Finite-element modeling of ferroelectric material behavior at morphotropic phase boundaries between tetragonal, rhombohedric and orthorhombic phases

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Abstract. The nonlinear response of ferroelectric/ferroelastic material below the Curie temperature is analyzed at morphotropic phase boundaries with account of tetragonal, rhombohedral and orthorhombic phases. The results are obtained by means of finite-element homogenization with using the micromechanical model taking into account the dissipative nature of the domain wall motion. The results of simulation have revealed the extremal values of spontaneous polarization and remanent strain at morphotropic phase boundaries for the tetragonal/rhombohedral and tetragonal/orthorhombic compositions.

1. Introduction

Lead-free ferroelectric/ferroelastic materials are among the most actively studied classes of materials up to date due to several reasons. Firstly, because of a wide range of applications of these materials in industries from automotive to microelectronics. Secondly, it is the environmental friendliness of lead-free ferroics compared to the more common ceramics based on lead titanate-zirconate (PZT) [1]. Thirdly, there is no overall acclaimed theory of the nonlinear behavior of ferroelectroelastic materials as well as there is no software product that allows computations of nonlinear ferroelectroelastic boundary value problems [2]. However, it was found that ceramics based on barium titanate and other lead-free perovskites taken close to the morphotropic phase boundary (MPB) depict piezoelectric and dielectric response at the levels compared to PZT ceramics.

The main objective of the study is to evaluate the ability of computational micromechanical models to predict the properties of multiphase polydomain ferroelectric materials with aim to be used in domain engineering and microstructural design of lead-free ferroelectric/ferroelastic materials.

2. Hysteresis behavior modeling

An algorithm for simulation of the ferroelectroelastic nonlinear behavior of materials close to the MPB that utilize the proposed earlier micromechanical model [3-8] based on the dissipative nature of the motion of domain walls is implemented into CES program (Constitutive Equation Studio) [9]. Even though, this model doesn’t take into account interphase transitions due to their complex physical mechanism, it allows the calculations for tetragonal, rhombohedral and orthorhombic phases, two- and three-phase mixtures with constant phase composition [10]. The possibilities for two-phase calculations are presented further.
In the general case in three-phase material, there are 26 domains: 6 tetragonal, 8 rhombohedral and 12 orthorhombic (see figure 1). The model assumes that all crystal cells of the same phase oriented in the same direction are combined into one domain. Each domain $I$ is described by a volume fraction $c_I$. There are possible 218 different switching processes in the considered model without the phase transitions.

![Figure 1. Possible polarization orientations in unit cell: (a) tetragonal system with 6 crystal variants; (b) orthorhombic system with 12 variants; (c) rhombohedral system with 8 variants.](image)

Constitutive equations for the crystal were obtained by averaging the strain fields (tensor $\varepsilon$) and dielectric displacements (vector $D$) under the condition of homogeneous fields of mechanical stresses (tensor $\sigma$) and electric field (vector $E$) (Reuss homogenization) [4]:

$$
\left\{ \begin{array}{l}
\varepsilon' \\
D'
\end{array} \right\} = \sum_{I=1}^{M} c_I \left( \begin{array}{c}
\frac{4}{3} S^E_i \cdot d_i^j \cdot \kappa_i^\sigma \\
E
\end{array} \right) \cdot \left\{ \begin{array}{l}
\varepsilon'_I \\
P'_I
\end{array} \right\} = \sum_{I=1}^{M} c_I \left( \begin{array}{c}
\frac{4}{3} S^E_i \cdot d_i^j \cdot \kappa_i^\sigma \\
E
\end{array} \right) \cdot \left\{ \begin{array}{l}
\varepsilon' \\
P'
\end{array} \right\},
$$

where $\frac{4}{3} S^E_i \cdot d_i^j \cdot \kappa_i^\sigma$ are tensors of compliance, piezoelectric coefficients and dielectric constants, corresponding to the $I$-th domain.

The evolution equations for the volume-averaged crystallite tensor of residual deformation $\varepsilon'$ and the polarization vector $P'$ are [4]:

$$
\left\{ \begin{array}{l}
\varepsilon' \\
P'
\end{array} \right\} = \sum_{I=1}^{M} \dot{c}_I \left\{ \begin{array}{l}
\varepsilon'_I \\
P'_I
\end{array} \right\} = \sum_{a=1}^{N} \dot{f}_a \left\{ \begin{array}{l}
\mu_{\alpha} \gamma_{a} \\
S_{a} P_{a}
\end{array} \right\},
$$

where $N$ is the number of possible transitions $\alpha$ from the $I$-th system to the $J$-th; $\mu_{\alpha}$ and $S_{a}$ are Schmidt tensor and vector, $\gamma_{a}, P_{a}$ are the shift and increment of polarization corresponding to the $\alpha$ transition; $\dot{f}_a$ is a function that determines the transition rate, depending on the driving force $G_{a}$ and volume fraction $c_I$, that is introduced by analogy with visco-plasticity [4]:

$$
\dot{f}_a = \dot{f}_0 \frac{G_{a}}{G_{c}} \left( \frac{c_I}{c_0} \right)^m,
$$
where $G_c = \mathbf{\sigma} \cdot \mathbf{\mu}_a \gamma_a + \mathbf{E} \cdot \mathbf{s}_a P_a + \mathbf{\sigma} \cdot \Delta \mathbf{d} \cdot \mathbf{E}$ is the driving force, $\dot{f}_0$, $G_c$, $n$, $m$, $c_0$ are material constants, $P_a$ and $\gamma_a$ are elementary cell unit spontaneous polarization and strain in ferroelectric state.

### 3. Model parameters

The parameters of the material model (1)-(3) such as $n$, $m$, $c_0$, $P_a$ and $\gamma_a$ for each phase separately and 9 $G_c$ parameters for all the possible types of ferroelectric switching ($90^\circ$ and $180^\circ$ for tetragonal phase; $71^\circ$, $109^\circ$ and $180^\circ$ for rhombohedral; $60^\circ$, $90^\circ$, $120^\circ$ and $180^\circ$ for orthorhombic) are to be defined. In the present studies for the reasons of simplicity $n$, $m$, $c_0$, $P_a$ and $\gamma_a$ for all three phases were taken the equal.

#### Table 1. Model parameters.

| $P_a$, C/m$^2$ | 0.5 |
|----------------|-----|
| $\gamma_a$    | 0.002 |
| $n$            | 10 |
| $m$            | 1 |
| $c_0$          | 0.01 |
| $G_c$, MPa     | 0.5 |
| $f_0$          | 1 |

#### Table 2. Material parameters.

| $d_{33}$, m/V | 1.57e-10 |
|---------------|-----------|
| $d_{31}$, m/V | 8e-011    |
| $d_{15}$, m/V | 1.94e-010 |
| $k_{33}$, F/m | 2.51e-008 |
| $E_1$, N/m$^2$ | 9.26e+010 |
| $v_{12}$      | 0.304 |
| $d_{33}$, m/V | 1.57e-10 |

Due to geometrical reasons the driving force constants for tetragonal, rhombohedral and orthorhombic phases switching directions might be connected with further equations:

$$
\begin{align*}
2G_c^{90,Tet} = G_c^{180,Tet} \\
\frac{1}{\sqrt{2}}G_c^{109,Rh} = G_c^{71,Rh} = G_c^{180,Rh} \\
\frac{2\sqrt{2}}{\sqrt{3}}G_c^{120,Orth} = G_c^{60,Orth} = G_c^{90,Orth} = G_c^{180,Orth}
\end{align*}
$$

(4)

To reduce the number of model parameters the assumption can be made that not only the parameters for one each phase are connected but those of different phases are connected as well. Such is the equality of the lower angle switching $G_c$ for three phases:

$$
G_c^{90,Tet} = G_c^{71,Rh} = G_c^{60,Orth} = G_c^{90,Orth} = G_c^{180,Orth}
$$

(5)

By assuming so all 9 $G_c$ parameters can be calculated through $\overline{G}_c$. Thus, the number of model parameters that describe nonlinear ferroelectric behavior is reduced to 6 mentioned in table 1. The material parameters that describe elastic behavior are collected in table 2.

### 4. Finite-element modeling

The results are obtained by means of finite-element homogenization method [11] with using the micromechanical model (1)-(3). The finite-element formulation of the ferroelectroelastic problem for the representative volume element of polycrystalline material allows taking into account the interaction between crystals that increases the accuracy of predictions of the model. The finite element program PANTOCRATOR v.7.19 [12] is applied for the solution of fully coupled nonlinear electromechanical problem with help of the vector potential formulation [13-15]. Three ferroelectric phases are simulated independently with no interphase transitions allowed.
A number of finite-element model boundary problems for two-phase compounds with varying phase fractions was solved. Each compound is described by $V_f$ parameter, which is the volume fraction of one phase in the two-phase compound: tetragonal ($V_T$) if tetragonal/rhombohedral or tetragonal/orthorhombic composition is studied, and orthorhombic ($V_R$) for rhombohedral/orthorhombic.

The cubic representative volume element of the polycrystalline material was modeled, divided onto 27 finite elements (216 crystals with random generated orientations) and loaded with the alternating electric field in the direction [001] with the triangular form of wave and the magnitude of $E = 2$ MV/m and the frequency $f = 0.025$ Hz. Figure 2 illustrates the axial remanent polarization and strain field distributions in a representative volume element under unloading.

![Figure 2](image.png)

**Figure 2.** Remanent polarization (a) and strain (b) in the 3x3x3 representative volume element under unloading after loading until $E = 2$ MV/m.

5. Results and discussion

Three series of hysteresis curves obtained for two-phases compositions are shown in figure 3 from which the general parameters such as remanent polarization $P_r$ and coercive electric field $E_c$ can be taken, which are shown in figure 4 and 5.

Thus, figure 4 and 5 depict that the maximum of $P_r$ is obtained in the tetragonal/rhombohedral system with the volume fraction of tetragonal phase being equal to $V_T = 0.2$; in the tetragonal/orthorhombic system it is obtained at $V_T = 0.4$; though, the rhombohedral/orthorhombic system shows the monotonic dependence of $P_r$ from $V_O$. It can be assumed that these obtained maximums correspond to the state of material close to MPB.

The coercive field changes monotonically with the change of phase fractions in compound from rhombohedral phase to orthorhombic and then to tetragonal.

The obtained numerically effect of extremal values of spontaneous polarization and remanent strain in the nearness of morphotropic phase boundaries is consistent with results observed in experiments [16, 17]. That points out the abilities of considered approach based on combination of finite-element homogenization with multiphase micromechanical models to predict the effect of phase combination on the properties of ferroelectric materials.

The absence of maximum in the rhombohedral/orthorhombic system might be explained by the inconsistency of model parameters or model assumptions, such as driving force constants connectivity (4)-(5). However, this leads to the problem of the parameters identification for the juxtaposition of the model predictions with physical experiments. This problem gets much more complicated when assumptions (4)-(5) are rejected and the number of parameters increase dramatically, even though it arise the prediction possibilities of the model.
The prospect for future work includes several main directions which are the model parameters identification, studying of three-phase MPBs and technical applications simulation.

Figure 3. Hysteresises for tetragonal/rhombohedral (a), tetragonal/orthorhombic (b) and orthorhombic/rhombohedral (c) phase compositions.

Figure 4. Dependence of remanent polarization $P_r$ on volume fractions for different phase compositions.

Figure 5. Dependence of coercive electric field $E_c$ on volume fractions for different phase compositions.

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