Flexoelectric effect in ceramic lead zirconate titanate

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Mechanical strain gradient generated electric polarization or flexoelectric effect was investigated in unpoled lead zirconate titanate (PZT) ceramics in the ferroelectric state by using a cantilevered beam based approach. Flexoelectric coefficient μ_{12} at room temperature was measured to be 1.4 μC/m in the PZT ceramic at small level of strain gradient. Temperature-dependent experimental investigations clearly showed that high dielectric permittivity in the ferroelectrics enhanced flexoelectric polarization: essentially a linear relation was found to exist between μ_{12} and dielectric susceptibility χ at lower permittivity level (2100–2800), while μ_{12} versus χ curve started to deviate from the straight line at the $\chi \sim 2800$ and nonlinear enhancement of μ_{12} with χ was observed, with μ_{12} value reaching 9.5 at $\chi \sim 11\,000$. The nonlinearity in the flexoelectric effect was associated with domain-related processes. It is suggested that flexoelectric effect can have a significant impact on epitaxial ferroelectric thin films and mesoscopic structures. © *2005 American Institute of Physics*.
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Flexoelectric effect is the coupling between mechanical strain gradient and electric polarization and can be described by

$$P_l = \mu_{ijkl}\frac{\partial \varepsilon_{ij}}{\partial x_k}, \tag{1}$$

where P_l is the flexoelectric polarization, μ_{ijkl} the flexoelectric coefficient, ε_{ij} the elastic strain, and x_k the position coordinate. μ_{ijkl} is a fourth-rank polar tensor and therefore has nonzero components in dielectric solids of any crystal symmetry. Theoretical estimations predicted that flexoelectric coefficients in simple dielectrics are generally small (of the order e/a or $\sim 10^{-10}$ C/m, where e is the electron charge and a the dimension of unit cell).[1–3] Earlier experimental work on polymers[4] supported the theoretical predictions. Recently we developed a cantilevered beam based approach[5] to perform reliable measurements of flexoelectric effect. Experimental investigations using the approach showed that flexoelectric coefficients in the ferroelectric materials are many orders of magnitude higher (10^{-6} to 10^{-4} C/m).[6,7] The cantilevered beam based approach is generally used for dynamic flexoelectric measurements at lower level of strain gradient. To investigate the flexoelectric effect at higher strain gradient we developed another approach based on four-point bending and used the approach in static measurements of the flexoelectric coefficients in ferroelectric materials.[8]

Based on flexoelectric effect, ideas for developing new types of piezoelectric composites[9] were proposed, where none of the components is piezoelectric. If we understood flexoelectric effect well and there were database of flexoelectric coefficients available, a range of properly engineered flexoelectric composite structures could provide completely new piezoelectric capability.

Ferroelectric thin films and mesoscopic structures have exhibited a lot of potential for device applications such as FERAM and MEMS.[10] Misfit strain certainly exists at the interface between the epitaxially grown thin film ferroelectric and the substrate or electrode material. Nonuniform relaxation of the misfit strain in the thin films can lead to strain gradient,[11] which can then influence the dielectric and polarization behaviors of the ferroelectrics. Experimentally, some new phenomena recently observed in the thin film ferroelectrics were suggested to be due to the consequences of flexoelectric effect, such as the mechanical stress induced imprint in PZT capacitor structures[12] and pyroelectricity in highly stressed quasiamorphous $BaTiO_3$ films.[13] Recently a phenomenological model[14] of flexoelectricity was also proposed, showing that flexoelectric effect could play an important role in reducing the dielectric maximum in ferroelectric thin films. Ferroelectric PZT based ceramics and thin films are a family of technologically important functional materials.[15] In this letter, we report experimental investigations of the flexoelectric effect in ceramic PZT.

The PZT samples are the same as those used before,[8] with dimensions 60 mm long, 7 mm wide, and 3 mm thick. Flexoelectric effect was investigated using the cantilevered beam based approach and the system used for the flexoelectric measurement is identical to that used in earlier studies of barium strontium titanate (BST) and lead magnesium niobate (PMN).[5–7] A series of 3-mm-diam thin sputtered gold electrodes were prepared on the sample surface along the bar length. The ceramic bar sample is rigidly clamped at one end and driven into transverse vibration at 1 Hz by a small moving coil loudspeaker. The ac mechanical strain as a function of position along the bar was measured using a Microstrain™ DVRT (differential variable reluctance transducer) and the generated current was measured using an SR830 DSP Lock-in amplifier. The measured mode shape was then used to calculate the strain gradient at positions of the electrodes using the free bar model.[5]

For an unpoled PZT ferroelectric ceramic at the morphotropic phase boundary, although individual grains may have lower symmetry (tetragonal or rombohedral) which permits

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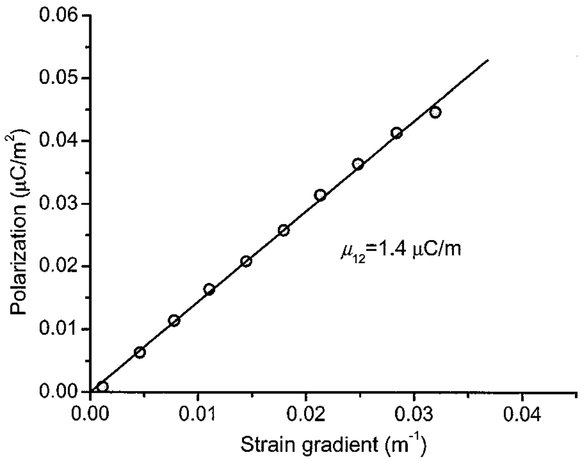

FIG. 1. Room temperature flexoelectric polarization vs strain gradient for unpoled PZT ceramic measured at 1 Hz near the clamped end ($x_1/L = 0.18$) of the cantilevered beam.

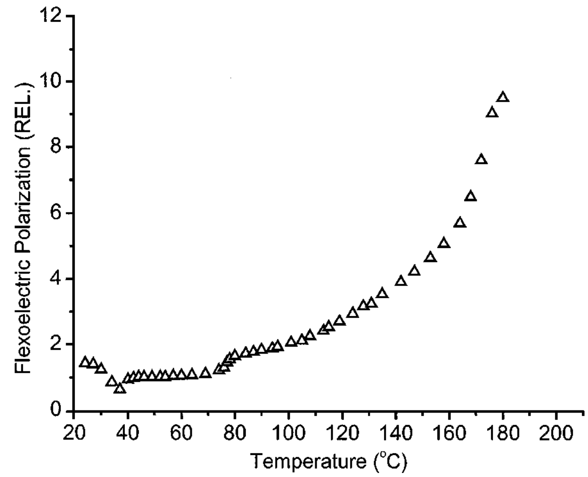

FIG. 2. Flexoelectric polarization (arbitrary unit) measured as a function of temperature in the ferroelectric state for the unpoled PZT ceramic.

piezoelectricity, in the volume of the ceramic one may expect a macroscopic symmetry of $\infty\infty m$, so the nonzero components for the flexoelectric tensor μ_{ijkl} should be μ_{1111}, μ_{1122}, and μ_{1212}, or in matrix notation μ_{11}, μ_{12}, and μ_{44}. In the unpoled PZT ceramic, no residual piezoelectricity could be detected by Berlincourt d_{33} meter and no evidence of piezoelectric resonance could be found in the impedance trajectory from 1 kHz to 1 MHz. By using the cantilevered beam based approach, any remnant piezoelectricity from the top and bottom halves of the sample bar is well balanced during the flexoelectric measurements. That some unbalance was affecting the measured value was however ruled out by the simple experiment of inverting the sample and noting that the measured signal did not change either in amplitude or phase. Clearly in ferroelectrics the free surface breaks the symmetry of the bulk and may affect the polarization behavior, however, in the present studies the effect of surface ferroelectricity[16] is unlikely due to the highly conductive metal electrodes on both free surfaces. Thus we believe that the measured electric polarization P_3 is solely due to the strain gradient in the x_3 thickness direction and can be written as

$$P_3 = \mu_{12}\frac{\partial \varepsilon_{13}}{\partial x_1}. \quad (2)$$

Figure 1 presents the room temperature (24 °C) flexoelectric polarization as a function of the transverse strain gradient obtained near the clamped end ($x_1/L = 0.18$) of the bar by using the cantilevered beam based dynamic approach. It is clear that the generated electric polarization is linearly proportional to the elastic strain gradient and the slope of the line gives a magnitude of μ_{12} of 1.4 μC/m, close to the early data of 0.5 μC/m[8] obtained by static measurements using a four-point bend fixture. Figure 2 presents the measurements of μ_{12} in the PZT ceramic as a function of temperature (24–180 °C). When heating up from room temperature (24 °C), unexpectedly the μ_{12} initially drops before it becomes stabilized at 40 °C, then flexoelectric polarization basically keeps flat at the temperature range of 40–70 °C but starts to rise prominently at 70 °C.

Clearly high dielectric permittivity in the ferroelectric materials can enhance flexoelectric coefficients[6,7] and μ_{12} can be related to dielectric susceptibility χ by

$$\mu_{12} = \gamma\chi\frac{e}{a}, \quad (3)$$

where γ is a scaling factor. In order to evaluate the impact of dielectric property on the flexoelectric effect, dielectric spectra from the PZT ceramic were measured and shown in Fig. 3, where a strong but rounded dielectric maximum suggests a diffuse phase transition around 220 °C. The plot of μ_{12} versus χ is shown in Fig. 4. Comparison of experimental data obtained in BST, PZT, and PMN reveals that, at similar level of relative dielectric permittivity, μ_{12} in BST is roughly one order of magnitude higher than that in PMN or PZT. It remains unclear as to why the Pb-based ferroelectrics should have lower values of flexoelectric coefficients.

As shown in Figs. 2 and 4, the initial drop of μ_{12} with χ is unexpected but may correspond to the increase of loss tangent (Fig. 3) in the temperature range (24–50 °C). A linear relation between μ_{12} and χ with $\gamma=1$ is seen to exist in the χ range of 2100–2800 (or temperature range of 40–74 °C). The μ_{12} versus χ curve deviates from the $\gamma=1$ line at the $\chi \sim 2800$ and the rise of μ_{12} with χ becomes essentially nonlinear, with μ_{12} reaching 9.5 at $\chi \sim 11\,000$.

Nonlinearity in flexoelectric coefficient was found in temperature-dependent experimental investigations of BST,[7] where μ_{12} was raised to 100 μC/m when approaching the dielectric peak from the paraelectric state. Such nonlinear

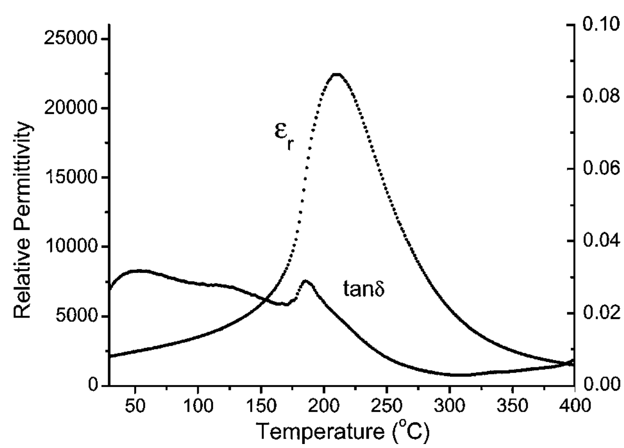

FIG. 3. Dielectric permittivity and loss tangent for the unpoled PZT ceramic measured as function of temperature at a frequency of 1 kHz.

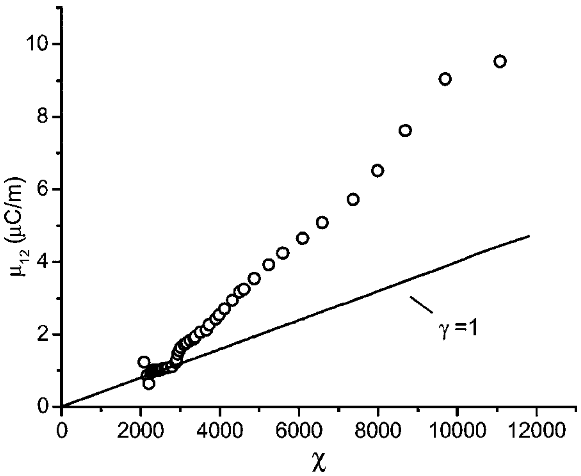

FIG. 4. Flexoelectric coefficient μ_{12} vs dielectric susceptibility χ for the unpoled PZT ceramic. The dotted line shows a linear relation between μ_{12} and χ at lower level of dielectric permittivity with a $\gamma=1$.

enhancement was suggested to be due to the survival of some ferroelectric domains in the BST ceramic above the Curie transition temperature T_C. In the previous studies of ceramic PMN,[6] nonlinear enhancement of μ_{12} with χ was also observed and found to be closely associated with the pre-existing polar microdomains in this prototypic relaxor ferroelectric material.[17] Apart from the nonlinear behavior of flexoelectric coefficient with dielectric permittivity, previous static investigations[8] in PZT ceramic revealed nonlinear relation between flexoelectric coefficient and mechanical strain gradient, where the jump of μ_{12} from 0.5 μC/m at lower strain gradients to 2 μC/m at much higher strain gradients was shown to be associated with the onset of domain wall motion induced by the very high level of inhomogeneous strain achievable with the four-point bend fixture. As discussed earlier, nonlinearity in the flexoelectric effect can be tentatively attributed to the domain-related processes in ferroelectrics and the scaling factor γ in Eq. (3) depends on the materials investigated, the level of dielectric permittivity, and the magnitude of strain gradient. The experimental findings of nonlinear phenomena are in good agreement with the theoretical studies by Catalan *et al.*,[14] where it was shown that flexoelectric coefficient is only a linear function of the strain gradient or permittivity when the induced flexoelectric polarization is small. In addition to the extrinsic influence of domain-related processes discussed earlier, it is possible that a part of the nonlinearity in the flexoelectric effect may also be of intrinsic origin as shown in the theoretical work of Catalan *et al.*[14]

In epitaxial ferroelectric thin films and mesoscopic structures, Curie phase transition temperature T_C or dielectric peak can be adjusted to around room temperature where ultrahigh dielectric permittivity becomes available, by appropriate selection of lattice misfit and film thickness as shown in recent theoretical[18] and experimental[19] studies. Likewise, strain gradient in these ferroelectric structures can also be adjusted by tailoring the structure dimensions or controlling the relaxation of the misfit strain. The nonlinear enhancement of flexoelectric coefficients with the dielectric permittivity and strain gradient can lead to a significant impact of flexoelectric effect in these properly engineered thin film ferroelectric heterostructures.

In summary, flexoelectric effect was investigated in the ferroelectric state of unpoled lead zirconate titanate (PZT) ceramics. Temperature-dependent flexoelectric investigations showed that μ_{12} essentially increases with relative dielectric permittivity and the nonlinear phenomenon was found at higher level of dielectric permittivity, which is suggested to be associated with domain-related processes.

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