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Relaxor and incipient ferroelectric phases in 6.5/65/35 PLZT ceramics

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Abstract

The linear and third harmonic nonlinear dielectric constants were measured in 6.5/65/35 PLZT hot-pressed ceramics. Linear dielectric data obtained on ooling show the transition from an ergodic to a nonergodic relaxor phase while, on heating, a ferroelectric to ergodic relaxor phase transition appears. The third harmonic di-electric response is reminiscent of an ergodic to nonergodic relaxor phase transition. Existence of the spontaneous polarization below the Vogel–Fulcher temperature at which the longest relaxation time diverges, indicates the possibility that the sample breaks up at low temperatures into relaxor glass-like and ferroelectric order dominated regions.

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

1. Introduction

Lanthanum-modified lead zirconate titanate solid solutions (PLZT) with La content between 5 and 14 at.% and with a Zr/Ti ratio of 65/35 are relaxor ferroelectrics.[1–3] A broad diffuse relaxor-like dielectric maximum appears due to substitution of Pb 2+ ions by aliovalent La 3+ ions which creates vacancies in the A-site of the perovskite ABO3 structured ferroelectric PZT ceramics. The incorporation of La ions and vacancies in the lattice is believed to break Preprint submitted to Elsevier Science 25 October 2002.the long-range interaction between ferroelectrically active oxygen octahedrals containing B-site cations. Above a critical (<9 at.%) La content, the decou-pling might be sufficiently strong for spontaneous macroscopic transformation to a long-range ferroelectrics state with micron-sized domains to be prevented; rather a state with locally polarized regions on a nanometer scale would be observed.[4] Their size is inversely proportional to the temperature.[2] Cor-respondingly, the macroscopic properties change from normal-ferroelectric to relaxor-ferroelectrics with increasing La content. In relaxor-like materials it is believed that correlations between polar nanodomains and subsequent freez-ing of polarization fluctuations into a state with glass-like characteristics at lower temperatures control the observed relaxor behavior. The coexistence of both relaxor and ferroelectric phase is assumed in the literature[1] for critical La content, however clear proof has not been obtained. We will show in the present study, that the combination of linear and nonlinear dielectric measurements point to the coexistence of both phases.

2. Experimental procedures

$(Pb_{1-3/2y}La_y)$ $(Zr_{1-x}Ti_x)_{1-y/4}O_3$ ceramics were used in this study. Samples were prepared by a mixed oxide method starting from high purity oxides ($<99.9\%$). The compounds were hot pressed at 1150 °C for 2 h in a PbO- excess environment. Gold electrodes were sputtered onto the sample. Linear complex dielectric permitivity was measured in the frequency range between 20 Hz and 1 MHz, using a Hewlett-Packard 4282A precision LCR meter. The amplitude of the applied ac

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excitation voltage was 1 V. The third harmonic dielectric response was measured in the frequency range between 1 Hz and 10 kHz by using a Hewlett-Packard 35665A Dynamic Signal Analyzer with an ac excitation voltage of 4.9 V. Both measurements were performed in the tem- perature interval between 20 and 185 °C on cooling and heating the samples with a temperature scanning rate of 30 °C/h. The measurement voltages were small enough to keep the amplitude of harmonics higher than the third order negligibly small.[5,6] Prior to each measurement the sample was annealed at 185 °C for at least 1h.

3. Results and analysis

The temperature dependence of the linear complex dielectric constant ε′, and of the dielectric loss factor $\tan(\delta)=\varepsilon_1''/\varepsilon_1'$, obtained on cooling and heating the sample respectively, is shown in Figs. 1 and 2.

Data taken on cooling differ from those obtained on heating the sample. While on cooling the sample from 185 °C, both the real part of the complex dielectric constant and the dielectric loss factor show continuous evolution, on heating the sample both quantities exhibit a more discontinuous-like increase near 139 °C. It was reported that this behavior is a consequence of a space charge field.[2] In PLZT ceramics a space charge field is built up by the redistribution of the defects and/or space charge. This field is stabilized by coupling with the spontaneous polarization. An internal field thus helps in inducing the ferro- electric state.[2] By heating the sample to 200 °C the space charge and the internal field completely disappear. Therefore, on cooling the internal field is much smaller than on heating, and consequently a difference in ε* (*T*) between the cooling and heating cycles appears. This means that the low temperature state, which was reached immediately after cooling the sample is not in equilibrium and conforms more to the relaxor glassy state. In time it slowly converts to the long-range incipient ferroelectric state as the space charge field builds up after the redistribution of the defects and space charges has taken place.

No distinct transition in the complex dielectric constant (Fig. 1a) and the di-electric loss factor (Fig. 1b) can be observed on cooling. This shows that there is no obvious macroscopic transformation on cooling from an ergodic relaxor phase towards a long-range normal ferroelectric state. The glassy nature of the state reached immediately after cooling is also evident from the analysis of the freezing dynamics. The temperature dependence of the characteristic relaxation frequency obtained from the temperatures corresponding to the diffuse imaginary dielectric maxima on cooling (Fig. 3)

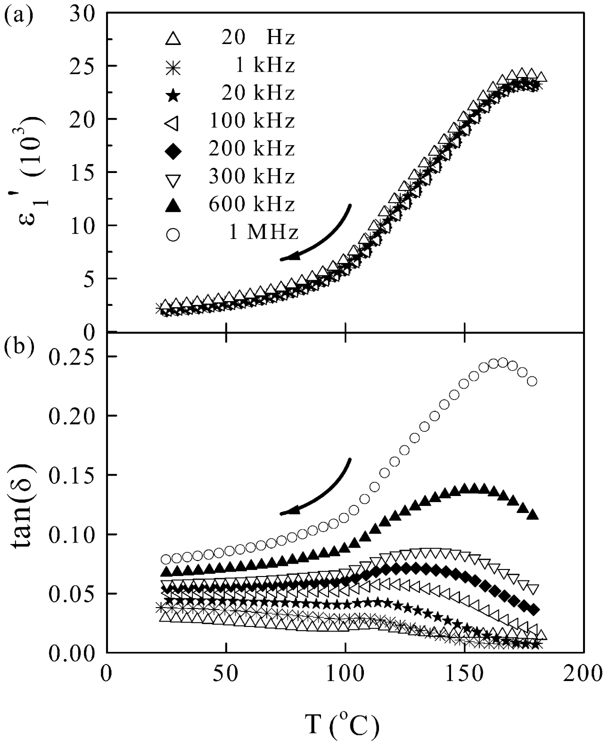

Fig. 1. (a) Linear complex dielectric constant ε′ and (b) the dielectric loss factor tan(δ) as a function of temperature at different measurement frequencies on cooling.

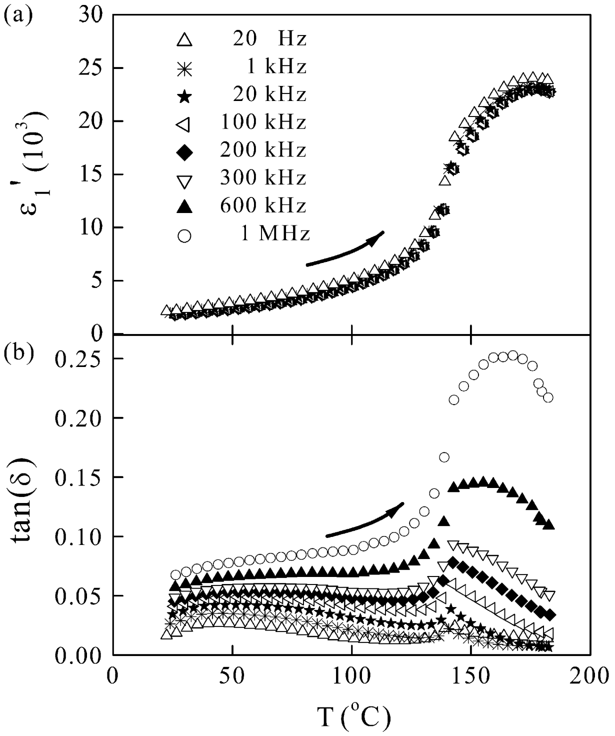

Fig. 2. (a) Linear complex dielectric constant ε′ and (b) the dielectric loss factor tan(δ) as a function of temperature at different measurement frequencies on heating.

obeys the Vogel–Fulcheransatz $f=f_0 \exp[-E_a/(T-T_0)]$ with $E_a=0.039$ eV, $f_o=132$ MHz and the freezing temperature $T_0=87\pm2$ °C.

Such behavior is characteristic of a freezing process from the ergodic to a non-ergodic relaxor phase.[7] Above the freezing temperature an ergodic relaxor phase is present; at T_0 the divergence of the longest relaxation time effectively breaks the ergodicity of the system, leading to the nonergodic relaxor state.[10] The observed dynamics are similar to the glassy dynamics reported for the pure relaxor 9/65/35 PLZT ceramics,[8] which do not show ferroelectric long range order in zero electric bias field. The glassy relaxor state and the electric field-temperature (*E–T*) phase diagram were recently successfully described within the spherical random bond random field (SRBRF) model.[5,7,9] Here the nanoclusters interact through random bonds in the environment of the random fields. Due to the gradual growth of the polar nanoregions in the relaxor phase on cooling, and due to the decreasing thermally activated reorientation of the polarization in nanoregions, the correlation between the nanoregions increases. Yet the stabilization of the polar regions is very slow at lower temperatures due to the interaction between the defects and the polar anoregions. Consequently the size of the polar regions also increases with time.[2] In about 100 h they reach the size of a few micrometers, which is comparable to the size of ferroelectric domains. Furthermore, a similar time dependence was reported [12,13] for ferroelectric hysteresis at room temperature. Thus these increased polar regions become ferroelectric domains.[2] Infact, some authors have stated that the ferroelectric phase is probably stabi-lized only in a very small fraction of the sample.[1] Xunhu et al. reported, using X-ray diffraction, the detection of both polar nanocluster state and micrometer-sized ferroelectric domain state,[1] i.e., the coexistence of both relaxor and ferroelectric phases at room temperature.

On the heating cycle, a change of slope is seen at 139 °C in the real part of the dielectric constant ε_1' (Fig. 2) and in the dielectric loss factor (Fig. 2b). The change of slope and the transition temperature hysteresis are indications of the weakly first order nature of the ferroelectric to relaxor transition.[9,11] Recent investigations, involving dielectric hysteresis and X-ray diffraction measure-6.ments, showed that it is possible that a spontaneous ferroelectric to ergodic relaxor phase transition takes place at this temperature.[1,2] The space charge field, which helped to induce the ferroelectric state, gradually disappears with increasing temperature, thus allowing the thermal fluctuations to destroy the long-range correlations between micro domains. A broad dielectric maximum is seen at 172 °C in the real and imaginary parts of the complex permitivity. This maximum was shown to be purely of dynamic origin.[8,10] Thermal activation of the orientation of the polarizations in nanoregions takes place due to the smaller size of polar nanoregions. Therefore a strong frequency dispersion of dielectric properties appears.[1,3,8,10] Whenever the longest relaxation time of the system exceeds the experimental time scale, the measured dielectric constant starts to deviate from the static response, resulting in a broad peak, at a temperature which depends on the measuring frequency.

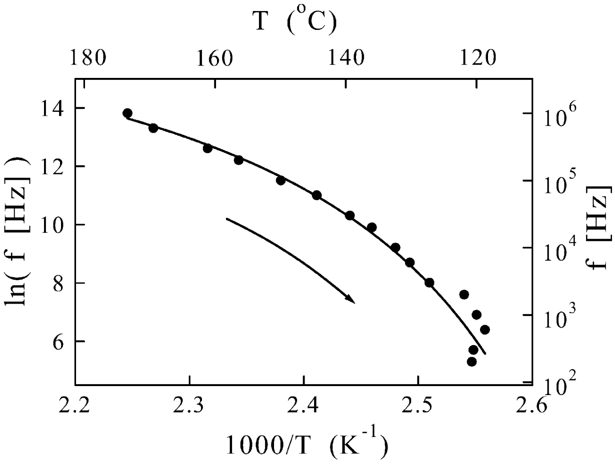

Fig. 3. The temperature dependence of the characteristic relaxation frequency *f*. The solid line represents the fit to the Vogel–Fulcher ansatz.

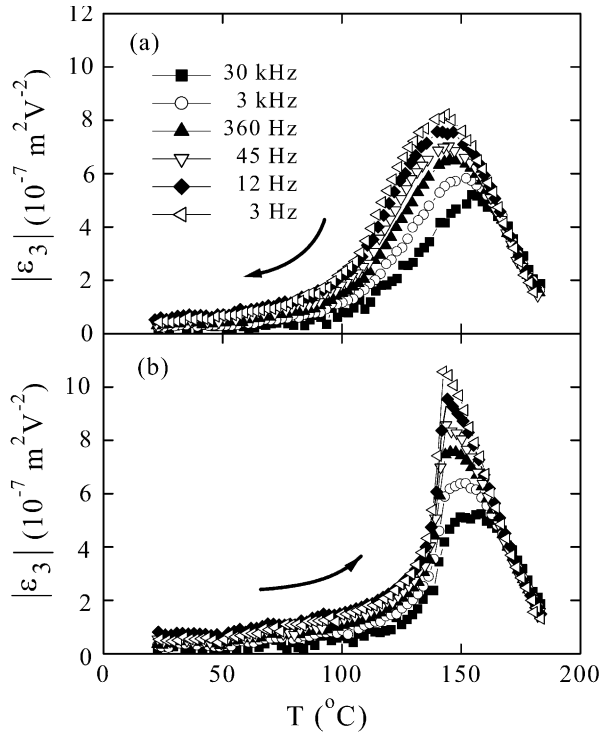

Fig. 4. Third harmonic dielectric constant $|\varepsilon_3|$ as a function of temperature (a—cooling run, b—heating run) at various frequencies.

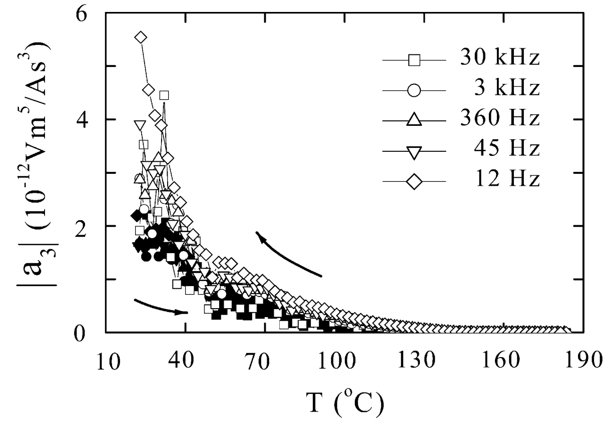

Fig. 5. Dielectric nonlinearity $[\alpha_3]$ as a function of temperature at various frequencies. Open and solid symbols represent cooling and heating data, respectively.

Additional proof of the coexistence of the ferroelectric and relaxor phases is given by the measurements of the third harmonic nonlinear dielectric response $|\varepsilon_3|$. Fig. 4 shows the temperature dependence of $|\varepsilon_3|$ on cooling and heating the sample. It should be noted that much sharper peaks in $|\varepsilon_3|$ are observed on heating than on cooling, indicating the different nature of the transitions, similar to the behavior observed in the linear dielectric constant $|\varepsilon_3|$. On heating, a sharper increase occurs in $|\varepsilon_3|$ near 139 °C, similarly to the change of slope of the linear dielectric constant and dielectric loss tan(δ). Peaks in $|\varepsilon_3|$ and in the linear dielectric constant remain fairly broad, even on heating the sample from the state with the established long-range ferroelectric order. This indicates the presence of a large volume of unconverted glassy polar nanoclusters, besides the ferroelectric domain regions.

It was shown recently that the nonlinearity $|a_3| = |\varepsilon_3|/\varepsilon_0^3\varepsilon_1^4$ could reveal the universality class of the system under study.[8] It was shown [5,8] that $|a_3|$ should decrease continuously through the relaxor to ferroelectric phase transition or rather steeply increase in the case of the glassy ergodic to nonergodic relaxor phase transition. Instead of decreasing, however, $|a_3|$ (Fig. 5) gradually increases with decreasing temperature, thus demonstrating the presence of a considerable volume of glassy polar nanoclusters in addition to the fer-roelectric microdomains. The small thermal hysteresis observed in $|a_3|$ data is in accordance with the first harmonic dielectric data (Figs. 1a and 2a) and is a consequence of the slow, time dependent relaxor to ferroelectric phase conversion.

4. Conclusions

Measurements of the linear and nonlinear dielectric response show that in 6.5/65/36 PLZT ceramics the ergodic to nonergodic relaxor phase transition occurs at 87±2 °C on cooling. At low temperatures slow conversion from the glassy relaxor state to the microdomain ferroelectric state takes place. As a consequence, the spontaneous transition from the ferroelectric to the ergodic relaxor phase occurs at 139±C on heating the sample and is reflected in a change of slope in the linear dielectric constant and in the dielectric loss factor. However, the remaining breadth of the peaks in the linear dielectric response and the temperature dependence of the dielectric nonlinearity $|a_3|$ show that both relaxor glass-like and ferroelectric dominated regions coexist at low temperatures.

Acknowledgements

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