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Anomalous toughening in nanoscale ferroelectrics with polarization vortices

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Abstract—Unusual mechanical behavior of cracks in nanoscale ferroelectrics, where spontaneous polarization characteristically forms closed-flux vortices, is investigated using state-of-the-art real-space phase-field modeling based on the Ginzburg–Landau theory. An anomalously large toughening effect is revealed in nanoscale ferroelectrics due to drastic stress release near the crack tip, which is almost one order of magnitude larger in stress intensity than that observed in macroscale materials. Such anomalous toughening is attributed to an unusual switching behavior of the polarization vortices in nanoscale ferroelectrics, which is no longer localized near the crack tip as in macroscale ferroelectrics, but expands to the entire structure through the splitting and multiplication of vortices. We further demonstrate that this local-to-global switching is intrinsically induced by strong cross-coupling between the ferroelectric polarization and mechanical strain that concentrates to the electro-elastic energy, not only in the vicinity of crack tip, but also to each polarization vortex due to its inhomogeneous distribution. Our finding provides a novel insight into nanoscale polarization vortices and leads to an entirely new strategy for the tailoring and improvement of fracture toughness in ferroelectric materials by engineering the microstructure of polarization vortices.

Keywords: Ferroelectric material; Crack; Polarization vortex; Polarization switching; Phase-field model

1. Introduction

Ferroelectric materials such as $PbTiO_3$ and $Pb(Zr,Ti)O_3$ solid solutions have been drawing continuous attention and interest due to their large ferroelectricity and related electromechanical properties such as a large piezoelectric response and high dielectric constant, and have thus been widely used for technological devices including nonvolatile random access memory (FeRAM) devices, sensors, actuators and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [1–4]. However, their inherent brittleness and low fracture toughness often lead to critical failure and malfunction of such devices [5–7] through the propagation of cracks that are typically formed during the growth or production processes [8–12].

The mechanical behavior of cracks in ferroelectric materials is generally complicated due to coherent nonlinear interactions between the mechanical and electric fields [13–15]. The intense stress concentration with the form of a singular field at a crack tip and significant cross-coupling between the ferroelectric spontaneous polarization and mechanical stress/strain induces local polarization switching near the tip [16–27], which often shields (or anti-shields) the crack from applied mechanical loads and thus apparently toughens (or weakens) these ferroelectric materials [17,18,25,27]. Therefore, an understanding of the mechanical behavior of cracks in ferroelectric materials is of central importance, not only for the reliability of ferroelectric devices, but also with respect to fundamental physics and mechanics. To date, the mechanical behavior of cracks and the polarization switching characteristics have been intensively studied both experimentally and theoretically [16–27], which has mostly elaborated on macroscale ferroelectrics where the cracks are simply assumed to behave in a uniform (monodomain) polarization.

Recent significant advances in manufacturing technology have enabled us to obtain nanostructured ferroelectric materials, such as thin films, nanowires, and nanodots. In such nanoscale ferroelectrics, the charge that appears on a surface due to the termination of electric dipoles generates a counter electric field inside the nanostructures (depolarization field) [4], which destabilizes the normal rectilinear polarization and instead leads to the formation of polarization vortices [28–43]. The clockwise-and-counterclockwise arrangement of polarization vortices

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that emerge to cover the entire structure of the nanoscale ferroelectric and the spatially continuous rotation of polarization vectors no longer allow us to understand the ferroelectric properties on the basis of conventional domains [40,41]. In addition, the formation of polarization vortices induces a complex internal stress distribution in nanoscale ferroelectrics, which is attributed to the coupling between polarization and stress [43]. Therefore, in the presence of a crack, such a spatially inhomogeneous polarization field of vortices may interact with the singular stress field near the crack tip in a totally different way from that with nearly-homogeneous (single-domain) polarization in macroscale ferroelectrics, and which would further complicate the mechanical behavior of crack. However, the mechanical behavior of cracks in nanoscale ferroelectrics has not yet been clarified.

The Ginzburg–Landau theory was proposed on the basis of the fundamental principles of thermodynamics and kinetics to describe the dynamic behavior of ferroelectrics using a polarization vector as an order parameter [44–50]. Phase field modeling based on the Ginzburg–Landau theory has been commonly used for the study of cracks in ferroelectric materials [51–54] because phase field modeling achieves self-consistency of the electrostatic and elastic interactions, which is essential to describe the electric and mechanical behavior near a crack tip [25,27,51–54]. In recent years, phase field modeling has been extended for simulation in real-space [51,55–61], which has enabled us to address any ferroelectric structures with arbitrary geometries and boundary conditions, and has successfully reproduced the polarization vortices in nanoscale ferroelectrics [40,41]. Therefore, real-space phase-field modeling is suitable and effective for the study of cracks in nanostructured ferroelectrics.

In this study, we investigate the mechanical behavior of cracks in nanoscale ferroelectrics, where a complicated coupling between the polarization vortices and singular stress field is expected, using real-space phase-field simulations based on the Ginzburg–Landau theory. We find a dramatically large toughening effect in the nanoscale ferroelectrics. The anomalous toughening is shown to be due to an unusual switching of polarization vortices that is no longer localized near the crack tip, but expands to the entire nanoscale ferroelectrics. We further demonstrate that a strong cross-coupling between polarization and mechanical strain plays a central role in the unusual switching of the polarization vortices.

2. Computational details

2.1. Real-space phase-field model for ferroelectrics based on the Ginzburg–Landau theory

The mechanical and ferroelectric behavior of cracks in ferroelectric nanocomponents is studied using real-space phase-field modeling based on the Ginzburg–Landau theory. The present phase-field modeling achieves self-consistency of the electrostatic and elastic interactions, which is essential to describe the electric and mechanical behavior near a crack tip [25,27,51–54]. In the phase-field model of ferroelectric materials, the polarization vector $\boldsymbol{P} = (P_1,\ P_2,\ P_3)$ is taken as the order parameter to describe the free energies of ferroelectric systems. The total free energy of the ferroelectric system F, can be described by [62]:

$$F = \int_V f dV = \int_V (f_{\text{Land}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{coup}} + f_{\text{elec}}) dV, \quad (1)$$

where f, f_{Land}, f_{grad}, f_{elas}, f_{coup}, and f_{elec} denote the total free energy density, the Landau energy density, the gradient energy density, the elastic energy density, the coupling energy density, and the electrostatic energy density, respectively. V is the entire volume of the ferroelectric system.

The Landau energy density is expressed by a six-order polynomial of the spontaneous polarization [63] as:

$$\begin{aligned} f_{\text{Land}} = {} & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) \\ & + \alpha_{12}(P_1^2P_2^2 + P_2^2P_3^2 + P_3^2P_1^2) + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) \\ & + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_1^2 + P_3^2) + P_3^4(P_1^2 + P_2^2)] \\ & + \alpha_{123}P_1^2P_2^2P_3^2. \end{aligned} \quad (2)$$

where α_1 is the dielectric stiffness, and α_{11}, α_{12}, α_{111}, α_{112}, and α_{123} are higher-order dielectric stiffness. The dielectric stiffness α_1 is given a linear temperature dependence based on the Curie–Weiss law:

$$\alpha_1 = (T - T_0)/2\kappa_0 C_0, \quad (3)$$

where T and T_0 denote the temperature and the Curie–Weiss temperature, respectively, C_0 denotes the Curie constant, and κ_0 is the dielectric constant of a vacuum [64]. The gradient energy density [65] in the second term of Eq. (1) is given by:

$$\begin{aligned} f_{\text{grad}} = {} & \frac{1}{2}G_{11}(P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2) + G_{12}(P_{1,1}P_{2,2} + P_{2,2}P_{3,3} + P_{3,3}P_{1,1}) \\ & + \frac{1}{2}G_{44}[(P_{1,2} + P_{2,1})^2 + (P_{2,3} + P_{3,2})^2 + (P_{1,3} + P_{3,1})^2] \\ & + \frac{1}{2}G'_{44}[(P_{1,2} - P_{2,1})^2 + (P_{2,3} - P_{3,2})^2 + (P_{3,1} - P_{1,3})^2], \end{aligned} \quad (4)$$

where G_{11}, G_{12}, G_{44}, and G'_{44} are the gradient energy coefficients, and $P_{i,j} = \partial P_i/\partial x_j$ denotes the derivative of the ith component of the polarization vector P_i, with respect to the jth coordinate x_j, and $i,j = 1, 2, 3$. The gradient energy represents the energy penalty for inhomogeneous spatial distribution of the polarization in a ferroelectric system, such as domain walls. The elastic energy density is a pure mechanical strain energy:

$$\begin{aligned} f_{\text{elas}} = {} & \frac{1}{2}c_{11}(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + c_{12}(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{22}\varepsilon_{33} + \varepsilon_{33}\varepsilon_{11}) \\ & + 2c_{44}(\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2), \end{aligned} \quad (5)$$

where c_{11}, c_{12}, and c_{44} are the elastic constants, and ε_{ij} is the elastic strain. The fourth term of Eq. (1) represents the energy density of piezoelectric coupling between the spontaneous polarization and mechanical strain, and is given by [63]:

$$\begin{aligned} f_{\text{coup}} = {} & -q_{11}(\varepsilon_{11}P_1^2 + \varepsilon_{22}P_2^2 + \varepsilon_{33}P_3^2) - 2q_{12}[\varepsilon_{11}(P_2^2 + P_3^2) \\ & + \varepsilon_{22}(P_1^2 + P_3^2) + \varepsilon_{33}(P_1^2 + P_2^2)] \\ & - 2q_{44}(\varepsilon_{12}P_1P_2 + \varepsilon_{13}P_1P_3 + \varepsilon_{23}P_2P_3), \end{aligned} \quad (6)$$