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Weak ferroelectricity in antiferroelectric lead zirconate

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Sawyer-Tower polarization (*P-E*) measurements have revealed dielectric hysteresis loops in antiferroelectric lead zirconate (PZ), suggestive of weak ferroelectric tendencies. Both polarization saturation and reemergence were observed which were on the order of 0.1 and 0.05 $\mu C/cm^2$, respectively. Laser interferometry investigations, then, revealed a strain of approximately 2×10^{-7} under a field strength of 15 kV/cm. The strain curve has a butterfly shape indicating a contribution from the piezoelectric effect. These results suggest that antiferroelectric PZ may possess a small reversible spontaneous polarization along the *c* direction, which is consistent with previous structural studies. The weak ferroelectricity is found to disappear in lanthanum-modified lead zirconate, excluding the possibility of defect-induced ferroelectricity in PZ. A competition between zone center (which leads to ferroelectricity) and zone boundary (which leads to antiferroelectricity) transverse phonon modes is discussed with respect to the observed weak ferroelectricity.

INTRODUCTION

Lead zirconate ($PbZrO_3$, denoted as PZ) is a well-known antiferroelectric and is the end member of the technologically important $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) crystalline solution series. Antiferroelectricity in PZ was observed by dielectric investigations.[1] Early x-ray studies[2] of the antiferroelectric PZ superstructure suggested an orthorhombic symmetry; however, tetragonal[3] and monoclinic[4] symmetries were also suggested by other investigators. A detailed x-ray and neutron diffraction investigation by Jona, Shirane, Mazzi, and Pepinsky[5] confirmed the orthorhombic structure and revealed that the origin of antiferroelectricity was an antiparallel shift of Pb ions along the [110] direction. This shift resulted in no net polarization along [110]; however, an antiparallel shift of oxygen atoms along the [001] direction remained unbalanced. Consequently, PZ is not an antiferroelectric in the theoretical sense suggested by Kittel.[6] Kitell's model crystal involved two or more sublattices containing equal and opposite polarizations, resulting in a centrosymmetric structure with no piezoelectricity. PZ fits this antiferroelectric definition only in two dimensions (the *a-b* plane); polarization (P_3) and piezoelectricity (d_{33}) may exist along the [001] direction due to unbalanced shifts of oxygen ions. The existence of a small but detectable d_{33} in prepoled PZ ceramics was reported by Robert in the early 1950's.[7] However, no subsequent reports of weak piezoelectricity or ferroelectricity in antiferroelectric PZ have been made. Investigations[8] have tried, unsuccessfully, to verify the existence of a remanent polarization along [001] in PZ single crystals by pyroelectric methods. The failure of this study has been attributed to sensitivity limitations of the techniques used and to the highly twinned nature of the crystals examined.[9,10] Fesenko and Smotrakov[11] have shown that if a spontaneous polarization exists it should be smaller than 0.1 $\mu C/cm^2$.

In this paper, we report weak ferroelectricity in PZ at room temperature observed by Sawyer-Tower polarization (*P-E*) and interferometric displacement (*s-E*) techniques. Studies on lanthanum-modified lead zirconate (PLZ) samples are also performed to examine the effect of "impurities" on the weak ferroelectricity.

EXPERIMENTAL TECHNIQUES AND PROCEDURE

PLZ ceramic specimens were prepared by a mixed-oxide method according to the formula $Pb_xLa_{1-x}ZrO_3$ (abbreviated as PLZ 100*x*) from high-purity (>99.9%) PbO, ZrO_2, and La_2O_3 powders. The compositions chosen for study included PZ, PLZ 1, 2, 4, 6, and 8. Ceramic disks were prepared by hot pressing at 1150 °C for 2 h and a subsequent postannealing at 1300 °C for 2 h in a PbO-rich environment. Dense ceramic specimens were obtained, which were second-phase free to x-ray diffraction.

The complex dielectric permittivity was measured using a Hewlett-Packard 4284A inductance-capacitance-resistance (LCR) meter which can cover a frequency range from 20 to 10^6 Hz. High-temperature dielectric data were obtained by putting the samples in a small tube furnace specifically equipped for such measurements.

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The P-E measurements were performed using a modified, computer-controlled Sawyer-Tower circuit. The data were carefully compensated by a linear capacitance and a linear conductance to determine the net contribution of the displacement current. Electric field strengths of 40 kV/cm were needed to drive the polarization into saturation. Corresponding field-induced strains were measured by a laser interferometric technique, which had a displacement resolution of 10^{-4} Å over a broad frequency bandwidth.[12]

RESULTS AND DISCUSSION

Figure 1 shows the dielectric response characteristics measured at 100 kHz as a function of temperature for PZ. A dielectric maximum of ~6000 can be seen near 240 °C in measurements on heating and 233 °C on cooling, in agreement with accepted values. Figure 2 illustrates a P-E curve for PZ at room temperature. The measurement frequency was 50 Hz. A single hysteresis loop can clearly be seen, resembling that expected for ferroelectrics rather than antiferroelectrics. However, the magnitudes of the spontaneous and remanent polarizations were nearly three orders of magnitude below that generally found for ferroelectric PZT. A remanent polarization of ~0.05 $\mu C/cm^2$, a coercive field of ~15 kV/cm, and a saturation polarization of ~0.09 $\mu C/cm^2$ can be seen in Fig. 2. No double hysteresis loops characteristic of a field-induced antiferroelectric-ferroelectric transition were observed below 40 kV/cm; the field needed to induce this transformation at room temperature presumably exceeded the dielectric breakdown strength.

Field-induced displacements were then measured by laser interferometer, in part to exclude the possibility that space-charge effects are the source of the polarization nonlinearity which is observed in Fig. 2. Space charges may move and possibly even saturate under ac bias, giving a hysteresis-loop-like response; however, space charge does not generate a lattice strain. Figure 3 illustrates the field-induced strain (s-E) at room temperature. The measured strain was along the applied field direction. A measurement frequency of 10 Hz was used. The strain achieved under a field strength of 15 kV/cm was on the order of 10^{-7}. The observed field-induced strains must have occurred via a piezoelectric and/or electrostrictive coupling mechanism(s).

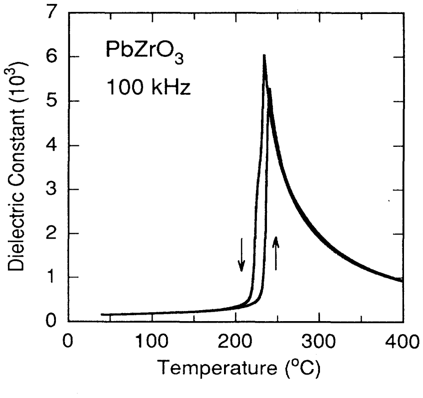

FIG. 1. Dielectric constant as a function of temperature for PbZrO$_3$. Arrows indicate measurements on heating and cooling.

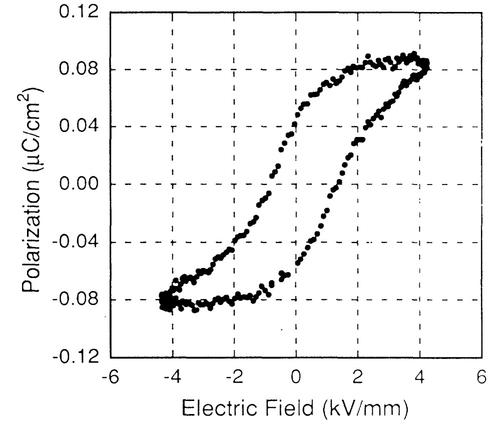

FIG. 2. Dielectric hysteresis loop of PbZrO$_3$.

It is known that the piezoelectric strain associated with polarization reversal (s-E) in a ferroelectric has a butterflylike hysteresis behavior. However, the electrostrictive strain is a parabolic function of the field strength, and is generally negligible relative to the piezoelectric strain at moderate field strengths in normal ferroelectrics. The s-E curve shown in Fig. 3 clearly shows butterflylike features, which strongly suggests a piezoelectric effect combining with polarization reversal. However, careful data analysis revealed that the strain cannot be fitted to either a linear piezoelectric relation

$$s = d_{33} E \, , \tag{1}$$

or a parabolic electrostrictive relation

$$s = Q_{11} E^2 \, , \tag{2}$$

in which E is the strength of applied electric field, s is the induced strain in the field direction, d_{33} is the piezoelectric coefficient, and Q_{11} is the electrostrictive coefficient.

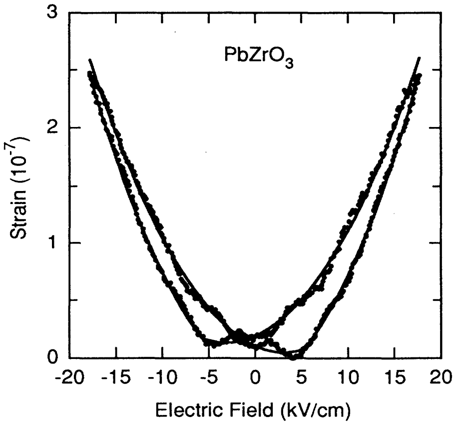

FIG. 3. Strain versus electric field curve of PbZrO$_3$. The dots are the experimental data and the lines are fittings using $s = d_{33}E + Q_{11}E^2$, which includes contributions from both piezoelectric and electrostrictive couplings.

The best agreement was obtained by fitting the total strain to a relation

$$s=d_{33}E+Q_{11}E^2 . \qquad (3)$$

This indicates that the contribution from electrostriction in PZ should not be neglected, and must be superimposed on a piezoelectric strain to yield the total strain. Nonlinear least-squares fitting to the total strain, shown in Fig. 3 by solid lines, yielded contributions from d_{33} of 3×10^{-14} C/N and Q_{11} of 7×10^{-20} C^2/N^2. The magnitude of d_{33} is so small that it has not been detected by traditional piezoelectric techniques, which generally have resolution limits of 10^{-12} C/N.

The expression for electrostriction $s=Q_{11}E^2$ is valid only when the polarization along the field direction follows the applied field in a linear manner, $P=\varepsilon_0\varepsilon E$ (ε_0 is the vacuum dielectric permittivity and ε is the relative dielectric constant). A more general definition of electrostriction is

$$s=Q'_{11}P^2 , \qquad (4)$$

where the longitudinal strain and polarization result from a common lattice distortion. Using a phenomenological approach, Haun[13] estimated that the upper and lower limits of Q'_{11} for polycrystalline PZ were 0.032 and 0.027 m^4/C^2, respectively. Following this model, Q'_{11} represents the electrostrictive contribution to the lattice strain from the antiferroelectric sublattice expansion under bias. By assuming a linear P-E behavior (which is certainly valid for the antiferroelectric contribution) and by estimating the value of the dielectric constant at room temperature from Fig. 1 ($\varepsilon=180$), the value of Q_{11} can be converted to an equivalent Q'_{11}. The value of Q'_{11} was estimated from our data to be 0.028 m^4/C^2, which is in excellent agreement with Haun's calculations. This close agreement clearly indicates that the electrostrictive strain arises from an antiferroelectric contribution, whereas the piezoelectric strain arises from a noncentrosymmetric polar contribution. These results strongly support the possibility of weak ferroelectricity in antiferroelectric PZ.

P-E and s-E studies were then performed on La-modified PZ samples, in part to exclude the possibility that impurities and/or defects are the source of the weak ferroelectricity by locally inducing a small volume fraction of a ferroelectric state. Lanthanum was chosen as the "impurity," as it is well known to be a good aliovalent dopant in PZ and the $Pb(Zr_{1-x}Ti_x)O_3$ crystalline solution series. Figures 4(a)–4(f) show the P-E re-

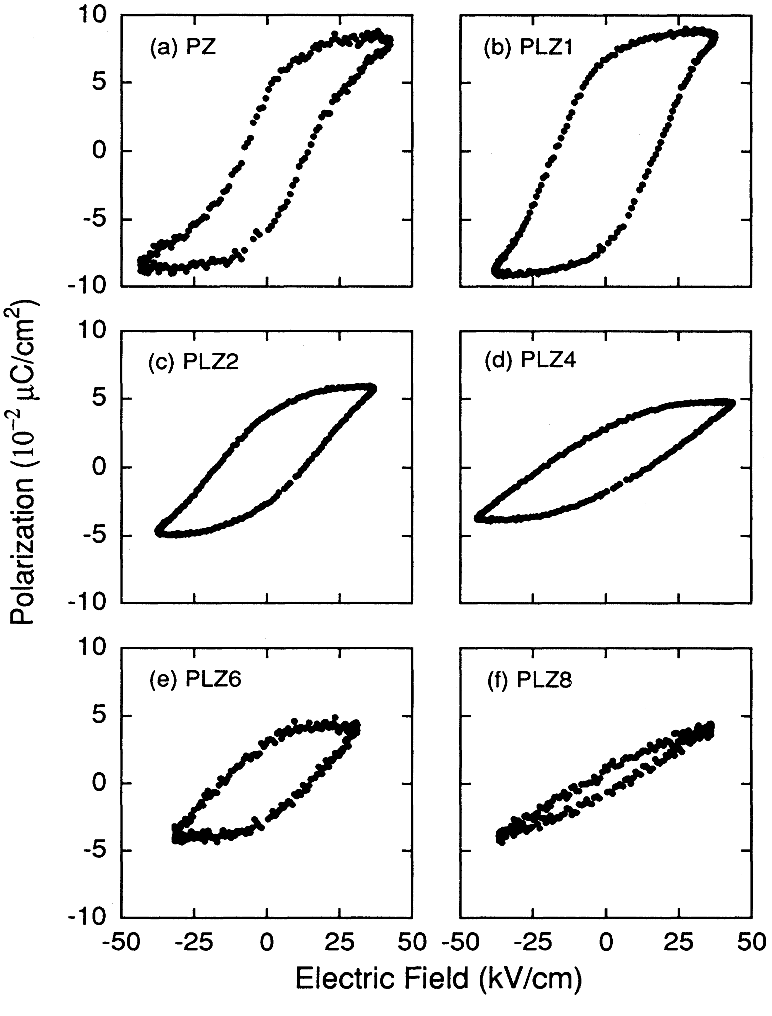

FIG. 4. P-E curves at room temperature of (a) PZ, (b) PLZ 1, (c) PLZ 2, (d) PLZ 4, (e) PLZ 6, and (f) PLZ 8.

sults for PZ, PLZ 1, 2, 4, 6, and 8. Evidence of weak ferroelectricity, characterized by the near-square hysteresis loops, is present for compositions up to PLZ 4. However, the saturation and remanent polarizations decrease with increasing La content, indicating a gradual loss of the weak ferroelectricity. Nonlinearity of the P-E curves becomes less evident for PLZ 6, and changes to a nearly linear response for PLZ 8. s-E curves for PZ, PLZ 2, 4, and 6 are presented in Figs. 5(a)–5(d). The butterflylike features persists from PZ to PLZ 4, reflecting a piezoelectric contribution to the induced strain in these compositions, and is consistent with the P-E studies. The s-E curve shows quadratic features without the butterfly shape for PLZ 6, suggesting a pure electrostrictive response. These results clearly show that impurities and vacancies are not the source of the polarization nonlinearity and piezoelectric coupling. La modification of PZT ceramics is known to relax the oxygen octahedra framework, also excluding the possibility of residual strains in the ceramic giving rise to local induced transformations. However, if residual strains in the ceramic gave rise to stress-induced transformations, these stress-induced transformations would not be expected to be switchable by an electric field. In addition, no evidence of second phase formation or the presence of local ferroelectric domains was found by extensively examining the PZ sample using transmission electron microscopy and selected-area electron diffraction techniques.[14] We believe that the observed weak ferroelectricity in PZ is clearly an intrinsic phenomenon.

Jona *et al.*[5] found unbalanced oxygen shifts along [001] and assigned PZ to the space group *Pba*2 at room temperature. This space group is acentric, allowing ferroelectricity and piezoelectricity. However, Fujishita and Hoshino proposed the centrosymmetric structure belonging to *Pbam* with no oxygen shifts.[15] The weak ferroelectricity observed in the present study supports Jona's conclusion of unbalanced oxygen shifts along [001]. A net polarization in PZ has also previously been suggested by Miller and Kwok from microscopic free-energy considerations.[16] The questions arise as to what is the origin of the weak ferroelectricity in PZ and what is the structural basis of the net remanence? A possible answer might be an intrinsic coexistence/competition between ferroelectric and antiferroelectric phonon modes in PZ.

PZ has been shown to undergo a first-order paraelectric-antiferroelectric transition near 235 °C,[17] as by dielectric anomaly in Fig. 1. The dielectric constant in the high-temperature region followed the Curie-Weiss relation, $\varepsilon = C/(T-T_0)$, with a Curie-Weiss constant (C) of 1.2×10^5 °C and a Curie temperature (T_0) of 185 °C.[1] The static dielectric constant (ε at wave vector $\mathbf{q}=0$) and lattice vibration frequencies are related through the generalized Lydane-Sachs-Teller relationship given in the equation

$$\varepsilon/\varepsilon_\infty = \prod_i [(\omega_L)_i^2/(\omega_T)_i^2] \ , \tag{5}$$

where ε_∞ is the high-frequency (or optical) dielectric constant and ω_L and ω_T are the longitudinal and transverse optical (LO and TO) phonon frequencies, respectively. According to Eq. (5), a large ε must be associated with the existence of a low-frequency ($\mathbf{q}=0$) TO mode (i.e., a ferroelectric mode). The weak ferroelectricity in antiferroelectric PZ confirms the two-mode competition theorem proposed by Samara[18] based on pressure- and temperature-dependent studies of the dielectric properties and phase transformation characteristics. That is, in PZ there are two temperature-dependent low-frequency

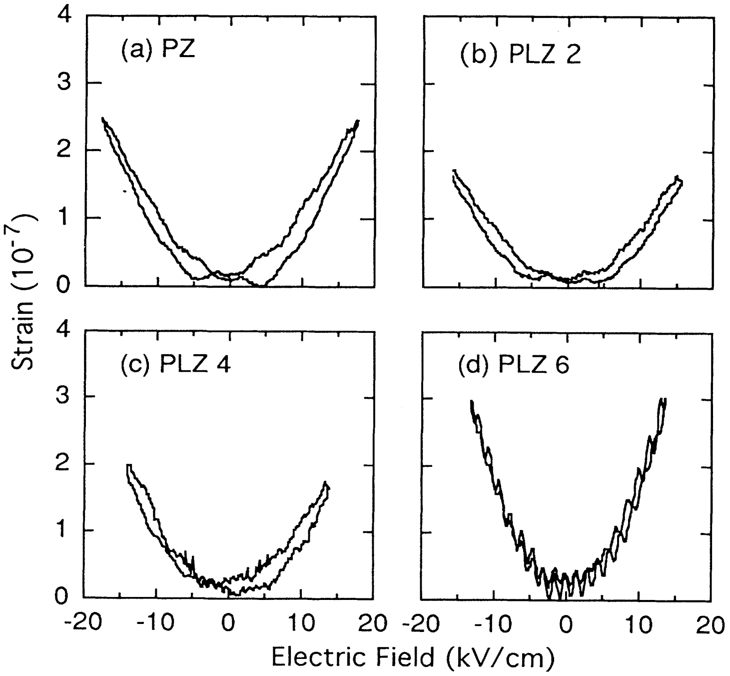

FIG. 5. Strain curves under applied electric field of (a) PZ, (b) PLZ 2, (c) PLZ 4, and (d) PLZ 6.

modes: a ferroelectric mode which determines the large polarizability above the paraelectric-antiferroelectric phase transition temperature, and an antiferroelectric mode(s) which drives the transformation to the antiferroelectric state.

As concerns the question of the structural basis of the net remanence, the components of spontaneous polarization on the *a*-*b* plane may align antiparallel due to strong short-range antiferroelectric couplings. As a result, the polarization on the *a*-*b* plane can be considered to be composed of two equal but opposite antiparallel polarizations, P_a and P_b, in a two-dimensional lattice. However, a component of the spontaneous polarization along [001], driven presumably by a ferroelectric mode as discussed above, exists which is not significantly affected by the antiferroelectric coupling in the *a*-*b* plane. Consequently, a net remanent polarization may exist in PZ.

The important conclusions of the present study can be summarized as follows.

(1) Extremely weak but detectable ferroelectricity is confirmed in antiferroelectric PZ at room temperature. The implication is that the space group of the antiferroelectric orthorhombic phase in PZ is noncentrosymmetric, as previously suggested by Jona *et al.*

(2) A net polarization may result due to the coexistence of ferroelectric and antiferroelectric mode(s), where the antiferroelectric order is two dimensional (confined to the *a*-*b* plane) and the reversible spontaneous polarization lies along [001].

ACKNOWLEDGMENTS

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