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Linear and nonlinear dielectric constant as function of bias electric field in relaxor materials

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Abstract

The quasistatic linear and nonlinear dielectric constants ε_S in 9/65/35 PLZT ceramics and PMN crystal were investigated by means of the charge accumulation technique and by monitoring the first, ε_1, and the third, ε_3, harmonic response. The zero field cooled and field cooled static susceptibilities show a crossover from a nonergodic relaxor to inhomogeneous ferroelectric behaviour. At electric fields above the critical value contribution from the saturated spontaneous polarization was observed. The temperature dependence of the total third order nonlinear response was determined in 9/65/35 PLZT ceramics.

Keywords: Dielectric properties; Ferroelectric properties; PLZT; Relaxor

1. Introduction

Investigations based on the linear and nonlinear dielectric studies resulted in the (E-T) phase diagram of lead lanthanum zirconate titanate ceramics $Pb_{1-x}La_x(Zr_y Ti_{1-y})_{1-x/4}O_3$ (PLZT) for the particular composition of $x = 0.09$ and $y = 0.65$ (denoted as 9/65/35 PLZT ceramics).[1,2] It was shown that no long-range ferroelectric order is established in the zero dc bias field,[3–5] hence the system undergoes a freezing transition from the ergodic to nonergodic relaxor phase similar as in lead magnesium niobate (PMN) crystal.[6,7] On the other hand, by cooling the relaxor material in an electric field higher than the critical field E_C, a long-range ferroelectric (FE) phase is formed.[6,8–10] Therefore, the PLZT system shows at lower electric fields properties of the relaxor materials, which are typically characterized by a broad frequency dispersion in the complex dielectric constant and slowing dynamics,[3–6] however, at higher fields it exhibits properties of inhomogeneous ferroelectrics.

The universality class of the freezing process in relaxor ferroelectrics, which has long been the subject of controversy,[3–11] should be revealed by studying the temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_S^4$. Indeed, it was shown recently that a crossover from the decreasing paraelectric-like to the rapidly increasing glass-like temperature dependence of a_3 exists in PMN and 9/65/35 PLZT materials,[12] which places these systems among spherical random bond–random field (SRBRF) glasses at low electric fields.[13]

The observation of the splitting between the field-cooled dielectric constant ε_{FC} and the zero-field-cooled dielectric constant ε_{ZFC} in both the PMN crystal and PLZT ceramics[6,7,14] provides an additional indication of the nonergodic behavior similar to the one observed in many glassy systems. The existence of the remanent polarization P_R in 8/65/35 and 9/65/35 PLZT ceramics was confirmed by earlier studies.[14,6] However, it was shown as well that the P_R obtained in zero-field-heating (ZFH) experiment depends strongly on the experimental time scale and on various history effects such as aging, which is a particularly strong effect in the PLZT relaxor.[6]

Until now no detailed investigation of the spontaneous polarization P_S and its development as a function of the dc bias electric field and temperature has been reported. Moreover, it was recently found that beside the third harmonic nonlinear coefficient additional nonlinear contribution of the third order, which is responsible for the strong nonlinear field dependence of the first harmonic,

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should be taken into account.[15] This opens the question, what is the total third order nonlinear response, which should be in a static limit compared with the theoretical predictions.

2. Experiments and discussion

The dc field dependence of the effective zero-field-cooled dielectric constant $\varepsilon_{ZFC} = 1 + P_{ZFC}(E, T)/\varepsilon_0 E$ was determined by cooling an annealed sample down to 100 K in zero field $E = 0$. There, an external electric field of E was applied, and the sample was slowly heated (1 K/min) up to 400 K while the corresponding polarization charge was measured by the Keithley 617 programmable electrometer.[16] At temperature $T = 400$ K the scanning rate was reversed (−1 K/min) and the effective field-cooled dielectric constant $\varepsilon_{FC} = 1 + P_{FC}(E, T)/\varepsilon_0 E$ was measured by cooling the system down to 100 K in the same external electric field E. After the electric field E was switched off at 100 K, a long-living remanent polarization P_R was observed and monitored on heating (1 K/min) the sample in zero field again up to 400 K. This procedure was than repeated for several electric fields between 0.02 and 8.5 kV/cm. Pyroelectric current was calculated from the derivative of the $P_R(T)$ data.

Quasistatic measurements of the FC and ZFC effective dielectric response obtained on 9/65/35 PLZT ceramics at $E = 2$ kV/cm are shown in Fig. 1. Results are very similar to those obtained previously at much lower fields[6] and to the results obtained on the 8/65/35 PLZT sample[14] and PMN relaxor.[7] Also the splitting between FC and ZFC dielectric constants is very similar to the one reported in various orientational glasses.

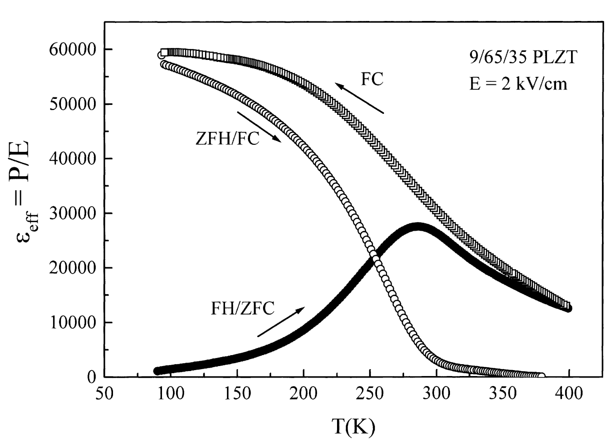

Fig. 1. Temperature dependence of the field-cooled (open boxes) and zero-field-cooled–field-heated (solid circles) quasistatic effective dielectric constant ε_{eff} of 9/65/35 PLZT ceramics at $E = 2$ kV/cm. Also shown is zero-field-heated after field-cooling dielectric response (open circles) due to the existence of the remanent polarization P_R.

On the other hand, for the electric fields higher than the critical one $E_C = 4.4$ kV/cm several new features appear as shown in Fig. 2 for $E = 8.5$ kV/cm. In particular, field-heated after zero-field-cooled (FH/ZFC) dielectric constant increases very sharply with increasing temperature and becomes equal to the FC dielectric constant at the temperature denoted by the arrow A in Fig. 2. This increase corresponds to the relaxor-to-ferroelectric conversion enforced by the electric field higher then the critical one. A hysteresis effect is observed between FC and FH/ZFC dielectric constants in the temperature range around the ferroelectric transition (denoted by arrows B and C in Fig. 2). The hysteresis effect could be a consequence either of the nanodomain structure, depinned impurities, or the smeared latent heat effect. Namely, it was shown that the ferroelectric transition may be of the weakly first order type.[1,2] The zero-field-heated after field cooling (ZFH/FC) effective dielectric constant (corresponding to the remanent polarization P_R) exhibits a very pronounced drop around the temperature where ergodicity is broken at lower electric fields (arrow D in Fig. 2). This is in striking contrast to the case shown in Fig. 1, where ZFH/FC dielectric constant (P_R) decreases continuously in a much broader temperature interval, thus demonstrating that the nature of the phase transition changes at higher electric fields.

Rescaled pyroelectric current peaks proportional to the dP_R/dT show the difference in the nature of the transition to the low temperature phase even more precisely. As shown in Fig. 3 the pyroelectric current peaks appear nearly at the same temperature for the electric fields below and above critical one. However, for the peak at $E = 2$ kV/cm the width at half maximum is almost 100 K. On the other hand, the peak at $E = 8.5$ kV/cm is only few K wide and its magnitude is 20 times larger. This demonstrates that the electric field easily converts glass-like relaxor state into the long range ordered ferroelectric one.

Experiments shown in Figs. 1 and 2 repeated at several dc bias fields enable quasistatic measurements of the polarization as a function of the field E. Fig. 4 shows the field dependence of the FC dielectric polarization at a particular temperature of 100 K deduced from different FC scans obtained at various dc electric fields. Two interesting features are observed. (i) After linear regime the polarization increases abruptly near the critical field $E_C \approx 4.4$ kV/cm. This demonstrates a phase transition in which the rapid conversion from the relaxor to the field-induced long range ordered ferroelectric state occurs. (ii) Above critical electric field E_C the polarization saturates in a practically field-independent plateau. This plateau corresponds to the spontaneous polarization P_S, which reaches the value of nearly 0.6 As/m^2 at low temperatures. It is interesting to note that the P_S vanishes nearly at the same temperature where the sharp peak in pyroelectric current is observed, i.e. at $T \approx 265$ K.

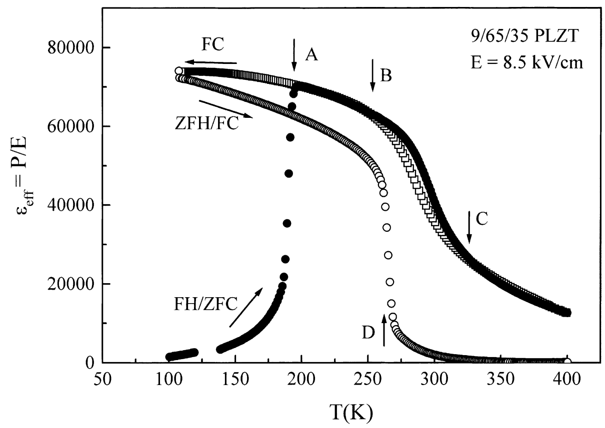

Fig. 2. Temperature dependence of the field-cooled (open boxes) and zero-field-cooled–field-heated (solid circles) quasistatic effective dielectric constant $\varepsilon_{\mathrm{eff}}$ of 9/65/35 PLZT ceramics at $E = 8.5$ kV/cm. Also shown is zero-field-heated after field-cooling dielectric response (open circles).

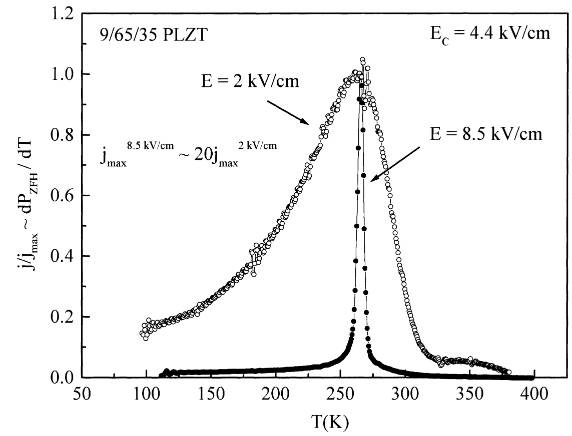

Fig. 3. Rescaled pyroelectric current peaks proportional to the $dP_{\mathrm{R}}/\mathrm{d}T$ obtained at $E = 2$ kV/cm (open circles) and at $E = 8.5$ kV/cm (solid circles). Note that the actual magnitude of the peak obtained at $E = 8.5$ kV/cm is 20 times larger than the peak obtained at $E = 2$ kV/cm.

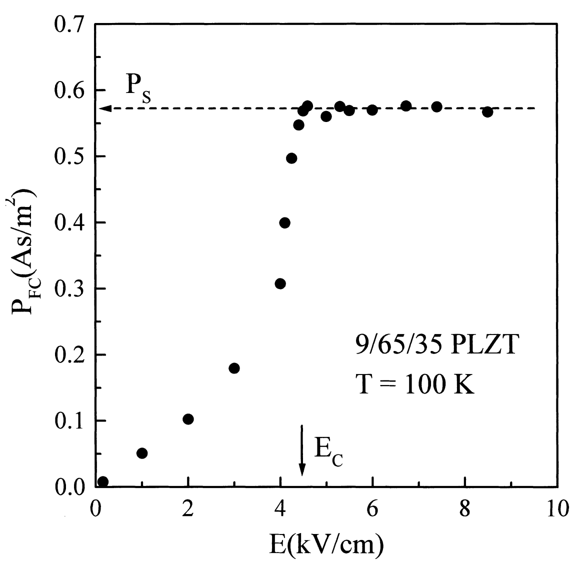

Fig. 4. The electric field dependence of the FC dielectric polarization P at 100 K deduced from different FC scans obtained at various dc electric fields E.

As shown in Fig. 4 the polarization exhibits significant nonlinear deviations from the linear field dependence below critical electric field $E_{\mathrm{C}} \approx 4.4$ kV/cm. This allows quasistatic determination of the temperature dependence of the third nonlinear dielectric response from the FC dielectric measurements. Namely, it was shown very recently[15] that the first harmonic ε_1 exhibits a nonlinear field dependence, which cannot be attributed simply to the ε_3 coefficient, but additional contribution must be taken into account. When applying an ac electric field $E = E_{\mathrm{AC}}\cos\omega t$ to the relaxor system the dielectric response can be written in terms of higher harmonics expansion as[15]

$$\varepsilon(\omega, E) = \left[\varepsilon_1(E=0) + (\Delta\varepsilon_{\mathrm{R\text{-}FE}} - 3/4\varepsilon_3)E_{\mathrm{AC}}^2\right]_\omega - \left[1/4\varepsilon_3 E_{\mathrm{AC}}^2\right]_{3\omega} + \dots. \quad (1)$$

It was proposed that the additional nonlinear contribution $\Delta_{\varepsilon_{\mathrm{R\text{-}FE}}}$ to the first harmonic and also to the static response originates in the shift of the state of the system through the relaxor to ferroelectric crossover region, i.e. through the electric field range $0 < E < E_C$.[15] It was also shown that $\Delta\varepsilon_{\mathrm{R\text{-}FE}}$ can be modelled within the spherical random bond-random field model by expanding a mean ferroelectric coupling constant $J_0(E)$ as a function of the electric field.[15] The second contribution to the first harmonic $-3/4\varepsilon_3 E_{\mathrm{AC}}^2$ was found to be in PMN and PLZT systems typically more than one order of magnitude smaller than $\Delta\varepsilon_{\mathrm{R\text{-}FE}}E_{\mathrm{AC}}^2$ (see also Fig. 5 where the ratio between these two contributions is calculated for 9/65/35 PLZT ceramics).

As mentioned in the introduction the universality class of the freezing process in relaxor ferroelectrics was revealed by studying the temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_{\mathrm{S}}^4$. However, in the above case a_3 was calculated by taking into account solely the third harmonic $\varepsilon_3(3\omega)$ contribution, excluding the dominant $\Delta\varepsilon_{\mathrm{R\text{-}FE}}$ term. This opens the question what is the temperature dependence of a_3 in the static limit when the total third order nonlinear response $\varepsilon_3^t = \Delta\varepsilon_{\mathrm{R\text{-}FE}} - \varepsilon_3$ is taken into account.

Fig. 6a shows the $\varepsilon_3^t = [\varepsilon_{\mathrm{FC}}(E) - \varepsilon_{\mathrm{FC}}(E \approx 0)]/3E^2$ calculated from the FC measurements of $\varepsilon_{\mathrm{FC}}$ at $E = 0.3$ and $E = 0.02$ kV/cm. It is interesting to note that the total static $\varepsilon_3^t(T)$ does not exhibit a peak, but rather saturates monotonously at low temperatures in a similar way to the static linear dielectric constant. Since the dominant contribution $\Delta\varepsilon_{\mathrm{R\text{-}FE}}$ to the total ε_3^t has a fer-

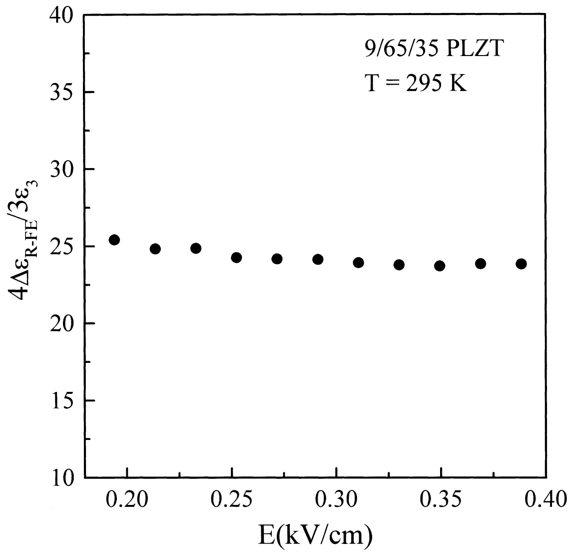

Fig. 5. The ratio between $\Delta\varepsilon_{R\text{-}FE}$ and $3/4\varepsilon_3(3\omega)$ calculated for 9/65/35 PLZT ceramics.

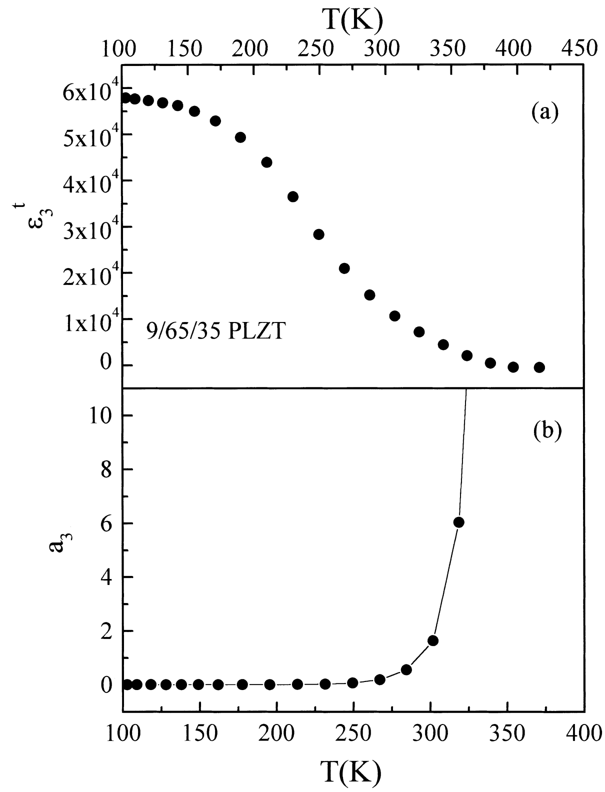

Fig. 6. (a) The total static third order nonlinear dielectric constant ε_3^t as a function of temperature. calculated from the SRBRF model in the vicinity of the relaxor to ferroelectric transition. (b) The temperature dependence of the nonlinearity $a_3 = \varepsilon_3^t/\varepsilon_S^4$ in 9/65/35 PLZT ceramics.

rolectric origin in the shift of the state of the system through the relaxor to ferroelectric crossover region one would expect that the static $a_3(T)$ calculated by taking into account the total static third order nonlinear response $\varepsilon_3^t(T)$ would exhibit only a monotonously decreasing temperature dependence as typically observed in ferroelectric materials.[12] As shown in Fig. 6b this was indeed observed in the case of 9/65/35 PLZT ceramics in a broad temperature range. The temperature dependence of the static total third order nonlinear response $\varepsilon_3^t(T)$ demonstrates that apart from the $a_3(T)$ calculated only from the third harmonics $\varepsilon_3(3\omega)$, which places these systems among SRBRF glasses at low electric fields, the ferroelectric nature may be dominant already in the relaxor to ferroelectric crossover region. It should be noted, that similar results were obtained also in a PMN single crystal.

3. Conclusions

In conclusion, the quasistatic linear and nonlinear dielectric constants obtained in 9/65/35 PLZT ceramics and PMN crystal show a crossover from a nonergodic relaxor to inhomogeneous ferroelectric behaviour. At electric fields above the critical value contribution from the saturated spontaneous polarization was observed. As a consequence of the above crossover the additional contribution to the total third order nonlinear dielectric response can be observed. This additional contribution exhibits a strong impact on the nonlinearity a_3 changing its temperature dependence typical for SRBRF glasses to the temperature dependence expected for ferroelectrics.

Acknowledgements

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