Perovskites at High Electric Fields: Electrostriction in $SrTiO_3$ Thin Films and Piezoelectricity in $BiFeO_3$

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Objective

The objective of this work is to probe the electromechanical behavior of dielectric and ferroelectric thin films at high electric field. All dielectric materials undergo electrostriction and are strained proportionally to the square of the electric field that is applied. Piezoelectric materials have a large strain linearly proportional to electric field in addition to electrostriction. There have been very few measurements of the electrostrictive strain and no successful attempts to measure electrostriction in a material that is also piezoelectric. $SrTiO_3$ is an ideal material to study electrostriction thanks to its large electrostriction coefficient and lack of piezoelectricity. This project aims to measure the electrostriction in $SrTiO_3$ and then to use the same technique to probe piezoelectricity in $BiFeO_3$ at high electric fields to see if there is an electrostrictive contribution to the strain at high field.

At the time of the beginning of the experiment, the $SrTiO_3$ sample was not ready because our collaborators' MBE chamber was being serviced. Rather than delay the project, we proceeded with the piezoelectricity in $BiFeO_3$ portion of the project.

Polarization Rotation in $BiFeO_3$

$BiFeO_3$ is a ferroelectric, antiferromagnetic material which is currently the object of intense study. It is widely believed that the ferroelectric and magnetic properties are coupled, but the exact mechanism is still poorly understood. Characterizing the electromechanical response is vital to making use of any multiferroic coupling. Once this is accomplished, $BiFeO_3$ could be used in magnetic field sensors and actuators. The most promising applications lie in electrically controlling the magnetization direction in magnetic tunnel junctions or read/write heads in magnetic memories.

At room temperature, the ferroelectric polarization direction lies along one of the crystallographic <111> directions. When an external electric field is applied, the material is piezoelectrically strained parallel to the field. If the applied field is not parallel to the ferroelectric polarization direction, there are additional forces which make a rotation of the polarization direction energetically favorable. Lisenkov et al. predicted the polarization (P) should begin to rotate near 10 MV/cm and reach the [001] direction around 20 MV/cm. [1] The polarization rotation is accompanied by a change in symmetry from the bulk

rhombohedral state. A tetragonal phase is predicted once P is parallel to the [001] direction. The tetragonal phase has been observed in highly strained $BiFeO_3$ thin films deposited on $LaAlO_3$ substrates. [2]

We predict that a tetragonal phase is forming at high electric field as a result of polarization rotation. The tetragonal phase will have a different lattice constant and the piezoelectric coefficient should change abruptly at the phase transformation. This can be distinguished from electrostriction by measuring the piezoelectric coefficient as a function of field. Electrostriction would give a characteristic strain proportional to E^2, but a phase transformation would be a sharp change in the linear piezoelectric coefficient at some critical electric field.

These electric fields are larger than the DC breakdown field. In previous studies we have found that the breakdown field increases if the duration of the pulse is shortened. For example, we have been able to apply hundreds of thousands of 25 ns pulses at fields ten times larger than the low frequency breakdown field in $Pb(Zr,Ti)O_3$ thin films. The phase transformation is predicted to occur above 10 MV/cm. [1] However, this type of calculation is known to predict fields several times higher than the observed value. [3,4] We expected the phase transformation to occur at a field of several MV/cm, well above the DC dielectric breakdown. Therefore it was necessary to apply the electric field to the $BiFeO_3$ film for 40 nanoseconds at most and measure only the photons which were scattered from the sample during that time.

Experimental Method

The experiment was split into two parts. The first part was the measurement of piezoelectric strain as a function of electric field. We measured the (002) $BiFeO_3$ reflection while the electric field was applied and calculated the lattice constant and strain as a function of electric field. The second portion of the experiment was to search for an (002) Bragg reflection from the tetragonal phase at high field. The tetragonal phase in $BiFeO_3/LaAlO_3$ has a larger c axis lattice constant (4.1 Å) so we expect the reflection to be at a smaller value of 2θ.

The sample was a 50 nm $BiFeO_3$ film on a 50 nm bottom electrode of conducting $SrRuO_3$. Both films were grown epitaxially on an (001) $SrTiO_3$ substrate using off-axis RF magnetron sputtering. Circular platinum top electrodes were sputtered through a shadow mask onto the top surface so an electric field could be applied to the $BiFeO_3$. The electric field was applied using a small electrical probe tip which was touched to the top electrode. The high bandwidth probe tip was connected directly to the output of a pulse generator (Agilent 8114A).

We used time-resolved microdiffraction to measure the piezoelectric strain and scattering at high fields. The capacitor top electrodes are small (25 μm) to minimize the rise time of the electric field. (The time until the maximum electric field is reached in a capacitor is inversely proportional to electrode area). Small electrodes require a small x-ray spot size, so that only the region under electric field is probed. 12.3 keV x-rays were focused by a compound refractive lens to a spot size approximately 2.5 μm by 2.5 μm. A schematic diagram of the experimental setup is shown in Figure 1(a).

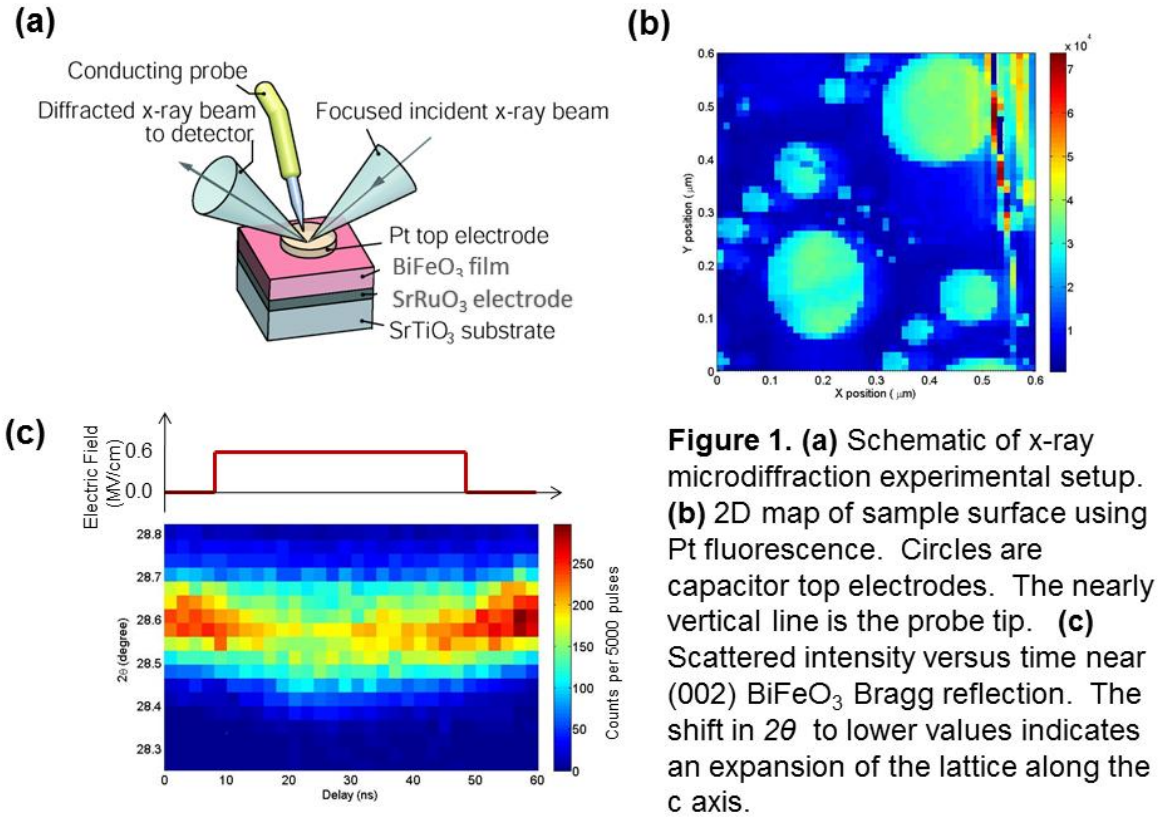


Figure 1. (a) Schematic of x-ray microdiffraction experimental setup. **(b)** 2D map of sample surface using Pt fluorescence. Circles are capacitor top electrodes. The nearly vertical line is the probe tip. **(c)** Scattered intensity versus time near (002) $BiFeO_3$ Bragg reflection. The shift in 2θ to lower values indicates an expansion of the lattice along the c axis.

It was necessary to count only the photons that were scattered from the sample while the electric field was applied. In order to avoid counting photons from multiple bunches, we used an avalanche photodiode detector (APD). The APD has output pulses with durations shorter than the time between electron bunches. We gated the output of the APD and synchronized the gate with the voltage pulses applied to the sample using the 508 MHz counter. Thousands of voltage pulses were applied and the counts from each pulse were summed in a scaler to obtain adequate counting statistics of at least 100 counts on the peak maximum. This was an adaptation of our previous technique [5] to account for the A bunch mode of the SPring-8 storage ring.

An AMPTEK fluorescence detector was used to help determine the position of the beam on the sample. Pt fluorescence indicated the beam was on a capacitor, and W fluorescence meant the beam was hitting the electrical probe tip. The sample was scanned under the focused beam to image the sample. (Figure 1(b).) There were multiple sizes of electrodes patterned onto the sample and the tip in Figure 1(b) is contacting a 25 μm diameter capacitor.

After ensuring the beam was positioned on the same capacitor as the probe tip, we checked the synchronization between the applied pulses and detected photons. The $BiFeO_3$ (002) Bragg reflection was found at zero field. A θ-2θ scan was measured while electrical pulses were being applied. Next, the delay between the electrical pulse and the photons was varied using a delay generator (DG645). This was repeated several times to measure the Bragg reflection versus time as shown in Figure 1(c). The center of the peak does not change after 50 ns when the electric field has decayed to zero.

Results

We selected a delay time in the middle of the pulse and measured a single θ-2θ scan. The center of the shifted peak can be used to calculate the c axis lattice constant. We repeated this scan at several different electric field values as shown in Figure 2 (a).

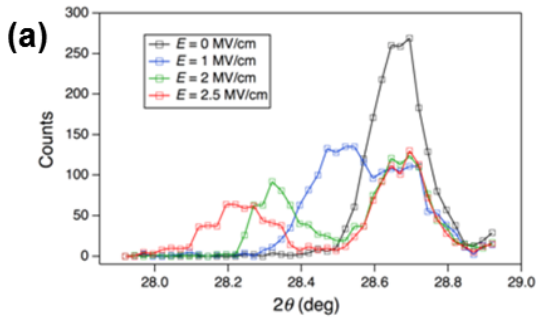
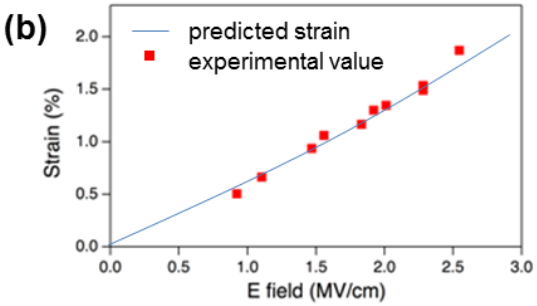


Figure 2. (a) *θ-2θ* scans of (002) reflection at various electric fields. The unresponsive peak is at 28.68°, while the responsive peak position decreases as *E* increases.

Figure 2 (b) Measured and predicted strain versus electric field. Predicted values are for piezoelectricity and electrostriction only. An abrupt change in the experimental value would indicate an electric field induced phase transformation.



It should be noted that there is a significant peak at the zero field 2θ value even while an electric field is applied. We believe that there is a portion of the film which does not have an electric field applied to it and would not show any shift due to piezoelectric expansion. We observe that the volume fraction of the unresponsive portion is not a function of electric field and is approximately equal in all capacitors and regions of the sample. This may be caused by several factors. One possibility is delamination of the top electrode in some portions of the capacitor, effectively removing the electric field from those regions. Another cause could be an interfacial layer of the film near the electrode that is no longer responsive. [6] Further study would be needed to conclusively determine the origin of the unresponsive peak. We believe that the unresponsive portion of the film does not significantly affect the piezoelectric response of the rest of the film.

We also observe that the shifted peak at lower 2θ decreases in intensity as a function of electric field. Rocking curves (changing the incident angle only) were measured to test whether or not the film was tilting under high field. The peak position did not change, ruling out a rotation of the film. There may be a slight increase in the width of the peak which could account for the missing intensity. Further data analysis will be conducted to determine if the peak width increases.

Discussion

The strain was calculated by fitting the θ-2θ scans to a double Gaussian function. The center of the peak at lower 2θ was used to determine the strain in the piezoelectrically responsive portion of the film. (Figure 2 (a)) It was not possible to measure at electric fields

higher than 2.5 MV/cm because the capacitors underwent dielectric breakdown after only a few thousand pulses. A typical scan required more than one million electrical pulses to be applied to the sample in order to detect 10-100 photons at the peak.

The predicted value for piezoelectric and electrostrictive strain is also plotted in Figure 2(b). This was calculated using the following formula

$$\text{Strain} = d_{33}E + Q_{11}\varepsilon_0 X E^2$$

where E is the applied electric field, d_{33} is the piezoelectric coefficient (57 pm/V), Q_{11} is the electrostriction coefficient (estimated at ~ 100), and X is the susceptibility (~ 0.6 C/m). d_{33} was measured in previous experiments at fields below 0.2 MV/cm. The electrostriction coefficient was estimated based on values from similar materials and the susceptibility was estimated using measurements of the induced polarization in $BiFeO_3$ capacitors. These values were not fit to the data in any way.

The data fit the piezoelectric – electrostrictive model quite well. ***We do not observe any abrupt change in the piezoelectric coefficient that would be associated with polarization rotation or a phase transformation.*** However, to be thorough, we searched for the potential tetragonal phase as well.

We predicted that the tetragonal phase would have a lattice constant larger than the low-field rhombohedral phase, but there was no way to estimate the exact lattice constant after piezoelectric expansion. We scanned along the entire [00L] rod to cover lattice constants from 4.5 Å to 3.96 Å. We also made a coarse reciprocal space map by opening the detector slits and making a two dimensional map, scanning both the incident angle and θ-2θ. Neither of these methods observed any scattering above the background and thickness fringes, approximately 9,000 counts/sec compared to 2.1 x 106 on the $BiFeO_3$ (002) reflection. Using this, it is possible estimate the maximum count rate of a tetragonal phase present that would be undetectable in our scans. We estimate the volume fraction of any potential tetragonal phase to be less than 0.5%, assuming incoherent scattering such that the diffracted intensity is proportional to N, the number of planes.

Summary

Time-resolved x-ray microdiffraction was used to measure the electromechanical response of $BiFeO_3$ thin films at high electric field. We developed a technique to measure the scattered intensity from single bunches synchronized with an electric field pulse. The (002) Bragg reflection was used to measure the lattice constant and calculate the strain. The strain was measured as a function of electric field up to 2.5MV/cm. No signature of a tetragonal phase caused by polarization rotation was observed. These results are consistent with a combination of piezoelectricity and electrostriction and suggest that there is no polarization rotation to a tetragonal phase at these electric fields.

References

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