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ac-field-dependent structure-property relationships in La-modified lead zirconate titanate: Induced relaxor behavior and domain breakdown in soft ferroelectrics

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The complex dielectric response was studied for various compositions in the $(Pb_{1-3/2y}La_y)(Zr_{0.65}Ti_{0.35})O_3$ (PLZT y/65/35) crystalline solution as a function of ac drive amplitude, frequency, and temperature. These studies reveal the presence of nonlinearities with respect to the amplitude of the ac drive. For $0.02<y<0.04$, the magnitude of the dielectric constant was observed to increase dramatically (~500–1000 %) and the temperature of the dielectric maximum (T_{max}) was observed to be shifted down significantly with increasing drive amplitude between 20 and 500 V/cm. In addition, strong frequency dispersion was observed in the nonlinear dielectric response, whereas the linear response was found to be frequency independent. For $0.06<y<0.10$, the magnitude of the nonlinearities were significantly decreased with increasing La content and the value of T_{max} was nearly independent of drive. Frequency dispersion was observed in the linear dielectric response; however, the nonlinear response was noticeably frequency independent. Sawyer-Tower polarization studies then revealed that the polarization behavior was linear in the range of electrical-field strengths used to measure the dielectric responses. These results indicate that the observed dielectric nonlinearities are not due to polarization nonlinearities, but rather related to the dynamics of various stable domainlike structures. On the basis of the results, an attempt is made to distinguish the similarities and differences between soft and relaxor ferroelectric behaviors. [S0163-1829(96)00222-6]

I. INTRODUCTION

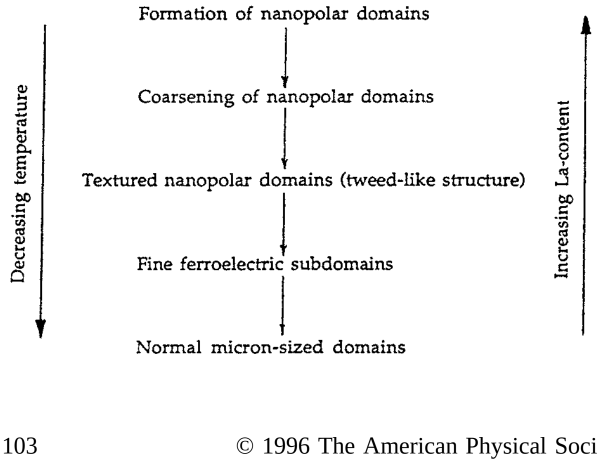
Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ [PZT $x/(1-x)$] crystalline solutions are technologically important and have been widely investigated. These materials are ferroelectric and are characterized by the presence of normal micron-sized domain structures in the low-temperature product state in the unpoled condition. La modification (y) of PZT ceramics [PLZT $y/x/(1-x)$] is known to result in the destabilization of the long-range ferroelectric order. With increasing La impurity content, the evolution of polar order has been shown to occur through a common sequence of domainlike states for PLZT y/65/35 and y/40/60,[1] including: normal micron-sized domains, tweedlike precursors and polar nanodomains (or clusters), as illustrated in Table I.

In the strongly disorder condition, relaxor ferroelectric behavior is observed. In these materials, the cluster state has been shown to be long lived at temperatures significantly below that of the average transformation temperature (T_{max}), as indicated by the dielectric response characteristics. Viehland *et al.*[2,3] have shown that this long-lived polar cluster state is characterized by glasslike behavior in the macroscopic response characteristics, similar to dipolar and quadrupolar glasses. The observed freezing behavior in relaxors clearly indicates the presence of a correlated freezeout of polarization fluctuations, however it is not yet clear whether this correlated freezeout involves a phase transformation into a state with a long-range ‘‘glassy’’ order parameter or rather the development of a finite-range order parameter on the mesoscopic scale.

In the less strongly disordered condition, transmission electron microscopy (TEM) studies have revealed the presence of tweedlike precursor structures,[1] which have strong morphological resemblance to those previously report in premartensitic states.[4,5] Recent investigations of PLZT have shown that these tweedlike structures are long-time present at temperatures significantly below that of the average transformation,[6] indicating that the ferroelectric transition is destroyed by the quenched impurities and that a pretransitory state is long-time stabilized. Kartha *et al.*[7] have previously developed a theory concerning the coupling of quenched disorder to martensitic phase transformations, and have predicted the presence of long-lived premartensitic states below the average transformation. In addition, polarization switching investigations of PLZT compositions in this intermediate La-content range have indicated that switching occurs through the tweedlike precursor structures,[6] rather than by the creation and motion of normal micron-sized domains.

In the weakly disordered condition, the macroscopic prop-

TABLE I. Common sequence of domainlike states observed with increasing La content in PZT ceramics.



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erties of PZT are characterized by decreases in the remanent polarization, coercive field, c/a ratio, and phase transformation temperature with increasing La content.[8] However, TEM studies have shown that normal micron-sized domain structures are maintained throughout this compositional range.[6] For PLZT y/65/35, a normal ferroelectric state cannot be maintained above ~4 at. %.[6] Studies of the polarization switching characteristics have been performed in this compositional range and it is generally believed that polarization switching occurs by the creation and motion of normal domain boundaries. Cao[9] has recently shown that the domain mobility makes a significant contribution to the dielectric and piezoelectric properties, over that predicted by the single-crystalline single-domain Landau theory.[10] These predictions are consistent with experimental investigations of ''soft'' PZT materials, which are well known to have significantly enhanced response characteristics over that of the corresponding undoped based compositions.

In spite of a large number of studies on PLZT's with micron-sized domains and polar clusters, the behavior of the intermediate states and the detailed transitional processes between normal and relaxor behaviors under external fields have not been studied in detail. Nonlinearity due to domain-wall motion and/or domain switching under high ac electrical fields have previously been reported by Li *et al.*[11,12] and Arlt *et al.*[13] in normal ferroelectric states. It might appear feasible to correlate changes in the domain configurations, domain-switching mechanisms, and long-range polar order by systematically investigating the nonlinearities in the dielectric response of various PLZT ceramics as a function of the ac drive amplitude. However, only limited studies of ac-field-induced (>1 kV/cm) dielectric nonlinearities in ferroelectrics have previously been reported.[14–16] Recently, Setter *et al.*[17] have studied the ac field dependence of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) relaxors. They observed an appreciable softening of the dielectric response using ac drive fields in excess of 1.5 kV/cm. Also, Li and Viehland[18] have recently observed a softening of the dc-bias-induced piezoelectric response of PMN-based relaxors with increasing ac drive amplitude. In addition, Viehland *et al.*[19] have previously reported an anomalous nonlinearity in the complex elastic response with respect to the amplitude of ac mechanical drive in dc-biased PMN relaxors. The purpose of the present study was to investigate the nonlinearities in the dielectric response with respect to the ac drive at lower drive amplitudes (<1 kV/cm) for various PLZT ceramics. It was hoped that these studies might reveal the characteristics of the dynamical responses of the various types of domainlike configurations which are known to exist.

II. EXPERIMENT

PLZT powders were batched according to the formula $Pb_{1-y}La_y(Zr_{1-x}Ti_x)_{1-y/4}O_3$ by a mixed oxide method starting from high-purity starting oxides (>99.9%). Excess PbO was incorporated in the formula to account for PbO loss during heat treatment. Ceramic pellets were formed by hot pressing at 1150 °C for 2 h at a pressure of 60 MPa, which was followed by an annealing at 1300 °C for 2 h in a PbO excess environment. The rhombohedral-structured PLZT compositions chosen for study were 0/65/35, 2/65/35, 3/65/35, 4/65/35, 6/65/35, 7/65/35, 8/65/35, 15/65/35.

The complex dielectric permittivity was measured using a Hewlett-Packard 4284A inductance-capacitance-resistance (LCR) meter which could cover a frequency range from 20 to 10^6 Hz with an ac driving field in the range 0.005–20 V. High-temperature dielectric data were obtained by putting the samples into a small tube furnace specifically equipped for such measurements. Low-temperature measurements were made by placing samples in a Delta Design 9023 test chamber. The P-E behavior was characterized using a computer-controlled, modified Sawyer-Tower circuit with a measurement frequency of 50 Hz. TEM specimens were prepared by ultrasonically drilling 3-mm discs which were mechanically polished to ~100 μm. The center portions of these discs were then further ground by a dimpler to ~10 μm, and argon-ion milled to perforation. Specimens were coated with carbon before examination. The TEM studies were done on a Phillips EM-420 microscope operating at an accelerating voltage of 120 kV.

III. RESULTS

A. Dependence of dielectric properties on ac drive amplitude

Figures 1(a)–1(f) show the 10^2 Hz dielectric response characteristics using various ac drive amplitudes between 10 and 500 V/cm for the compositions 0/65/35, 2/65/35, 4/65/35, 6/65/36, 8/65/35, and 15/65/35, respectively. For the composition 0/65/35, (undoped PZT), the dielectric response can be seen to be only slightly changed with increasing ac drive between 22 and 445 V/cm, as shown in Fig. 1(a). In this figure, the temperature of the dielectric maximum (T_{max}) can be seen to be shifted down slightly (~4 °C) with increasing drive, in addition the value of the permittivity maximum was only slightly increased (~5%) in the temperature range between 320 and 360 °C.

Upon increasing the La content to 2 at. %, the dependence on the ac drive was found to be strongly changed, as can be seen in Fig. 1(b). For this composition, the average transformation temperature was shifted down from ~310 °C using a drive amplitude of 19 V/cm to ~285 °C using a drive amplitude of 478 V/cm. In addition, the magnitude of the dielectric constant can be seen to be increased significantly over a wide range of temperatures between 200 and 300 °C. For example, at 285 °C the value of the dielectric constant increased from ~4000 using a drive of 19 V/cm to ~44000 using a drive of 476 V/cm. These results unambiguously demonstrate a significant increase in the nonlinearity of the dielectric constant with small increments in the La content. Upon further increment of the La content to 4 at. %, the dependence of the dielectric response on the ac drive was further increased and was in fact the maximum for all the compositions in the y/65/35 sequence which were investigated. The average transformation temperature was shifted down by ~50 °C with increasing drive amplitude between 16 and 313 V/cm, in addition the magnitude of the dielectric constant was significantly increased in the temperature range between 150 and 250 °C. For example, the magnitude of the dielectric constant at 225 °C was found to be increased from 5000 to ~25 000 with increasing drive. These results clearly show the presence of a strong dependence of the dielectric response characteristics on ac drive amplitude in the La-

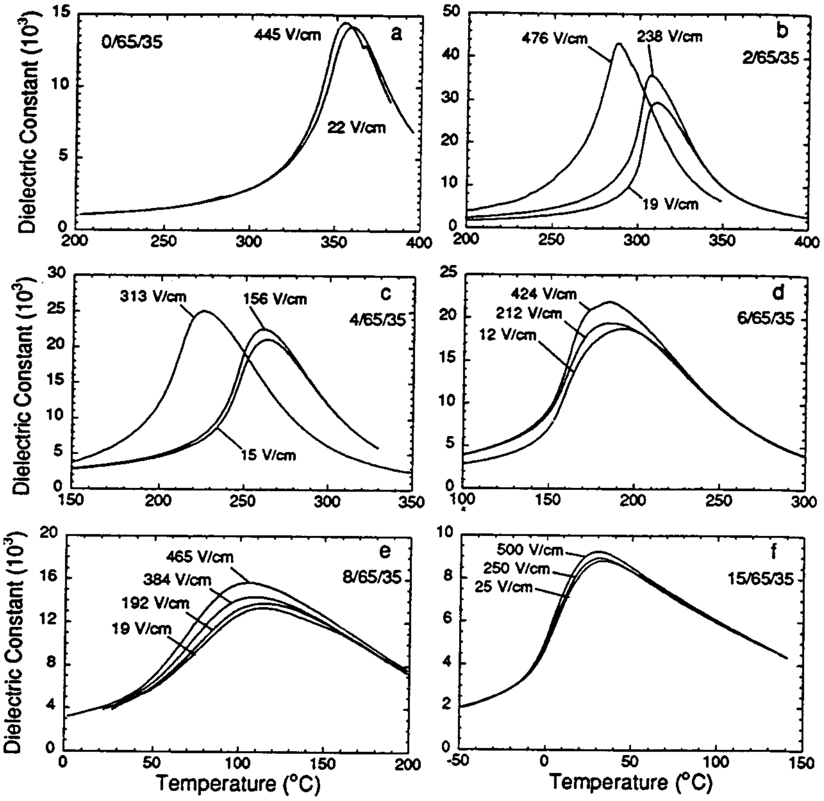

FIG. 1. Dependence of the 10^2 Hz dielectric constant for various PLZT y/65/35 compositions on the amplitude of the ac drive between approximately 10 and 500 V/cm. (a) $y=0$, (b) $y=0.02$, (c) $y=0.04$, (d) $y=0.06$, (e) $y=0.08$, and (f) $y=0.15$.

content range between 2 and 4 at. %. In this compositional range, normal micron-sized domain structures have previously been reported to be maintained.[6] However, the limit of stability of the long-range-ordered ferroelectric phase has been reported to be close to the composition where the maximum nonlinearities were observed.[6] Above this stability limit, relaxorlike ferroelectric behavior begins to emerge.

At higher La contents, the dependence of the dielectric response on drive amplitude was found to be significantly reduced, as can be seen by inspection of Figs. 1(d)–1(f). For the composition 6/65/35, the value of $T_{\max}$ was shifted down only slightly (<10 °C) with increasing drive between 12 and 424 V/cm. Correspondingly, the magnitude of the nonlinearity in the dielectric constant was greatly reduced; the largest nonlinearity was found near $T_{\max}$ and was equal to ~20%. With additional increment in the La content, the nonlinearities in the dielectric response can be seen to be further decreased; however no dramatic changes were found as for that between 4 and 6 at. %. In the compositional range between 6 and 10 at. % La, the shift in $T_{\max}$ decreased from ~10 °C to less than 1 °C and the degree of nonlinearity in the dielectric constant decreased from ~20% to less than 5%. For the composition 8/65/35, it is interesting to note the similarities of the results shown in Fig. 1(e) taken at various drive amplitude using a constant frequency to results previously reported at various frequencies using a constant drive amplitude.[20,21] Similar relaxational effects in the dielectric constant and shifts in $T_{\max}$ can be seen to be induced with changes in the drive amplitude between 19 and 465 V/cm, as would be expected with drive frequency between 20 and 10^6 Hz. In addition, for 8/65/35 the dependence of the dielectric constant on drive can be seen to decrease dramatically below the temperature range 40–50 °C.

The temperature-dependent dielectric loss spectra ($\tan\delta$) taken using various ac drive amplitudes between 20 and 1000 V/cm at a constant drive frequency of 10^2 Hz are shown in Figs. 2(a)–2(f) for the compositions 0/65/35, 2/65/35, 4/65/35, 6/65/35, 8/65/35, and 15/65/35, respectively. These figures clearly reveal a significant increase in the value of $\tan\delta$ with increasing drive amplitude for every composition investigated. The largest nonlinearity was found for 2/65/35, where the magnitude of $\tan\delta$ increased by nearly a factor of 20. At both higher and lower La contents, the dependence of $\tan\delta$ was significantly reduced. Also, the peak value of $\tan\delta$ was shifted to lower temperatures with increasing drive amplitude. For 2/65/35 and 4/65/35, the peak values of $\tan\delta$ were shifted down by ~25 and 50 °C, respectively, consistent with the relatively large shifts observed in the real component of the response [see Figs. 1(b) and 1(c)]. At higher La contents, the peak values of $\tan\delta$ were significantly less sensitive to the drive amplitude in the range investigated; in fact for these compositions the edges of the $\tan\delta$ curves were shifted to higher temperatures with increasing amplitude.

The most pronounced changes with La content in the nonlinearity of $\tan\delta$ were found in the compositional range between 2 and 4 at. %. In this range, the degree of nonlinearity decreased from ~2000% for 2/65/35 to ~500% for 4/65/35. Upon further increment in the La content between 6 and 15 at. %, the degree of nonlinearity further decreased to ~100% for 8/65/35 and then to ~30% for 15/65/35. Inspection of Fig. 2 will reveal that the magnitude of $\tan\delta$ for 4/65/35 was close in value to that for the relaxor compositions. For the compositions between 4/65/35 and 15/65/35, the value of $\tan\delta$ was nearly constant at ~0.1%, using a drive amplitude of ~500 V/cm. The larger nonlinearities for 4/65/35 than

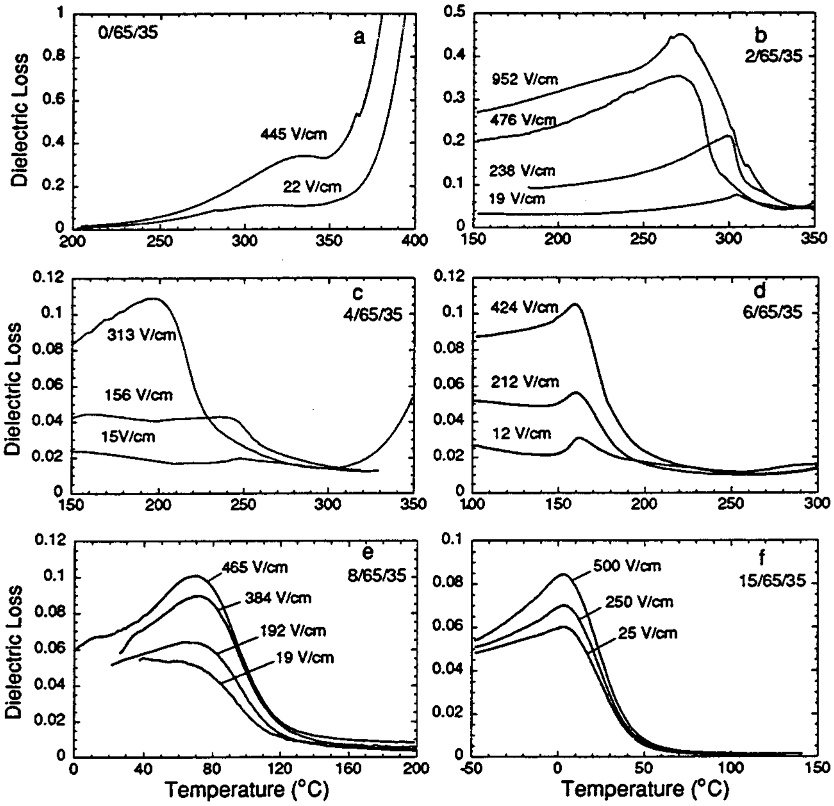

FIG. 2. Dependence of the 10^2 Hz dielectric loss factor for various PLZT y/65/35 compositions on the amplitude of the ac drive between approximately 10 and 500 V/cm. (a) $y=0$, (b) $y=0.02$, (c) $y=0.04$, (d) $y=0.06$, (e) $y=0.08$, and (f) $y=0.15$.

15/65/35 were not due to higher tanδ values under higher drives, but rather lower values under weaker drives. It is also interesting to note the similarities between the effects of increasing frequency and drive amplitude on tanδ for the relaxor compositions. It can be seen in Figs. 2(e) and 2(f) that the effects of increasing drive amplitude are similar to those previously reported with increasing frequency. These trends are in distinct comparison to those for the real component of the response, where with increasing drive amplitude the dielectric constant increased; however, with increasing frequency it has previously been shown to decrease.

In order to determine the possibility that the strong nonlinearities in the complex dielectric response might be due to electrically induced nonlinear polarization effects, the polarization electric field (P-E) hysteresis behavior was measured using a modified Sawyer-Tower circuit. Figure 3 shows the P-E behavior for 2/65/35 at various maximum ac drive fields. In this figure, the P-E behavior can be seen to be linear for field levels below 1.2 kV/cm. Strong nonlinearities and hysteresis effects were not induced until significantly higher field levels. These results clearly demonstrate that the strong nonlinearities observed in the complex dielectric response (Figs. 1 and 2) are not due to the development of a macroscopic polarization under an electrical field.

Figure 4 shows the temperature dependence of the dielectric constant at various field levels between 19 and 952 V/cm for the composition 2/65/35. In this figure, the dielectric response characteristics can initially be seen to be shifted down with increasing drive amplitude. However, upon more closely approaching the field strength necessary to begin to induce polarization reversal, the transition peak was shifted back to higher temperatures, broadening out significantly over a wide enough temperature interval, which was sufficient to encompass the responses of all the lower field measurements. We believe that these results demonstrate that the nonlinearities observed in the complex dielectric responses shown in Figs. 1 and 2 are related to the dynamics of the intrinsic domain states, rather than induced polarization switching and the growth of preferred domains.

The combination of the dielectric and the P-E data clearly indicates two different types of dielectric nonlinearities. One is associated with induced polarization effects and macrohysteretic behavior, and the other is probably associ-

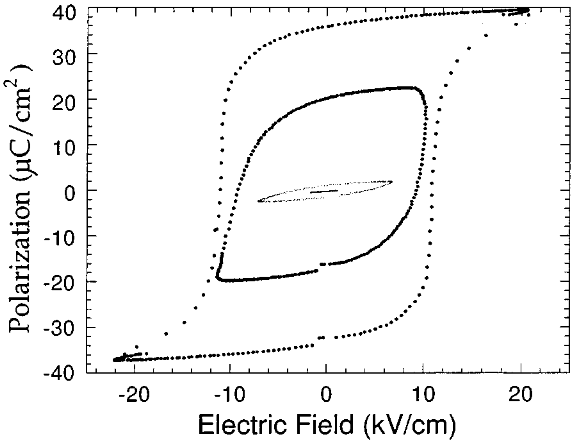

FIG. 3. P-E behavior for 2/65/35 at various maximum electric field strengths.

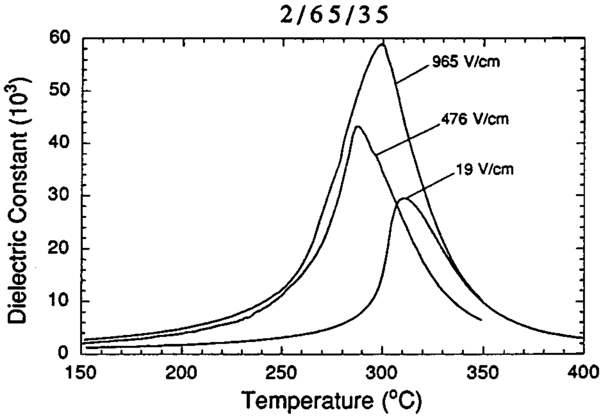

FIG. 4. Dependence of the 10^2 Hz dielectric constant for 2/65/35 on the amplitude of the ac drive between approximately 19 and 1000 V/cm.

ated with local domain boundary excitations and microhysteretic effects. We believe that the anomalous amplitude dependence of the complex dielectric response (Figs. 1 and 2) for the lower La content specimens is related to the later mechanism. Domain boundaries are well known to be pinned by defect structures resulting in the presence of thermally activated processes in displacive systems, i.e., thermal martensite. Aliovalent La modification of PZT results in the introduction of A-site vacancies, which may not only interrupt the coupling between ferroelectrically active BO_6 octahedral,[22] but might also provide a source of quenched defects on which domain walls could become pinned. Large amplitude drives [in excess of the coercive field (E_c)] would result in the long-range motion of domain boundaries, the development of remanent polarization, and saturation effects. However, under smaller ac drives $(E<E_c)$, domain boundaries might be continuously depinned around an average pinning site, without long-range boundary motion. The dielectric nonlinearities associated with these fluctuation effects might be significantly larger than those from induced polarization effects, due to the lack of saturation.

The pronounced lowering of the average transformation temperature by ac electrical drive for 2/65/35 and 4/65/35 might also be explained by considering this continuous depinning (or roughening, as we will call it below) of the domain boundaries under excitation. The pinning of boundaries by random quenched-in defects would result in the stabilization of the boundary to higher temperatures than would be expected in the unpinned condition, due to a lowering of the energy of the boundary via interactions with defects. Consequently, if the boundaries are electrically excited away from the frozen pinning sites, the average transformation temperature might be observed to be effectively moved down in temperature, due to additional extrinsic contributions to the permittivity from the boundary motion. However, we believe that such a simple picture, although it gives correct insights, does not provide an adequate explanation in detail for the observed changes. If this were the case, the shift down in $T_{\max}$ would occur by a broadening of the transformation with the high-temperature side of the response left unchanged, as in the paraelectric state domain mechanisms can not contribute to the permittivity. However, inspection of Figs. 1(b) and 1(c) will reveal that the entire permittivity curves are shifted down in temperature with increasing drive amplitude, without signs of significant broadening effects. We believe that a possible explanation is that the ferroelectric coupling within a characteristic distance (ζ) of the boundary is being weakened by the continuous depinning process. At higher temperatures, this decoupling may result in the stabilization of the paraelectric state, shifting $T_{\max}$ down. At lower temperatures, the decoupling may result in a roughening and coarsening of the domain boundaries. If the boundaries are then driven hard enough that polarization switching occurs, long-range domain motion is induced and a remanent polarization develops; consequently, $T_{\max}$ increases due to the expulsion of the roughened boundaries.

The changes in the degree of dielectric nonlinearity with composition undoubtedly reflect changes in the common sequence of domain like states with increasing La content,[1,6] as shown in Table I. The maximum nonlinearity and shift in $T_{\max}$ was found for the composition 4/65/35, which is close to the crossover between normal micron-sized domain structures and tweedlike states.[6] Close to this composition, the domain boundaries may become increasingly roughened and coarsened due to an increasing number of pinning sites and the influence of moderate ac excitations; consequently, the degree of dielectric nonlinearity may be increased. In fact, TEM studies revealed a change in the stable domain like state after moderate ac excitations. Figures 5(a) and 5(b) show bright-field images for 4/65/35 taken from specimens which had not been and had been excited by moderate ac drives, respectively. These specimens were cut from the same sintered ceramic disc, just prior to the investigation. Figure 5(a) reveals the presence of normal micron-size domains, which possessed subdomain structures. However, after moderate ac excitations, only the presence of subdomain tweedlike structures were present, as can be seen in Fig. 5(b). These results can be explained in terms of a roughening of the domain boundaries by moderate ac excitations that reduce local ferroelectric orderings within a distance ζ, resulting in a change in the stability of the domainlike state.

On increment of the La content between ~4 and 5 at. %, tweedlike structures are known to become the stable domain state, with or without a prior applied moderate ac excitation. Correspondingly in this compositional range, a strong decrease in the dielectric nonlinearity and shift in $T_{\max}$ were observed in the present study. We believe that these changes can be explained by conjecturing the possibility that the subdomain structures and polar clusters are not pinned in this compositional range, but rather the long-range polar order is broken by the aliovalent substitution of La^{3+} for Pb^{2+}. Consequently, a pretransitory state is long-time stabilized and the normal phase transformation prevented, as recently reported.[23] Large enhancements in the dielectric constant are then not incurred due to the continuous depinning. However, moderate ac excitations could influence the kinetics of any fluctuation effects in the tweedlike and polar cluster states.

B. Frequency effects at various drive amplitudes

Figure 6(a) shows the dielectric response for the composition 2/65/35 as a function of temperature at various frequencies between 10^2 and 10^6 Hz using drive amplitudes of 19, 238, and 476 V/cm, respectively. Using the low ac drive, no frequency dispersion was observed in the dielectric re-

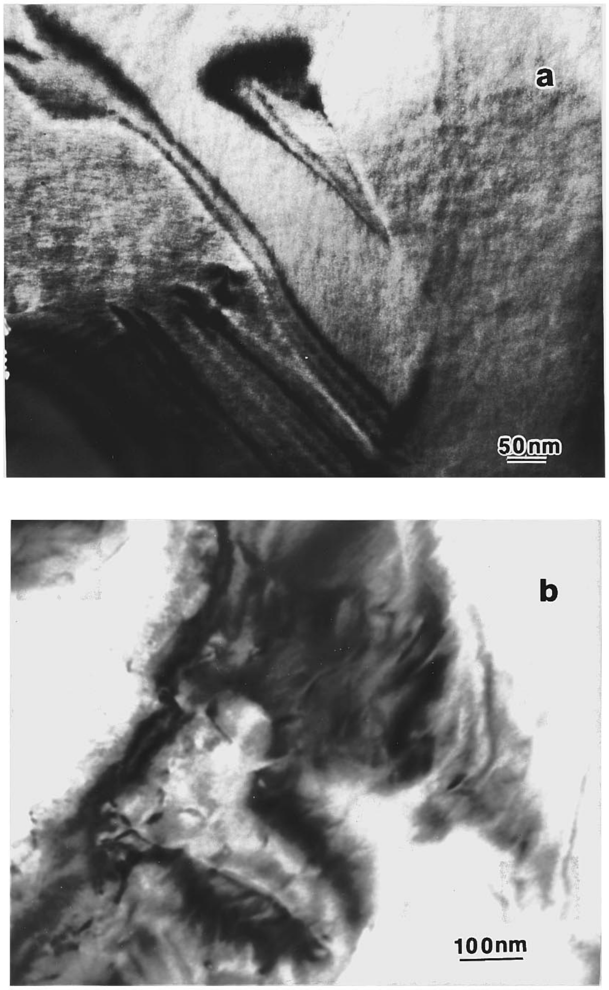

FIG. 5. Bright-field images for 4/65/35 before (a) and after (b) ac electrical excitation.

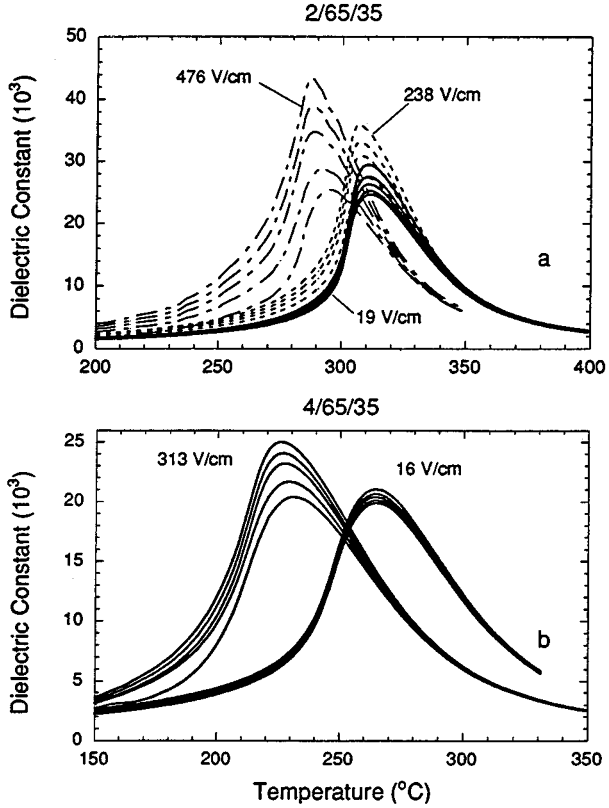

FIG. 6. Frequency-dependent dielectric response for several PLZT compositions using various drive amplitudes between approximately 20 and 500 V/cm. (a) 2/65/35 and (b) 4/65/35. The measurement frequencies from the top to the bottom curves for under each ac drive are 10^2, 10^3, 10^4, 10^5, and 5×10^5 Hz.

sponse. Rather, the response resembled that of a normal long-range ferroelectric state. However, upon increasing the drive amplitude to 238 V/cm, strong frequency dispersion became evident. The magnitude of the dielectric constant at low frequencies was increased by ~50% by the increased drive; however, the enhanced dielectric softness was significantly reduced with increasing frequency. Using a frequency of 10^6 Hz, the dielectric constant was nearly equal for both drive amplitudes. Upon further increasing the drive amplitude to 476 V/cm, the dielectric response was shifted down in temperature and enhanced frequency dispersion was observed. Again, with increasing frequency, the enhanced dielectric softness was observed to relax, however the shift in the average transformation temperature remained unchanged. Similar results were obtained for the composition 4/65/35, as shown in Fig. 6(b). The only noticeable differences in the dielectric response for 4/65/35 relative to that for 2/65/35 were an enhanced broadening of the temperature-dependent response, stronger frequency relaxation near $T_{\max}$ under low drives, and a larger shift in $T_{\max}$ with increasing drive amplitude.

Figures 7(a) and 7(b) show the dielectric responses for the composition 6/65/35 taken at drive amplitudes of 19 and 384 V/cm, respectively. From these figures, it can readily be observed that the frequency dependence of the dielectric constant and $T_{\max}$ are both increased with increasing drive. Again, the nonlinearities were largest at the lowest drive frequencies. The difference between the 10^6 Hz response was nearly negligible between the two drive levels used. The frequency-dependent response characteristics under larger drives were identical to that expected for a relaxor, however at lower drives this was not the case. These results clearly demonstrate for the first time that relaxor ferroelectric behavior can be induced by ac electrical drive. Upon further increment in the La content to 8 at. %, relaxor behavior was observed in both the low- and high-amplitude responses, as can be seen by inspection of Figs. 8(a) and 8(b), respectively. Increasing ac drive had some effects on the dielectric response, however the nonlinearities were weak in the field range investigated. In addition, with increasing La content in the relaxor region, the magnitudes of the nonlinearities further decreased, as can be seen by inspection of Figs. 8(c) and 8(d) for 15/65/35.

It has previously been reported that the addition of less than 4 at. % La in PZT does not result in the appearance of relaxor behavior.[24] However, these results clearly demonstrate that relaxorlike characteristics can be induced in the dielectric response of a normal ferroelectric using higher ac drive amplitudes, which are insufficient to induce polarization nonlinearity in the P-E behavior. Relaxorlike characteristics were present in the magnitude of the dielectric response; however, no significant shifts in $T_{\max}$ were observed with increasing frequency, as would be expected for a relaxor. Rather, $T_{\max}$ was shifted down with increasing ac drive and did not shift back up with increasing measurement frequency. The frequency dispersion of the dielectric constant for 2/65/35 and 4/65/35 demonstrates the presence of a relaxational phenomenon. Increasing drive amplitude may roughen or disorder the domain structures, however the extrinsic contribution to the dielectric response from these boundary excitations relaxes rapidly with increasing frequency.

One might be able to explain the compositional trends between 6/65/35 and 8/65/35 by again considering the stable domainlike states, illustrated in Table I. Tweedlike subdomains have been shown to exist in the bright-field images for 6/65/35, at temperatures far below $T_{\max}$. These subdomains preserve a high degree of regularity between tweeds along particular crystallographic directions. Previous dielectric investigations for this composition using low-amplitude drives have revealed a broadened response which exhibited some frequency relaxation, however it is generally believed not to be a relaxor ferroelectric,[24] rather, the term ''incipient'' relaxor has been used.[9] Under moderate ac excitations, the tweedlike structures may undergo driven fluctuations, resulting in the partial interruption of local polar order. Consequently, the polar cluster state may be stabilized over the tweedlike under excitation, resulting in the development of enhanced relaxorlike characteristics. For the composition 8/65/35, only weak nonlinearities were observed; corre-

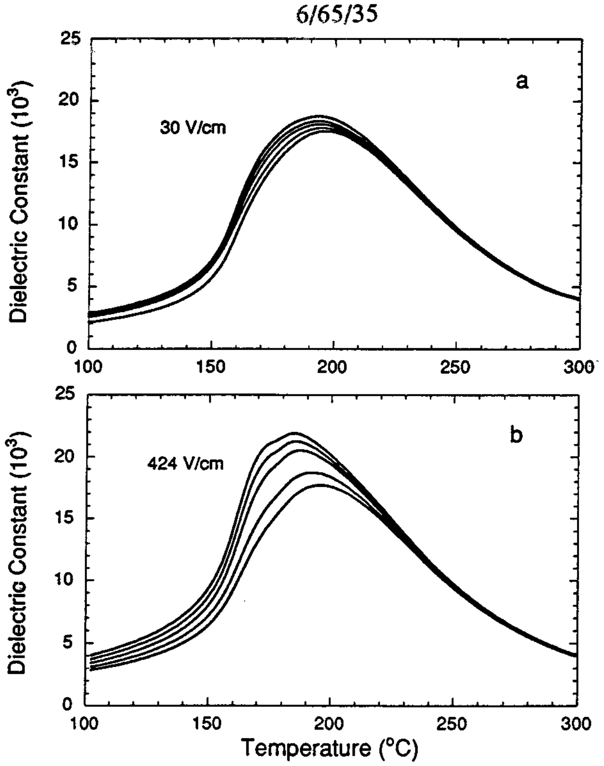

FIG. 7. Frequency-dependent dielectric response for 6/65/35 using various ac drive amplitudes. (a) 20 V/cm and (b) 384 V/cm. The measurement frequencies from the top to the bottom curves for under each ac drive are 10^2, 10^3, 10^4, 10^5, and 5×10^5 Hz.

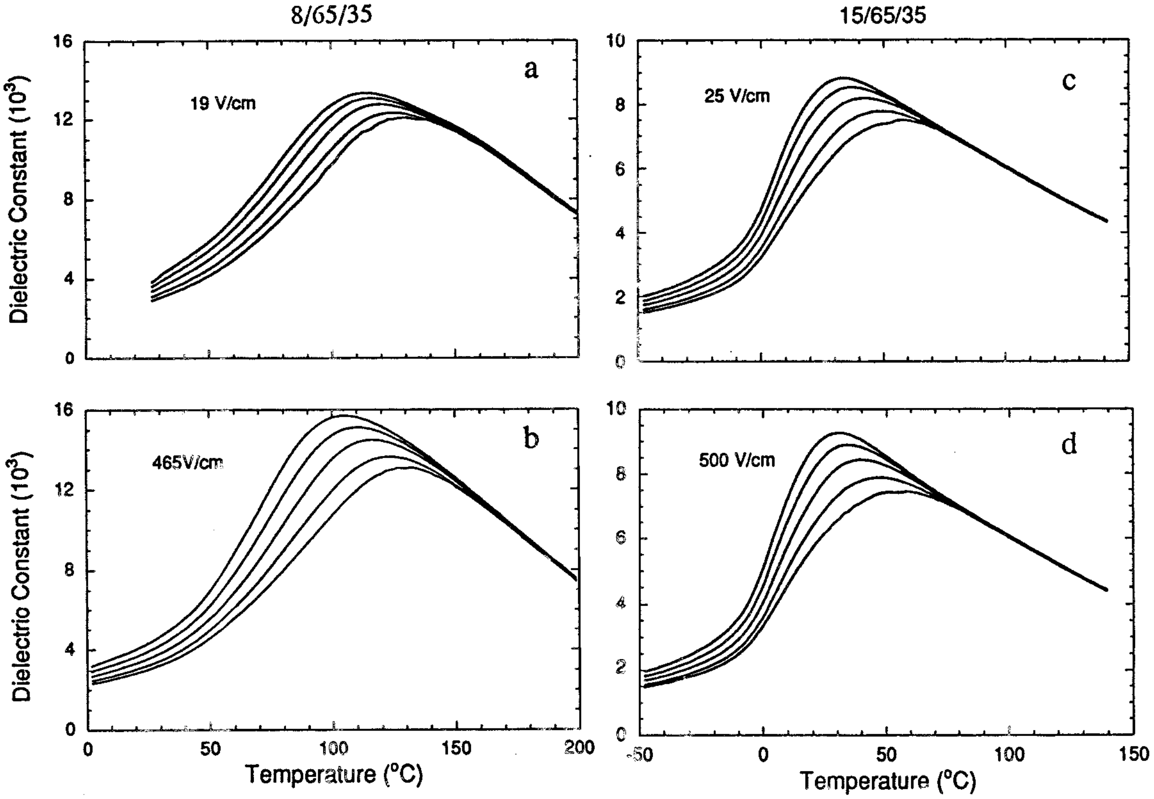

FIG. 8. Frequency-dependent dielectric response for several PLZT compositions using various ac drive amplitudes. (a) 8/65/35 under 12 V/cm, (b) 8/65/35 under 465 V/cm, (c) 15/65/35 under 25 V/cm, and (d) 15/65/35 under 500 V/cm. The measurement frequencies from the top to the bottom curves for under each ac drive are 10^2, 10^3, 10^4, 10^5, and 5×10^5 Hz.

TABLE II. Generalization of the influence of ac drive amplitude on the dielectric response for the various PLZT compositions.

Low La-FE	FE dielectric behavior, normal micron-sized domains ↓ increasing AC drive relaxor-like dispersion with nonlinear response to AC drive, domain roughening
Critical LA-FE	Soft FE behavior, micron-sized domains ↓ increasing AC drive induced relaxor-like characteristics in nonlinear dielectric response, but no strong frequency dependence of T_{max}, tweed-like structures
Intermediate La-relaxors	"Incipient" relaxor, stable tweed-like structures ↓ increasing AC drive relaxor FE state, coarse nanopolar domains
High La-relaxors	Relaxor characteristics in linear dielectric response, nanopolar domains ↓ increasing AC drive weak nonlinearities to AC drive, nanopolar domains

spondingly, the polar cluster state is known to be stable. Higher ac drives (>1 kV/cm) have been reported to induce stronger nonlinearities; however, these nonlinearities are weak compared to 4/65/35.

The presence of weak nonlinearity in the relaxor compositions (8/65/35 and 15/65/35) demonstrates that the kinetics of the polarization fluctuations can be driven by ac excitation. In fact, the influences of increasing amplitude and decreasing frequency were similar, as mentioned in Sec. III A. Based on these results, one could conjecture that there may be a gradual freezing of polarization fluctuations [with respect to the time constant of the measurement frequency (τ_{meas})]. A possible interpretation is that the system is beginning to settle into a series of metastable states over a relatively wide temperature range and under excitation the system exhibits microhysteresis around these metastable minima. Inspection of the data for the composition 8/65/35 (Fig. 8) will reveal the presence of pronounced nonlinearities only in the temperature range between 40 and 120 °C. Correspondingly, previous polarization studies[3] have shown that the onset of remanence (T_f) occurs near ~40 °C, demonstrating that the polarization fluctuations can be driven by moderate ac drives only in the temperature range between T_{max} and T_f. Based on these results and the fact that the degree of dielectric nonlinearity decreased significantly with increasing frequency, one could conjecture that the gradual freezing of the polarization fluctuations into metastable minima is cooperative in nature. This cooperative nature indicates that the freezing process is not local (i.e., single clusters), but rather a correlated freeze out of many clusters.

IV. SIMILARITIES AND DIFFERENCES BETWEEN SOFT PZT's AND RELAXORS

The results presented above clearly demonstrate a general trend with increasing La content, as illustrated in Table II. For low La-content materials, relaxorlike dispersion can be induced by increased ac drive, presumably due to domain boundary roughening, however a true relaxor state is not induced. Upon increasing the La content to a critical range, moderate ac excitations result in the destabilization of the normal micron-sized domains, resulting in tweedlike structures and enhanced relaxorlike characteristics. However, a strong frequency dependence of T_{max} was not observed in the range of ac drives investigated. Upon increasing the La content to the range of 6 at. %, the tweedlike domains were inherently stable with ''incipient'' relaxor characteristics. However, under moderate ac drives, a relaxor ferroelectric state was induced. Upon further increasing the La content, the drive level needed to induce the relaxor state decreased, until it was presumably intrinsically present under an infinitely small drive (>8 at. % La), i.e., relaxor characteristics were present in the linear response and are driven by thermal fluctuations.

These results require an extension of the definition of what constitutes a relaxor state, including both weak- and strong-field drives, or more correctly whether the relaxational process occurs in the linear or nonlinear dielectric responses. This extension should allow us to distinguish the similarities and differences between a soft PZT and a relaxor state. In the relaxor state, the linear component of the dielectric response is intrinsically frequency dispersive. The nonlinear contribution is weak and does not add significantly to the overall degree of frequency dispersion. These intrinsic linear relaxations indicate inherent fluctuations in the stability of the state, which undoubtedly are due to the presence of pretransitorylike structures (tweeds and clusters). In the soft PZT's, a phase transformation does occur into the low-temperature product state. For these compositions, only the nonlinear contributions to the permittivity are frequency dependent. The linear terms are nondispersive.

It is clear that both soft PZT and relaxor behaviors are defect-induced states, whose macroscopic response characteristics are related to the metastabilities of their respective domainlike configurations. However, the nature of the metastabilities for soft PZT's is significantly different than that for relaxors. The metastability of soft PZT's arises due to the pinning of transformed regions which are of macroscopic size. Consequently, the number of metastable states and the difference between them are both relatively small. However, the metastability of relaxors arises due to the correlated freezing of pretransitory states, which are of nanometer size. Consequently, the number of possible degenerate metastable states through which the system can evolve is enormous. As a results of this near continuous degenerate sequence of metastable states and the strongly correlated nature of the freeze out, the relaxor may be best viewed in terms of a glassy polarization state.

V. CONCLUSIONS

Investigations of the ac field dependence of the dielectric constant have been performed for various La contents across the PLZT y/65/35 crystalline solution. These studies have revealed the presence of strong nonlinearities and large shifts in T_{max} for $0.02<y<0.04$. At higher La contents, the magnitude of the nonlinearities was found to be significantly decreased and only minor shifts in $T_{\max}$ were observed with increasing drive amplitude. In addition, it was demonstrated that relaxorlike characteristics could be induced in the nonlinear dielectric response for $x<0.06$ with increasing drive amplitude. However, for higher La contents the linear component of the response was strongly frequency dependent, whereas the nonlinear response was relatively independent. These results require an extension of the concept of what a relaxor is, including both weak-and strong-field drives, or more correctly whether the relaxational process occurs in the linear or nonlinear dielectric responses.

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