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Combining experiments and modeling to characterize field driven phase transformations in relaxor ferroelectric single crystals

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Abstract—Field induced phase transformations in $[0\,1\,1]_C$ cut and poled relaxor ferroelectric single crystals can be induced by electrical or mechanical loading. Concurrent electrical and mechanical loading drives the ferroelectric rhombohedral to ferroelectric orthorhombic phase transformation at lower threshold levels than either load alone. The current experimental technique for characterization of the large field behavior including the phase transformation requires an extensive set of measurements performed under electric field cycling at different stress preloads and stress cycling at different bias electric fields repeated at multiple temperatures. Here, a mechanism based model is combined with a more limited set of experiments to obtain the same results. The model utilizes a work–energy criterion that calculates work required to induce the transformation by overcoming an energy barrier. In the relaxor single crystals, the energy barrier of phase transformations distributed over a range of field values is represented by a normal distribution of step like transformations. The results of the combined experiment/modeling approach are compared to the fully experimental approach and error is discussed.

Keywords: Field induced phase transformations; Relaxor ferroelectric; Work–energy model; Characterization

1. Introduction

Relaxor ferroelectric single crystals exhibit many electromechanical properties superior to those of ferroelectric ceramics [1–3]. This has resulted in their use in applications that include advanced sonar and medical ultrasound transducers [4–8], energy harvesters [9], and as a platform to study the behavior of magnetoelectric heterostructures under biaxial strain loading [10,11]. The electromechanical behavior is limited by electrical, mechanical, and thermally driven phase transitions [12–16]. Although this limits the linear behavior desired in acoustic transducer applications, it provides extraordinarily large changes of polarization and strain that are beneficial to the energy harvesting and magnetoelectric heterostructure applications.

The $[0\,0\,1]_C$ and $[0\,1\,1]_C$ cut and poled rhombohedral phase crystals are referred to as "domain engineered". Domain engineered crystals exhibit reduced hysteresis due to the near elimination of domain wall motion [3]. This results in a stress and electric field loading regime with linear behavior and very low loss. $[0\,1\,1]_C$ crystals are often mechanically pre-loaded with stress (σ_{22}) in the $[1\,0\,0]_C$ direction and unipolar electric field (E_3) in the $[0\,1\,1]_C$ direction. When this loading exceeds a transformation threshold, a field induced phase transformation from the ferroelectric rhombohedral phase (FE_R) to the ferroelectric orthorhombic phase (FE_O) occurs [17–19]. This phase transition results in non-linearity and hysteresis. The combined effects of σ_{22} and E_3 act cooperatively to drive the FE_R to FE_O phase transformation. Concurrent $[1\,0\,0]_C$ mechanical loading and $[0\,1\,1]_C$ electrical loading drive the FE_R–FE_O phase transformation at lower threshold levels than either load alone.

Fig. 1 shows a schematic of the domain engineered state and the polarization reorientation associated with the FE_R–FE_O transformation in $[0\,1\,1]_C$ single crystals under electrical (Fig. 1(b)) and mechanical (Fig. 1(c)) loading. The observed effect of transformation is a jump in strain and electric displacement as well as a decrease in the compliance, piezoelectric, and dielectric coefficients by nearly an order of magnitude [13,20]. The FE_R–FE_O phase transformation can display either a sharp discontinuous strain and electric displacement or a more gradual transition distributed over a range of applied field levels [20]. The relationship between the coordinate axes and the Miller indices used in the following discussion is also defined in Fig. 1.

Recent experimental characterization of $[0\,1\,1]_C$ ternary ferroelectric single crystal lead indium niobate–lead magnesium niobate–lead titanate, $x\mathrm{Pb}(\mathrm{In}_{1/2}\mathrm{Nb}_{1/2})\mathrm{O}_3$–$(1-x-y)\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$y\mathrm{PbTiO}_3$ (xPIN–$(1-x-y)$PMN–yPT) provides examples of distributed and discontinuous transformation behavior [21,22]. Fig. 2 (a) shows the

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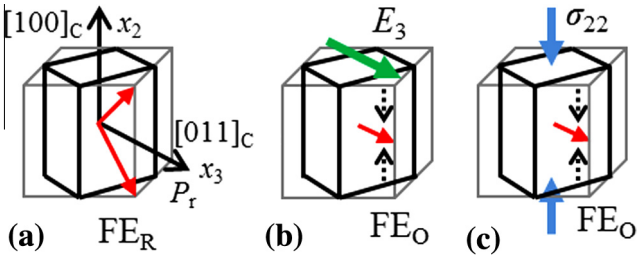

Fig. 1. Polarization reorientation under loading for $[0\,1\,1]_C$ cut and poled relaxor ferroelectric single crystals. (a) At room temperature with no external loads the crystal is in a two variant rhombohedral state with volume average polarization (P_r) in $[0\,1\,1]_C$. Application of (b) electrical loads in $[0\,1\,1]_C$ and (c) mechanical loads in $[1\,0\,0]_C$ above the transformation threshold induce a FE_R–FE_O phase transformation to a single variant orthorhombic state with polarization in the $[0\,1\,1]_C$ direction.

distributed strain–electric field (ε_{22}–E_3) transformation behavior of 0.24PIN–0.48PMN–0.28PT and Fig. 2 (b) shows the discontinuous transformation behavior of 0.24PIN–0.44PMN–0.32PT under electrical loading. The electric displacement–electric field (D_3–E_3), strain–stress (ε_{22}–σ_{22}) and electric displacement–stress (D_3–σ_{22}) curves display similar phase transformation profiles [21,22].

Modeling of the distributed field phase transformation is based on the observed behavior of relaxor ferroelectrics. Relaxor ferroelectrics display a phase transition when cooled from the cubic phase that is distributed about a mean Curie temperature [23]. Chemical heterogeneity at the nanometer length scale is understood to be the origin of the broad Curie temperature region and frequency-dispersive properties of relaxor ferroelectrics [19,24]. Hierarchical domain structures have been observed in single crystal lead magnesium niobate–lead titanate $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–xPT) with compositions close to the morphotropic phase boundary (MPB). The domain sizes range from nanometers to millimeters and the spatial configuration of the domains is dependent on the thermal and electrical history of the specimen [25]. The material behavior and crystal structure are temperature dependent. At high temperatures the material is paraelectric. A transformation from paraelectric to the ergodic relaxor phase occurs when cooled below the Burns temperature. This cooling results in the development of nano-polar regions associated with randomly distributed dipoles that give rise to enhanced dielectric and piezoelectric behavior [24]. Spontaneous polarization develops as temperature is reduced below the Curie temperature (T_C ~200 °C for PIN–PMN–PT) and the material enters a ferroelectric phase. The morphotropic phase boundary that separates the rhombohedral phase from the tetragonal phase is tilted in the composition – temperature phase diagram. For compositions that are near this boundary and pass through it upon cooling, when the temperature is below the rhombohedral to tetragonal phase transformation temperature ($T_{R/T}$ ~137 °C for PIN–PMN–PT), the ferroelectric tetragonal structure transforms to the FE_R structure [26–30] passing through a monoclinic phase.

Webber et al. [31] proposed a model based on the concept that spatial chemical and structural heterogeneities play a similar role in the distributed field-induced transformations in ferroelectric single crystals. They modeled the observed phase transformation behavior based on the volume average of the behavior of many small regions, with each region displaying an idealized discontinuous transformation. Fluctuations in the material properties about their mean values were assumed to result in a distribution of transformation threshold fields that follow a normal distribution, with the center of the transformation defined in terms of a mean value and the spread in terms of the standard deviation. This led to simulations that closely matched experimental data. Similar models have been used in simulations of 180° domain switching [32].

The success of Webber's modeling approach suggested the possibility of greatly reducing the number of experiments necessary to fully characterize the field induced phase transformations as a function of stress, electric field, and temperature. Experimentally characterizing field induced phase transformations in relaxor single crystals requires using simultaneous combinations of stress, electric field, and temperature loading [12,13,15,22]. This experimental characterization technique requires a mechanical load frame, a high voltage power supply, a strain gauge amplifier, a Sawyer Tower circuit (or equivalent method to measure the charge on the specimen), and a temperature controller. Electric field is cycled at multiple stress preloads and stress is cycled at multiple bias electric fields. This procedure is repeated at multiple temperatures. Details of the experimental procedure have been previously published [22]. The collection and analysis of this type of data is time consuming.

The following sections describe a characterization approach that combines experiments with a modified modeling methodology. The model is validated through a comparison of a full set of measured stress, strain, electric displacement, and electric field plots to those generated from a single D_3–ε_{22}–E_3 measurement plus the compliance of the FE_R phase and the error is discussed.

2. Model methodology

McLaughlin et al. [13] and Dong et al. [33] measured a scalar energy barrier to a field induced phase transformation. They showed that when a combination of mechanical and electrical loading that does positive work during the transformation is sufficient to overcome the energy barrier, the transformation takes place. The mechanical work density (w^m) is expressed in Eq. (1) as the integral of the ε–σ loading path and the electrical work density (w^e) is expressed in Eq. (2) as the integral of the D–E loading path:

$$w^m = \int \sigma_{ij} d\varepsilon_{ij} \tag{1}$$

and

$$w^e = \int E_m dD_m, \tag{2}$$

where σ_{ij} is the applied stress, E_m is the applied electric field, ε_{ij} is the strain, and D_m is the electric displacement. The indices vary from 1 to 3. For $[0\,1\,1]_C$ crystals the only non-zero components of stress and electric field are σ_{22}, and E_3, and the resulting work conjugate variables are ε_{22}, and D_3. The energy barrier depends on temperature and composition and is assumed to be independent of loading path [22]. The energy barrier to the start of the transformation is taken to be equal to the work done (w^C) to start the transformation and can be determined by applying Eq. (3) along a measured data loading path: