A phase field study of frequency dependence and grain-size effects in nanocrystalline ferroelectric polycrystals

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Abstract—In this study we take the view that frequency dependence of ferroelectric hysteresis is a result of direct competition between the speed of polarization evolution and the speed of external loading. We used the Ginzburg–Landau kinetic equation to evaluate the evolution of polarization vectors. We also devised a polycrystal model with a core–shell grain configuration to reflect the effect of the grain-boundary (GB) affected zone. The phase-field results showed that the coercive field tended to increase with frequency, but remnant polarization increased only slightly while the dielectric constant and piezoelectric constant d_{33}, tended to decrease. We also found that, while both hysteresis and butterfly loops exhibited the familiar sharp tails at low frequencies, the tails disappeared and the loops became elliptic- and kidney-shaped, respectively, at high frequencies. The calculated low-frequency phenomena are widely supported by experiments, but the high-frequency ones are not commonly found in the literature. We substantiated both types of findings with details of the underlying domain dynamics. They clearly showed a complete 180° polarization reversal at low frequencies, but stopped mostly at 90° at high frequencies. We also examined the influence of the kinetic coefficient and the loading amplitude, and found that, as either increases, the elliptic and kidney shapes of the loops would occur at a higher frequency. The calculated grain-size effects indicated that the remnant polarization, dielectric constant, and d_{33} all decreased with decreasing grain size. This is again widely supported by experiments. But we also found that the grain-size effect of coercive field is more complicated. It may increase or decrease, and it is the magnitude of spontaneous polarization of the GB affected zone that determines its outcome.
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1. Introduction

Ferroelectric ceramics represent a unique class of multifunctional materials due to their strong electromechanical coupling and possession of domain variants. Due to the spontaneous polarization, the domain variants are metastable and may experience domain reorientation upon applied electric field or mechanical stress. The reorientation process leads to microstructural evolution and adds nonlinearity to the overall response. This process can be exploited to tune the coupled behavior to meet the desired functions. Domain reorientation – or more precisely the evolution of polarization vectors on a finer scale – is a kinetic process and inherently rate-dependent. As such, ferroelectric characteristics are naturally frequency-dependent. The study of frequency dependence in ferroelectrics has a long history that could be dated back to the experimental investigations of Wieder [1] and Pulvari and Kuebler [2] for single crystals, Song et al. [3] for thin films, and Viehland and

Chen [4], Lente et al. [5], and Eiras and Lente [6] for bulks, among others. A common feature of the reported data is that the coercive field tends to increase with loading frequency.

The dynamics of domain evolution in crystals is very complex. It is a spatially and temporally dependent microscopic process. In this study we take the view that frequency dependence in ferroelectric hysteresis is a result of direct competition between the speed of microstructural evolution and the speed of external loading. Due to its kinetic nature the speed of microstructural evolution tends to stay behind the speed of loading, but at low frequencies it can sufficiently catch up. At high frequencies, however, it could fall much behind. This will have strong implications on the frequency-dependence of coercive field and other characteristics. This sort of frequency dependence is unlike the frequency dependence in ordinary viscoelastic solids where microstructural evolution is not a factor and damping plays the key role.

To understand this complex phenomenon, we will adopt the time-dependent Ginzburg–Landau (TDGL) kinetic equation to evaluate the evolution of polarization vectors. This will be done in conjunction with the free energy

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density of Landau, Ginzburg, and Devonshire [7–9]. While the phase-field approach has been widely used to study various ferroelectric characteristics, the issue of frequency dependence differs from others in one significant way. In traditional phase-field modeling, the evolution of polarization vectors from TDGL is given as much time as needed to reach the equilibrium state, but this cannot be the case for the frequency study, especially at high frequencies. It turns out that, even with a sufficiently high magnitude of applied electric field, polarization reorientation could not always fully undergo the 180° switch, and in many cases it would stop at 90°. This has a profound effect on the shape of hysteresis and butterfly loops. In particular, it will be shown that the loops will exhibit the widely recognized sharp corners and tails under low frequencies, but they will turn into elliptic and kidney shapes respectively at high frequencies. We shall substantiate these findings with details of the underlying domain dynamics.

Our study of frequency dependence will be directed toward nanocrystalline ferroelectric polycrystals. This has the added advantage of providing some insights into this new subject. Due to the continuous desire of miniaturization of microelectronic devices, there is a dire need to understand the ferroelectric characteristics of nanocrystalline materials as the grain size decreases down to the nanometer range. As it is now possible to process dense $BaTiO_3$ ceramics within the grain size of 100 nm, this has become a realistic goal [10]. To study the grain-size effect, it is essential to consider the variation of grain structure near the grain boundary (GB). High resolution images of scanning transmission electron microscopy have indicated that grain boundaries were atomically sharp and crystallinity was well maintained right up to the boundary, but there existed a GB affected zone near the grain boundary with a weaker mechanical strength [11,12]. In ferroelectric ceramics, we consider the GB affected zone to be a layer with a lower dielectric constant and reduced spontaneous polarization. The "dead layer" model of Buscaglia et al. [13] could be considered as a special case that its spontaneous polarization is zero. The thickness of GB affected zone was reported to span over 7–10 atomic spacing and 1–3 nm for the dead layer. As will be shown later, the presence of GB affected zone is crucial to the grain-size effect of nanocrystalline materials.

In retrospect there is a large body of literature on the phase field studies of ferroelectrics. These include, among others, the works of Cao and Cross [14], Chen and his associates [15–21], Wang et al. [22], Wang and Zhang [23], and Hong et al. [24]. Additional contributions can also be found in Zhang and Bhattacharya [25,26], Su and Landis [27], Su and his associates [28–31], and Zhang et al. [32]. In the context of frequency dependence, the problem was considered in Zheng et al. [33], Xu et al. [34] and Zhou et al. [35], but only for the low frequency response of single crystals. The issue of grain-size dependence was considered only in Shu et al. [36] and Liu et al. [37]. The former used a four-square block model separated by cross channels of various widths to represent the nano-grained polycrystal, while the latter used a dielectric phase to represent the grain boundary. It has become evident that the general characteristics of frequency dependence spanning over the low and high frequency range as well as the origins of grain-size effect in nanocrystalline polycrystals remain as yet unexplored by the phase-field approach.

2. The basics of this phase-field model in ferroelectric crystals

There are two major components in this phase-field model. The first one is the time-dependent Ginzburg–Landau (TDGL) kinetic equation and the second one is the Landau–Ginzburg–Devonshire energy density function. In addition, the quasi-static form of the Maxwell equation and the mechanical equilibrium must also be satisfied.

2.1. The phase-field approach to the microstructural evolution

The objective of this approach is to seek for the attainable minimum energy state of the system. Its total free energy, F, is given by the volume integral of the energy density, ψ, as:

$$F = \int_V \psi(P_i, P_{i,j}, \varepsilon_{ij}, D_i) dV, \tag{1}$$

where P_i is the polarization vector, $P_{i,j}$ its gradient ($P_{i,j} = \partial P_i / \partial x_j$), ε_{ij} the strain tensor, and D_i the electric displacement vector. In phase field, P_i is taken as the order parameter of the system.

As the system evolves toward equilibrium, its total free energy continues to decrease. Its variation with respect to time, t, can be evaluated from its variational derivative (e.g. [38]), as:

$$\frac{dF}{dt} = \int_V \frac{\delta F}{\delta P_i} \frac{\partial P_i}{\partial t} dV < 0; \quad \text{where} \quad \frac{\delta F}{\delta P_i}$$
$$= \frac{\partial \psi}{\partial P_i} - \frac{\partial}{\partial x_j}\left(\frac{\partial \psi}{\partial P_{i,j}}\right). \tag{2}$$

From the integrand it can be identified that the term, $\delta F / \delta P_i$, is the thermodynamic conjugate to $\partial P_i / \partial t$, and thus its negative also serves as the thermodynamic driving force for the evolution of the polarization vector, P_i. Its form is identical to the left-hand side of the Euler–Lagrange equation in classical mechanics. In the simplest case one may take the evolution of P_i to be proportional to its driving force, as:

$$\frac{\partial P_i(x,t)}{\partial t} = -L_{ij}\frac{\delta F}{\delta P_j(x,t)}; \quad \text{or} \quad \beta_{ij}\frac{\partial P_j}{\partial t}$$
$$= \frac{\partial}{\partial x_j}\left(\frac{\partial \psi}{\partial P_{i,j}}\right) - \frac{\partial \psi}{\partial P_i}, \tag{3}$$

where L_{ij} are the components of the positive-definite kinetic coefficients, and β_{ij} the components of the inverse mobility tensor. Eq. (3) is the well-known time-dependent Ginzburg–Landau (TDGL) kinetic equation for the evolution of the order parameter, P_i. It provides the fundamental means of describing the kinetics of the polarization vectors as a function of the thermodynamic driving force. From (2) and (3), it can be seen that the total free energy of the system will continue to decrease as the domain structure evolves from a non-equilibrium toward the equilibrium state, with the end point marked by $-\delta F / \delta P_i \rightarrow 0$.