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E–T phase diagram of the 6.5/65/35 PLZT incipient ferroelectric

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Abstract

The electric-field–temperature (E–T) phase diagram for lanthanum modified lead zirconate (PLZT) 6.5/65/35 hot-pressed ceramics was determined by measurements of the quasistatic field-cooled–field-heated (FC/FH) dielectric susceptibilities. Approximately linear dependence of the phase transition line between the ergodic relaxor and ferroelectric phases on the bias electric field was found. In zero electric bias field the incipient ferroelectricity is established at nonzero phase transition temperatures. From the field-cooled polarization measurements a quasistatic spontaneous polarization of 0.37 As/m^2 was determined at 25 °C. Measurement of the frequency dependent, linear complex dielectric constant as a function of the bias electric field shows a significant change in its temperature dependence as well as in the temperature dependence of the characteristic relaxation time, indicating freezing of those sample regions dominated by the disordered nanocluster relaxor state, to the nonergodic glass-like relaxor state.

Keywords: Dielectric properties; Ferroelectric properties; Hot pressing; PLZT; Relaxor

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1. Introduction

Lanthanum doped lead zirconate-titanate ceramics $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT), with La content varying between 4 and 12 at.%, belong to the ferroelectrics relaxor systems.[1] All these materials show a shift of the maximum of frequency dependent dielectric permitivity with decreasing temperature, the absence of any macro-symmetry changes, a characteristic slowing dynamics according to the Vogel–Fulcher law and a strong deviation from Curie–Weiss behavior. This behavior is believed to be a consequence of a compositional and/or structural heterogeneity which acts to break the translational invariance of the polarization.[2]

It is commonly recognized that all relaxors are highly inhomogeneous materials.[3] Nanocluster regions result because of the fluctuation of composition and the appearance of lattice defects due to the method of their preparation (powder sintering), which favors chemical heterogeneity and residual stress.[1] These nanopolar regions behave like spins feeling local electric random fields and interacting via random bonds.[4,5] It has recently been shown that, for glassy relaxor systems like x/65/35 PLZT ceramics for $7<x<12$, the temperature dependence of the static linear and the third order nonlinear dielectric susceptibilities and the E–T phase diagram could be well described within the spherical random bond random field (SRBRF) model.[4–6] In these systems no long range ferroelectric phase is established on cooling the system in zero electric field, but rather, the system freezes into an nonergodic glass-like relaxor phase.[7,8] Lanthanum doping in ferroelectric perovskites is believed to disturb the long-range Coulomb interaction, which drives the formation of spontaneous polarization below T_c. The formation of ferroelectric domains is strongly inhibited as La-content increases. The ferroelectric phase could only be stabilized in glassy relaxor systems by cooling the system above the critical electric field E_C.[5,9]

It was shown that in ($x<7$)/65/35 PLZT ceramics cooled in zero electric bias field at low temperatures, regions are dominated by both ferroelectric and relaxor states. Optical and electrical measurements reported the coexistence of micro-sized ferroelectric domains and also nano-sized glassy polar regions.[10–12] At room temperature their size in (6–7)/65/35 PLZT is 1–3 μm and ≈10 nm, respectively.[10,12] The E–T phase diagram has

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been studied only in glassy relaxor systems showing no incipient ferroelectricity in zero bias electric field.[5,9,13–15] Recently, it was shown that the ferroelectric state in x/65/35 PLZT relaxors ($4<x<12$) can be induced by mechanical stress or by dc electric bias field.[7,9]

An external electric field can overcome the random local fields in such a way that a normal ferroelectrics phase may be induced. This transition is often referred to in the literature as the field induced micro to macro domain transition.[2] By applying an electric field, the favorable oriented clusters grow until the ferroelectric phase is induced.[16] Thus, when an electric field is applied the nano domains will grow in size and merge to form large polar regions, which results in micro domains. Moreover, it was reported that the applied bias electric field could induce the ferroelectrics phase even at higher temperatures, where thermal fluctuations normally prevent the onset of long-range order.

In this article we present the E–T phase diagram and study the influence of the bias electric field on the formation of a long range ferroelectric phase from polar nanoclusters in 6.5/65/35 PLZT ceramics.

2. Experimental procedures

Measurements were made on three PLZT 6.5/65/35 ceramic samples with thickness from 0.26 to 0.32 mm. Samples were prepared by a mixed oxide method starting from high purity oxides (>99.9%). After being hot pressed at 1150 °C for 2 h in PbO excess environment, gold electrodes were sputtered onto the sample by the evaporation technique. Complex dielectric permitivity was measured using a Hewlett-Packard 4282A Precision LCR meter. The amplitude of the ac excitation voltage was 1 V. The measurement voltages were small enough to neglect the influence of the ac field on dielectric constant values. Measurements were performed on cooling the sample from 180 to 22 °C in several dc bias electric fields from 0 to 5 kV/cm. The temperature cooling rate was typically −60 °C/h and the frequency range was between 20 Hz and 1 MHz.

The dc field dependence of the effective quasistatic field-cooled (FC) dielectric constant $\varepsilon_{FC}=1+P_{FC}(E,T)/\varepsilon_0 E$ was determined by cooling an annealed sample down to 22 °C in a dc bias electric field E. At 22 °C the scanning rate was reversed and the sample was slowly field-heated (FH) (60 °C/h) up to 180 °C while the corresponding polarization charge was measured by the Keithley 617 programmable electrometer.[17] This procedure was then repeated for several electric fields between 0.1 kV/cm and 5 kV/cm.

Since it is well known that history-dependent effects play an important role in relaxor systems, the sample was annealed at 180 °C for 1 h before each measurement, in order to ensure identical conditions for all measurements and to eliminate the effects of previous treatments.[8,18]

3. Results and analysis

Quasistatic measurements of the FC/FH effective dielectric response obtained on 6.5/65/35 PLZT ceramics at $E=1$ kV/cm are shown in Fig. 1. Results are very similar to those obtained previously at similar fields on the glassy relaxor systems (8–9)/65/35 PLZT ceramics[8,19,20] and on PMN relaxor.[21] In particular, the FC dielectric constant increases very sharply with decreasing temperature and nearly saturates at lower temperatures. This increase corresponds to the relaxor-to-ferroelectric conversion which takes place even in a zero-field cooled run and can be seen as a step-like anomaly in the temperature dependence of the frequency dependent real part of the dielectric constant.

A hysteresis effect is observed between FC and FH quasistatic dielectric constants in the temperature range around the ferroelectric transition. This effect could be a consequence either of the nanodomain structure, depinned effects due to impurities, or the smeared latent heat effect. It was shown that the ferroelectric transition may be of the weakly first order type.[9]

The experiments shown in Fig. 1, repeated at several dc bias fields, enable quasistatic measurements of the polarization as a function of the field E. Fig. 2 shows the field dependence of the FC dielectric polarization, at a particular temperature of 25 °C, deduced from different FC scans obtained at various dc electric fields. After an approximately linear regime the polarization saturates in an almost field-independent plateau. This plateau corresponds to the spontaneous polarization P_S, which reaches a value of nearly 0.37 As/m^2 at low temperatures.

It is interesting to note that this value obtained in the incipient ferroelectric 6.5/65/35 PLZT ceramics is much lower than the value of 0.6 As/m^2 obtained in the field

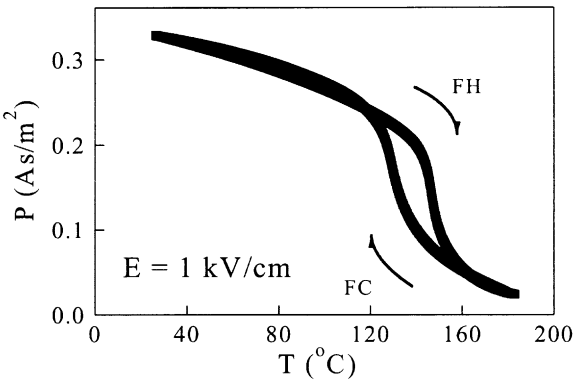

Fig. 1. Temperature dependence of FC/FH effective dielectric polarization P, measured at $E=1$ kV/cm. Arrows indicate heating and cooling run.

induced ferroelectric state of the glassy relaxor 9/65/35 PLZT ceramics.[19]

It should also be noted that P_S vanishes at the same temperature where the sharp peak in pyroelectric current is observed. The pyroelectric current was calculated from the derivative of the $P_{FC/FH}(T)$ data. This allows determination of the ergodic relaxor to ferroelectric (RF) transition temperatures from the temperature positions of the pyroelectric current peaks.

The RF phase transition temperatures are presented in Fig. 3a as a function of the applied bias electric field, which is determined from the temperature positions of the pyroelectric current peaks. In zero bias electric field the ferroelectric phase transition temperature was found to be 110 °C on cooling and 140 °C on heating. On increasing the bias electric field a nearly linear increase in RF phase transition temperature was observed (+11 °C per 1 kV/cm on cooling).

On the other hand, analysis of the frequency dependent complex dielectric constant (Fig. 4) reveals that, in small bias electric fields, part of the sample still freezes into the glass-like nonergodic relaxor state even below the RF transition temperature. The freezing transition temperature of this glassy relaxor state is shown as a function of the bias electric field in Fig. 3b. Here, the temperature dependence of the characteristic relaxation frequency, determined from the temperature positions of the diffuse imaginary dielectric maxima obtained at different bias electric fields (inset to Fig. 4), obeys the Vogel–Fulcher ansatz $f=f_0\exp[-E_a/(T-T_0)]$ with the freezing temperature T_0 strongly dependent on the bias electric field E.

Furthermore, temperature positions of the diffuse peaks of the imaginary part of the dielectric constant become almost frequency independent, as one would expect for the critical slowing down near the ferroelectric phase transition. This is reflected in the very steep curves (inset to Fig. 4), which become more and more activated-like as more and more of the sample

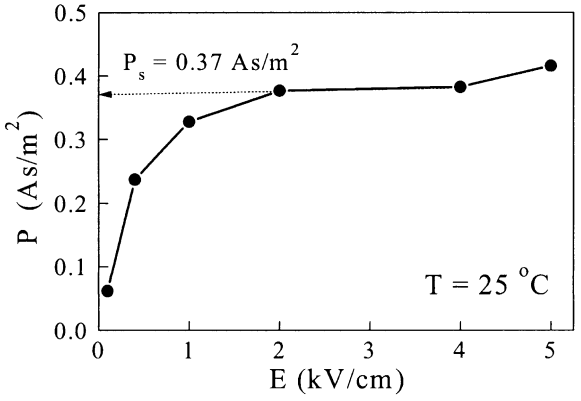

Fig. 2. Dielectric polarization measured at 25 °C. The value of spontaneous polarization at 25 °C is also shown.

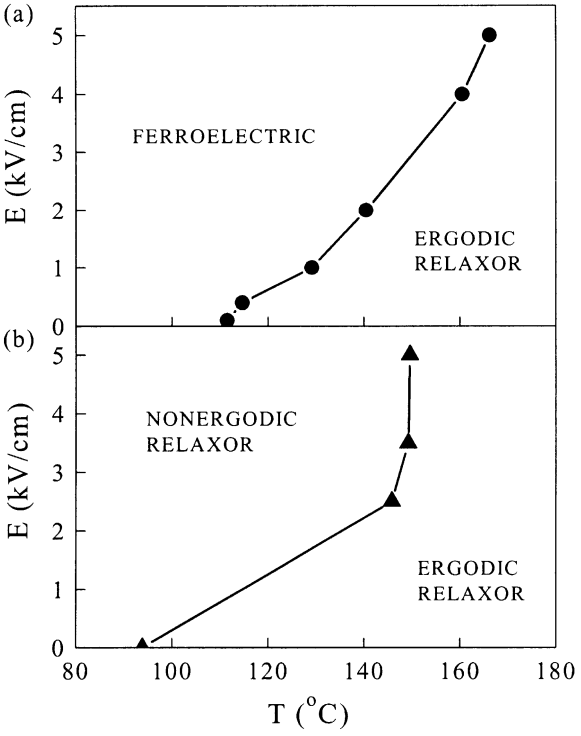

Fig. 3. (a) RF transition temperature and (b) freezing temperature on cooling as a function of the electric field in 6.5/65/35 hot-pressed PLZT ceramics.

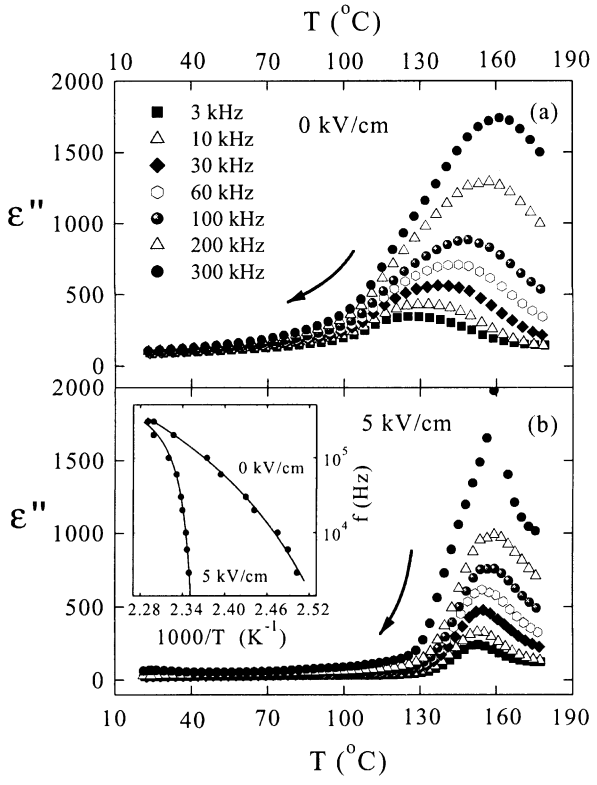

Fig. 4. Imaginary part of the linear dielectric constant as a function of the temperature on cooling in zero bias electric field (a) and in $E=5$ kV/cm (b). The inset shows the characteristic relaxation frequency as a function of the inverse temperature in zero bias electric field and in $E=5$ kV/cm.

converts to the ordered ferroelectric state with the increasing bias field.

It seems that at even higher electric bias field a ferroelectric state would be dominant, as relaxor polar nanoregions would tend to convert into ferroelectric micron-sized domains. In this case a more sharp first order ferroelectric phase transition exhibiting a divergence in the dielectric response should be seen. In addition a critical-slowing-down anomaly should appear in the Arrhenius temperature dependence of the characteristic relaxation frequency.

4. Conclusions

Measurement of the complex dielectric constant and FC/FH quasistatic dielectric polarization show incipient ferroelectricity in 6.5/65/35 PLZT ceramics with the coexisting relaxor and ferroelectric states at small bias electric fields. The value of the spontaneous polarization was found to be lower than in the 9/65/35 PLZT ceramics. The E–T phase diagrams for both relaxor and ferroelectric states show increase of the transition temperatures with increasing bias electric field. The coexistence of multidomain states in PLZT 6.5/65/35 is most probably stabilized by a random distribution of local fields. Additional nanoscale polar regions, which still coexist with ferroelectric micro domains, slowly convert with increasing bias field to the ordered ferroelectric state. The linear dielectric response at higher values of the bias electric field becomes more similar to the response one would expect for the critical slowing down near the proper ferroelectric transition.

Acknowledgements

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References

1. Farhi, R., El Marsii, M., Dellis, J-L., Picot, J-C. and Morell, A., On the nature of the glassy state in 9/65/35 PLZT ceramics. *Ferroelectrics*, 1996, **176**, 99–106.
2. Xunhu, D., Xu, Z. and Viehland, D., The spontaneous relaxor to normal ferroelectric transformation in La-modified lead zirconate titanate. *Phyl. Mag. B*, 1994, **70**(1), 33–48.
3. Viehland, D., Jang, S. J. and Cross, L. E., Freezing of the polarization fluctuations in lead magnesium niobate relaxors. *J. Appl. Phys*., 1990, **68**(6), 2916–2921.
4. Blinc, R., Dolinšek, J., Gregorovič, A., Zalar, B., Filipič, C., Kutnjak, Z., Levstik, A. and Pirc, R., Local polarization distribution and Edwards–Anderson order parameter of relaxor ferroelectrics. Phys. *Rev. Lett*., 1999, **83**, 424–427.
5. Bobnar, V., Kutnjak, Z. and Levstik, A., Glassy to inhomogeneous-crossover in (Pb,La)(Zr,Ti)O_3 ceramics. *Appl. Phys. Lett*., 2000, **76**(19), 2773–2775.
6. Kutnjak, Z., Pirc, R. and Blinc, R., Field-cooled static nonlinear response of relaxor ferroelectrics. *Appl. Phys. Lett*., 2002, **80**(17), 3162–3164.
7. El Marssi, M., Farhi, R., Dellis, J.-L., Glinchuk, M. D., Seguin, L. and Viehland, D., Ferroelectric and glassy picture states in La-modified lead zirconate titanate ceramics: a general picture. *J. Appl. Phys*., 1998, **83**(10), 5371–5380.
8. Kutnjak, Z., Filipič, C., Pirc, R., Levstik, A., Farhi, R. and Mimoun El, M., Slow dynamics and ergodicity breaking in a lanthanum-modified lead zirconate titanate relaxor system. *Phys. Rev. B*, 1999, **59**(1), 294–301.
9. Bobnar, V., Kutnjak, Z., Pirc, R. and Levstik, A., Electric-field-temperature phase diagram of the relaxor ferroelectric lanthanum-modified lead zirconate titanate. *Phys. Rev. B*, 1999, **60**(9), 6420–6427.
10. Dellis, J. L., El Marssi, M., Tilloly, P., Farhi, R. and Viehland, D., A dielectric study of the X/65/35 lanthanum-modified lead zirconate-titanate series. *Ferroelectrics*, 1997, **201**(1–4), 167–174.
11. Xunhu, D., Xu, Z. and Viehland, D., Long-time relaxation from relaxor to normal ferroelectric states in Pb0.91La0.06(Zr0.65-Ti0.35)O3. *J. Am. Ceram. Soc*., 1996, **79**(7), 1957–1960.
12. Krumins, A., Shiosaki, T. and Koizumi, S., Sponatneous transition between relaxor and ferroelectric states in lanthanum-modified lead zirconate titanate (6–7)/65/35. *Jpn. J. Appl. Phys*., 1994, **33**, 4940–4945.
13. Colla, E. V., Koroleva, E., Okuneva, N. M. and Vakhrushev, S. B., Long time relaxation of the dielectric response in lead magnoniobate. *Phys. Rev. Lett*., 1995, **74**, 1681–1684.
14. Sommer, R., Yushin, N. K. and van der Klink, J. J., Polar metastability and an electric-field-induced phase transition in the disordered perovskite $PbMg_{1/3}Nb_{2/3}O_3$. *Phys. Rev. B*, 1993, **48**, 13230–13237.
15. Westphal, V., Kleemann, W. and Glinchuk, M. D., Diffuse phase transitions and random-field-induced domain states of the "relaxor" ferroelectric PbMg1/3Nb2/3O3. *Phys. Rev. Lett*., 1992, **68**, 847–850.
16. Bottger, U., Biermann, A. and Arlt, A., Phase transitions in PLZT ceramics. *Ferroelectrics*, 1992, **134**, 253–258.
17. Levstik, A., Filipič, C., Kutnjak, Z., Levstik, I., Pirc, R., Tadić, B. and Blinc, R., Field-cooled and zero-field-cooled dielectric susceptibility in deuteron glasses. *Phys. Rev. Lett*., 1991, **66**, 2368–2371.
18. Burkhanov, A. and Shilnikov, A., Aging and after-affects in PLZT X/65/35 ferroelectric ceramics. *Ferroelectrics*, 1989, **90**, 39–43.
19. Kutnjak, Z., Filipič, C. and Levstik, A., Linear and nonlinear dielectric constant as function of bias electric field in relaxor materials. *J. Eur. Ceram. Soc*., 2001, **21**, 3162–3164.
20. Viehland, D., Li, J. F., Jang, S. J., Cross, L. E. and Wuttig, M., Glassy polarization behavior of relaxor ferroelectrics. *Phys. Rev. B*, 1992, **46**, 8013–8017.
21. Levstik, A., Kutnjak, Z., Filipič, C. and Pirc, R., Glassy freezing in relaxor ferroelectric lead magnesium niobate. *Phys. Rev. B*, 1998, **57**, 11204–11210.