VISCOPLASTIC MODELS FOR FERROELECTRIC CERAMICS

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Abstract

Nonlinear hysteretic phenomena in polycrystalline ferroelectric ceramics are simulated using viscoplastic (rate-dependent) models without a switching condition. Viscoplastic models describe the domain structure evolution effectively: in terms of rate equations for the volume fractions of orientation variants. The results of a comparative study of two viscoplastic models for polycrystalline ferroelectrics undergoing a cubic-to-tetragonal phase transition are discussed. Both models allow for 90° and 180° polarization switching, but differ in the number of accessible domain orientations, which is six and forty-two, respectively. While the model with six polarization orientations provides a reasonable description of ferroelectric ceramics under uni-axial loading, the model with forty-two orientations reproduces the typical isotropic behaviour of polycrystalline materials and can be parameterized for multi-axial loading. Examples of the viscoplastic models application to rate-dependent phenomena in soft PZT ceramics and to a 3D finite element analysis of microstructural inhomogeneities in ferroelectric multi-layer films are given.

Keywords: B Defects; C Ferroelectric properties; C Plasticity; D PZT; Modelling

1. Introduction

The polarization switching in ferroelectric crystals is a kinetic process. It is determined by the kinetics of the processes occurring on the atomic level, such as the motion of domain walls in the potential relief of various obstacles. Commonly, the polarization switching criteria for

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ferroelectrics are formulated in terms of a critical field or energy release (driving force) [1-2] necessary for domain reorientation. There are also attempts [3] to describe the response of ferroelectrics to multi-axial loading using a *yield* or *switching* surface (in the combined electric field and stress space), within which switching does not occur. Although such time-independent models can reproduce many important features of the switching process, strictly speaking, due to the thermally activated nature of domain wall motion, this description is valid only at 0 K. The experimental data [4-5] show that in soft PZT ceramics the rate effects are pronounced already at electric field frequencies of 0.1-1.0 Hz. Therefore, the time scale for the rate dependent processes in these materials corresponds to seconds. In the present study the rate dependence of the domain reversal is simulated using a viscoplastic model. Its functional form is similar to that used in [3]. The difference between the two models is in the number of accessible polarization directions used to reproduce the isotropic response of a polycrystal.

2. Viscoplastic model: physical background

Taking into account the thermally activated character of the domain wall motion in ferroelectrics, one can formulate a *viscoplastic model* without a switching criterion. We consider a ferroelectric material with n orientation states (variants), for example, n = 6 for tetragonal materials. Each variant r is characterized by its volume fraction ξ_r. The decrease in the volume fraction of the r-type domains with time (transformation rate) due to their switching into a more energetically favourable state s is expressed by an Arrhenius type kinetic equation

$$\dot{\xi}_{rs} = \rho_{rs} < S > V_c \exp\left[-\frac{\Delta G(\boldsymbol{E},\boldsymbol{\sigma})}{kT}\right], \tag{1}$$

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where ρ_{rs} is the density of the mobile domain walls separating the *r*- and *s*-type domains (transformation system), ΔG is the Gibbs free energy required for a domain wall to overcome an obstacle (activation energy), V_c and $< S >$ are the wall velocity at zero activation energy and its average area, respectively. The activation energy strongly depends on the nature of pinning defects and is to be found from atomic scale calculations. However, like in the case of dislocation plasticity limited by discrete obstacles, one can use some empirical expressions for ΔG. Here, we suggest that it depends on the components of the electric field $\boldsymbol{E}$ and stress tensor $\boldsymbol{\sigma}$ only via the driving force $f_{rs} > 0$ for the domain switching. Following [6], one has

$$\mathit{\Delta} G(\boldsymbol{E},\boldsymbol{\sigma}) = \mathit{\Delta} G_0(1-(f_{rs} / f_c)^p), \tag{2}$$

where ΔG_0 is the activation energy at zero driving force, f_c is the obstacle strength and the parameter *p* characterises the obstacle shape. The parameters $\mathit{\Delta} G_0$, f_c, and *p* in eqn. (2) depend on the domain wall type. In tetragonal ferroelectrics there are six variants and two types of domain walls, which correspond to 90° and 180° domain switching. Therefore in this case one needs two sets of the parameters. As $f_{rs} \to f_c$, the approximation (2) yields for the transformation rate a power-law (viscoplastic) form

$$\dot{\upsilon}_{rs} = \dot{\upsilon}_c \left(\frac{f_{rs}}{f_c} \right)^m . \tag{3}$$

The viscoplastic index $m = p\Delta G_0 / kT$ decreases with increasing temperature. Typically $m >> 1$ and the power-law (3) provides a reasonable approximation for $\dot{\upsilon}_{rs}$ in the whole range $0 \le f_{rs} \le f_c$. In the athermal regime ($f_{rs} > f_c$) the viscoplastic law fails and a pure viscous dependency $\dot{\upsilon}_c \sim f_{rs}$ seems to be more pertinent. However, the power-law form may be useful also in this case, though the index *m* cannot be longer considered as a temperature dependent parameter. We further assume that the factor $\dot{\upsilon}_c$ in eqn. (3), which depend on the domain structure, can be expressed in terms of the volume fraction ξ_r of the *r*-domains. According to [3], saturation of a transformation system rs is controlled by the volume fraction ξ_r. Hence, the transformation rate $\dot{v}_{rs}$ can be written in the form

$$\dot{v}_{rs} = \dot{v}_c \left(\frac{f_{rs}}{f_c} \right)^m \left(\frac{\xi_r}{\xi_0} \right)^\alpha \tag{4}$$

and is vanishing as $\xi_r \to 0$. The parameter $\dot{v}_c$ in eqn. (4) now is independent of the domain structure. In fact, the analysis described above concerns a single polydomain grain with *n* orientation variants consistent with symmetry change in the phase transition from paraelectric to ferroelectric state. In polycrystalline ceramics one has a random distribution of grain orientations described by a continuous function. Here two discrete approximations (models I and II) for this function will be used. While the model I is based on one system of six variants and corresponds to one possible grain orientation in the paraelectric cubic phase, the model II employs seven systems of six variants in each. The total number of accessible polarization directions in the model II is forty-two. However, there is no polarization switching between orientation variants, which belong to different systems. The relative arrangement of domains in both models is shown in Fig.1.

3. Rate effects

Under uni-axial electrical loading $E_3 = E \sin \omega t$ the driving force f_{rs} in the model I reduces to $2P^s E_3$ or $P^s E_3$ for 180° or 90° domain switching, respectively, where the spontaneous polarization P^s is a model parameter. For calibration of the viscoplastic models it is convenient to introduce two parameters $\omega^{(90)} = \dot{v}_c^{(90)} (P^s E_0 / f_c^{(90)})^m$ and $\omega^{(180)} = \dot{v}_c^{(180)} (2P^s E_0 / f_c^{(180)})^m$ with a dimension of frequency. These parameters

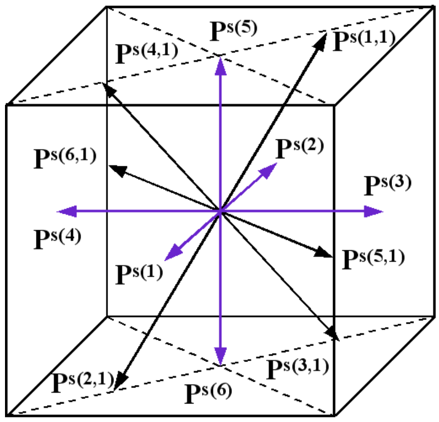

Fig. 1. Polarization directions in the models I and II. Six polarization orientations $P^{s(r)}$ (r = 1,…,6) of the model I are situated along the cube axes (x_1, x_2, x_3). In the model II six additional sets of polarization $P^{s(r,n)}$ (r, n = 1,…,6) are situated in the diagonal planes of the cube. Only one set $P^{s(r,1)}$ is shown. The remaining five sets are related to other diagonal planes.

characterize the effective mobilities of the 180° and 90° domain walls under a reference electric field with amplitude E_0. The dependence of the wall mobilities on an electric field amplitude E is given by a power-law $\sim (E/E_0)^m$. In this study the value of 2.0 MV/m is used for both E_0 and E. The simulated strain hysteresis curves for the frequencies of 0.01, 0.1 and 1.0 Hz are shown in Fig. 2. The model I was parameterised to reproduce qualitatively the experimental data [4] of the commercial soft PZT piezoceramic PIC151 in the quasi-static regime with a frequency of 0.01 Hz. The model parameters have the following values: m = 8, α = 3, $\omega^{(90)}$ = 10 Hz and $\omega^{(180)}$ = 10 Hz (Parameter set 1). The corresponding experimental curves are shown in Fig. 3. The results of the simulations are in good agreement with experiment for the loading rates of 0.01 and 0.1 Hz. However, there is a discrepancy in prediction of the remnant strain (corresponding to E_3 = 0) at a frequency of 1.0 Hz. Although both the viscoplastic model and experiment show incomplete saturation of strain at the maximum field, the dependence of the remnant strain on frequency is different. The simulated remnant strain decreases with frequency, whereas in experiment [4] this behaviour is observed only at electric field amplitude of 1.0 MV/m. Better agreement between simulated and measured strain curves at $\omega = 1.0$ Hz is achieved by changing the value of α in the Parameter set 1 from 3.0 to 0.8 (Parameter set 2). The strain hysteresis curves for two sets of parameters are shown in Fig. 4. Interestingly, the polarization reversal in the viscoplastic model is achieved mostly by two 90° switching. However the minimum strain remains positive.

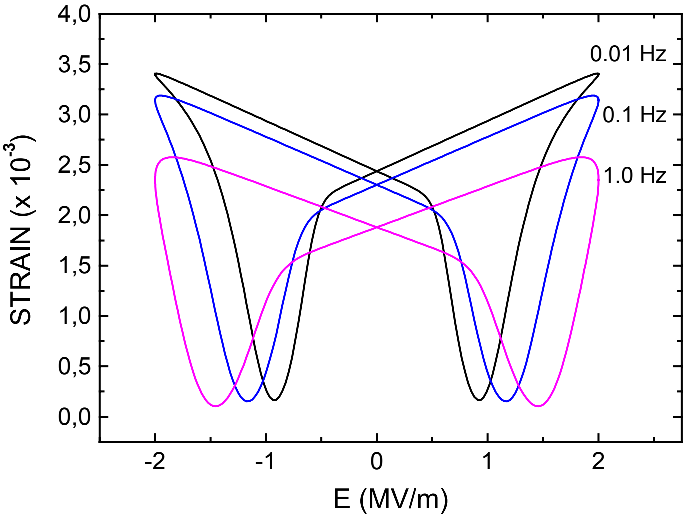

Fig. 2. Strain versus sinusoidal electric field hysteresis curves simulated for the loading rates of 0.01, 0.1 and 1.0 Hz (Parameter set 1).

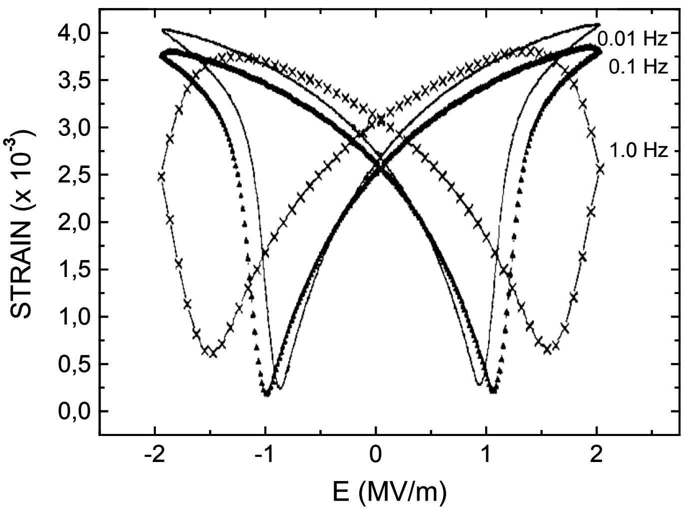

Fig. 3. Strain versus triangular electric field hysteresis curves in commercial soft PZT piezoceramic PIC151 for the loading rates of 0.01, 0.1 and 1.0 Hz according to [5].

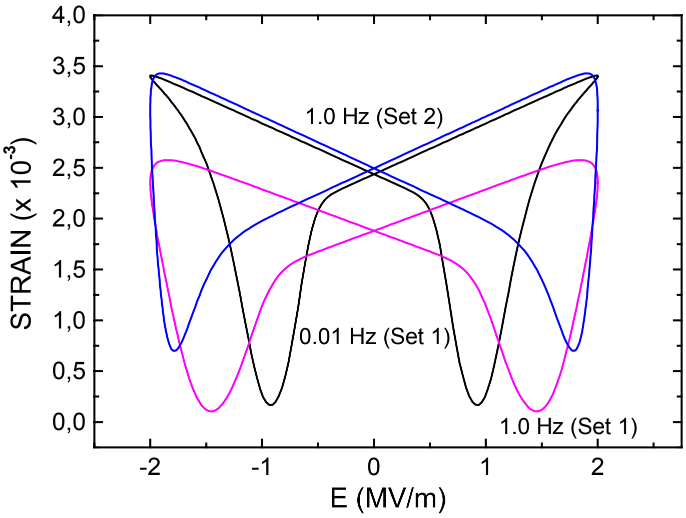

Fig. 4. Strain versus sinusoidal electric field hysteresis curves simulated at the loading rate of 1.0 Hz (Parameter sets 1 and 2). The strain hysteresis curve for $\omega = 0.01$ Hz and Parameter set 1 is added as a reference.

4. Multi-axial loading and finite element implementation

The response of ferroelectric ceramics described by the viscoplastic models I and II to multi-axial electrical loading was investigated for the following parameter set: $m = 8$, $\alpha = 3$, $\omega^{(90)} =$ 10 Hz and $\omega^{(180)} = 1$ Hz (Parameter set 3). The sinusoidal electric field with amplitude of 2.0 MV/m and a frequency of 0.01 Hz was applied at an angle θ to the polarization direction of one of the orientation variants (x_3-axis) as shown in Fig. 1. The projection of the remnant polarization on the direction of the electric field was calculated as a function of θ and the azimuth ϕ (in x_1x_2 plane). Since the material was initially in the unpoled state, this function should be isotropic. The results of the simulation presented in Fig. 5 for two values of ϕ clearly show that model 1 is too anisotropic and can describe the response of a polycrystal to multiaxial loadings only qualitatively. The difference between the maximum and minimum values of the remnant polarization in the model II does not exceed 20%, which is a considerable improvement over the model I.

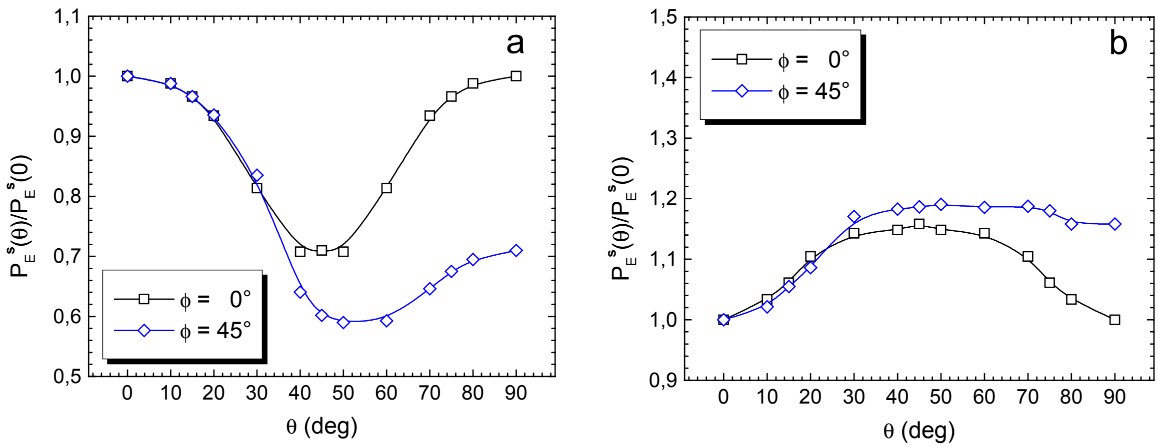

Fig. 5. Projection of remnant polarization on the electric field direction for the viscoplastic models with six (a) and forty-two (b) orientation variants.

The viscoplastic models can be applied to the analysis of local polarization distributions near inhomogeneities in PZT double-layer films consisting of a thin upper layer and a thick substrate film. Such films are of interest for application as a ferroelectric printing form and non-polarizable defects like pores can considerably influence the printing quality. As an unpoled double-layer film containing a pore is subjected to an electric loading perpendicular to the film plane, the poling process near the pore is hindered due to the electrical boundary condition on its surface. The resulting inhomogeneous polarization distribution depends on the pore size and depth, and also on the thin layer thickness. The non-linear analysis of the poling process was carried out using the viscoplastic model I with the Parameter set 3. The volume fractions of the orientation variants now depend on the spatial coordinates R and x_3 = Z due to the axial symmetry of the problem. The rate equations are integrated in time and at every time step the electric field and stress inside the film are found by solving an axially-symmetric electro-elastostatic problem. This is done numerically using a finite element code FlexPDE[7]. The material parameters are taken from [8]. The dielectric displacement distribution in the double-layer film upon unloading is illustrated in Fig. 6. The poling was performed by a sinusoidal electric field with a frequency of 0.1 Hz and total loading-unloading time was 31.4 s. For the geometrical parameters of this simulation, the material above the pore remains non-polarized upon unloading.

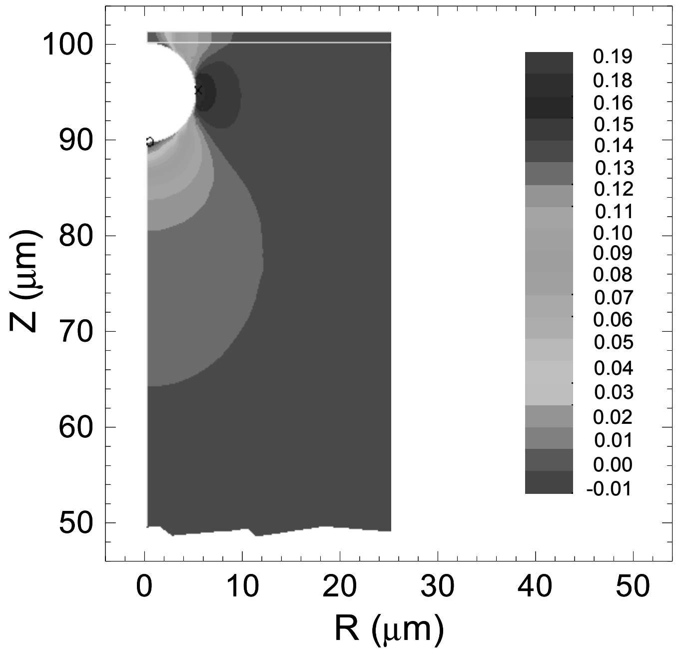

Fig. 6. Distribution of the dielectric displacement D_3 in a double-layer film with a pore. The values of D_3 are given in C/m^2. The thick film and thin layer have a thickness of 100 μm and 1 μm, respectively. The pore diameter is 10 μm and its depth below the thick film surface is 0.1 μm. The bottom surface was set to zero potential and the upper surface to the potential of –202 V, corresponding to the average electric field of 2.0 MV/m in the double-layer film.

5. Conclusion

Viscoplastic modelling is a computationally efficient approach to the analysis of nonlinear processes in ferroelectric ceramics, including rate-dependence of the polarization and strain hysteresis. A viscoplastic model with forty-two polarization orientations discussed here can reproduce with good accuracy isotropic behaviour inherent to polycrystalline materials with random distributions of grain orientations. Two viscoplastic models investigated here can describe the polarization reversal in terms of either one direct 180° domain switching or two consecutive 90° domain switchings. The relative significance of these two polarization reversal mechanisms is controlled only by a few parameters, which have to be found from experimental data. The efficiency of the viscoplastic models was demonstrated in a 3D finite element modelling of the poling process in ferroelectric films with defects.

Acknowledgements

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