Phase-Field Simulation of Ferroelectric Domain Microstructure Changes in BaTiO$_3$

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Phase-field method has recently been extended and utilized across many fields of materials science. Since this method can systematically incorporate, the effect of coherency strain induced by lattice mismatch and applied stress as well as external electrical and magnetic fields, it has been applied to many material processes including solidification, solid-state phase transformations, and various types of complex microstructure changes.

In this article, we focus on the ferroelectric domain microstructure changes followed by the structural phase transition from cubic to tetragonal phase in BaTiO$_3$, and its morphological developments are simulated on the basis of the phase-field method. The circuit structure of polarization moments of ferroelectric domains including twin defects is simulated, and the domain morphology is controlled by both the electric dipole-dipole interaction among polarization moments and the elastic interaction among domains with different tetragonal distortion. The ferroelectric domain exchange induced by external electric field is also simulated, then the dielectric property, i.e., the polarization hysteresis curve, is calculated by integrating all the $x$ components of polarization moment vector over the microstructure. Furthermore, the simulation of the reversible ferroelectric domain switching, which is a new phenomenon recently discovered by Ren, is also simulated as an advanced application of the present simulation model.

Keywords: phase-field method, ferroelectric material, polarization domain, polarization hysteresis, time dependent Ginzburg-Landau (TDGL) equation

1. Introduction

Phase field method has been successfully applied to various materials processes including solidification, solid-state phase transformations and microstructure changes.

Using phase field methodology, one can deal with the evolution of arbitrary morphologies and complex microstructures without explicitly tracking the positions of interfaces. It is rather straightforward to incorporate the effect of coherency and applied stresses, as well as the electrical and magnetic fields.

The phase-field simulation method of the structural phase transition in ferroelectric materials and the polarization domain exchanges by external electric field has been proposed by Li et al., where the material employed for calculation was the lead zirconate titanate (PZT) thin film. Recently, the temperature-strain phase diagram for BaTiO$_3$ thin films was also calculated based on the phase-field method. As the practical application to the ferroelectric random access memory, the ferroelectric domain switching in the memory has been analyzed on the basis of the phase-field model by Dayal and Bhattacharya. Therefore, the simulation method has been well established, currently.

On the other hand, the reversible ferroelectric domain switching controlled by thermal treatment has been recently discovered by Ren in BaTiO$_3$ based ferroelectric materials. Since this phenomenon induces the extremely large piezoelectric strain, this phenomenon has been expected as a new type of a piezoelectric actuator.

In this paper, firstly, we focus on the ferroelectric domain microstructure changes followed by the structural phase transition from cubic to tetragonal phase in BaTiO$_3$, and simulate its morphological developments on the basis of the phase-field method. Then the microstructure development during the ferroelectric domain exchange induced by external electric field and the polarization hysteresis curve with this microstructure changes are simulated. Finally, we modify the conventional simulation method so as to be able to calculate the reversible ferroelectric domain switching newly discovered by Ren, and simulate the domain microstructure changes and polarization hysteresis curve during this reversible ferroelectric domain switching.

2. Simulation Method

In this section, firstly, the phase-field simulation method of calculating the structural phase transition from cubic to tetragonal phase and the ferroelectric domain microstructure changes in BaTiO$_3$ is explained. Secondary, we account for the mechanism of the reversible ferroelectric domain switching and propose its modeling method based on the phase-field simulation.

2.1 Phase-field simulation of the ferroelectric domain microstructure changes

The order parameter describing the ferroelectric domain structure is spontaneous polarization moment $P(r,t) = (P_1(r,t), P_2(r,t), P_3(r,t))$ which is the function of spatial position $r$ and time $t$. This order parameter $P(r,t)$ is regarded as the phase field order parameter in the phase-field method. The temporal evolutions of the polarization $P(r,t)$, i.e., the structural phase transition and ferroelectric domain microstructure changes, are described by the time dependent Ginzburg-Landau (TDGL) equation:

$$\frac{\partial P_i}{\partial t} = -L_g \frac{\delta G_{sys}}{\delta P_i},$$

(1)
where $L_P$ is the relaxation kinetic coefficient and we set $L_P = 1$, which means the time $t$ is normalized to $L_P$ and the symbol of normalized time is denoted as $\tau$ in this paper. $G_{sys}$ is the total free energy of the system, and the quantity $\delta G_{sys}/\delta P_i$ is the thermodynamic driving force for the spatial and temporal evolution of $P(r, t)$. The total free energy $G_{sys}$ is expressed as

$$G_{sys} = \int_{\Omega} \left[ G_c(P_i, T) + \frac{1}{2} \kappa_p \sum_{i=1}^{3} |\nabla P_i|^2 \right] \, d\Omega$$

where $G_c(P_i, T)$ is a bulk free energy density, $E_{str}$ is an elastic strain energy, $E_{dipole}$ is a dipole-dipole interaction energy among polarization moments in the microstructure, $E_{appel}$ is an electric potential energy induced from the external electric field, and the second term in the integrant is a ferroelectric domain wall energy which is expressed by the same form as the gradient energy in phase-field method.

The total free energy density of the BaTiO$_3$ system under a stress-free boundary condition is described by a Landau-Devonshire polynomial as

$$G_c = \alpha_i (P_i^2 + P_i^4) + \alpha_{ij} (P_i P_j + P_j P_i)$$

where $\alpha_i, \alpha_{ij}, \alpha_{ik}$ and $\alpha_{ijk}$ are adjusted to the BaTiO$_3$ single crystal properties, and the values of which have been determined by Li et al.\textsuperscript{16}

The elastic strain energy is given as

$$E_{str} = \frac{1}{2} \int_{\Omega} C_{ijkl} \epsilon_{ij}^{0^*}(\mathbf{r}) \epsilon_{kl}^{0}(\mathbf{r}) \, d\Omega$$

where $C_{ijkl}$ is the elastic stiffness tensor, $\epsilon_{ij}^{0^*}(\mathbf{r})$ and $\epsilon_{ij}^{0}(\mathbf{r})$ are the total strain and the stress-free strain, respectively. The elastically homogeneous case and the cubic symmetry are assumed in this study, then the employed values of $C_{ijkl}$ are $C_{12} = 2.48 \times 10^{11}$ (Pa), $C_{13} = 1.57 \times 10^{11}$ (Pa) and $C_{44} = 0.91 \times 10^{11}$ (Pa).\textsuperscript{17} The stress-free strain $\epsilon_{ij}^{0}(\mathbf{r})$ is expressed by the function of the polarization moment $\mathbf{P}(\mathbf{r})$ as

$$\epsilon_{ij}^{0}(\mathbf{r}) = Q_{ij} P_i P_j$$

where the coefficients $Q_{ij}$ represents the electrostrictive coefficient, and the values of the BaTiO$_3$ single crystal case are obtained from Ref. 16. The total strain $\epsilon_{ij}^*(\mathbf{r})$ is calculated based on the Khachaturyan’s mesoscopic elasticity theory\textsuperscript{18}

$$\epsilon_{ij}^*(\mathbf{r}) = \frac{1}{2} \left[ \Omega_{pq}(\mathbf{n}) n_q n_p + \Omega_{pq}(\mathbf{n}) n_q n_p \right]$$

where $\mathbf{k}$ is a reciprocal vector in Fourier space and $\mathbf{n} = k / |k|$ is unit vector along $k$ direction. $\Omega_{pq}(\mathbf{n})$ is the inverse matrix of $\Omega_{pq}(\mathbf{n}) \equiv C_{ijkl} n_i n_j$, and $\epsilon_{ij}^*(\mathbf{k})$ is the Fourier transform of $\epsilon_{ij}^*(\mathbf{r})$.

The dipole-dipole interaction energy among polarization moments in the microstructure is given as

$$E_{appel} = - \int_{\Omega} E_{appel}(\mathbf{r}) \, d\Omega$$

where $E_{appel}$ is a vector component of external electric field and the $\mathbf{P}_i$ is an spatial average of $P_i(\mathbf{r})$. Since the periodic boundary condition of the microstructure is employed in this study, there is no surface so the depolarization energy is neglected in this study. Numerical simulation of the microstructure changes is performed based on the conventional deference method.

### 2.2 Phase-field simulation of the reversible ferroelectric domain switching

Figure 1 shows the schematic illustration explaining the mechanism of the reversible ferroelectric domain switching, which has been proposed by Ren.\textsuperscript{11} The light and dark gray regions in Fig. 1(a) represent the ferroelectric domains having tetragonal crystal structure with deferent orientation, respectively. The black arrows in (a) indicate the direction of the c-axis of the tetragonal phase. The small white squares and rectangles in the figure represent the spatial symmetry of the point defects (dopant/impurity ions and Oxygen-ion vacancies) in ferroelectrics, and the square shape means the isotropic spatial distribution of the point defects. On the other hand, the rectangle shape in (b) and (c) indicates that the point defects are preferentially rearranged according to the crystal symmetry of tetragonal phase in which the defects are embedded. Since the defects rearrangement needs short or long range atomic diffusion, this rearrangement is taken place under the thermal treatment such as an aging process. Therefore, Fig. 1(b) shows the situation that the defects arrangement is stabilized by aging. It should be emphasized that the rearranged defects store the orientation of c-axis in its memory through the local atomic bonding or the local strain field. If the external electric field pointing downward direction is imposed on the microstructure of (b), the...
Schematic illustration explaining the mechanism of the reversible domain switching, which has been proposed by Ren. The light and dark gray regions in (a) represent the ferroelectric domains having tetragonal crystal structure with different orientation, respectively. The black arrows in (a) indicate the direction of the c-axis of the tetragonal phase. The small white squares and rectangles represent the spatial symmetry of the point defects (dopant/impurity ions and Oxygen-ion vacancies) in ferroelectrics.

Fig. 1

The behavior of ferroelectric domain exchanges with the external electric field is simulated from (a) to (f). Initially, the external electric field is set to be constant and the value of which is (see the upper right arrow). The applied external electric field applied along horizontal direction (see (d)–(f)), where the interface between brighter and darker parts is the twin boundary. This twin microstructure is formed due to relax the elastic constraint induced from the structural phase transition. Furthermore, the continuous circuit of the polarization moments is formed by the dipole-dipole interaction among polarization moments (see the arrows in (f)). Note that the twin domain boundary of the tetragonal phase is coincident with the 90° ferroelectric domain boundary, and the 180° ferroelectric domain boundary is located inside a twin domain.

Figure 2 shows the two-dimensional simulation of the structural transformation from cubic to tetragonal phase in BaTiO$_3$ at 298 K, where the black part is a cubic phase, and the gray and white parts correspond to the tetragonal phase. The gray level also indicates the orientation of polarization moment vector which is indicated by arrows in Fig. 2(f), the direction of which is parallel to the c-axis of the tetragonal phase.

At early stage of structural transformation from cubic to tetragonal phase, the tweed-like structure having the structural modulation along the diagonal direction is developed (see (a)–(c)). Then the microstructure gradually changes to the twin domain morphology during coarsening of domains (see (d)–(f)), where the interface between brighter and darker part is the twin boundary. This twin microstructure is formed due to relax the elastic constraint induced from the structural phase transition. Furthermore, the continuous circuit of the polarization moments is formed by the dipole-dipole interaction among polarization moments (see the arrows in (f)). Note that the twin domain boundary of the tetragonal phase is coincident with the 90° ferroelectric domain boundary, and the 180° ferroelectric domain boundary is located inside a twin domain.

Figure 3 shows the two-dimensional simulation of the polarization domain microstructure change induced by the external electric field applied along horizontal direction (see the upper right arrow). The applied external electric field is set to be constant and the value of which is 4 × 10^6 (V/m), and the Fig. 2(f) is employed as the initial microstructure for this simulation, so Fig. 3(a) is the same as Fig. 2(f).

The behavior of ferroelectric domain exchanges with the external electric field is simulated from (a) to (f). Initially,
Fig. 2 Two-dimensional simulation of the structural transformation from cubic to tetragonal phase in BaTiO$_3$ at 298 K.

Fig. 3 Two-dimensional simulation of the polarization domain microstructure change induced by the external electric field applied along horizontal direction (see the upper right arrow).
the domains having polarization moment along the vertical direction, which is perpendicular to the external electric field, start to disappear (see (b)–(d)), because these domains are energetically unstable not only for the potential energy by the external electric field but also for the elastic strain energy. Then, the domains having polarization moment pointing left hand side shrink, gradually (see (d)–(f)). In this case, since the entire region is a single twin domain, i.e., tetragonal single crystal, the elastic strain energy does not exist. Therefore, the driving force for microstructure changes is only the potential energy induced by the external electric field. Since we confirmed from this result that the ferroelectric domain exchanges is taken place with the external electric field, we further tried to simulate the ferroelectric domain microstructure changes induced by the external alternating electric field.

Figure 4 shows the two-dimensional simulation of the polarization domain microstructure changes induced by the external alternating electric field. Since the phase-field method can not calculate nucleation process, the some nucleation site is artificially introduced on the four sides of each figure. The dielectric property, i.e., the polarization hysteresis curve, is calculated by integrating all the x components of polarization moment vector in the microstructure (horizontal direction is x-axis), and the calculated dielectric hysteresis curve corresponding to the microstructure changes in Fig. 4 is represented as Fig. 5, where the abscissa is an external alternating electric field and the vertical axis indicates the average polarization moment along horizontal direction. The solid circles (a) to (h) in Fig. 5 are calculated from the figures (a) to (h) in Fig. 4, respectively. The dielectric hysteresis is reasonably calculated in accordance with the morphological microstructure changes of the ferroelectric domains.

3.2 Simulation results of the reversible ferroelectric domain switching

Figure 6 shows the two-dimensional simulation of the reversible ferroelectric domain switching induced by the external alternating electric field. The initial microstructure morphology of (a) is artificially set up, where the polarization moment $P_i(r)$ takes equilibrium value depending on the morphology of the domain microstructure. The order parameter field $\rho_i(r)$ is fixed so as to satisfy the relation $\rho_i(r) = P_i(r)$, which corresponds to the state of the minimum interaction energy (see the third term in the integrant of eq. (10)). Furthermore, since we want to calculate the typical
case in which the field $\rho_i(r)$ strongly constrains the polarization moment field $P_i(r)$, the parameters $W$, $\alpha_\rho$, $\kappa_\rho$ and $L_\rho$ are assumed to be $W = 500$ (J/mol), $\alpha_\rho = 1$, $\kappa_\rho = 0$ and $L_\rho = 0$, respectively. As a result, $\rho_i(r)$ does not change from the initial setting.

The polarization hysteresis curve is calculated by integrating all the $x$ components of polarization moment vector in the microstructure, and the calculated dielectric hysteresis curve corresponding to the microstructure changes in Fig. 6 is represented as Fig. 7. The circles (a) to (l) in Fig. 7 are calculated from the microstructures (a) to (i) in Fig. 6. The feature of the ferroelectric domain microstructure changes is almost same as that observed in Fig. 3, and the reversible domain switching behavior is calculated, reasonably.

### 4. Conclusions

The ferroelectric domain microstructure changes followed by the structural phase transition from cubic to tetragonal phase in BaTiO$_3$, and the ferroelectric domain microstructure changes are simulated on the basis of the phase-field method. Furthermore, the simulation of the reversible domain switching, which is a new phenomenon recently discovered by Ren, is also simulated as an advanced application of the present simulation model. The results obtained are as follows:

1. The circuit structure of polarization moments of ferroelectric domains including twin defects is simulated, and the domain morphology is controlled by both the electric dipole-dipole interaction among polarization moments and the elastic interaction among domains with different tetragonal distortion.

2. The ferroelectric domain exchange induced by external electric field is simulated, and the polarization hysteresis curve is calculated, simultaneously, by integrating all the $x$ components of polarization moment vector over the microstructure.

3. The reversible ferroelectric domain switching in BaTiO$_3$ is reasonably modeled by using the calculation method for the rubber-like behavior in reversible martensitic transformation.

![](Fig_6.png)

**Fig. 6** Two-dimensional simulation of the reversible ferroelectric domain switching induced by the external alternating electric field.

![](Fig_7.png)

**Fig. 7** Calculated dielectric hysteresis curve corresponding to the microstructure changes in Fig. 6.
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