Journal of the European Ceramic Society 21 (2001) 1319–1322

www.elsevier.com/locate/jeurceramsoc

Nonlinear dielectric response of relaxor PLZT ceramics in a dc bias electric field

Vid Bobnar, *, Zdravko Kutnjak, Adrijan Levstik

Jožef Stefan Institute, PO Box 3000, 1001 Ljubljana, Slovenia

Received 4 September 2000; received in revised form 30 September 2000; accepted 5 October 2000

Abstract

The temperature dependences of the first, ε_1, and the third, ε_3, harmonic dielectric responses have been simultaneously measured in 9/65/35 PLZT ceramics in a dc bias electric field, higher than the critical field. Additional peaks in both, ε_1 and ε_3, superimposed on the broad dispersive relaxor background were observed, indicating induced ergodic relaxor to ferroelectric phase transition. It is shown that the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_1^4$, as predicted by the spherical random bond-random field model of relaxor ferroelectrics, indeed monotonously decreases when approaching the relaxor to ferroelectric transition temperature.

Keywords: Dielectric properties; Ferroelectric properties; PLZT; Relaxor

1. Introduction

Since their discovery more than 40 years ago,[1] relaxor ferroelectrics have been under extensive experimental studies. These perovskite materials are typically characterized by a broad frequency dispersion in the complex dielectric constant and slowing dynamics[1–3] and are believed to provide a conceptual link between ferroelectrics and dipolar glasses. Namely, in zero electric field no long-range ferroelectric state is established, however, at freezing temperature, where the longest relaxation time diverges, relaxors undergo a transition from the ergodic relaxor phase, where all relaxation times are finite, into the nonergodic phase.[3–6] On the other hand, by cooling the relaxor material in an electric field E higher than the critical field E_C a long-range ferroelectric phase is formed.[6,7]

PLZT ceramics is a very promising material for numerous applications. Moreover, for certain compositions, including the 9/65/35 PLZT, it belongs to relaxor materials and thus allows studies of their properties. Recent studies of the electric-field–temperature phase diagram[8] show that by applying a dc bias field higher than $E_C \sim 5$ kV/cm during cooling a long-range ferroelectric order is established, while no long range order is formed below E_C in 9/65/35 PLZT ceramics. Furthermore, dielectric and pyroelectric studies performed in zero dc electric field indicate a glass-like freezing process in 9/65/35 PLZT ceramics, similar to one observed in the lead magnesium niobate (PMN) and dipolar glasses.[4]

After some contradictory experimental results of the temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_1^4$ were reported,[9,10] very recently a crossover from the decreasing to the increasing temperature dependence in a_3 when approaching the freezing transition was observed in zero dc bias field in the PMN single crystal and in 9/65/35 PLZT ceramics.[11] This suggests that the nonergodic relaxor phase is rather glassy phase than a ferroelectric state broken up into nanodomains. Namely, the scaling theory of the second order phase transition predicts that a_3 should vanish at the ferroelectric transition[12] and diverge at the freezing transition in dipolar glasses[13] as indeed observed.[14]

The observed crossover in a_3 is actually predicted by the spherical random bond-random field (SRBRF) model of relaxor ferroelectrics.[10,11] On the other hand, the SRBRF model predicts different temperature dependence of a_3 on approaching the relaxor to ferroelectric

* Corresponding author. Tel.: +386-1-477-3763; fax: +386-1-219-385.

E-mail address: vid.bobnar@ijs.si (V. Bobnar).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00009-7

transition temperature.[10,11] Therefore, in this work we present a detailed description of measurements of the temperature dependences of the first, ε_1, and the third order, ε_3, dielectric constants in 9/65/35 PLZT ceramics in a dc bias electric field, higher than E_C. It is shown that a_3 determined from this measurement monotonously decreases when approaching the relaxor to ferroelectric transition temperature, as predicted by the SRBRF model.

2. Experimental procedure

The 0.52 mm thick platelet of 9/65/35 PLZT hot pressed ceramics was covered with evaporated gold electrodes having surface dimensions of 4.7×3.5 mm^2. It has already been shown that the field induced transition from the ergodic relaxor phase to the long-range ferroelectric phase can be studied by measurements of the complex dielectric constant in a zero-field-heating run following the field-cooling run (FC-ZFH susceptibility).[8] In this case, an additional peak in ε_1, superimposed on the broad dispersive relaxor background appears at the ferroelectric to ergodic relaxor phase transition temperature. Therefore, the PLZT sample was first cooled from 410 down to 150 K in a dc bias field higher than E_C. At 150 K the dc bias field was switched off and the sample was short-circuited. Then, the sample was heated back to 410 K. The cooling and heating rates were ±25 K/h. During heating run, the first, ε_1, and the third, ε_3, harmonic dielectric responses were measured simultaneously by using a HP 35665A dynamic signal analyzer. It should be noted that ε_1 and ε_3 here denote the real parts of the corresponding complex dielectric constants. Prior to each measurement, the samples were annealed for 1 h at 410 K in order to ensure equal conditions for all measurements and to eliminate the effects of previous treatments.

3. Results and discussion

Fig. 1 shows the first, ε_1, and the third order, ε_3, dielectric constants, measured in the zero-field-heating run on the sample cooled in a dc bias field of 8.5 kV/cm. Besides the broad dispersive dielectric maximum, typical for relaxors, also a peak at $\approx$265 K can be observed in both, ε_1 and ε_3. It has already been shown that the maximum value of the peak in ε_1 is frequency dependent, however, its temperature position is not dependent on the frequency, contrary to the broad peaks associated with the relaxor phase.[8] This peak therefore indicates the ferroelectric to ergodic relaxor phase transition.

The dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_1^4$ has been calculated in the vicinity of the transition temperature T_C

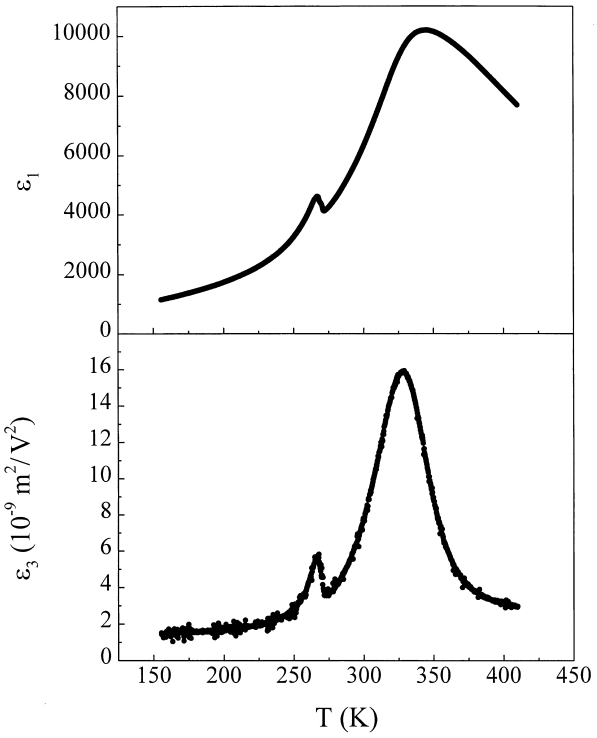

Fig. 1. The temperature dependences of the first, ε_1, and the third order, ε_3, dielectric constants, measured at 400 Hz in 9/65/35 PLZT ceramics in the FC-ZFH run at 8.5 kV/cm. The peaks superimposed on the broad dispersive relaxor background indicate ferroelectric to ergodic relaxor phase transition.

from the ε_1 and ε_3 data, shown in Fig. 2. These data were obtained from the FC-ZFH run results (cf. Fig. 1) after the subtraction of the background coming from the broad relaxor dielectric peak. The resulting temperature dependence of a_3 is shown in Fig. 3(a). While in zero dc bias field, where no long-range order is established, a_3 shows a crossover from the decreasing to the increasing temperature dependence on approaching the freezing transition,[11] here a_3 monotonously decreases on approaching the relaxor to ferroelectric transition temperature T_C.

Similarly to crossover from the decreasing to the increasing temperature dependence of a_3 on approaching the freezing transition in zero bias field,[11] the obtained dependence in a_3 in the vicinity of the relaxor to ferroelectric transition temperature is actually predicted by the SRBRF model. SRBRF model predicts the glassy behavior of the system to be due to the reorientable polar clusters embedded in a random array of chemically ordered nanodomains.[10] Random bonds are characterized by the mean value of coupling J_0 and variance J, and random fields are characterized by the variance Δ. Numerical solutions of equations for the spherical glass order parameter q and polarization P,[10]

$$q = \beta^2 J^2\left(q + \Delta/J^2\right)(1-q)^2 + P^2, \tag{1}$$

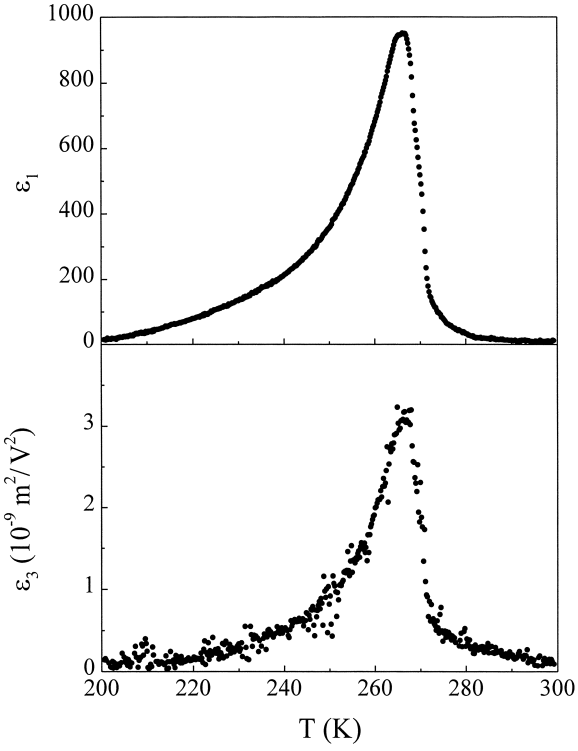

Fig. 2. The temperature dependences of ε_1 and ε_3, obtained in 9/65/35 PLZT ceramics in the FC-ZFH run (cf. Fig. 1) after subtraction of the background.

$$P = \beta(1-q)(J_0 P + E), \tag{2}$$

where $\beta = 1/kT$ yield derivatives such as $\varepsilon_1\ (E, T) = 1 + \partial P/\partial E$ and $\varepsilon_3\ (E, T) = -(1/6)\partial^3 P/\partial E^3$ leading to $a_3 = \varepsilon_3/\varepsilon_1^4$. It should be noted that if $J_0 < \sqrt{J^2 + \Delta}$ a spherical glass without long range order is formed, whereas a ferroelectric state becomes stable if $J_o > \sqrt{J^2 + \Delta}$.[10]

Fig. 3(b) shows the temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_1^4$ calculated from the SRBRF model in the vicinity of the relaxor to ferroelectric transition. As experimental data, calculated a_3 also monotonously decreases when approaching the relaxor to ferroelectric transition temperature. However, it can be seen that the model predicts the change of the sign of a_3 at the transition temperature, while the experimental data do not change the sign at T_C. This can be explained by the fact that the theoretical predictions are based on the results of the continuous second-order phase transition, whereas it was shown that 9/65/35 PLZT ceramics exhibit a weak discontinuous first-order relaxor to ferroelectric transition,[8] perhaps as a consequence of the strain-polarization coupling. It should be pointed out that earlier theoretical results based on the thermodynamic theory have already predicted that the third-order nonlinear dielectric constant changes sign at the second-order paraelectric to ferroelectric transition, while there is no change in sign in the case of the first-order transition.[15]

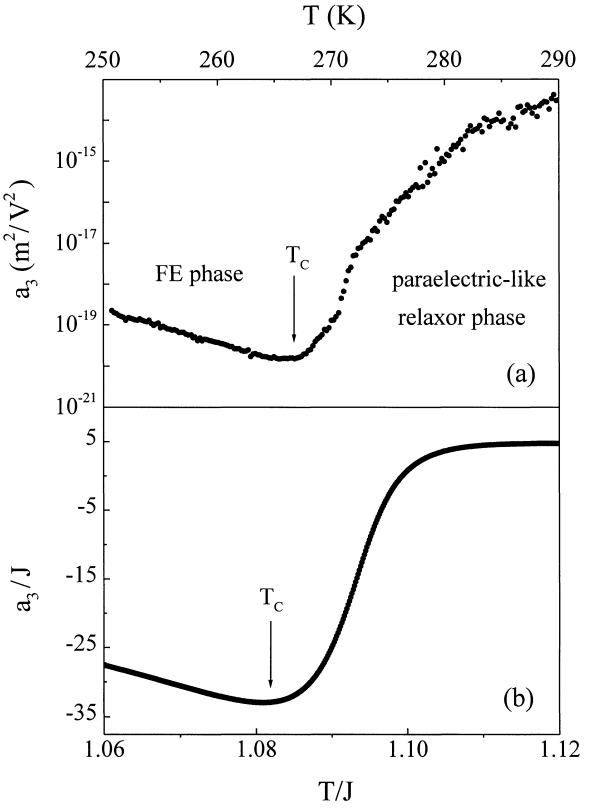

Fig. 3. (a) The temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_1^4$ in the temperature interval around the relaxor to ferroelectric transition temperature in 9/65/35 PLZT ceramics, calculated from ε_1 and ε_3 data presented in Fig. 2. (b). The temperature dependence of a_3 calculated from the SRBRF model in the vicinity of the relaxor to ferroelectric transition.

4. Conclusions

Simultaneous measurements of the temperature dependences of the first, ε_1, and the third, ε_3, harmonic dielectric responses have been performed in 9/65/35 PLZT ceramics in a dc bias electric field, higher than the critical field E_C. Contrary to the results in zero dc bias electric field, where the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_1^4$ shows a crossover from decreasing to increasing temperature dependence when approaching the freezing transition from above, here the a_3 data monotonously decreases when approaching the relaxor to ferroelectric transition temperature, as is predicted by the spherical random bond-random field model of relaxor ferroelectrics.

Acknowledgements

This work was supported by the Ministry of Science and Technology of Slovenia.

References

1. Smolenskii, G. A., Isupov, V. A. and Agranovskaya, A. I., Dielectric polarization of solid solutions in the system (Ba,Sr)$(Ta,Nb)_2O_6$. *Sov. Phys. Solid State*, 1959, **1**, 909–911.
2. Cross, L. E., Relaxor ferroelectrics. *Ferroelectrics*, 1988, **76**, 241–267.
3. Viehland, D., Jang, S. J., Cross, L. E. and Wuttig, M., Deviation from Curie–Weiss behavior in relaxor ferroelectrics. *Phys. Rev. B*, 1992, **46**, 8003–8006.
4. Kutnjak, Z., Filipič, C., Pirc, R., Levstik, A., Farhi, R. and El Marssi, M., Slow dynamics and ergodicity breaking in lanthanum-modified lead zirconate titanate relaxor system. *Phys. Rev. B*, 1999, **59**, 294–301.
5. Levstik, A., Kutnjak, Z., Filipič, C. and Pirc, R., Glassy freezing in relaxor ferroelectric lead magnesium niobate. *Phys. Rev. B*, 1998, **57**, 11204–11210.
6. Colla, E. V., Koroleva, E.Yu., Okuneva, N. M. and Vakhrushev, S. B., Long time relaxation of the dielectric response in lead magnoniobate. *Phys. Rev. Lett.*, 1995, **74**, 1681–1684.
7. 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.
8. 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**, 6420–6427.
9. Tagantsev, A. K. and Glazounov, A. E., Does freezing in $PbMg_{1/3}Nb_{2/3}O_3$ relaxor manifests itself in nonlinear dielectric susceptibility? *Appl. Phys. Lett.*, 1999, **74**, 1910–1912.
10. Blinc, R., Dolinšsek, 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.
11. Bobnar, V., Kutnjak, Z., Pirc, R., Blinc, R. and Levstik, A., Crossover from glassy to inhomogeneous-ferroelectric nonlinear dielectric response in relaxor ferroelectrics. *Phys. Rev. Lett.*, 2000, **84**, 5892–5895.
12. Stanley, H. E., *Introduction to Phase Transitions and Critical Phenomena*. Clarendon Press, Oxford, 1971 p. 187.
13. Fischer, K. H. and Hertz, J. A., *Spin Glasses*. Cambridge University Press, Cambridge, 1991 p. 187.
14. Hemberger, J., Ries, H., Loidl, A. and Böhmer, R., Static freezing transition at a finite temperature in a quasi-one-dimensional deuteron glass. *Phys. Rev. Lett.*, 1996, **76**, 2330–2333.
15. Ikeda, S., Kominami, H., Koyama, K. and Wada, Y., Nonlinear dielectric constant and ferroelectric-to-paraelectric phase transition in copolymers of vinylidene fluoride and trifluoroethylen. *J. Appl. Phys.*, 1987, **62**, 3339–3342.