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Effects of a bias on the permittivity of PLZT 9/65/35

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Abstract. We have measured the low-field dielectric response, $\varepsilon(\omega)$, in the relaxor $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ with $x = 0.09$ and $y = 0.65$ (PLZT 9/65/35) subjected to an external field E varying linearly in the 0–800 V cm^{-1} range. In the experimental temperature domain, we point out two regimes of ε-variations, which are attributed to electromechanical coupling: electrostriction at high temperature and domain wall motions at low temperatures. The cross-over is found close to T_m, the temperature of permittivity maximum in the zero-field condition ($E = 0$). It is proposed that the external field induces metastable long-range ordering correlations, leading to the observed time-dependent effects. An exponent $\beta(T)$ related to the distribution of relaxation time has been determined through a non-Debye relaxation analysis.

1. Introduction

Studies of the perovskites PLZT have shown that these systems exhibit, for some compositions, typical relaxor ferroelectric properties. Relaxors are characterized by a broad peak in the dielectric permittivity measured as a function of the temperature which shifts towards higher temperature with increasing measurement frequency (figure 1) and by the lack of any sudden x-ray line splitting when lowering the temperature. On the contrary, additional peaks were shown to continuously increase in intensity and shift towards smaller angles as the temperature was lowered [1]. Relaxors are highly inhomogenous materials and usually show a diffuse phase transition (DPT). From the measurement of the temperature dependence of the refractive index and strain, Burns and Dacol [2] evidenced local polarization at much higher temperatures than the temperature of the permittivity maximum (T_m). Smolenski and Agranovskaya [3] suggested that the DPT arose due to locally varying ferroelectric transition temperatures. Viehland *et al* [4] proposed the formation of randomly oriented polar microregions (PMRs) in the paraelectric phase with thermally activated polarization fluctuations above a freezing temperature. As the temperature is lowered, the development of short-range correlations between PMR was assumed to lead to a freezing into a glassy state and to the observed relaxor behaviour. Recently, Westphal *et al* [5] excluded any glassy state at low temperature in PMN from the observation of Barkhausen jumps during poling and proposed a mechanism of random electric fields originating from charged compositional fluctuations to account for the diffuse character of the transition.

The effect of an external field on the dielectric susceptibility has been extensively studied in ferroelectrics and relaxors because it gives interesting informations about the nature and the mechanism of the onset of polarization in these systems. Kher *et al* [6] have evidenced successive processes (i.e. nucleation and growth) in the poling of $BaTiO_3$ single crystals according to the applied field amplitude. In relaxors, Colla *et al* [7] have

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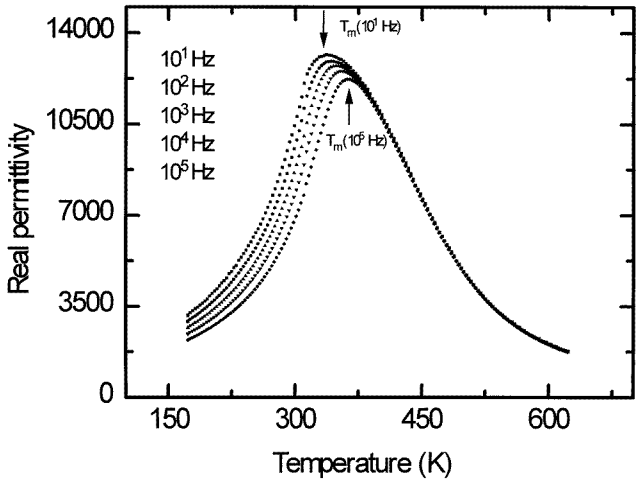

Figure 1. The weak-field permittivity of PLZT 9/65/35. The temperature at which the permittivity peaks depends on the frequency and is denoted T_m. (From [14].)

measured the time dependences of the PMN permittivity in the ZFC (zero-field cooled) state after switching on a DC field E. They observed a stepwise change after some time $\tau(E, T)$ that they attributed to a relaxor–ferroelectric phase transition. Glazounov *et al* [8] studied the dynamics of PMR by measuring the variations of the permittivity as a function of the amplitude of the applied AC field. The application of an electric field is known [9] to align the PMR, transforming the relaxor to a long-range ordered (LRO) state. It is the aim of the present paper to report experimental results obtained by measuring the low-field permittivity when submitting PLZT of composition $x = 0.09$, $y = 0.65$ to isothermal bias ramps. The observed variations of the permittivity are of importance in view of the understanding of the mechanisms of polarization in the relaxors and their possible transition to normal ferroelectric state.

2. Experimental procedure

PLZT 9/65/35 samples were transparent (hot-pressed) ceramics ($4 \times 4 \times 0.5$ mm^3). They were polished, sputtered with gold on both faces to form electrodes which were coated with a conductive painting in order to prevent the gold layers from being scratched by the sample holder. Dielectric experiments have been carried out between 300 and 400 K using the standard two-electrodes technique associated to a Schlumberger 1260 impedance meter. This device allows us to determine the low-field permittivity with the possibility of increasing linearly the bias voltage from 0 to 40 V according to a suitable slope. Most measurements were made using a ramp from 0 to 40 V followed by a plateau at this value (inset of figure 2). Once this DC voltage was reached, the variations of the permittivity were studied as a function of time. The samples were placed in a Linkam stage, which can be operated between 100 and 850 K. The temperature stability of the system is about 0.2 K.

Isothermal measurements were made in the ZFC state (unpoled). The sample was heated up to 600 K in the paraelectric phase for a few minutes, cooled down to the working temperature and the measurements were performed after a waiting time of 1 h. This ensures

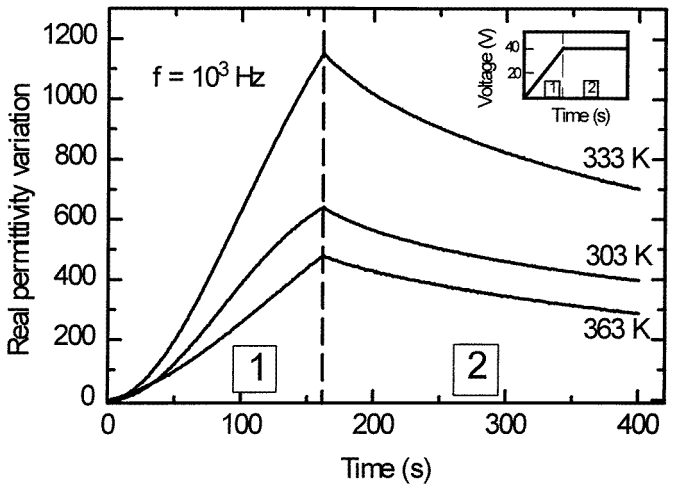

Figure 2. Variations at different temperatures of the permittivity as a function of the bias (part 1 of the figure) and as a function of time (part 2). The inset shows the variations of the applied field and the dashed line the end of the ramp.

the reproductibility of the results. At the end of a ramp or before changing the working temperature, the sample was reheating and the procedure repeated.

3. Results and discussion

3.1. Bias ramps

At all temperatures the permittivity is found to increase with increasing DC bias but this effect is weaker at the higher and the lower temperatures of the experimental domain, and is maximum at an intermediate temperature T_{mb} which depends on the measuring frequency ω (left part of figure 2). It can be seen from this figure that the permittivity variations can reach 10% of the equilibrium value. The increase of the permittivity with the bias is more pronounced when the slope of the ramp is steeper but the temperatures $T_{mb}(\omega)$ were found to be independent of the slope. This means that, although the effect is obviously kinetic, the temperatures $T_{mb}(\omega)$ are intrinsic. In analogy with spin glasses, the ZFC state is generally attributed to the breakdown of ergodicity in the frozen state [10]. In this regime the bias must act to overcome the chemical heterogeneities which normally prevents LRO. A switching from local equilibrium in the ZFC state to a global equilibrium under bias [11] and not only an orientational mechanism can explain the increase of permittivity [12], which reflects the correlations in the sample.

The isothermal variations of the permittivity were analysed by the expression

$$\varepsilon(E) = \varepsilon_0 + \varepsilon_1 E + \varepsilon_2 E^2 \tag{1}$$

where ε_0 is the equilibrium permittivity at $E = 0$ and ε_1 and ε_2 adjustable parameters. As can be seen from figure 3, these variations were almost linear at higher temperatures and quadratic at lower temperatures. The quadratic part is however continued by a linear variation at higher field which leads us to suppose that ε_1 and ε_2 depend themselves on the field (or on time) as already similarly observed by Kher *et al* [6]. This has not been studied

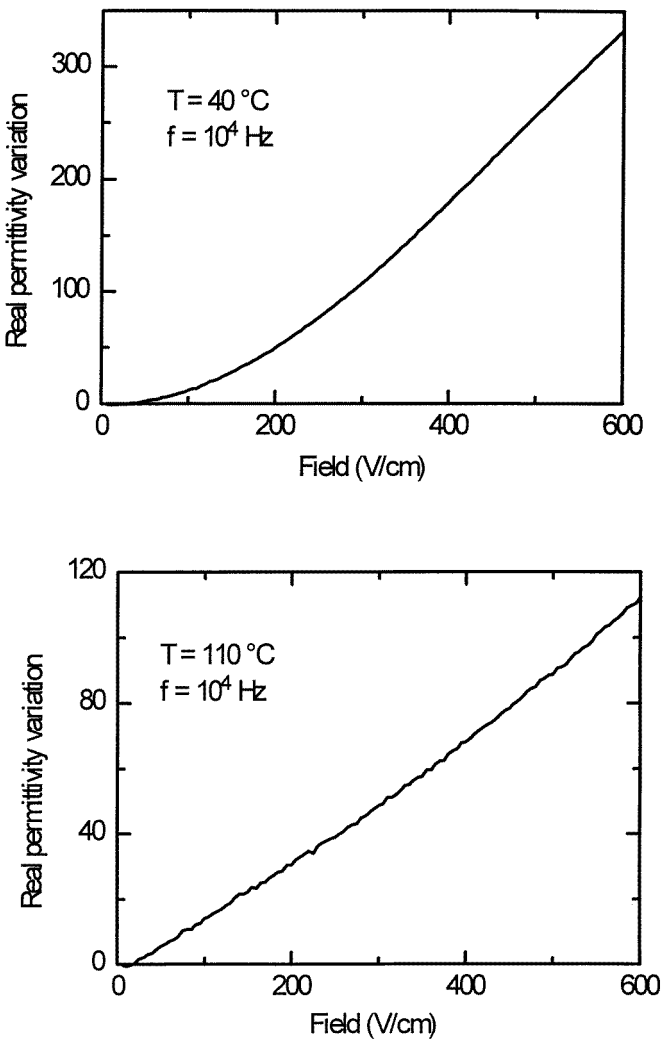

Figure 3. Variations of the permittivity at low temperature (top) and at high temperature (bottom).

here and data were analysed in the low-field part of the experimental domain in such a way that expression (1) was strictly verified. ε_1 and ε_2 are plotted versus temperature in figure 4. ε_1 presents peaks at temperatures close to T_m while the ε_2 maxima lay at lower temperatures, denoted T_{mb}.

These results point out two different behaviours of the effective permittivity under a linearly varying electrical bias. On the one hand at high temperatures, i.e. above T_m, the permittivity variations $\varepsilon(E) - \varepsilon_0 \propto E$ could be explained by both the effect of the nucleation of new nanodomains and the growth of already existing polar nanodomains in the paraelectric phase contributing to electrostriction [13]. On the other hand, at temperatures below T_m, a different mechanism has to be adduced. We suggest that, as the temperature is lowered in the ZFC state, the PMR density rises and, gradually, PMRs interact, leading

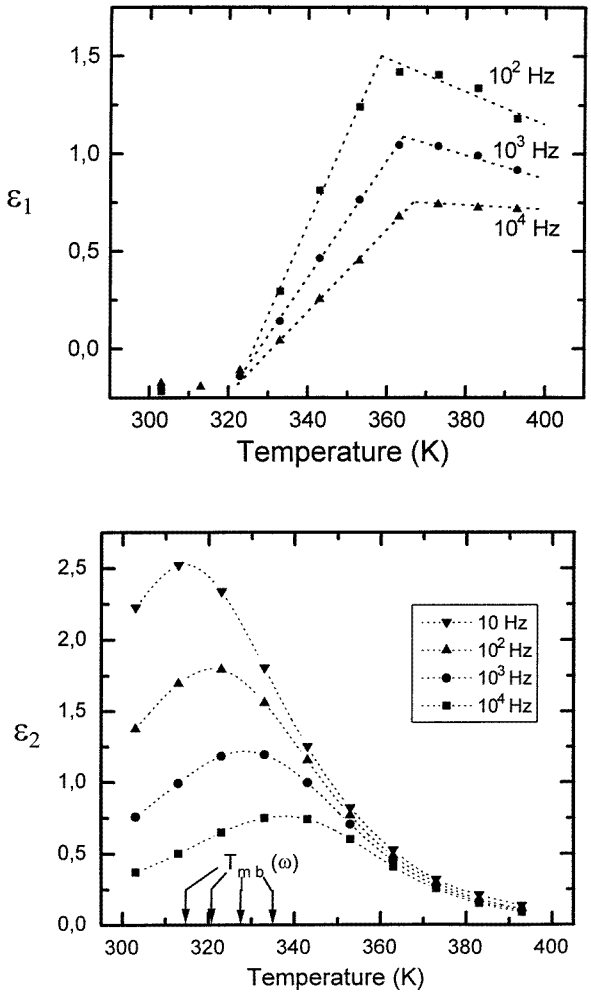

Figure 4. Variations of the parameters ε_1 and ε_2 versus temperature. The arrows indicate the temperatures at which $\varepsilon_2(\omega)$ are maximal.

finally at some lower temperature T_c to a domain wall structure of the PLZT sample [14]. The mechanism of polarization under an electric field of these interacting PMRs is the motion of domain walls. As the material was thermally depoled, the curve (P, E) is the first polarization one and could be described by

$$P = \varepsilon_0 E + \tfrac{1}{3}\varepsilon_2 E^3$$

leading to the observed variations of the permittivity (1)

$$\varepsilon = \varepsilon_0 + \varepsilon_2 E^2$$

with the non-linear term ε_2 related to the irreversible motions of domain walls. At $T > T_c$, since the PMR remains embedded in the paraelectric phase, the walls discussed here have to be considered rather as boundaries between regions in which correlations are strong and whose core is polar than actual boundaries between ferroelectric regions.

The cross-over from the nucleation-growth mechanism of PMR to growth by the domain wall motion mechanism at lower temperature corresponds to the slim to square loop transition usually observed in relaxors. Although these two mechanisms are different, both include induced piezoelectricity since the bias lowers the symmetry of the polycrystalline sample from spherical (thermally depoled material without piezoelectric properties) to conical symmetry (partially poled material). Thus, the observed ε-variations can be understood by assuming that $\varepsilon(E) - \varepsilon_0$ is related to the induced piezoelectric coefficient d_{33} during poling. This can be explained by stating that the sample is free to change its shape. So, on the one hand, electrical field directly causes polarization, defining the dielectric constant at constant strain. On the other hand, field causes a strain x which in turn, by the piezoelectric effect, produces a polarization. This additional contribution arising from the path $(E \rightarrow x \rightarrow P)$ would give rise to the observed increase in the effective dielectric constant.

This interpretation is supported by the very recent piezoelectric measurements on PLZT of the $x/65/35$ series reported by Li *et al* [15]. Indeed, they found that the dominant electromechanical coupling mechanism was electrostriction, $d_{33} \propto E$ in the nanopolar domain state (isolated PMRs). In the normal micrometre-sized domain state (interacting PMRs) nonlinearity in d_{33} was observed on increasing the bias (typically from 0 to 5 kV cm^{-1}) until it remains constant at higher field reflecting normal piezoelectricity. However, their results did not show any frequency dependence of d_{33} as we could expect from our observations (figure 4).

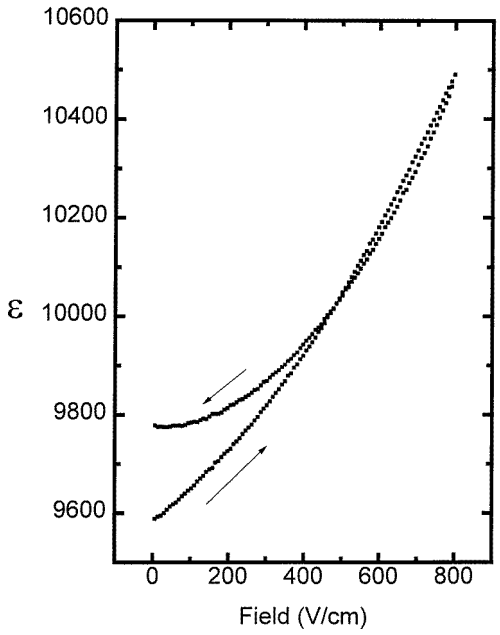

Figure 5. The linear to quadratic cross-over of the permittivity variations at T slightly above T_m. The frequency measurement was 10^3 Hz.

Therefore, we propose that the correlations induced by a field at high temperature are electromechanical in nature. If the bias effect were only an orientational mechanism, the permittivity would be expected to decrease. When, at high temperature, the sample is

submitted to a positive bias ramp followed by a negative one in order to bring back the bias to zero, the permittivity variation is

(i) on increasing, linear at low field;
(ii) on reverse bias, quadratic decrease (figure 5).

As mentioned above, the bias induces a somewhat LRO driving the system from ZFC state to FC state, so at sufficiently high field and when the bias is brought back, the ε variations are those observed at lower temperatures where correlations between PMRs are stronger. Finally, at $E = 0$, the permittivity decreases slowly with time, reflecting the metastability of the field induced LRO.

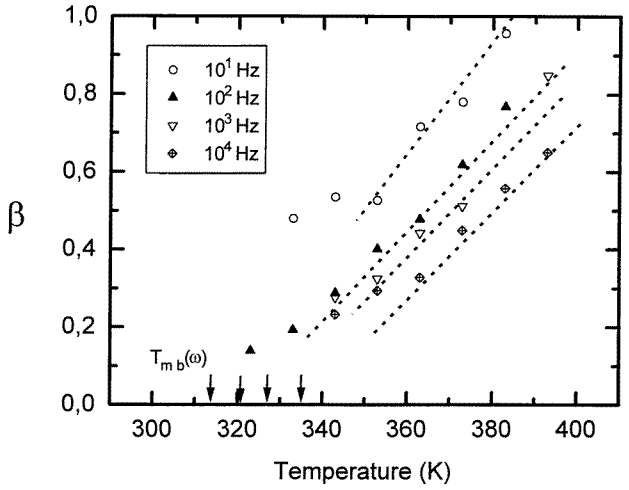

Figure 6. Variations of the exponent β versus temperature. The arrows indicate the temperatures at which $\beta(\omega)$ can be extrapolated to zero from their linear variations.

3.2. Relaxation

As emphasized above, in the ZFC state all these experiments are made under non-equibrilium conditions. Indeed, even if the slope of the field ramp is small, when the field increase is stopped and E is maintained at its maximum value, the permittivity immediately decreases (right part of figure 2). This relaxation has been analysed by the well known stretched exponential:

$$\varepsilon(t) = \varepsilon(\infty) + \{\varepsilon(0) - \varepsilon(\infty)\} \exp(-(t/\tau_0)^{\beta}).$$

Unfortunately only the variations $\beta(T)$ give reliable results, shown in figure 6. The exponent β varies linearly at high temperature (i.e. between 320 and 390 K) and exhibits a plateau in the low-temperature range. Extrapolation of the linear part of $\beta(T)$ to $\beta = 0$ leads to temperatures $T_{\beta=0}(\omega)$ identical to $T_{mb}(\omega)$. When formally interpreted as a 'spectrum of relaxation times' through the identity

$$\int g(\tau) \exp(-t/\tau)\, \mathrm{d}(\log \tau) \equiv \exp(-(t/\tau_0)^{\beta})$$

smaller β corresponds to a broader 'spectrum'. Recently, Lu and Calvarin [16], by supposing an exponential-type distribution for the volume of the PMR, have modelled the dielectric behaviour of ferroelectric relaxors. They found an empirical linear relationship between an exponent n inversely proportional to the width of the distribution and the temperature: $n = \alpha(T - T_{n=0})$ with $T_{n=0}$ corresponding to the temperature at which microdomains would develop into macrodomains as in normal ferroelectrics. In relaxors this only occurs under the effect of an external field, which explains the deviation of β from linear behaviour above $T_{\beta=0}$. The identity $T_{\beta=0} \equiv T_{mb}$ reflects both the clamping of PMRs in a nanoscale domain structure with slowing down of fluctuations and a corresponding maximum in the growth by the domain wall motion mechanism. Although our results are very similar, the situation is not clear for the time being. Indeed, in our experiments the exponent β depends on the frequency and consequently the temperatures $T_{\beta=0}(\omega) \equiv T_{mb}(\omega)$. It can simply be explained by the fact that the physical property whose relaxation is measured depends on the frequency itself. So one can interpret this dispersion by making the assumption that the temperature $T_{mb}(\omega)$ corresponds to the freezing of the entities that are probed by the measurement signal at the frequency ω. This is coherent with the fact that the temperature $T_{mb}(\omega)$ obeys a Vogel–Fulcher law:

$$\omega = \omega_0 \exp\{-A/(T_{mb}(\omega) - T_c)\}$$

with $\omega_0 = 2.6 \times 10^{13}$ Hz, $A = 1760$ K and $T_c = 254$ K the temperature below which an FE state induced by an electrical field is stable as shown by our results (pyroelectric current, Raman scattering and permittivity experiments made in FC–ZFC sequences) published elsewhere [14].

4. Conclusion

The dielectric behaviour of the relaxor PLZT 9/65/35 has been studied as a function of an increasing external field. Two regimes of polarization are evidenced whose cross-over lies closely at the temperature of the maxima in weak-field permittivity T_m. The high-temperature mechanism was attributed to electrostriction associated with the nucleation and growth of PMR. The low-temperature mechanism would be due to domain wall motions under the effect of the electrical field.

The exponent $\beta(\omega)$ characterizing the slowing down of the relaxation was found to vary linearly with temperature. Its extrapolation to the value $\beta(\omega) = 0$ gave temperatures which obey a Vogel–Fulcher law with a freezing temperature T_c identical to those, determined by other techniques, where one determines a field induced nano–microsized domain transition.

Experiments on various La contents of the $x/65/35$ PLZT series are now being undertaken and will be published in another paper.

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