Memory of Multiple Aging Stages above the Freezing Temperature in the Relaxor Ferroelectric PLZT

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The dynamic dielectric susceptibility and the elastic compliance of the relaxor ferroelectric lanthanum lead zirconate titanate (PLZT) 9/65/35 have been measured under different cooling and heating protocols in order to study aging and memory. The memory of multiple aging stages at different temperatures has been found (several dips in the susceptibility curves on heating), as in spin glass systems below the glass transition. Remarkably, in PLZT the memory of several aging stages is retained also above the freezing temperature deduced from the dynamic susceptibilities. The results are discussed in light of the existing models of aging and memory in spin and dipolar glasses.

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Aging, rejuvenation, and memory are considered manifestations of the frozen spin glass state. In the case of the dynamic susceptibility $\chi(\omega, T)$, aging consists in a slow reduction of χ during a stay at a constant temperature T_1 *below* the glass transition temperature T_g [1–3]. On further cooling, χ may recover the values found before aging, rejoining the reference curve that is measured during continuous cooling; this is called rejuvenation, since the susceptibility behaves as if aging at T_1 did not occur. On subsequent heating through T_1, χ may completely or partially retrace the dip formed during aging, and this is called memory. A peculiarity of spin glasses is that aging stages at several $T_n < T_g$ may be recalled, giving rise to susceptibility curves measured on continuous heating with dips at the various T_n [4]. Tentative explanations of this phenomenon involve the concept of a hierarchy in the potential landscape of the metastable states as a function of temperature, below the glass transition temperature [5].

Relaxor ferroelectrics are often considered among the possible realizations of spin glasses, with electric instead of magnetic dipoles, since they exhibit most of the phenomena characterizing spin glasses, including aging, rejuvenation, and memory [6,7]. These materials, mostly of the perovskite-type, have substantial disorder in the valence and/or size of the cation sublattices, so that long range order in the electric polarization is never established (unless a bias field above a certain threshold is applied). Below the so-called Burns temperature T_B, which corresponds to the Curie temperature T_C for a solid solution with a pure ferroelectric, fluctuating polar clusters of nanometer size start forming. On cooling at a much lower temperature [8], the freezing of these polar clusters gives rise to the typical frequency dispersion in the ac susceptibility, as found in spin glasses.

Many properties of the relaxor ferroelectrics may be explained in terms of the recently proposed spherical random-bond random-field model [9], reminiscent of the Sherrington–Kirkpatrick model of spin glasses [10]; the latter is the basis for various theoretical treatments of aging and memory [3,11].

The material under study here is $(Pb/La)(Zr/Ti)O_3$ with La concentration $x = 0.09$ and Zr/Ti ratio 65/35 [lanthanum lead zirconate titanate (PLZT) $x/65/35$]. The parent lead zirconate titanate (PZT) 65/35 is a normal ferroelectric below $T_C = 627$ K [12]. The partial substitution of Pb with La induces the formation of the polar nanoclusters below $T_B \simeq T_C(\text{PZT } 65/35) \simeq 627$ K and the relaxor behavior with the frequency dispersive maximum of the dielectric susceptibility around 340 K for $x = 0.09$.

Here we show that in PLZT 9/65/35 the memory of multiple aging stages, which is generally considered peculiar of the frozen spin glass state, is found even above the freezing temperature indicated by both the dielectric and elastic susceptibilities.

The ceramic material was prepared by the solid state reaction of the starting oxides according to the formula $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ ($x = 0.09$) with the vacancies compensating La^{3+} for Pb^{2+} in the Zr/Ti sublattice. The oxide powders were calcined for 4 h at 850 °C and sintered at 1200 °C for 2 h and at 1300 °C for 2 h. The density was 97% of the nominal value, and the mean grain size was about 3 μm. The structure determined by x-ray diffraction was pure perovskite without any pyrochlore phase. The dielectric ac susceptibility $\chi \simeq \varepsilon = \varepsilon' - i\varepsilon''$ was measured with an HP 4194 A impedance bridge with a four wire probe and a signal level of 0.5 V/mm, between 200 Hz and 1 MHz, and its mechanical equivalent, the dynamic compliance $s = s' - is''$, through the electrostatic excitation of the flexural modes (1 and 13 kHz) in the linear regime, as described in Ref. [13]. All the measurements presented here were made on the same sample with dimensions $45 \times 4 \times 0.5$ mm^3.

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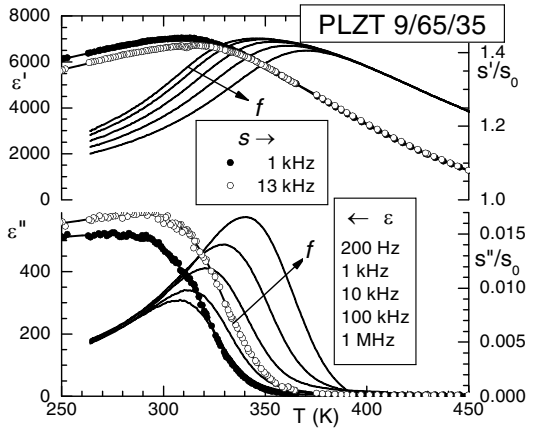

FIG. 1. Real and imaginary parts of the dielectric susceptibility (lines, left hand ordinates) and elastic compliance (circles, right hand ordinates) of PLZT 9/65/35.

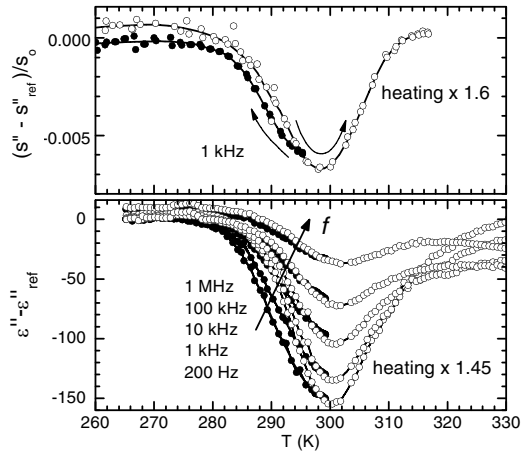

FIG. 2. Rejuvenation on cooling (solid symbols) after aging 24 h at 298 K and memory on heating (open symbols) in the elastic compliance (top panel) and dielectric permittivity (bottom panel). The reference curves of Fig. 1 have been subtracted.

The ε curves are shown in Fig. 1 and agree with most of the measurements of PLZT 9/65/35 in the literature [14], with a frequency dispersion typical of a freezing process at some temperature below the susceptibility maxima, namely $T_f < 340$ K.

The dynamic compliance is normalized to a reference value s_0. The maxima of s' are shallower and shifted to lower temperature, indicating that the dynamics of dipolar type (affecting ε but not s) and of quadrupolar-type (affecting s) are different. In fact, ε probes the fluctuations of electric dipoles, while s probes the fluctuations of local distortions; the latter, being symmetric strain tensors, are quadrupoles [15]. For the present purposes it is sufficient to note that the quadrupolar dynamics exhibits an even lower freezing temperature. The curves in Fig. 1 are the references against which aging and memory curves will be compared.

Figure 2 shows the memory effect in both the susceptibilities, after aging 24 h at 298 K. Before the aging experiments, the sample was brought to a reference state by heating to $\gtrsim 550$ K and cooling at 1.5 K/min to the first aging temperature. The solid symbols are measured on cooling and the open symbols after subsequent heating. The reference curves measured during continuous cooling have been subtracted from the data, and the heating curves are multiplied by a factor F in order to overlap with those on cooling; F^{-1} provides a measure of the memory effect, which turns out to be almost the same in the anelastic (63%) and dielectric (69%) cases. We also measured the isothermal decays of the susceptibilities during aging at and above room temperature but did not find any major difference between the dielectric and elastic responses.

A run with multiple aging stages (24 h each) at 374, 349, and 324 K is presented in Fig. 3; notice that the first two aging temperatures are certainly above T_f. The dips on heating are better seen after dividing by the reference curves; this is shown for the real part of the dielectric permittivity in Fig. 4. The memory is almost complete for the last aging stage at 324 K, while the other two stages are only partially retraced. Similar effects are found also in the compliance curves (not shown here).

The degree of memory can be estimated by fitting the three dips with Gaussians and defining the degree of memory as the ratio of the amplitude of these Gaussians to the lowest values reached during aging. In this manner, one finds 90%, 50%, and $\lesssim 80\%$ memory of the three aging stages, starting from the lowest temperature. The Gaussian form has been adopted, since it fits very well to the heating curve after a single aging stage, as in Fig. 2; yet, the effects of multiple agings may be nonadditive, and, moreover, the Gaussians are broader at higher temperature. The frequency dependence of the dips at lower temperature is due to differences in aging and not in memory, and the temperature dependence of aging is in agreement with previous results [6].

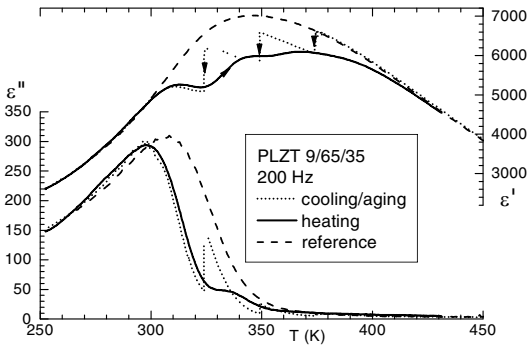

FIG. 3. Dielectric permittivity at 200 Hz during multiple aging stages (24 h each) and subsequent heating curves with memory, compared with the reference curve measured on continuous cooling.

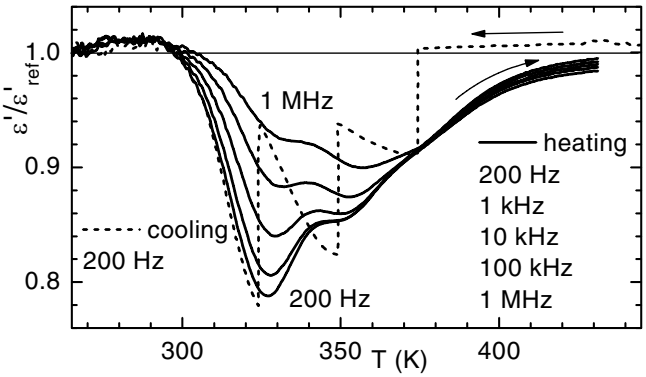

FIG. 4. Relative change of the real part of the permittivity measured with the temperature protocol of Fig. 3 with respect to the reference.

In traditional spin glasses, aging and memory effects are found below the glass transition temperature T_g, and their presence is even considered a signature of the spin glass state (see, e.g., Ref. [1]). This is true for both experiment and for various models of the spin glass state, although it may be debated whether a true transition temperature exists and is experimentally accessible, or rather it is hindered by the exceedingly slow dynamics on approaching it. In the hierarchical scenario derived from the Sherrington–Kirkpatrick model, the roughening of the potential landscape, held responsible for these out-of-equilibrium phenomena, starts below T_g [3,16], and the number of metastable minima increases extremely fast with the reduced temperature $t = (T_g - T)/T_g$ [11,16]. In addition, the heights of the barriers between the metastable states have been experimentally shown to increase with cooling below T_g [11]. Similarly, in models derived from the droplet picture [17] and adapted to explain memory [4], the height of the barriers between the metastable states vanishes at T_g.

The remarkable feature of the results in Fig. 3 is that the memory of multiple aging stages in PLZT is retained also above the temperature of freezing of the polar fluctuations. This is at variance with other glassy systems, including canonical Ising and Heisenberg spin glasses [2] and dipolar glasses [18], where nonergodic phenomena occur only below a glass transition [18].

The definition of a glass transition temperature in PLZT is not obvious, but, by analogy with other model and real spin glass systems, it should be very close to and in any case below the temperature at which the relevant degrees of freedom appear to freeze. For relaxor ferroelectrics, the polarization dynamics is the relevant one and is probed by the dielectric susceptibility, so that we can state that T_g is below the temperature of the maxima of the ac susceptibility. To be more quantitative, we may adopt the usual argument that, at the maximum, the susceptibility is probing fluctuations with characteristic relaxation time $\tau \sim \omega^{-1}$ and fit the temperature $T_m(\omega)$ of the susceptibility maximum with the Vogel-Fulcher expression $\omega = \tau^{-1} \sim \tau_0^{-1} \exp[-E/(T_m - T_{VF})]$. Under these naive assumptions, the maxima of $\varepsilon'(\omega, T)$ in Fig. 1 indicate that the relaxation time diverges at $T_{VF} = 320.5$ K with $\tau_0 = 2.1 \times 10^{-11}$ s and $E = 449$ K. On the other hand, within a scaling approach[2,19] with $\tau \sim [(T - T_g)/T_g]^{-z\nu}$, a fit of $T_m(\omega)$ yields $T_g = 337$ K and $z\nu = 6.8$. The data of Fig. 1 do not allow the two $\tau(T)$ laws to be distinguished, but certainly indicate that the system cannot be considered frozen above 337 K. One can compare the frequency dependence of the susceptibility maximum with that of spin glasses[19] and superparamagnets [20], finding that both the Vogel-Fulcher and the dynamical scaling parameters are typical of the first class of materials: $E/k_B T_{VF} = 1.4$ is between the values 0.85 and 2 found in the canonical spin glasses $Cu_{1-x}Mn_x$ and $Eu_{1-x}Gd_x$, while $E/k_B T_{VF} = 11$ for superparamagnets based on Fe particles; $z\nu = 6.8$ is within the range 4–8 found for spin glasses, whereas superparamagnets may have $z\nu$ as high as 40.

Another signature of the onset of a nonergodic state is the splitting between the field cooled and zero field cooled susceptibilities or of the magnetization for magnetic spin glasses and polarization for relaxor ferroelectrics. In PLZT 9/65/35 this occurs around 325 K, in correspondence with the maximum of the static susceptibility [21] and in agreement with the above estimates.

On the other hand, dielectric measurements over an extremely broad range of frequencies in the relaxor ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and PLZT [21] allow the distribution function of the relaxation times to be measured and suggest the definition of an even lower freezing temperature, namely, the temperature at which the longest relaxation time τ_{max} diverges [8]. Below the Burns temperature $T_B \simeq 627$ K, there is a strong broadening of the dielectric spectra with τ_{max} following the Vogel-Fulcher law with$T_{VF} \simeq 230$ K [8] or 250 K [21] in PLZT 9/65/35, depending on the type of analysis.

Summarizing, in PLZT one can identify a characteristic temperature for the freezing of the polarization in different ways, but, however defined, this is below the temperature T_m of the maxima of the dynamic dielectric susceptibility (340 K in the present case). We therefore expect a glasslike state with proliferation of metastable states below T_m, as usual in spin glasses, and it is striking to find that the memory of multiple aging stages extends above that temperature. One could consider other degrees of freedom, freezing at $T > T_m$, as responsible for the formation of a glassy state and therefore of multiple memory phenomena. In a relaxor ferroelectric such as PLZT, the other relevant degrees of freedom are the elastic distortions (quadrupoles), probed by the elastic compliance $s(\omega, T)$; however, the maxima of s are at even lower temperature than those of ε (see Fig. 1), indicating

that the quadrupolar dynamics is faster and is not a possible source of hidden freezing before the dipolar freezing.

Another possible source of aging is the migration or reorientation of defects and free charges, and is well known as the phenomenon of clamping of the domain walls in ferroelectrics [22]. In fact, aging has recently been reported to occur also above the temperature of the dielectric maximum in PLZT [6], and the phenomenology, more complex than in the other relaxor ferroelectric PMN-$PbTiO_3$, has been assigned to multiple aging mechanisms, possibly including the slow motion of defects. It is in fact conceivable that the slow rearrangement of defects may cause memory, if during aging they leave a template defect configuration that remains frozen during cooling, and induces the same highly pinned configuration on subsequent heating. Such a mechanism, however, would work with any ferroelectric and could not produce the imprinting of several agings. In fact, it requires that the defect configuration remains frozen at temperatures below the first aging and therefore cannot account for the imprinting of the subsequent agings at lower temperatures. The present results, instead, demonstrate the imprinting of *several* aging stages above T_f.

Other perovskite systems presenting electric polarization freezing, aging, and memory are the so-called dipolar glasses, such as $K_{1-x}Li_xTaO_3$ or $KTa_{1-x}Nb_xO_3$. The nonequilibrium effects in these systems are at least an order of magnitude smaller than those found here, but they have been extensively studied [23], and the aging part of susceptibility has been attributed to the domain walls reconformation, when the domains slowly evolve toward the equilibrium size [23].

The same ideas have been used to explain the memory of multiple aging stages in spin glasses by Bouchaud *et al.* [4], who proposed a qualitative picture that derives from the droplet model of spin glasses but satisfies also the hierarchical scenario. The main ideas are as follows: (i) The time necessary for a reconformation of a domain or domain wall is $\tau \sim \tau_0 \exp(U/T)$; (ii) the barrier for reconformations over a length scale l is $U \sim \Upsilon l^\theta$, with $\theta > 0$; (iii) the barrier vanishes at the glass transition temperature T_g, $\Upsilon = \Upsilon_0 |1 - T/T_g|^{-\nu}$. In this manner, particularly in virtue of hypothesis (iii), there is a strong separation of the time scales necessary for reconformations over different lengths and temperatures. Therefore at each temperature T the system is in equilibrium over a length scale $l < l(T)$ but almost frozen over $l > l(T)$. Aging at T_1 produces reconformations over $l \leq l(T_1)$, while aging at $T_2 < T_1$ is effective only at $l \leq l(T_2)$; if the scale separation between T_1 and T_2 is sufficient, then, after coming back at T_1, the system restarts aging where it was left, except for a very fast initial equilibration of the faster degrees of freedom that had changed during aging at T_2. The reasoning can be extended to several aging temperatures T_n, if there is sufficient separation in the time and therefore length scales, and hypothesis (iii) has been found essential to obtain such a strong separation [4]. If the above scenario applies also to PLZT, then the present data suggest that the hypothesis of vanishing barriers at the freezing temperature may be lifted, and still multiple memory effects are observable, although partially. The ground for supposing vanishing barriers at T_g in the domain wall scenario [4] is the analogy with the ferromagnetic case, where the wall stiffness Υ vanishes at the ferromagnetic transition. In the case of PLZT and other relaxor ferroelectrics, the onset temperature of the ferroelectric correlations is the Burns temperature $T_B \gg T_g$, and the barriers for domain wall motion are expected to vanish at that temperature.

The degree of (single aging) memory has been found to depend on temperature [6], and it may be considered as a measure of the separation between the length scales involved in aging or equivalently of the degree of hierarchization of the system. The heating curves in Fig. 3 indicate that memory does not disappear above T_g but gradually fades out above the susceptibility maximum. It remains to be clarified whether the aging and memory effects above T_f are still evidence of a hierarchical organization of metastable states and what its origin would be.

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