^2$] | 0.398 | $b_1 - b_{11}$ |
| $j_6$ [eV Å$^2$] | $-0.083$ | $2(c_1 + 2c_{11})$ |
| $j_7$ [eV Å$^2$] | $-0.204$ | $2(c_{11} - 2c_{11})$ |

The new parameters can be easily derived from the previous ones. We list values of all the parameters used in our simulations and how they are related to the previous work in Table I.

**B. Simulation Details**

Heating-up and cooling-down MD simulations are performed with our original MD code feram [http://loto.sourceforge.net/feram/]. Details of the code can be found in Ref. [30]. Temperature is kept constant in each temperature step in the canonical ensemble using the Nosé-Poincaré thermostat. This simplectic thermostat is so efficient that we can set the time step to $\Delta t = 2 \text{ fs}$. In our present MD simulations, we thermalize the system for 20,000 time steps, after which we average the properties for 20,000 time steps. We used a supercell of system size $N = L_x \times L_y \times L_z = 32 \times 32 \times 32$ and small temperature steps in heating-up (+1 K/step) and cooling-down (−1 K/step) simulations. The heating-up simulation from 100 K to 900 K is started from an $z$-polarized initial
configuration generated randomly: \( \langle u_x \rangle = \langle u_y \rangle = 0 \), \( \langle u_z \rangle = 0.33 \text{ Å} \), \( (u_x^2) - \langle u_x \rangle^2 = (u_y^2) - \langle u_y \rangle^2 = (0.045 \text{ Å})^2 \), and \( (u_z^2) - \langle u_z \rangle^2 = (0.021 \text{ Å})^2 \), where brackets denote \( R \)-average in supercell \( \langle u_\alpha \rangle = \frac{1}{N} \sum_R u_\alpha(R) \). The cooling-down one from 900 K to 100 K is started from random paraelectric initial configuration: \( \langle u_x \rangle = \langle u_y \rangle = \langle u_z \rangle = 0 \) and \( (u_\alpha^2) - \langle u_\alpha \rangle^2 = (0.15 \text{ Å})^2 \).

IV. RESULTS AND DISCUSSION

From the temperature dependence of averaged lattice constants (shown in Fig. 3), a tetragonal-to-cubic ferroelectric-to-paraelectric phase transition is clearly observed in the heating-up simulation at 677 K. However, a strange behavior in lattice constants is found in the cooling-down simulation at \( T=592 \text{ K} \). The average temperature of these two transition temperatures (634 K) is in good agreement with the earlier Monte Carlo simulations and slightly lower than the experimental value \( T_C = 763 \text{ K} \). Indeed, the observation of an orthorhombic phase during cooling-down simulations is intriguing.

To understand this interesting behavior of lattice constants in cooling-down simulations, we perform a detailed analysis of the configurations (snapshots) during our MD simulations. From a snapshot of dipoles in the supercell (shown in Fig. 4), we find that the apparently orthorhombic nature of the phase is due to a 90° domain structure. Although the 4 unit cell = 1.6 nm of the domain size is much smaller than experimentally observed ones as shown in Sec. II B, the width of a simulated domain wall estimated to be \( \sim 1 \text{ unit cell} \) is in good agreement with our experiment. Each domain has the \( a = b < c \) tetragonal structure of PbTiO\(_3\), but their average value in whole crystal gives smaller \( c' \) than \( c \) and larger \( a' \) than \( a \). The lattice constant \( b' \) has almost the same values as \( a \), because the polar directions of two kind of domains are perpendicular to the \( b' \)-axis. It should be noted that this domain structure is found in MD simulations in bulk under periodic boundary condition (PBC), but we have not simulated thin films. Under the PBC, there is no depolarization field inside the bulk. Moreover, this domain structure can be easily reproduced in cooling-down simulations from any random paraelectric initial configurations and any seeds for the pseudo random number generator. There was no evidence for such unusual behavior in simulations of bulk BaTiO\(_3\) [37].

To understand the reason of stability of the 90° domain structure seen here, even in bulk PbTiO\(_3\), we compare “total energy surfaces” between single and 90° domain structures. The total energy surface of single domain structure with [001] polarization is the same as in Refs. 37 and 50. For the total energy surface of 90° domain structure, we focus on a snapshot of the supercell at 300K shown in Fig. 3 and represent it with \( \{ u_{90°,300K}(R) \} \). We now obtain a sequence of configurations by multiplying a factor \( \frac{u}{u_{90°,300K}} \) for all \( R \)

\[
u(R) = \frac{u}{u_{90°,300K}} u_{90°,300K}(R) ,
\]

and compute total energy as a function of \( u \), where \( \langle u_{90°,300K} \rangle \) is the averaged length of dipoles in the 300 K snapshot

\[
\langle u \rangle_{90°,300K} = \frac{1}{N} \sum_R |u_{90°,300K}(R)| = 0.32 \text{ Å} .
\]

Calculated total energy surfaces of single and 90° domain structures for PbTiO\(_3\) are shown in Fig. 5 with solid and dashed lines, respectively. For comparison, those for BaTiO\(_3\) are also plotted assuming the same 90° domain structure by using the set of parameters in \( H^{\text{eff}} \) listed in Ref. 37. While the 90° domain structure of PbTiO\(_3\) exhibits a minimum at \( u \neq 0 \), that of BaTiO\(_3\) costs energy. This is why the 90° domain structures can be found in simple cooling-down simulations of PbTiO\(_3\), but not in those of BaTiO\(_3\).

Minima are indicated with (a)–(c) in Fig. 5. To uncover the origin of this contrasting behaviour, interaction energy terms at the minimums are listed in TABLE I. For the BaTiO\(_3\), because there is no minimum, interaction energies of configuration at (d) in Fig. 5 (of \( u = 0.10 \text{ Å} \)) are listed.

From TABLE I It is clear that the energy losses in \( V^{\text{harmonic}}, V^{\text{elas, inhomo}}, \) and \( V^{\text{coup, inhomo}} \) in forming the 90° domain structure in PbTiO\(_3\) are compensated by the energy gains in \( V^{\text{unharmonic}}, V^{\text{elas, homo}}, \) and \( V^{\text{coup, homo}} \). In contrast, such recovery is not sufficient in BaTiO\(_3\) to form a \( u \neq 0 \) minimum or non trivial 90° domain structures. In stabilization of the 90° domain structures in PbTiO\(_3\), our analysis conclusively highlights the role of two microscopic interactions: (a) lower elastic energy cost arising from the smaller strain from compensation along \( c \)
FIG. 4: (Color online) Snapshot of three “sides” of the $32 \times 32 \times 32$ supercell at $T = 300K$ in a cooling-down simulation of PbTiO$_3$. Dipole moments of each site are projected onto the side planes and indicated with arrows. Dipoles of $u_z > 0.2 \AA$ are indicated with red color. Dipoles of $u_z \leq 0.2 \AA$ are indicated with green. Crystalline directions are indicated with $a'$, $b'$, and $c'$ as indicated in Fig. 3.

TABLE II: Comparison of interaction energies $V^x$ in the effective Hamiltonian of Eq. (1) for two kinds of domain states of PbTiO$_3$ and BaTiO$_3$. $V^{\text{harmonic}}$ is the sum of $V^{\text{dpl}}$, $V^{\text{short}}$, and the harmonic terms in $V^{\text{self}}$. $V^{\text{unharmonic}}$ is the unharmonic terms in $V^{\text{self}}$. Unit of energy is eV.

| x of interaction energy $V^x$ | PbTiO$_3$ | BaTiO$_3$ | PbTiO$_3$ | BaTiO$_3$ |
|-------------------------------|------------|------------|------------|------------|
| (a) single | (b) 90° | (c) single | (d) 90° |
| domain | domain | domain | domain |
| harmonic | $-0.22106$ | $-0.14393$ | $+0.07713$, | $-0.0386$ | $0.03541$ | $+0.07427$ |
| unharmonic | $0.33435$ | $0.17249$ | $-0.16186$, | $0.04754$ | $0.00695$ | $-0.04059$ |
| elast.homo | $0.21946$ | $0.04441$ | $-0.17505$ | $0.02609$ | $0.00131$ | $-0.02478$ |
| elast.inho | $0.00000$ | $0.05171$ | $+0.05171$, | $0.00000$ | $-0.00262$ | $-0.00262$ |
| coup.homo | $-0.43891$ | $-0.08881$ | $+0.35010$, | $-0.05218$ | $0.00089$ | $+0.05307$ |
| coup.inho | $0.00000$ | $-0.10342$ | $-0.10342$, | $0.00000$ | $-0.00178$ | $-0.00178$ |
| total | $-0.10616$ | $-0.06755$ | $+0.03861$, | $-0.01741$ | $0.04016$ | $+0.05757$ |

| $u$ [Å] | 0.34 | 0.29 | 0.16 | 0.10 |
and a axis, and (b) inhomogeneous (local) strain coupling with polarization at the domain wall. The latter does not contribute much to transition behavior in the bulk, but has rather significant impact on the properties of domain wall. Noting that a 90° domain structure is not energetically favorable in BaTiO$_3$ simulated as a perfect bulk crystal and coupling of soft modes with higher energy modes is weak, we believe that the experimentally observed 90° domain structures in BaTiO$_3$ is most likely due to inhomogeneities in the samples and/or the specific electric and mechanical boundary conditions.

V. SUMMARY

In this article, TEM observation of PbTiO$_3$ thick films revealed 90° domain structures, which have been often observed in BaTiO$_3$. The domain size perpendicular to domain boundaries was 50–200 nm. The width of domain wall was corresponding to 1 or 2 unit cell.

We also have performed heating-up and cooling-down MD simulations of PbTiO$_3$. In cooling-down simulation, 90° domain structure is found to form spontaneously. By comparing “total energy surfaces” of single and 90° domain structures, we understand that a 90° domain structure is metastable in bulk PbTiO$_3$, but not in bulk BaTiO$_3$. The origin of this contrast is traced to significantly larger polarization-strain coupling in PbTiO$_3$. Hence, while 90° domain structures can form spontaneously in PbTiO$_3$, they seem to arise in BaTiO$_3$ mostly from special boundary conditions and/or defect-related inhomogeneities.

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