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強鐵性材料大應變之開發研究 (2/2)

A Novel Approach to Large Strain in Ferroelectrics (2/2)

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中文摘要

強電性材料乃主動材料中的一種，具有多種相變狀態和由此引發的非線性現象。經由微觀結構或晶域排列的控制，超大應變之開發是極具可行性。本研究計劃藉由能量最小原理，成功發展出一理論模型來解釋強電性材料的行為。透過此一模型，吾人可預測單晶強電材料之晶域排列與其宏觀行為。我們證明晶域轉變所需之最小能量路徑與超大應變致動器開發亦可由本模型求得，同時我們發現所得之結果與實驗觀察之應變非常吻合。

NSC PROGRESS REPORT

A Novel Approach to Large Strain in Ferroelectrics (2/2)

Project Number: NSC 90-2212-E-002-189

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1 Abstract

Ferroelectrics are one of active materials which can exploit various phase transformations and other inherently nonlinear phenomenon. This gives rise to unusually large strain by manipulating their microstructure or domain patterns via electric field and load. We have developed a model to study the behavior of ferroelectrics based on energy minimization. Using this model, we have examined the domain patterns and the macroscopic behavior of single crystals of ferroelectric material. A low-energy path is identified for domain switching and a novel configuration that yields very large electrostriction is identified.

2 Introduction

Ferroelectric crystals are widely used in a variety of applications including transducers, capacitors, and non-volatile data storage elements [3]. In particular, poled ceramics of ferroelectric materials are used commonly for their piezoelectric property in actuator applications. Their many advantages include a linear response of the induced strain to applied electric field, very little hysteresis and very high frequency response. The strains and displacements that they display, however, are quite small. An improvement in the strain-level would lead to an explosion of the applications of these materials as miniature solid-state actuators and sensors in a variety of structural applications. It has recently been recognized that it is possible to obtain large strains through electrostriction in single crystals [2].

We study the domain patterns and the macroscopic properties of single crystals of ferroelectrics, and proposes a new way of obtaining large electrostriction. We first propose a variational theory that describes the behavior of a ferroelectric single crystal. We write the total energy of the crystal as a sum of the free (or stored) energy, the energy of the applied electrical and mechanical loads, the energy of the induced electric field and the domain wall energy; and the state of the ferroelectric crystal is obtained as minimizers of this total energy. The stored energy density encodes phenomenologically the information that the crystal prefers a few given spontaneously polarized and distorted states, and can be non-convex with multiple wells due to the presence of multiple such states. We allow for finite deformations in this model which are quite important as the strains become large. In addition, we carefully account for the energy of the electric field, both applied and induced. This turns out to be quite important in deciding between different shaped specimens. Finally, we do not restrict ourselves to polynomials but use very general functions and impose only the conditions required by symmetry.

We show that energy minimization based on this theory automatically leads to domain patterns, and accurately predicts the observed domain patterns in common ferroelectric materials based on very few parameters. In addition, we study electrostriction through domain switching, and propose a novel large strain actuator using a carefully chosen configuration and electro-mechanical loading path. The basic idea is that domain switching can give rise to large strains, and this can be enabled by a suitable geometry and electro-mechanical loading path. The predictions of our theory have been recently verified experimentally by [1] in BaTiO$_3$ single crystals, and show an excellent match compared to their experiment.

3 Continuum Model

3.1 Energy of a Single Crystal

Consider a ferroelectric single crystal occupying a region Ω in its reference configuration. Since we anticipate large strains, we use the setting of finite deformations. The deformation of this crystal is $\mathbf{y}(\mathbf{x})$ where $\mathbf{x}$ is a typical material point and the polarization $\mathbf{p}(\mathbf{y})$. Note that it is natural to define the polarization in the current configuration; however, we shall use its "pull-back" $\mathbf{P}(\mathbf{x}) = \mathbf{p}(\mathbf{y}(\mathbf{x}))$ sometimes.

Suppose this crystal is subjected to an external electric field $\mathbf{e}_0$ and a dead load corresponding to nominal stress $\mathbf{T}_0$. Then the total energy of the single crystal at temperature θ undergoing a deformation $\mathbf{y}(\mathbf{x})$ and polarization $\mathbf{p}(\mathbf{y})$ is given by

$$\begin{aligned} & \mathcal{E}_\theta(\mathbf{y},\mathbf{p}) \\ = & \int_\Omega \left\{ \frac{1}{2} \nabla_\mathbf{x}\mathbf{P} \cdot \mathbf{A}\nabla_\mathbf{x}\mathbf{P} + W(\nabla_\mathbf{x}\mathbf{y}, \mathbf{p}, \theta) \right. \\ - & \left. \mathbf{e}_0 \cdot \mathbf{p}\,(\det \nabla_\mathbf{x}\,\mathbf{y}) - \mathbf{T}_0 \cdot \nabla_\mathbf{x}\,\mathbf{y} \right\} d\mathbf{x} \\ + & \frac{\epsilon_0}{2} \int_{\mathbb{R}^3} |\nabla_\mathbf{y}\phi|^2 d\mathbf{y}, \end{aligned} \tag{1}$$

where $\mathbf{A}$ is the positive definite second order tensor, $\nabla_\mathbf{x}$ and $\nabla_\mathbf{y}$ are the gradient operators with respect to the reference and current configurations, W is the stored energy density of the crystal, $\epsilon_0 = 8.85 \times 10^{-12} \frac{\mathrm{C}^2}{\mathrm{N \cdot m^2}}$ is the coefficient of permittivity of the free space, and $\phi(\mathbf{y})$ is the electric potential such that the electric self-field is

$$\mathbf{e}(\mathbf{y}) = -\nabla_\mathbf{y}\,\phi(\mathbf{y}).$$

Above, the electric potential ϕ must satisfy the Maxwell's equation

$$\nabla_\mathbf{y} \cdot (-\epsilon_0 \nabla_\mathbf{y}\,\phi + \mathbf{p}\,\chi_{\mathbf{y}(\Omega)}) = \rho_f \quad \text{on} \quad \mathbb{R}^3, \tag{2}$$

where ρ_f is the free charge density and $\chi_A(\mathbf{y})$ is the characteristic function such that $\chi_A(\mathbf{y}) = 1$ if $\mathbf{y} \in A$ and $\chi_A(\mathbf{y}) = 0$ if $\mathbf{y} \in \mathbb{R}^3 \backslash A$.

We find the deformation and the polarization by minimizing the total energy over all possible deformations $\mathbf{y}$ and polarization $\mathbf{p}$.

4 Application to Design of Large Strain Actuators

4.1 Flat Plate Configuration

Consider a ferroelectric crystal in the shape of a flat plate with electrodes on the two faces as shown in Figure 1. Let $\Omega^{(h)}$ be the reference domain of the crystal:

$$\Omega^{(h)} = \{\mathbf{x} \in \mathbb{R}^3 : (x_1, x_2) \in S, \quad 0 < x_3 < h\}, \tag{3}$$

where S is the cross-section (bounded Lipschitz domain in two dimensions), h is the thickness of the ferroelectric plate, and $\{x_1, x_2, x_3\}$ is relative to an orthonormal reference basis $\{\boldsymbol{\xi}_1, \boldsymbol{\xi}_2, \boldsymbol{\xi}_3\}$. A uniaxial compressive stress and an electric field are applied to the crystal as also shown in Figure 1. We show that if the thickness of the crystal is much smaller than the

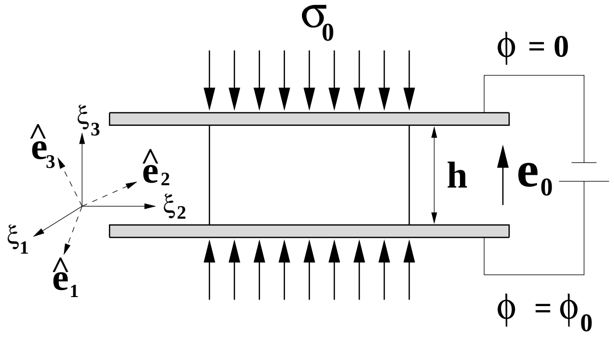

Figure 1: A ferroelectric crystal in the shape of a flat plate subject to uniaxial compressive stress with magnitude σ_0 and electric field $\mathbf{e}_0$ obtained from a potential ϕ_0. The physical and crystal bases are $\boldsymbol{\xi}_i$ and $\hat{\mathbf{e}}_i$ as shown.

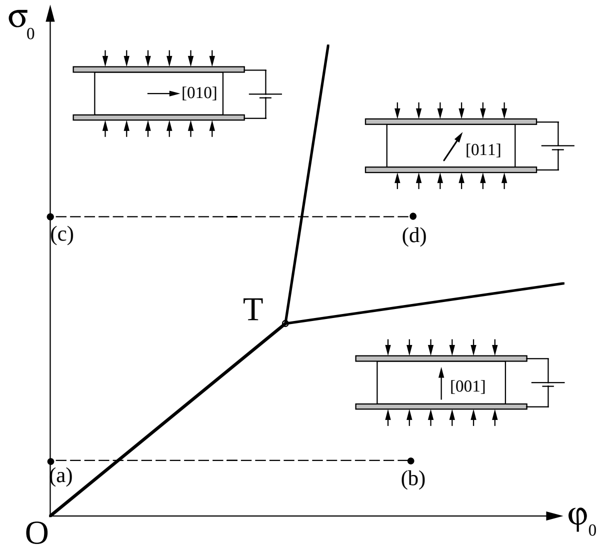

Figure 2: The field-stress phase diagram at room temperature for BaTiO$_3$. The basic experimental idea is to apply a constant load and varying electric field to traverse the dashed lines (a)-(b) or (c)-(d).

lateral size and we apply a fixed electric field $\mathbf{e}_0$ and mechanical load derived from a constant tensor $\mathbf{T}_0$; i.e., $\mathbf{t}_0 = \mathbf{T}_0\hat{\mathbf{n}}$ on $\partial\Omega$, then we can find the state of the crystal by minimizing the much simpler function

$$G(\mathbf{F},\mathbf{p};\mathbf{e}_0,\mathbf{T}_0) = W(\mathbf{F},\mathbf{p}) - \mathbf{e}_0 \cdot \mathbf{p}\,(\det\mathbf{F}) - \mathbf{T}_0 \cdot \mathbf{F} \quad (4)$$

instead of the functional $\mathcal{E}$ defined in (1).

The idea behind replacing $\mathcal{E}$ by G is the following. For the configuration under consideration, the electrostatic energy is negligible since the ferroelectric is shielded on the top and bottom faces, and the lateral surface is of negligible area. Furthermore, the minimizers are not forced to refine in the absence of the electric field, and therefore even the exchange energy is negligible. We are left with an integral over the body, which is minimized when the integrand (4) is minimized.

4.2 Phase Diagram

The energy density W has multiple wells as described in Section 2. The function G inherits this multi-well structure; however, the heights of the individual wells are controlled by the applied loads σ_0 and ϕ_0. In particular, G does not satisfy the material symmetry condition, and thus the different variants do not necessarily have the same energy. In short, the applied fields and loads can bias one variant over others; similarly it can change the transformation temperatures. This information can be summarized in a "$\sigma_0 - \phi_0$ phase diagram" which shows the variant that minimizes G for a given pair (σ_0, ϕ_0).

For example, consider a BaTiO$_3$ single crystal at room temperature oriented such that the pseudo-cubic [001] axis is normal to the plate (i.e., the crystal axes $\{\hat{\mathbf{e}}_i\}$ coincides with the physical axes $\{\boldsymbol{\xi}_i\}$). The phase diagram is shown schematically in Figure 2. All tetragonal variants are equally preferred in the absence of applied field and load (at the point O). If we apply a moderate field and a small load as in (b), the crystal prefers the [001] polarized state; in contrast if we apply a moderate load and a small field as in (a), the crystal prefers either a [100] or a [010] polarized state. The exchange of stability takes place across the line OT. Finally, if we apply a very large field and load as in (d), the crystal transforms to the orthorhombic phase and is either [101] or [011] polarized. Note that T is the triple point where all the different states have equal energy. The details of this

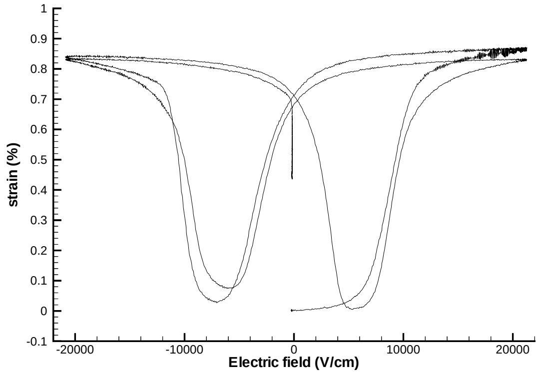

Figure 3: Experimental observation of actuation strain versus various electric voltage for $BaTiO_3$. A constant uniaxial compressive stress with magnitude about 3.5 MPa is applied on the specimen.

phase diagram and others for different temperatures and different crystal orientations will be presented elsewhere.

4.3 Comparison with Experiment

Burcsu *et al* [1] have designed and built an experimental setup to apply a constant mechanical load and variable electric field. They use a [001] oriented single crystal (approximately 5mm × 5mm × 1mm) as suggested by the theoretical considerations above, apply a loading along the path $(a)-(b)$ (see Figure 2) and measure the strain. Their experimental result is shown in Figure 3. Notice that the strain is almost 0.9% for moderate fields of about 2 KV/mm, and that this is close to the theoretically predicted value of 1.1%. We do not know the reason for this small discrepancy at this moment, but speculate the following. First, our theory finds absolute minimum while the material has to follow a suitable kinetic path which may get trapped in local minimum. Second, the aspect ratio of the thickness to the lateral size of the specimen is 1:5 which may not be small enough to make the electrostatic end fields negligible. Further, there is some electric leakage on the electrodes in reality, giving rise to incomplete charge compensation. If the leakage is significant, the neglect of the depolarization energy is questionable. Finally, the specimen is not defect-free: some microcracks extending from the edges to the center of the specimen were observed prior to the experiment. This would cause electric concentration around the crack tips which in turn could change the patterns of polarization switch. In any case, the agreement is encouraging and these specific issues will be addressed in future work.

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