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ESRF	**Experiment title:** Investigation of Mesoscale Constitutive Behavior of Ferroelectrics	**Experiment number**: ME-542
Beamline: ID-11	**Date of experiment**: from: 17/04/2003 to: 22/04/2003	**Date of report**: 28/08/2003
Shifts: 15	Local contact(s)**:** **Larry Margulies**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

E. Üstündag*: Materials Science Department, California Institute of Technology

R.C. Rogan*: Materials Science Department California Institute of Technology

C.M. Landis: Mech. Eng. & Mat. Sci. Department, Rice University

U. Lienert*: Advanced Photon Source, Argonne National Laboratory

H.F. Poulsen*: Materials Research Department, Risø National Laboratory

M.R. Daymond*: ISIS Neutron Scattering Facility, Rutherford Appleton Laboratory

G.L. Messing: Materials Science and Engineering Department, Penn State University

Report

Ferroelectric ceramics are widely used in a diverse set of devices including sensors, actuators, transducers and ultrasonic motors. In these applications, these materials exhibit a complicated behavior in response to both electrical and mechanical loads which produce large internal stresses that eventually lead to failure. Efforts to model and predict the behavior of ferroelectrics ceramics have often been hindered by the lack of sound, experimentally verified constitutive relations that accurately describe the electromechanical response of these materials. Applying information collected in single crystal experiments to polycrystalline simulations is problematic because the boundary conditions imposed by neighboring grains are absent. Specifically, the evolution of elastic strains associated with nonlinear changes in crystal texture due to domain switching has not been well characterized. The reported experiment at ESRF has provided critical information at the mesoscale which covers sub-grain domain structures and extends into the several grain level. This study therefore bridges the gap between the responses of single crystals and polycrystals observed in our previous work [1-3]. By performing *in-situ* 3-D XRD experiments on polycrystalline $BaTiO_3$ under electrical loading at beamline ID-11, we have been able to obtain information on the constitutive behavior of individual, embedded grains. Here we report, for the first time, the evolution of ferroelectric domains and elastic strains within grains as a function of applied electric field.

At room temperature, $BaTiO_3$ is tetragonal and ferroelectric [4]. Individual unit cells each possess a small electric dipole aligned with the extended *c* axis, producing internal electric fields. Because of the difference in lengths of the *a* and *c* axes, strains are produced during the tetragonal phase transformation from the high temperature cubic phase (leading to internal stresses). In order to balance the internal stresses, twin structures form within grains which produce alternating regions of *a* and *c* domains related through 90° domain boundaries [4]. Additionally, 180° domain boundaries form to alleviate internal electric fields. (Since 180° domains do not contribute significantly to elastic strains due to crystal symmetry and since diffraction cannot distinguish between 180° symmetry operations, these domains are not of interest in this study, and will not be discussed further.) In a sintered polycrystal, domains are randomly oriented. By

applying a large electric field (called the poling field) above a certain critical value (E_c), domains are forced to reorient and align their dipoles with the external field [4]. This process occurs through domain wall motion, which converts one domain variant into another, i.e., *a* domains are transformed into *c* domains through 90° "switching" or vice versa depending on the orientation of the domain variants. Significant elastic strains are associated with the domain switching process due to the mismatch between the *a* and *c* axes. After poling, the material exhibits piezoelectric behavior and is suitable for sensor and actuator applications. Because of the initial random distribution of grain and domain orientations, the poling process cannot completely align all of the dipoles within a polycrystal due to the limited geometries available to the domain switching process. If, for instance, an *a* or *c* domain within a grain is oriented at 45° to the poling field, no form of 90° switching will completely align the dipoles with the electric field (unless the entire grain rotates). This does not mean, however, that domain switching will not occur to relieve local internal stresses or electric fields generated by switching in neighboring grains.

In this experiment, $BaTiO_3$ ceramics prepared by templated grain growth and of varying grain sizes and engineered grain structures were employed (see Proposal ME-542 for specimen details). By using an experimental setup analogous to that depicted in Figure 1(a) at beamline ID-11, various samples were investigated to determine the optimal grain size for resolved single grain information. The essential questions we attempted to answer in this first experiement were: Is it possible to index all the reflections from an embedded grain and therefore locate it within the polycrystal? Can the individual contributions of domains within a grain be isolated? And finally, are we able to observe changes in domain states as a function of applied electromechanical load?

Proof of experimental concept proceeded quickly as even a sample with homogenous small grains (~20-50 μm) yielded information from single grains (and thus we were able to measure a significantly higher number of grains than anticipated). Figure 1(b) depicts a portion of a diffraction ring from a typical XRD pattern, in which one can clearly observe the peak splitting associated with 90° domain variants within a single grain. By rotating the sample through a 60° arc in ω, a large portion of the diffraction space of the sample was probed. Using the GRAINDEX procedure [5-7], we were able to index reflections generated at various ω angles and determine their grain of origin within the specimen. Using a validation scan, fully illuminated grains within the sample were identified. At this time, a partial analysis has already yielded a set of 10 bulk grains (far from surfaces) of various orientations which are suitable for complete characterization.

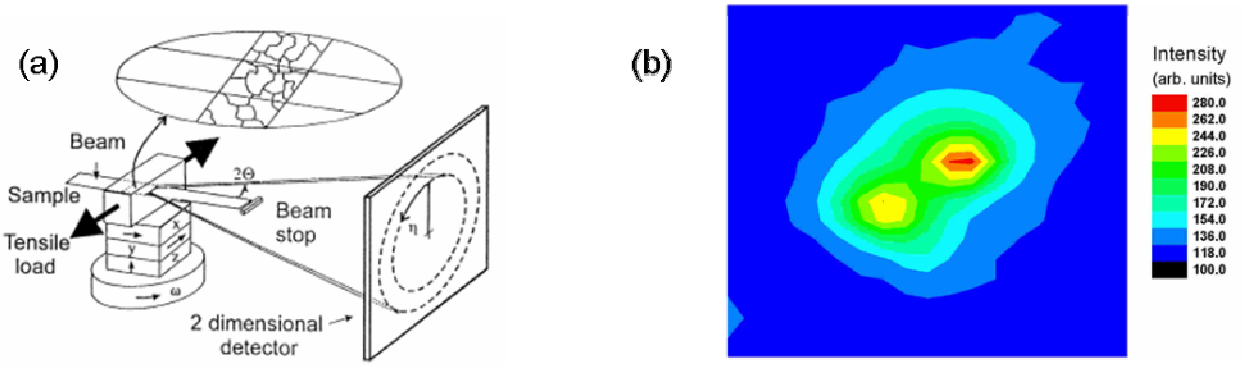

Figure 1: (a) Schematic of experimental geometry; for electrical loading experiments field was applied along the tensile axis. (b) Selected area of a typical diffraction pattern in the region of $\eta = -38°$. The double peak indicates the presence of 90° domain variants within a single grain.

With confirmation that single grain domain information was readily observable, we proceeded with an electrical loading experiment. A poled sample of $BaTiO_3$ was placed in the beam and electrically cycled to both positive and negative fields in order to capture the full ferroelectric portion of the constitutive behavior. When the external electric field, in combination with the local internal stresses and electric fields, induces domain switching within a grain, scattered intensity is transferred from one peak to another depending on the domain transformation taking place. After performing the GRAINDEX procedure, individual grain positions are known, and domains can be selected for detailed domain fraction and elastic strain analysis. Any reorientation of the entire grain is manifested through alterations in the diffraction condidion so that diffraction spots move in ω-η space, changes which are also recorded in the GRAINDEX procedure. Thus after the completion of the full analysis, we will be able to measure the fraction of

individual domain variants within an embedded single grain, and observe the multiaxial nature of the evolution of domain fractions and strain states as a function of applied electrical load.

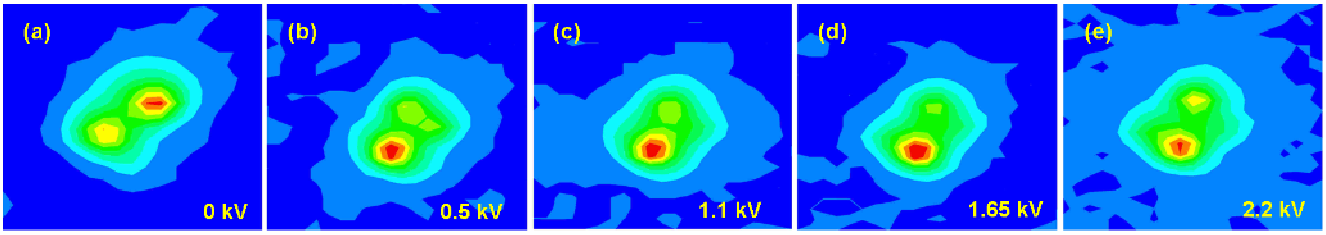

Figure 2: Changes in a diffraction pattern representing two domain variants within a single grain as a function of applied electric field (intensity scale in arb. units). The spot on the upper right is the (200) reflection, and the spot on the lower left is the (002) reflection related by a 90° twin. Changes in intensity indicate variations in domain volume fractions while elastic strain is represented by changes in the 2θ poisition of each spot.

Figures 2(a)–(e) depict the evolution of a set of domain variants in an individual grain. Since the sample was poled to –2.2 kV before placing it in the beam, the 0 kV scans correspond to a poled state. Initially, the (200) diffraction spot is of higher intensity, indicating that the majority of domains in this grain are of the *a* type as a result of poling. At 0.55 kV, intensity is quickly reallocated to the (002) spot of the *c* variant, corresponding to domain switching from *a* to *c*. This occurs well below the E_c value of single cyrstal $BaTiO_3$ (approximately 1.85 kV). Since this grain was scattering at –38° in η, it was not ideally oriented to take full advantage of *c*-to-*a* domain switching to relax internal stresses and electric fields during the poling process (thus we see both *a* and *c* variants in this grain). This suggests that the critical driving force for the reverse transformation in this grain is lower than that of the single crystal because the domain does not lie in the energetic minimum of the poled state. Also note that the relative positions of the diffraction peaks change with electric field. This is a direct result of lattice strain in the two variants due to domain switching.

In conclusion, we have verified the power of 3-D XRD for quantifying constitutive behavior in ferroelectrics. We were able to unambigously locate single grains within a polycrystalline sample. Additionally, we have proven that the technique is capable of capturing information on the fraction of domains within a grain, while simultaneously measuring the strain evolution resulting from domain switching under loading conditions. When full analysis is complete, we expect to have data for ~50 grains. From these grains we will be able to determine the relationship between orientation within the polycrystal and ferroelectric switching behavior. This information is crucial to multiaxial models for ferroelectric behavior, and has been previously unatainable. Thus the 3-D XRD technique pioneered at beamline ID-11 has shown immense promise for aiding the development of ferroelectric polycrystalline models. While much work is needed to analyze the complete set of data, the preliminary results show that these intital experiments have provided a solid basis for future work.

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