Mechanics of large electrostriction in ferroelectrics

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ABSTRACT

The complex arrangement of domains observed in ferroelectric crystals is a consequence of multiple energy minima of the crystal free energy density. Since the total energy is a sum of the free energy, and electrical and mechanical work, switching between the different energetically equivalent domain states can be achieved by both electrical and mechanical means. For many ferroelectric materials, this results in an electrostrictive phenomenon resulting from domain switching. In the current study, the electrostrictive behavior of single crystal ferroelectric perovskites has been investigated experimentally. Experiments have been performed in which a crystal of barium titanate is exposed to a constant compressive stress and an oscillating electric field and global deformation is measured. The combined electromechanical loading results in a cycle of stress and electric field induced 90-degree domain switching. The domain switching cycle results in a measurable strain response theoretically limited by the crystallographic unit cell dimensions. Induced strains of more than 0.8% have been measured in barium titanate. Larger strains of up to 5% are predicted for other materials of the same class.

Keywords: ferroelectric crystals, barium titanate, domain switching, electrostriction

1. INTRODUCTION

Ferroelectric materials are used in a variety of sensor and actuator applications. These are generally in the form of piezoelectric or electrostrictive, polycrystalline ceramics. Applications include micropositioning, ultrasonics, stress measurement, active damping and damage detection. The behavior of conventional materials is characterized by good high frequency response and low hysteresis, though strains are limited to about 0.1%. A variety of methods have been developed for creating large displacement actuators by using monomorph or bimorph benders, functionally graded ceramics and single crystals. Research on single crystal ferroelectric materials for sensor and actuator applications have recently focused on relaxor based systems, such as PMN-PT, formulated near the morphotropic phase boundary, that take advantage of phase transition to produce actuation strains of greater than 1%.[1]

The current investigation is a study of the electromechanical response of barium titanate ($BaTiO_3$). Barium titanate is a ferroelectric material of the perovskite class and has been extensively studied.[2] At high temperature it has the cubic structure of perovskite, as shown in figure 1. When cooled below 120^oC, it transforms to a tetragonal phase. In addition to the strain induced by the lattice distortion, there is a spontaneous polarization along the axis of the unit cell as indicated in the figure. Thus, at phase transition the unit cell can take any of six crystallographically equivalent combinations of strain and polarization. Furthermore, different regions of a single crystal or single grain in a polycrystal can take on different directions of polarization. A region of constant polarization is known as a ferroelectric domain. Domains are separated by 90^o or 180^o domain boundaries, as shown in figure 2, which can be nucleated or moved by electric field or stress. The process of changing the polarization direction of a domain by nucleation and growth or wall motion is known as domain switching. If the process is induced by electric field, it is known as *ferroelectric* switching. If it is induced by stress, it is known as *ferroelastic* switching.

Domain switching is important for a number of reasons. Globally it leads to change in the macroscopic polarization direction and, in the case of 90^o domain switching, an associated strain that can be quite large – up to 5%. A

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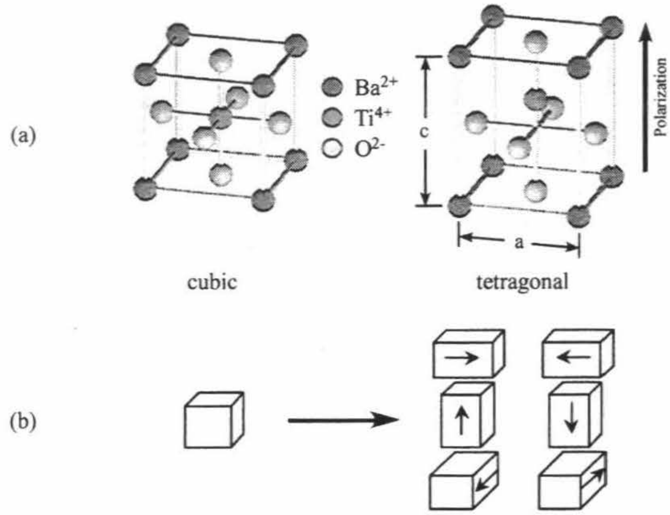


Figure 1. (a) The cubic (high temperature) and tetragonal (room temperature) structures of barium titanate. The tetragonal structure has both an induced strain and polarization. (b) Upon the cubic to tetragonal phase transition, the unit cell can take any of six equivalent combinations of strain and polarization. The arrow indicates the direction of polarization.

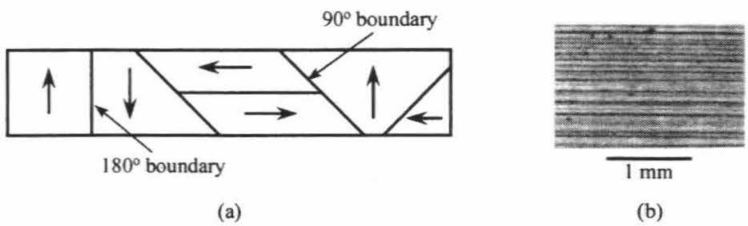


Figure 2. (a) Schematic diagram of the subgranular structure of domains, or regions of constant polarization separated by 90^o or 180^o boundaries. (b) 90^o domain boundaries photographed using a polarizing microscope.

ferroelectric material must have a direction of average polarization in order to be piezoelectrically active.[3] However, a polycrystal, while microscopically polarized, will be macroscopically non-polar due to the random orientation of grains. Domain switching makes it possible to pole the material macroscopically by exposing it to a strong electric field. By the same token, a piezoelectric material can be depoled by electric field or stress. The details of the poling and depoling process in polycrystals is very complex due to residual stresses and grain boundary mismatch. There have been a number of experimental and theoretical studies devoted to this subject. Most studies focus on ferroelectric switching.[4] Stress and electric field induced domain switching was studied by Lynch by measuring the nonlinear electromechanical response of PLZT ceramics subject to uniaxial stress.[5,6] Both strain and polarization were measured as a function of electric field at different stress levels.

To understand the fundamental mechanisms governing domain switching and avoid the inherent complexity of the polycrystal system, there have been many studies of electric field induced domain wall motion in single crystals.[7,8] Stress induced, 90^o domain switching was observed by Li, et. al. in $BaTiO_3$ and $PbTiO_3$.[9] They used a loading mechanism to generate a compressive stress along the [100] axis of a crystal and observed the domain switching behavior using micro-Raman spectroscopy. For $BaTiO_3$, 90^o domains were shown to be nucleated by a compressive stress of 0.22 MPa. Removal of 90^o domains was initiated at a stress of 1.1 MPa. The current investigation focuses on the combined electromechanical response of barium titanate single crystals by looking at the effect of compressive stress on electric field induced domain switching and the subsequent electrostrictive response. Such a system may be a useful for development of a model of domain switching in grains of polycrystals.

2. THEORY

2.1. Energy of a Single Crystal

A theoretical model of a ferroelectric single crystal has been developed by Shu and Bhattacharya using the framework of finite deformation continuum mechanics.[10] This model is summarized below. Consider a ferroelectric single crystal occupying a region Ω in its reference (undeformed) configuration. The deformation of this crystal is $y(x)$ where x is a typical material point and the polarization is $p(y)$. Note that it is natural to define the polarization in the current configuration. Suppose this crystal is subjected to an external electric field E_o and dead load corresponding to nominal stress T_o. Then the total energy of the single crystal at temperature θ undergoing a deformation $y(x)$ and polarization $p(y)$ is given by

$$\mathcal{E}[y,p;\theta] = \int_{\Omega} \{\alpha|\nabla_x P|^2 + W(\nabla_x y, P, \theta) - (\det \nabla_x y)E_o \cdot P - T_o \cdot \nabla_x y\}\, dx + \frac{1}{2}\int_{\mathbb{R}^3} |\nabla_y \phi|^2 dy \tag{1}$$

where $P = p(y(x))$ and the electric potential ϕ is determined by solving Maxwell's equation,

$$\nabla_y \cdot (-\nabla_y \phi + p) = \rho \quad \text{on } \mathbb{R}^3 \tag{2}$$

where ρ is the free charge density and we use the convention that $p = 0$ outside $y(\Omega)$.

The first term penalizes changes in the polarization, and is thus the domain wall energy. The second is the free energy density W which depends on the 'deformation gradient' (or strain), the polarization and temperature. The third describes the interaction with the applied electric field and the fourth the interaction with the applied mechanical load. Finally, the second integral is the 'electrostatic' energy associated with the electric field generated by the spontaneous polarization. The equilibrium deformation and polarization can be found by minimizing the total energy over all possible deformations y and polarizations p.

The energy density W, depends on the deformation gradient $F = \nabla_x y$ (a 3×3 matrix), the polarization P (a vector) and temperature θ. It is frame-indifferent, i.e.,

$$W(QF, QP, \theta) = W(F, P, \theta) \quad \text{for all rotation matrices } Q \tag{3}$$

satisfies material symmetry and has ground states (minima) corresponding to the observed spontaneously polarized state of the crystal. For barium titanate, in the absence of any field or load, material symmetry implies that at room temperature it can be polarized in any of the six $\langle 100 \rangle$ directions with its associated deformation. These are the crystallographically equivalent structures mentioned earlier. Thus there are six symmetry related ground states for which W is minimized. Minimization of the total energy dictates that external mechanical or electrical work can result in an exchange of stability between different ground states.

2.2. Flat Plate Configuration

For a flat plate configuration with electrodes on each face, the minimization problem can be simpified significantly. If the plate is thin and is bounded by electrodes on the two faces, the last integral in equation (1) can be neglected. In addition, if the size of the crystal is much larger than the domain wall, the domain wall energy can be neglected. The problem can then be reduced to the minimization of the following energy density function:

$$G(F, P, \theta) = W(F, P, \theta) - (\det F)E_o \cdot P - T_o \cdot F \tag{4}$$

The possible equilibrium configurations for a crystal of barium titanate cut in a flat plate configuration with a (100) orientation under combined electromechanical loading, are shown in figure 3. Any configuration with the polarization oriented in-plane will be energetically equivalent. This is shown as state (1), with some combination of stress and electric field for which this state is stable. At some different combination of compressive stress and electric field, the stable equilibrium configuration will be state (2), the out-of-plane configuration. It also happens that for very high values of compressive stress and electric field, the orthorhombic phase is the equilibrium configuration, shown as state (3). Minimization of equation (4) results in a phase diagram outlining the equilbrium boundaries of the three configurations. The phase diagram for barium titanate at room temperature is shown in figure 4. It is important to note that the configurations mentioned are equilibrium states. The problem of switching between equilibrium states is kinetic in nature.

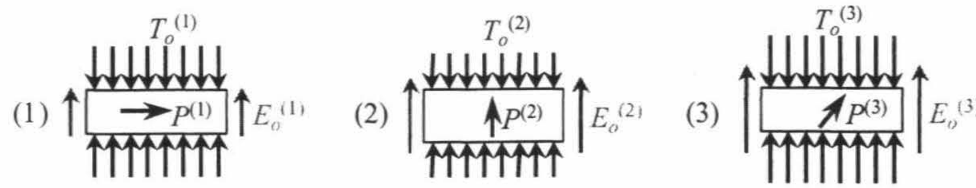


Figure 3. Possible flat plate equilibrium configurations under compressive stress and electric field loading.

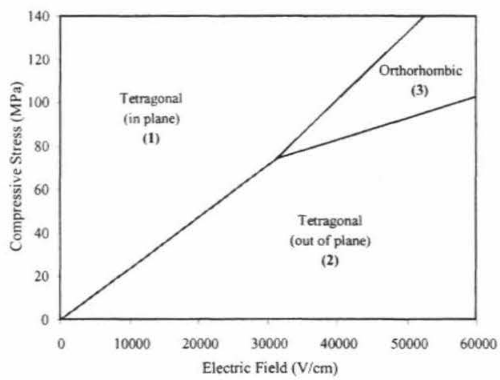


Figure 4. Compressive stress-electric field phase diagram of barium titanate at room temperature.

2.3. Mode of Electrostrictive Actuation

The exchange of stability between the in-plane and out-of-plane configurations discussed in the previous section suggests a potential mode of operation for an electromechanical actuator. This mode of operation takes advantage of the change in strain associated with switching between states (1) and (2) shown in figure 3. A single crystal ferroelectric in a flat plate configuration, with (100) orientation is subjected to a constant, uniaxial compressive prestress with no electric field. The equilibrium configuration is thus state (1). A voltage is introduced of sufficient magnitude to switch the crystal to state (2). The voltage is subsequently removed and compressive stress causes the crystal to return to state (1). The combined electromechanical loading allows a cyclic change in the domain pattern resulting in an electrostrictive strain limited by the c/a ratio of the given crystal. For barium titanate this corresponds to a strain of 1.1%. Other materials could produce higher strains, as large as 5%. A similar mode of operation was suggested for polycrystals by Lynch who pointed out a number of drawbacks.[5] The drawbacks and limitations, such as cracking and hysteresis, are mentioned in the experimental discussion that follows.

3. EXPERIMENT

The theoretical analysis suggested the experiment described below. Experiments were performed on single crystals of barium titanate of 5x5x1mm dimensions and (100) orientation (Superconix, Lake Elmo, MN). Barium titanate was chosen because it has been studied extensively and can be obtained in single crystal form. Because of the difficulty in obtaining single domain crystals, experiments were performed on crystals that were initially polydomain.

An experimental setup has been designed to provide a constant compressive stress and variable electric field to a ferroelectric crystal and measure the induced electrostrictive strain. The experimental setup consists of a loading mechanism, displacement measurement transducer, electrodes and CCD camera. A schematic diagram is shown in figure 5. Load is generated using a dead weight, W, and a lever mechanism to deliver a constant force to a loading frame. The force is transmitted to a pair of optically flat, glass plates that sandwich the specimen. A semi-transparent gold film of approximately 300-400 angstroms is sputtered on the surface of each optical flat to

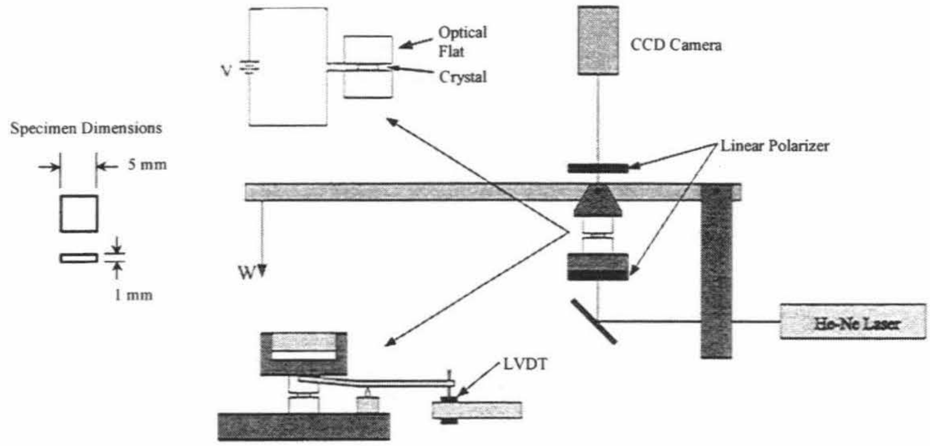


Figure 5. Schematic diagram of experimental setup and specimen dimensions

function as an electrode. The use of the glass plates and transparent electrodes allows direct observation of the specimen during the test. Wires are attached to the electrodes using a conductive epoxy (Chemtronics CW2400). The electrode wires are connected to a high voltage power amplifier (Trek, Inc. Model 10/10B) used to generate large electric fields. Electric field and current are measured by monitoring the amplifier voltage and current outputs and are recorded with a digital oscilloscope.

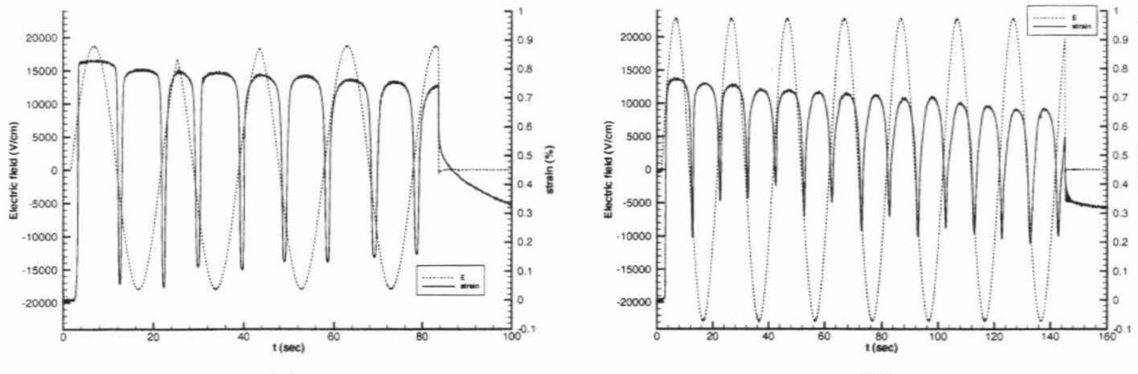
The crystal strain is measured by recording the load frame displacement during the course of the experiment, which corresponds to the change in thickness of the specimen. The displacement is measured using a high-resolution LVDT (Lucas-Schaevitz 025-MHR). The LVDT core is attached to a beam which is actuated at the center of the loading frame, as shown in figure 5. This mechanism allows actuation of the transducer proportional to load frame translation while eliminating any effects of angle change. The core moves a proportional amount to the loading frame relative to the LVDT coil. The signals from the LVDT pass through a signal conditioner and are recorded by a digital oscilloscope. Because the force remains constant during each experiment, load frame compliance is not an issue in strain measurement.

A helium-neon laser is used to illuminate the specimen from below. The light passes through crossed polarizers, one below the specimen and one above, and the image is captured on video using a CCD camera. Tetragonal barium titanate is optically birefringent within the (100) and (010) planes but is optically isotropic in the [001] direction. For this reason, 90^o domain boundaries can be observed with polarized light. At this point, the video images have only been used for observational purposes.

4. RESULTS

Experiments have been performed at different levels of compressive stress. Figure 6 shows the strain history for two experiments with compressive stress of (a) 3.6 MPa and (b) 2.0 MPa. The dashed curve is the input electric field signal which is sinusoidal with a frequency of 1/20 Hz. The solid curve is the strain history. Note that the response is electrostrictive in nature since it is the same for both positive and negative field polarity. The maximum strain occurs during the first cycle for each experiment with strain of about 0.83% for the 3.6 MPa case and 0.77% for the 2.0 MPa case. These values are less than the theoretical maximum of 1.1%. The 3.6 MPa experiment ends midway through the fifth cycle at which point arcing occurs. The arcing event causes the current limit for the power supply to be exceeded, automatically cutting off the input signal. Note that the strain continuously decays at zero electric field after the input signal is cut off. An arcing event occurs at the beginning of the eighth cycle in the 2.0 MPa case.

The same data are shown in figure 7 with strain plotted as a function of electric field. The curves bear strong resemblance to the familiar 'butterfly' strain hysteresis loops. In each case the signal begins at point (0,0). As the electric field increases, the strain increases linearly up to a critical value of electric field, at which point the strain



(a) (b)

Figure 6. (a) Strain vs. time for a compressive stress of 3.6 MPa. (b) Strain vs. time for a compressive stress of 2.0 MPa. The dashed line is the input electric field signal. The solid line is the strain response.

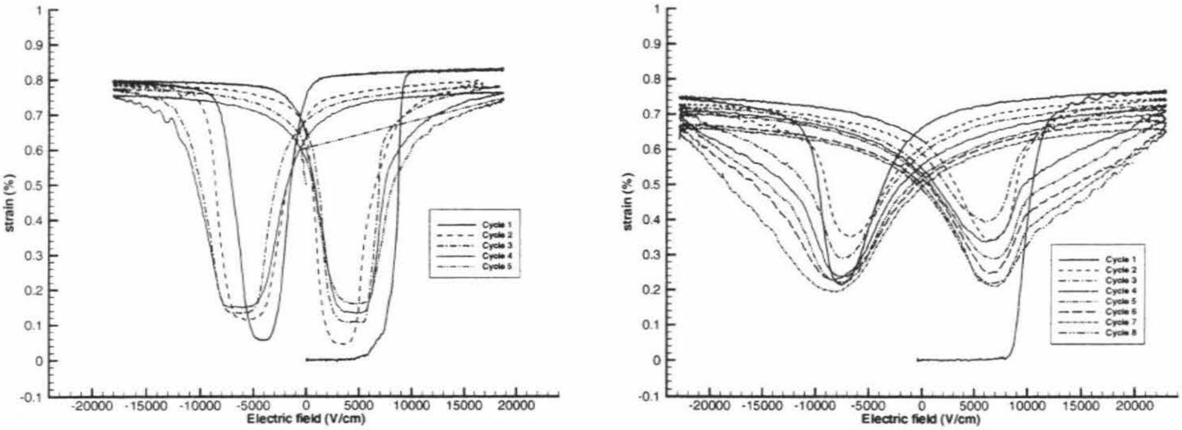
increases much more rapidly. At a higher value of electric field, the strain levels off and increases in an approximately linear fashion up to the maximum electric field with a strain of 0.83% for the first case and 0.77% for the second case. As the electric field is decreased, the strain decreases slowly and then drops suddenly. The strain reaches a minimum, though it does not return to zero and the minimum does not occur at zero electric field as proposed in section 2.3. The strain again increases as the magnitude of the electric field continues to increase. As it exceeds a critical value, the strain levels off again. With a decrease in magnitude of the electric field, the strain again decreases and reaches a minimum at some positive value of electric field. For each half-cycle (half of the sinusoidal input cycle), the amount the strain increases from its relative minimum will be referred to as the *strain envelope* for the half-cycle. The subsequent decrease in strain will be referred to as the *strain recovery.*

In the number of cycles considered, the hysteresis loops do not reach a steady state. Each cycle is somewhat different from the previous. In the later cycles the strain does not level off as much and the strain recovery decreases. This is especially evident in the 2.0 MPa case. The strain recovery during the initial cycle is about 0.55% with an initial strain envelope of 0.77%. The hysteresis loops shift downward with each cycle and, for the later cycles, do not level off at the maximum electric field. The same is true for the 3.6 MPa case, but to a lesser extent. In this case the initial strain recovery is about 0.77% with an initial strain envelope of 0.83%. The changes in the hysteresis loops with time may be due to the formation of cracks. The video images and inspection after the experiment reveal that cracks form during domain switching. Experiments have shown that these cracks initially form during the ferroelectric switching rather than the ferroelastic recovery.

The data are summarized in figure 8 for several cases with (a) the strain envelope and (b) the strain recovery at zero electric field as a function of the normalized time, τ (time/period of input signal). The previous two cases are included along with two others, a second 3.6 MPa case at 1/8 Hz. input signal and a 7.2 MPa case. The 7.2 MPa case ended due to arcing during the second half of the first cycle so there is limited data for this case. For each case, the maximum strain envelope occurs during the initial cycle and it decreases with time. For the 3.6 MPa cases, the envelope decreases steadily with time. In the 2.0 MPa case, the strain envelope decreases rapidly and then stabilizes. The magnitudes of the strain recovery at zero electric field are much smaller than that of the strain envelope, between 0.1 and 0.2% for the lower stress cases and about 0.3% for the 7.2 MPa case. In addition, the recovery at zero field appears to be independent of stress for the 3.6 and 2.0 MPa cases. This indicates a strong kinetic influence on the switching process.

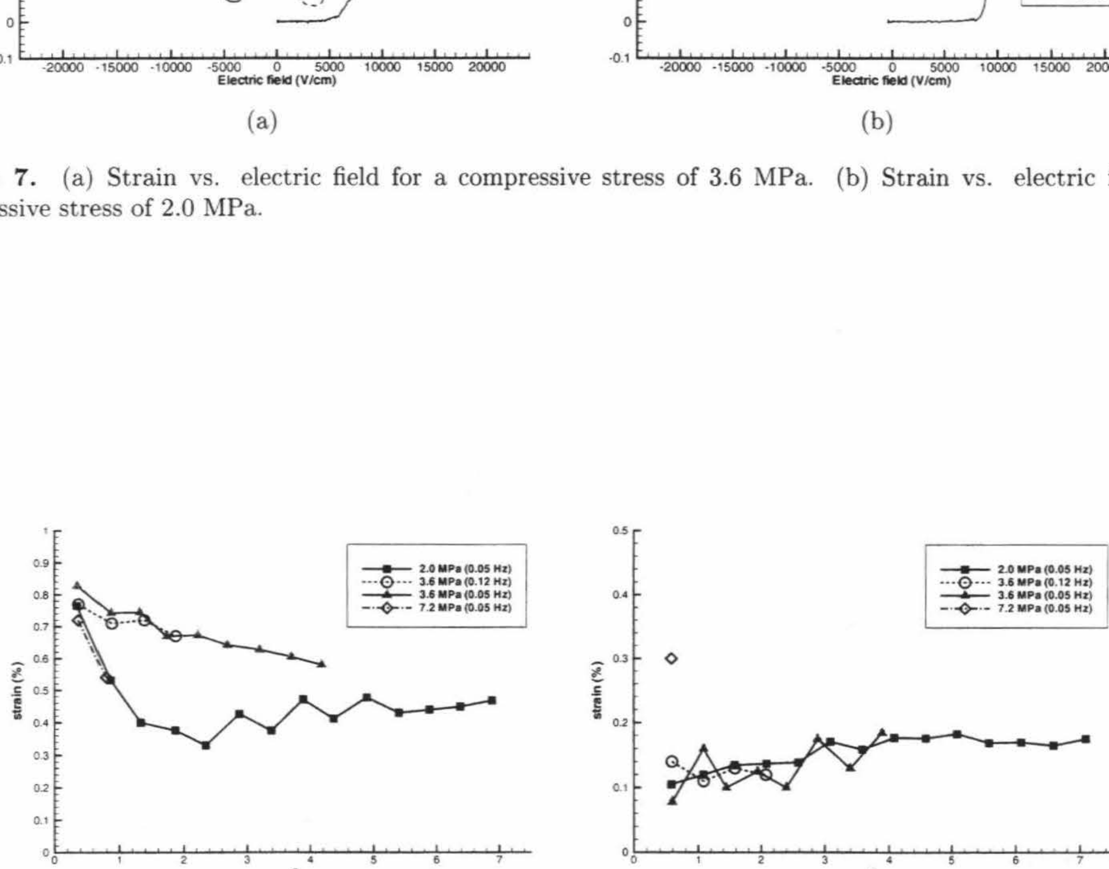
5. DISCUSSION

In the experiments, the strain envelope does not reach the theoretical maximum strain of 1.1% indicating that complete domain switching does not occur. Incomplete domain switching may be due to cracks that develop during the experiment and friction at the crystal-electrode interface that prevents some domains from switching. In most



(a) (b)

Figure 7. (a) Strain vs. electric field for a compressive stress of 3.6 MPa. (b) Strain vs. electric field for a compressive stress of 2.0 MPa.



(a) (b)

Figure 8. (a) Strain envelope (difference between maximum and minimum strain for a given cycle) as a function of normalized time. (b) Strain recovery at zero electric field (difference between maximum strain and strain at zero electric field) as a function of normalized time.

of the experiments that have been attempted, the experiment ends prematurely due to arcing. This arcing problem does not appear to be due to dielectric breakdown or contamination on the outside of the crystal. Instead it appears to be related to cracking of the crystal. In several cases, the spark path was observed in the interior of the crystal, along a crack surface. Most of the cracks are observed to initiate during the initial poling and the process continues during subsequent cycles. This may be responsible for the observed decay in the strain envelope with time.

For compressive stresses of 3.6 and 2.0 MPa, there is a stress dependence on strain envelope but not on strain recovery at zero electric field. For both cases, the strain recovery at zero electric field is quite low, however, at the end of the experiments, there is a greater recovery of the strain after the input signal is cut-off. The time scale for this decay, however, is on the order of the input signal period. This suggests a strong kinetic influence on 90^o switching, at the current loading conditions. The introduction of a field of opposite polarity is able to overcome the activation energy of 90^o domain nucleation and growth, thus the minimum strain occurs at a negative (or positive) electric field bias. Further experiments are needed to investigate the effect of stress on the frequency response of domain switching.

The problem can be looked at in another way. Since there is effectively a 180^o switch between strain peaks in the experiments, the mechanism of polarization reversal should be considered. In polycrystals, the mechanism for polarization reversal has been observed to consist of two 90^o domain rotations, rather than a direct 180^o switch.[4] This observation is consistent with the results of Lynch[5] whose data show that compressive stress has little effect on the strain envelope of polycrystalline PLZT, though it does effect the shape of the hysteresis loops. A single crystal, however, is not subject to the same residual stresses or mismatch at grain boundaries, so the two step process need not occur. In fact direct 180^o switching has been observed in single crystals in absence of compressive stress.[7,8] In the presence of a compressive stress, it seems reasonable that a two step mechanism should occur, however there is again a kinetic influence. Assuming that a two step mechanism occurs, not all domains need switch at the same time. The global strain will be determined by the fraction of domains in the original, rotated and reversed polarization states. The magnitude of compressive stress will have an influence on the evolution of combinations of these states with time. In addition, at low stresses, a dual mechanism of one step and two step reversal may occur. The specifics of the influence of stress on the switching mechanism should be a subject for further research and may be useful in modeling domain switching in a grain of a ferroelectric polycrystal.

Finally, the experimental results bring insight into the applicability of the proposed mode of electrostrictive actuation and the difficulties and limitations associated with its implementation. First of all, there is a large hysteresis associated with actuation. This would limit use of actuators of this mode of operation to switching rather than continuous displacement applications. This precludes its use in many current applications for piezoelectric actuators, however there are other applications where a large strain switching device could be useful. Application of a compressive prestress would be required, but this could be incorporated by appropriate design of the structure. Finally, there is the problem of reliability due to cracking and the arcing that is associated with it. It is possible that there may be other materials of the same class that are more resistant cracking. In addition other changes in design, such as use of an appropriate lateral confining stress, may limit the cracking to an acceptable level. Considering the potential for applications of large strain electromechanical actuators, further investigation of this operating mode is warranted.

6. CONCLUDING REMARKS

An experimental setup has been designed to investigate electrostrictive strain in a ferroelectric single crystal. Experiments have been performed on single crystals of barium titanate ($BaTiO_3$) exposed to a constant compressive stress and variable electric field. The experiments have demonstrated that large electrostrictive strains of greater than 0.8% can be generated, somewhat lower than the maximum predicted strain of 1.1%. The influence of compressive stress on the strain envelope of the electric field-strain hysteresis curves has been demonstrated. It has been found that for some range of stress, the strain envelope increases with increasing compressive stress. Further work is necessary to further investigate the effect of stress on the electrostrictive response as well as the frequency dependence and the mechanism of polarization reversal.

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REFERENCES

1. S. E. Park and T. R. Shrout, "Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals," *J. Appl. Phys.* **82**, pp. 1804–1808, 1997.
2. F. Jona and G. Shirane, *Ferroelectric Crystals*, Dover, New York, 1993.
3. L. E. Cross, "Ferroelectric materials for electromechanical transducer applications," *Jpn. J. Appl. Phys. Pt. 1* **34**, pp. 2525–2532, 1995.
4. S. P. Li, A. S. Bhalla, R. E. Newnham, L. E. Cross, and C. Y. Huang, "90-degrees domain reversal in $Pb(Zr_xTi_{1-x})O_3$ ceramics," *J. Mater. Sci.* **29**, pp. 1290–1294, 1994.
5. C. S. Lynch, "The effect of uniaxial stress on the electro-mechanical response of 8/65/35 PLZT," *Acta mater.* **44**, pp. 4137–4148, 1996.
6. W. Chen and C. S. Lynch, "A micro-electro-mechanical model for polarization switching of ferroelectric materials," *Acta mater.* **46**, pp. 5303–5311, 1998.
7. R. C. Miller and A. Savage, "Motion of 180^o domain walls in metal electroded barium titanate crystals as a function of electric field and sample thickness," *J. Appl. Phys.* **31**, pp. 662–669, 1960.
8. E. A. Little, "Dynamic behavior of domain walls in barium titanate," *Phys. Review* **98**, pp. 978–984, 1955.
9. Z. Li, C. M. Foster, X.-Z. Dai, X.-Z. Xu, S.-K. Chan, and D. J. Lam, "Piezoelectrically-induced switching of 90^o domains in tetragonal $BaTiO_3$ and $PbTiO_3$ investigated by micro-Raman spectroscopy," *J. Appl. Phys.* **71**, pp. 4481–4486, 1992.
10. Y. C. Shu and K. Bhattacharya, "Domain patterns and macroscopic behavior of ferroelectric materials," in preparation.