Strain-gradient-induced electric polarization in lead zirconate titanate ceramics

Wenhui Ma[a)]
Max-Planck-Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany

L. Eric Cross
Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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Strain-gradient-induced polarization or flexoelectricity was investigated in unpoled soft lead zirconate titanate (PZT) ceramic where the texture symmetry $\infty\infty m$ forbids macropiezoelectricity. Even under high strain gradient ($1\ \mathrm{m}^{-1}$) the induced polarization is small ($1.6\ \mu\mathrm{C/m}^2$) at 20 °C. Higher strain gradients induce ferroelastic poling and an additional extrinsic contribution to the flexoelectric coefficient μ_{12} raising the value from 0.5 to 2.0 μC/m. Cooling through the Curie point (T_C) under maximum stress (80 MPa) where the peak permittivity (~20 000) could raise μ_{12} to 20 μC/m, the equivalent electric field is still only ~1 kV/m, inadequate to achieve significant ferroelectric poling. The situation may be different in thin PZT films where much larger strain gradients can occur. [DOI: 10.1063/1.1570517]

The well-known elastoelectric coupling effects include piezoelectric effect, electrostrictive effect, and Maxwell stress effect. Piezoelectric ceramics[1] and more recently single crystals[2] have demonstrated the capability for broad applications in sensor, actuator, and transducer devices. In soft polymers, it is shown recently that Maxwell stress effect (attractive forces between opposite charges on the electrodes) can generate ultrahigh strain responses and exhibit great potential for a variety of electromechanical device applications.[3] All the earlier-mentioned physical effects, however, generally assume the situations of uniform stress or strain. In nature, there is elastoelectric coupling caused by inhomogeneous deformation where stress or strain gradient associated polarization effects (flexoelectric effects) need to be considered. Overall, mechanical stress or strain can generate electric polarization in a deformable dielectric material through the following two mechanisms:

$$P_i = d_{ijk}\sigma_{jk} + \mu_{ijkl}\frac{\partial \varepsilon_{jk}}{\partial x_l}. \tag{1}$$

In Eq. (1) and thereafter Einstein summation convention is assumed ($i,j,k,l=1,2,3$). The first term on the right-hand side refers to the well-known direct piezoelectric effect, where σ_{jk} is the stress uniformly distributed across the sample and d_{ijk} is the piezoelectric coefficient, a third-rank polar tensor. The second term on the right-hand side refers to the strain gradient ($\partial\varepsilon_{jk}/\partial x_l$) induced polarization and μ_{ijkl} is the flexoelectric coefficient, a fourth-rank polar tensor. In centrosymmetric materials, $d_{ijk} \equiv 0$, so the piezoelectric term in Eq. (1) can be eliminated, therefore

$$P_i = \mu_{ijkl}\frac{\partial \varepsilon_{jk}}{\partial x_l}, \tag{2}$$

where P_i is the electric polarization induced solely by strain gradient.

a)Electronic mail: mawenhui@mpi-halle.de

When reviewing the history of flexoelectric investigations, it is noted that while the concept was originally formed in early 1960s,[4,5] not until 1981 was such effect in crystalline solids given the name "flexoelectric."[6] Based upon an ionic model,[7] Tagantsev analyzed the flexoelectric effect and suggested possible larger effects in ferroelectrics. In soft polymers Marvan *et al.*[8] observed flexoelectric coefficients of the order of 10^{-11}–10^{-10} C/m. Up to now very little attention has been paid to test the magnitude of flexoelectric coefficients and the mechanism remains unclear. Recently we measured the flexoelectric coefficients (μ_{12}) in lead magnesium niobate (PMN)[9,10] (a well-known relaxor ferroelectric material) and barium strontium titanate (BST)[11,12] (a normal ferroelectric material). Both materials were tested in the phase region with macroscopic cubic symmetry, moreover the samples were measured in the form of a cantilevered beam so that any remnant piezoelectric contributions from the top and bottom halves of the beam would cancel. In this letter, we investigate the flexoelectric effect in a well-known lead zirconate titanate (PZT) piezoelectric ceramic in the ferroelectric phase by using a four-point bend fixture to generate a uniform strain gradient.

In this work several interesting questions were explored: (i) using a four point bending fixture is it possible to induce and measure a quasistatic flexoelectric polarization generated by μ_{12}; (ii) is the flexoelectric polarization enhanced or inhibited by the onset of ferroelastic domain wall motion which will be evidenced by change of the flexural stiffness and the development of remnant curvature in the sample; and (iii) is it possible in soft PZT to reach levels of flexoelectric induced field sufficient to pole the ceramic into a piezoelectric form.

The samples used were unpoled PZT–5H ceramics (doped with La and Sn) fabricated by TRS Ceramics Company, State College, Pennsylvania. Dielectric measurements performed using an HP4284A LCR meter show a weak field permittivity of 2200 at 20 °C and a strong but rounded dielectric maximum ($\varepsilon_3 \approx 20\,000$) without little dispersion

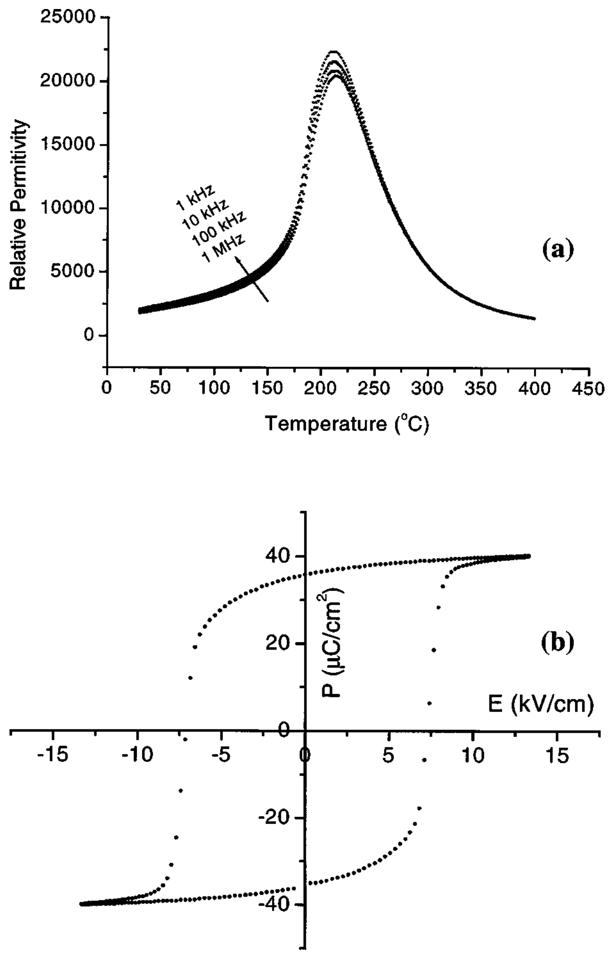

FIG. 1. (a) Weak field dielectric permittivity ($E \sim 10$ V/cm) as a function of frequency and temperature in the soft PZT–5H sample measured; (b) dielectric hysteresis (P vs E) in the soft PZT–5H composition.

over the frequency range of 1 kHz–1 MHz [Fig. 1(a)], suggesting a diffuse phase transition without strong relaxor character. Polarization hysteresis loops measured using a modified Sawyer–Tower circuit show remnant polarization of 35 μC/cm^2 and coercive field of 7 kV/cm [Fig. 1(b)] with no discernable bias. Young's modulus was measured to be 70 GPa by a dynamic resonance method.

A uniform strain gradient was generated using a four-point bend fixture schematically illustrated in Fig. 2(a). Samples for measurement had dimensions 60 mm long, 7 mm wide, and 3 mm thick. Surfaces were carefully polished and the samples were annealed at 700 °C to relieve surface stresses. Sputtered gold electrodes with dimensions 10×7 mm^2 were applied to upper and lower surfaces in the center of the beam. No residual piezoelectricity could be detected by Berlincourt d_{33} meter, and the impedance trajectory from 1 kHz to 1 MHz was free from evidence of piezoelectric resonance. The bend test was carried out according to the ASTM C-1161-94 by using an Instron machine model 4202 with a 10 kN load cell. Outer and inner spans of the fixture are 40 and 20 mm, respectively. The generated electric charge was detected by a Keithley 6517 electrometer that can resolve 10 fC and will measure up to 2.1 μC. Before measurement the electrometer was carefully calibrated for voltage burden and input offset current.

The stress distribution along the sample length direction

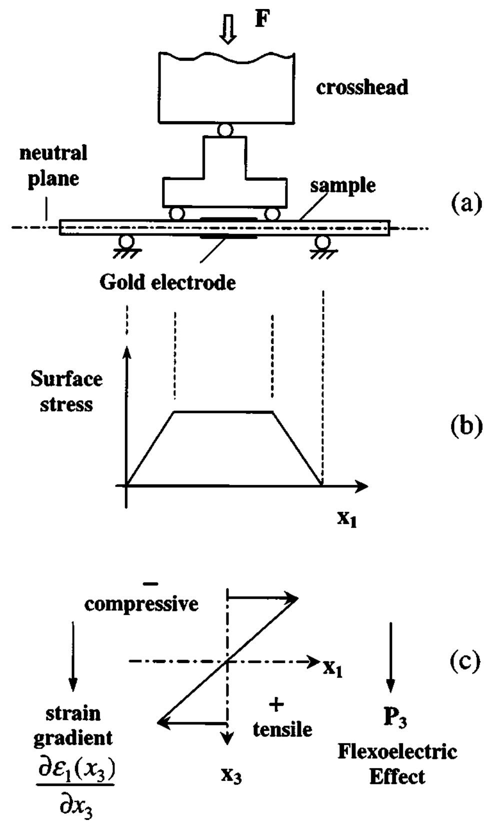

FIG. 2. Schematic illustration of strain gradient induced quasi-static polarization measurement, (a) typical four-point bending fixture; (b) stress distribution; (c) schematic of strain gradient and the induced polarization along the thickness of the sample.

(x_1) is shown in Fig. 2(b). Within the inner span the stress $\sigma_{11}(x_1)$ is uniform along the length, while along the thickness direction (x_3) the stress $\sigma_{11}(x_3)$ varies and there is a stress or strain gradient as shown by Fig. 2(c), which can generate electric polarization through the flexoelectric effect. Because the bar length is much greater than the bar thickness, we omit the shear stress and strain and only consider the principal stress and strain. Therefore, for simplification here only one suffix was used for describing the stress and strain tensors. The absolute value of surface stress was calculated using the following equation:

$$\sigma_1(x_3)|_{x_3=\pm d/2} = \frac{3FL}{4wd^2}, \tag{3}$$

where F is the load, w is the width, d is the thickness, and L is the outer span of the bend fixture.

The strain gradient in the thickness direction is given by

$$\frac{\partial \varepsilon_1(x_3)}{\partial x_3} = \frac{12st}{L^2}, \tag{4}$$

where s is the crosshead speed and t the time gone by.

Figure 3 presents data on the surface stress versus strain curves for tests carried out at 1 and 0.2 mm/min crosshead speed. As shown in Fig. 3(a), the flexure strength is measured to be 85 MPa. The softening of the samples at certain stress/speed levels (e.g., around 30 MPa for 1 mm/min crosshead speed) we believe corresponds to the onset of ferroelastic domain motion. As expected in PZT the sample becomes softer at lower loading rates due to the relaxational nature of

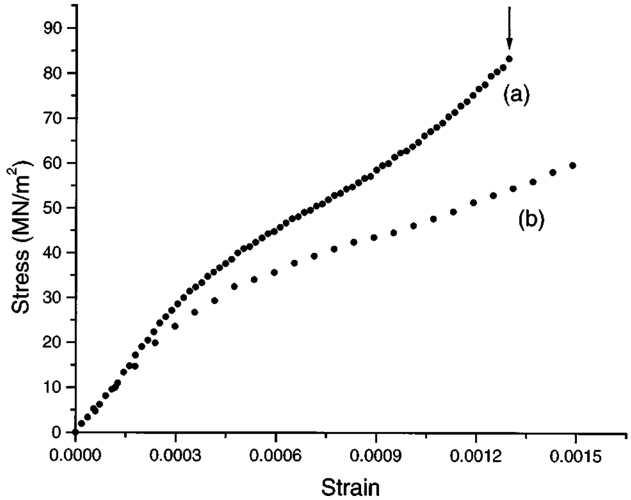

FIG. 3. Surface stress as a function of strain measured at two different crosshead speeds on PZT−5H bar, (a) 1 mm/min crosshead speed (the arrow indicates the level of stress at which the sample broke); (b) 0.2 mm/min crosshead speed.

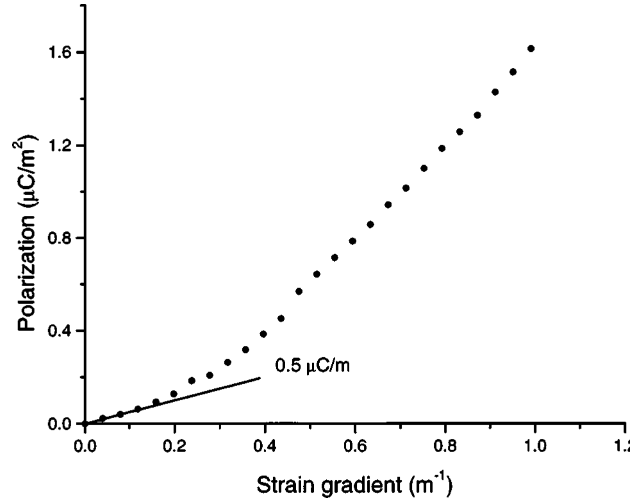

FIG. 4. Polarization vs strain gradient for an unpoled PZT−5H sample induced during a four-point bend test carried out at a crosshead speed of 0.2 mm/min.

ferroelastic domain switching. That ferroelastic switching has occurred at the higher loading levels is evident by a static remnant curvature in the sample after testing.

Flexoelectric polarization versus strain gradient is displayed in Fig. 4. It is clear that the behavior is not linear, showing a low-gradient and high-gradient linear behavior but of different slope. The changeover occurs at the gradient $\sim 0.3\ \mathrm{m}^{-1}$ corresponding to the onset of ferroelastic switching. At very small strain level, the sample is only subjected to elastic deformation, so the measured electric polarization response represents the intrinsic flexoelectric effect. The low-gradient slope corresponds to a flexoelectric coefficient $\mu_{12} \approx 0.5\ \mu\mathrm{C/m}$, and the high-gradient slope takes $\mu_{12} \approx 2.0\ \mu\mathrm{C/m}$ showing that ferroelastic domain wall motion aids the response.

The measured flexoelectric polarization is very small compared to the remnant polarization, only $1.6\ \mu\mathrm{C/m}^2$ at a strain gradient of $1\ \mathrm{m}^{-1}$. By using a relative permittivity value of $\varepsilon_r = 2200$ (at 1 kHz), we figure out that a strain gradient of $1\ \mathrm{m}^{-1}$ is equivalent to an electric field of 100 V/m, which is obviously too small compared to the coercive field. In high-permittivity ferroelectrics we may expect from elementary theory of flexoelectricity[7] that μ_{ij} be proportional to dielectric susceptibility χ_{ij} following a relation:[11]

$$\mu_{ij} = \gamma \chi_{ij} \frac{e}{a}, \tag{5}$$

where γ is a constant of value close to unity. For the PZT unpoled ceramic at low gradient levels the normalized flexoelectric coefficients μ_{12}/χ_{22} at 20 °C is 0.23 nC/m giving $\gamma \approx 0.57$. In PMN from our earlier study,[9,10] μ_{12}/χ_{22} is 0.26 nC/m giving $\gamma \approx 0.65$, both in reasonable accord with the elementary theory. For BST ceramic at 25 °C, however, $\mu_{12}/\chi_{22} \approx 3.72$ nC/m yielding a value $\gamma = 9.3$[11] much higher than those in the lead-based systems.

It may be noted that in earlier investigations of the thermopolarization effects Strukov *et al.*[13] found exceedingly high values for the normalized thermopolarization coefficient (b_{ij}^0) in triglycine sulfate which they attributed to the order-disorder nature of the ferroelectric phase change in this compound. We note that in $Ba_xSr_{1-x}TiO_3$,[13] there is strong evidence of a local order-disorder component between polarization vectors in the unit cell. It will be interesting to measure μ_{12} in potassium niobate tantate, where again order-disorder has been identified,[14] to see if the coefficients are again anomalously large.

In conclusion, the PZT ceramic does exhibit modest flexoelectricity and ferroelastic domain wall motion enhances the response, but it is not possible in our samples using stress levels up to the full fracture strength to induce ferroelectric poling, although ferroelastic poling was patently obvious.

In the PZT thin films epitaxially grown on lattice-mismatched substrates the strain gradient between surfaces and strain-relieving dislocations can be exceedingly large and the flexoelectric effects could be of major importance in these systems.

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