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An *in situ* diffraction study of domain wall motion contributions to the frequency dispersion of the piezoelectric coefficient in lead zirconate titanate

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The contribution of non-180° domain wall displacement to the frequency dependence of the longitudinal piezoelectric coefficient has been determined experimentally in lead zirconate titanate using time-resolved, *in situ* neutron diffraction. Under subcoercive electric fields of low frequencies, approximately 3% to 4% of the volume fraction of non-180° domains parallel to the field experienced polarization reorientation. This subtle non-180° domain wall motion directly contributes to 64% to 75% of the magnitude of the piezoelectric coefficient. Moreover, part of the 33 pm/V decrease in piezoelectric coefficient across 2 orders of magnitude in frequency is quantitatively attributed to non-180° domain wall motion effects. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4789903]

The properties of ferroelectric ceramics can change dramatically as a function of frequency.[1–6] Although it is commonly accepted that ferroelectrics can demonstrate a characteristic relaxation in the GHz range attributed to domain wall vibration,[7] the piezoelectric properties of certain ceramic materials have also been shown to change as much as 50% across the frequency range of 0.01–100 Hz.[8] For example, the piezoelectric coefficient of Nb-doped lead zirconate titanate (PZT) varies linearly as a function of the logarithm of frequency in this frequency range.[9] A logarithmic frequency dependence of a property can be observed in systems where the property is controlled by interface pinning.[10–12] The frequency dependence of the piezoelectric coefficient has often been explained in terms of displacement of domain walls (interfaces) and their interaction with the defects present in the material (pinning centers).[13] To date, this explanation of frequency-dependent properties has been phenomenological in nature as the experimental verification of this interpretation has proven challenging. However, neutron diffraction instrumentation has recently became available that can be used for *in situ* measurement of domain wall motion during cyclic electric field application.[14] In the present work, the contribution of non-180° domain wall motion to the frequency dependence of d_{33} in PZT is determined experimentally. Neutron diffraction was used to probe the average behavior of local crystallographic responses in the material to electric fields of various frequencies. Time-resolved data acquisition (the detector used for these measurements has a timing accuracy of 10 μs[15]) allowed for the material response to electric fields of time periods as short as 0.3 s to be measured *in situ*. Here, we show that non-180° domain wall motion in soft PZT is frequency dispersive at low frequencies in the range of 0.06 to 3 Hz.

Commercial PZT ceramics of tetragonal phase and exhibiting "soft" ferroelectric characteristics (K350, Piezo Technologies, Indianapolis, Indiana) were used in these experiments. Commercial samples were chosen as their piezoelectric properties and domain structures have been well characterized.[16,17] Samples of dimensions $4 \times 3.5 \times 1$ mm and $40 \times 3 \times 1$ mm were used for the piezoelectric coefficient measurements and *in situ* neutron diffraction measurements, respectively. The coercive field of K350 at 100 °C and was determined to be 1 kV/mm at a frequency of 1 Hz. The samples were poled for 5 min in a silicone oil bath maintained at 100 °C using an electric field of 1 kV/mm.

For the piezoelectric coefficient measurements, a bipolar cyclic electric field was used. The converse longitudinal piezoelectric coefficient, d_{33}, was calculated by measuring the electric-field-induced displacement of the material with a linear variable differential transformer (LVDT). The coercive field of K350 at room temperature and was determined to be 1.5 kV/mm at a frequency of 1 Hz. The d_{33} was measured using a subcoercive bipolar sinusoidal field of amplitude 700 V/mm at frequencies of 0.06, 0.6, and 3 Hz. These conditions were chosen because they represent intermediate conditions in amplitude[18] and frequency[8,9] at which dispersion has been observed previously in PZT. The measured peak-to-peak strain, $\mathcal{E}_{33,\mathrm{max}} - \mathcal{E}_{33,\mathrm{min}}$ was used to calculate d_{33} using the equation[19]

$$d_{33} = \frac{\varepsilon_{33,max} - \varepsilon_{33,min}}{2E_o}, \tag{1}$$

where $2E_o$ is the peak-to-peak value of the bipolar electric field signal.

Time-resolved, *in situ* neutron diffraction patterns were measured on poled ceramics during application of cyclic, bipolar electric fields on the Wombat[15] diffractometer at the Australian Nuclear Science and Technology Organisation (ANSTO). A vertically focused monochromatic neutron beam

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of wavelength 2.9562 Å was used. The sample was completely immersed inside the incident neutron beam, and the diffraction patterns were collected using a two dimensional curved detector with a solid angle of 120°. The sample was oriented to enable measurement of non-180° domain wall motion between 100(a-axis)- and 001(c-axis)-type domains that are approximately parallel to the electric field direction. To reduce background, all measurements were completed while a radial collimator oscillated in front of the detector with a 1-min period. A stroboscopic data collection technique was employed in which the detected neutrons are time stamped and are subsequently binned in a given time window within the cycle of the applied electric-field waveform. Diffraction images collected over multiple cycles are summed together and are represented with respect to a single cycle of the applied electric waveform.[20,21] Images were collected until sufficient statistics were obtained to allow the detection of the crystallographic changes in the material. For instance, under the bipolar electric field of 3 Hz, the sample was subjected to approximately 1.3×10^5 electric field cycles, and images were collected for approximately 12 h in order to obtain sufficient diffraction statistics. Unlike the macroscopic measurements which were made using a sinusoidal electric field, the use of a bipolar square wave enabled measurement of any apparent relaxation in non-180° domain wall motion. It has been previously demonstrated[19] that this difference in the waveform does not significantly affect the results. The field amplitudes and frequencies applied during diffraction were identical to those used during the macroscopic measurements.

Figure 1 shows selected regions of the diffraction pattern containing the (002), (200), and (111) type reflections during the positive and negative polarity of the electric field. The difference pattern shown in Figure 1 emphasizes the crystallographic changes taking place during the positive and negative portions of the bipolar electric field cycle. The shift in the position of the (111) peak indicates the change in interplanar spacing between the different polarities of the electric field. The (111) peak positions were analyzed as a function of time during the waveform by fitting a pseudo-Voigt profile shape function to the (111) peak in each time window. The change in the (111) peak positions were then used to calculate the time-dependent (111) lattice strain.[21] Figure 2 shows the time-dependent response of the (111) lattice strain to an applied bipolar electric field of frequency 3 Hz. When the positive polarity of the electric field cycle begins (0 s), the material displays an initially instantaneous strain response followed by a larger positive response for the remainder of the positive polarity of the electric field cycle. Similarly, when the negative polarity of the electric field cycle begins (0.165 s), the material displays an initially instantaneous negative strain response followed by a larger negative strain response for the remainder of the electric field cycle. This type of response is expected in materials that respond both piezoelectrically (intrinsic response) and with the motion of ferroelectric domain walls (extrinsic response and possible relaxation). However, no significant time-dependent relaxation in strain is observed at the presently measured conditions.

Figure 1 also shows changes in the relative intensity of the (002) and (200) reflections. In tetragonal PZT, all non-180° domain walls are of type 90° and the volume fraction of 90° domains parallel to a particular direction can be determined from the intensity of the (002) and (200) diffraction peaks.[20] The change in intensities, or equivalently the change in the 90° domain volume fractions, between the positive and negative polarity of the electric field implies the motion of the 90° walls separating these domains. The extent of 90°domain reorientation ($\Delta\eta_{002}$) was calculated from these intensities (see supplementary material).[22] These values can be further combined with the unit cell dimensions to determine the strain in the material due to 90° domain reorientation, $\mathcal{E}_{90^\circ}$ (see supplementary material).[22] The contribution of 90° domain wall motion to the longitudinal piezoelectric coefficient, $d_{33,90^\circ}$ can be subsequently calculated using the relation[19]

$$d_{33,90^\circ} = \frac{\varepsilon_{33,90^\circ}}{2E_o}. \tag{2}$$

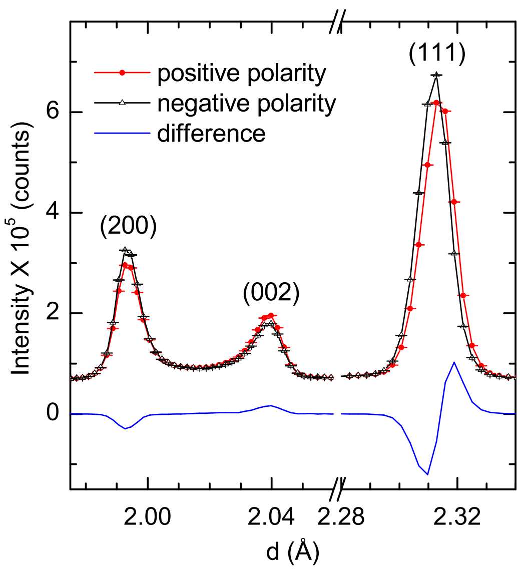

FIG. 1. Selected region of the diffraction pattern showing (002), (200), and (111) type reflections of the diffraction pattern under a positive and negative polarity of an electric field of frequency 3 Hz.

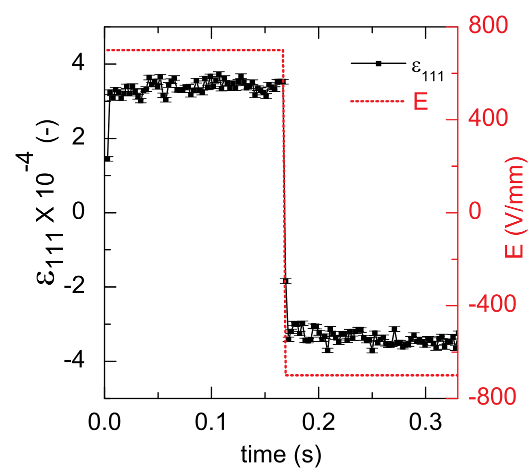

FIG. 2. Time-dependent response of the (111) lattice strain to an applied bipolar electric field of frequency 3 Hz. Strain is measured at 2.58 ms intervals.

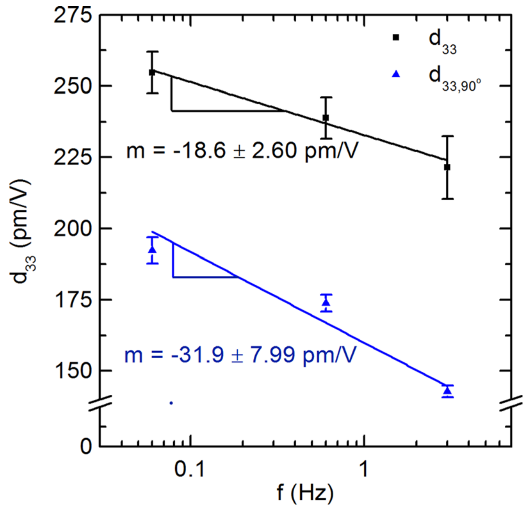

FIG. 3. Contribution of 90° domain wall motion to the macroscopic piezoelectric coefficient. The solid and dashed lines are linear fits to d_{33} and $d_{33,\,90°}$ respectively.

At the electric field amplitude used for these measurements, $\Delta\eta_{002}$ was found to be frequency-dependent. The value of $\Delta\eta_{002}$ at 0.06, 0.6, and 3 Hz was determined to be 0.03896 ± 0.0009, 0.03521 ± 0.0006, and 0.02891 ± 0.0004, respectively. This means that approximately 3% to 4% of 90° domains, which are oriented parallel to the electric field are reoriented between the positive and negative polarities of the waveform, leading to a measurable contribution to $d_{33,90°}$. The values of both d_{33} and $d_{33,90°}$ are shown in Figure 3 as a function of frequency. It can be said that the absolute value of $d_{33,90°}$ is approximately 75%, 72%, and 64% of the value of macroscopic d_{33} measured at the frequencies of 0.06, 0.6, and 3 Hz, respectively. Therefore, it can be concluded that 90° domain wall motion contributes directly to approximately 64% to 75% of the macroscopic piezoelectric coefficient in the frequency range of 0.06 to 3 Hz.

Figure 3 also demonstrates that $d_{33,90°}$, like d_{33}, varies linearly as a function of log frequency: d_{33} changes by 33 pm/V across the measured frequency range and $d_{33,90°}$ changes by 50 pm/V. A linear fit in d_{33} is applied to the d_{33} and $d_{33,90°}$ values as a function of log frequency. The linear fitting procedure takes into consideration the error at each data point and yields R^2 values of 0.96 and 0.88 for d_{33} and $d_{33,90°}$, respectively. The slopes of the frequency-dependent d_{33} and $d_{33,90°}$ are -18.6 ± 2.60 pm/V and -31.9 ± 7.99 pm/V, respectively. As slope of $d_{33,90°}$ is greater than the slope of d_{33} (by a factor of 1.7 ± 0.5), it is concluded that the contribution of 90° domain wall motion to strain is more frequency dispersive than the piezoelectric coefficient itself. This indicates that in addition to 90° domain wall motion, other mechanisms also affect the frequency dependence of the piezoelectric coefficient. In an analogous study that examined domain wall contributions as a function of field amplitude (instead of frequency), Pramanick *et al.*[19] found that $d_{33,90°}$ contributes to approximately half of the field-amplitude dependence of d_{33} in 2 at. % La-substituted PZT. Pramanick *et al.* suggested that nonlinearity in domain wall motion may be coupled with lattice strain, giving rise to an extrinsic lattice strain effect with additional nonlinearity.[18] In this prior work, the sum of these two contributions yielded the approximate nonlinearity in the property coefficient d_{33} as a function of field amplitude. Such a coupled mechanism is one possible explanation for the differences in frequency dispersion measured in the present work.

In conclusion, diffraction measurements have shown that 90° domain wall motion contributes to approximately 64% to 75% of the measured piezoelectric coefficient. Moreover, the effect of 90° domain wall motion on strain in tetragonal PZT is frequency-dependent in the range of 0.06–3 Hz, contributing partially to the frequency dispersion of the property coefficients.

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[22]See supplementary material at http://dx.doi.org/10.1063/1.4789903 for detailed calculations for the determination of the contribution of 90° domain wall motion to longitudinal strain.