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Non-linear dielectric properties in based-PMN relaxor ferroelectrics

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Abstract

The investigation of the non-linear dielectric response in ferroelectric materials has become one of the most important issues in the field of ferroelectricity due to its technological and scientific interest. Rather, from the practical point of view the understanding of the non-linear dielectric properties is essential to improve the performance of ferroelectric multilayer capacitors and actuators devices, which commonly operate at high field levels. On the other hand, the non-linear (NL) dielectric response to large electric fields has been revealed as a powerful technique to investigate the physical origin of the dielectric relaxor state. In this work, low frequency dielectric measurements were performed in $0.9[\mathrm{Pb(Mg_{1/3}Nb_{3/2})O_3}]$–$0.1\mathrm{PbTiO_3}$ (PMN–PT) relaxor ceramics in a wide frequency and temperature range. The non-linear dielectric properties were investigated by using the measurements of the dielectric permittivity of the PMN–PT as a function of the dc "bias" driving field. The obtained results were analyzed within the framework of the current models for the dielectric response of relaxor ferroelectrics.

Keywords: Niobates; Dielectric properties; Ferroelectric properties; Relaxors

1. Introduction

Over the last decades intense studies have been conducted for the understanding of the physical nature of the dielectric response in relaxor ferroelectrics.[1] These efforts are justified by a wide applicability range in the electronic industry.[2] Indeed, such applications include multilayer capacitors, actuators and field-induced piezoelectric transducers,[3] which often are operated at high field regime. Thus, it is very important to investigate the physical properties of relaxors at high field levels, where the non-linear dielectric features become essential. From the fundamental point of view, these investigations are also interesting to improve the understanding of relaxor ferroelectrics, since this research may contribute to the identification of the mechanisms that governs the dielectric nature of relaxors.

The origin of the relaxor behavior in relaxor ferroelectric materials has been studied for 40 years, but it is only in the last decade that microscopic mechanisms, with solid experimental evidence to support them, were proposed. The relaxors do not undergo a macroscopic phase transition from the paraelectric phase into a ferroelectric one, but they become rather 'frustrated' ferroelectrics.[1,2] They are complex materials where the origin of the 'frustration' has been associated to compositional inhomogeneity on a nanometer scale that results from partial compositional disorder in a specific lattice site.[1] This disorder prevents the macroscopic transformation into ferroelectric phase. A picture coherent with the experimental results is a paraelectric matrix in which ferroelectric nano-sized regions are formed upon cooling, without the evolution of a coherent macroscopic ferroelectric phase.

In this context, several phenomenological models have been proposed to explain the physical origin of the observed relaxor features.[4,5] Probably, the most known models are the spherical random bond-random field model (SRB-RF)[5] and vibration of the boundaries of the polar region (PRBV).[4] Nevertheless, none of them has yet gained a universal acceptance due to some contradictory experimental results. Rather, the basic question of whether the relaxor state in zero electric field is a ferroelectric state broken into nano-domains under a constraint of quenched random electric fields[4] or a glass state similar to one in dipolar glasses with randomly interacting polar nano-regions in the presence of random fields,[6] is still unclear. In general, it is accepted that is impossible to get a unique answer, for the whole temperature interval, because the interactions in relaxor systems may change their nature (i.e. from individual dipoles at high temperatures to domain walls at low ones). Therefore, the identification of the nature of the dielectric response in relaxors requires additional experimental information, which can be obtained from the measurements of the non-linear dielectric response.

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In this work, the electrical permittivity of $0.9[Pb(Mg_{1/3}Nb_{3/2})O_3]–0.1PbTiO_3$ relaxor ceramics was investigated in a wide range of frequency and temperature. In order to investigate the non-linear dielectric response, the dielectric measurements were performed as a function of the applied dc “bias” driving field. The results were analyzed and discussed within the framework of the models proposed in the literature.

2. Experimental procedure

$(1-x)[Pb(Mg_{1/3}Nb_{2/3})O_3]–(x)PbTiO_3$ ceramics, with $x = 0.1$ [PMN–0.1PT] (rhombohedral), were prepared through the columbite method by conventional sintering technique. This procedure was described in details elsewhere.[7] PMN–0.1PT was chosen because it is a prototype of relaxor ferroelectrics that present excellent physical properties, which are of high technological interest.[8] Briefly, the analytical graded precursor oxides were mixed in a ball mill using isopropyl alcohol. After that, the powder was calcined at 1173 K for 4 h. The conventional ceramics were sintered at 1473 K for 3 h in a saturated PbO atmosphere. X-ray diffraction analysis revealed only the perovskite phase without secondary phases.[7] The sintered ceramic bodies were cut into a bar shape of 5 mm × 4 mm and polished to a thickness of 0.5 mm for dielectric and ferroelectric measurements. After that, they were annealed at 900 K for 1 h to release mechanical stresses introduced during polishing. Gold electrodes were sputtered into the sample surfaces.

Ferroelectric hysteresis loops were characterized at room temperature by applying a triangular electric field of amplitude of 15 kV/cm at 1 Hz.[9] The real and imaginary components (ε' and ε'', respectively) of the dielectric permittivity were measured in the frequency and temperature range of 1–100 kHz and 100–450 K, respectively, using an Impedance Analyzer HP 4194A. Non-linear dielectric measurements were performed by using a LRC meter AG 4284A. A dc “bias” electric field with variable amplitude E_{dc} up to 5 kV/cm was superimposed on the small ac driving field. The non-linear effect was characterized by the non-linear component (NL) of the dielectric permittivity $\Delta\varepsilon_{dc}$ according to the dc “bias” effects.[4]

3. Results and discussion

As previously reported,[7] the results obtained by the fracture surface micrographs of the sintered ceramics revealed a homogeneous grain size (average grain size of 5 μm) with very low porosity level. The surface microstructure analysis revealed highly densified ceramic bodies with a homogeneous and crack free microstructure, and no secondary segregated phases. In addition, typical ferroelectric hysteresis slim loop was obtained, which reveals the relaxor characteristics of the investigated material.

Fig. 1a shows the frequency and temperature dependence of the linear (small signal) dielectric permittivity for the PMN–0.1PT sample. As can be seen, a strong dielectric dispersion is observed only near the temperature of the maximum dielectric permittivity ($T_m \sim 317$ K), which is typical of relaxor ferroelectrics.

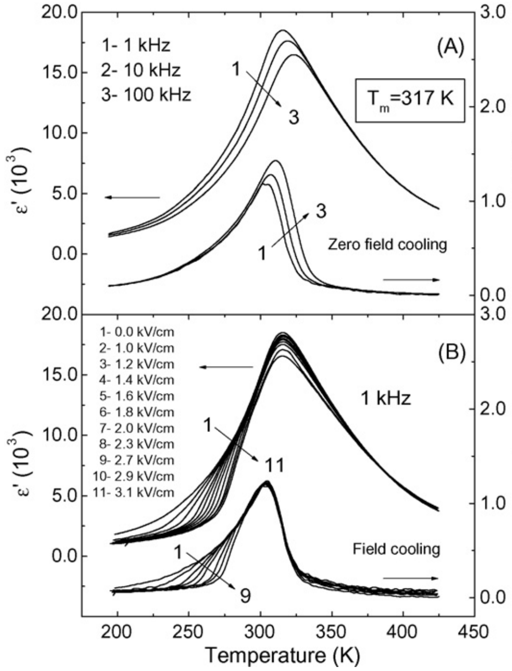

Fig. 1. Real and imaginary components of dielectric permittivity as a function of the temperature for the PMN–0.1PT ceramics: (a) zero field cooling for different frequencies; (b) field cooling measurement applying a dc “bias” electric field of variable magnitude.

On the other hand, the influence of a bias electric field (E_{dc}), superimposed to the small 1 kHz ac signal, on the temperature dependence of the dielectric permittivity is shown in Fig. 1b. As can be seen, the dielectric permittivity shows a behavior analogous to that obtained for zero field cooling measurements, which means ε' becomes smaller in magnitude with the increase of the magnitude of the applied dc field. Moreover, no change in T_m is noticed for the same frequency. The dielectric relaxor behavior observed in Fig. 1(a) (frequency dispersion near T_m) prevails even when an applied dc bias electric field of moderated magnitude is applied. However, it is important to point out that under a dc bias field the dielectric dispersion vanishes quickly just above and bellow T_m (figure not shown here), when compared to that obtained for zero field cooling measurements.

One of the most widespread methods employed to investigate the dielectric properties of the ferroelectric materials at high electric field regimes is the investigation of the electric “bias” field dependence of the non-linear dielectric permittivity. In order to investigate in more details the influence of a bias field on the electrical permittivity, the non-linear component of dielectric permittivity [$\Delta\varepsilon_{dc} = \varepsilon(E_{dc} \neq 0) - \varepsilon(0)$] was calculated from the dielectric measurements showed in Fig. 1(a) and (b).[4] The temperature dependence of the NL component of the dielectric permittivity at 1 kHz is shown in Fig. 2. Like the linear dielectric permittivity (Fig. 1a), it is seen that the temperature dependence of $\Delta\varepsilon_{dc}$ clearly demonstrates that the NL dielectric component has two regimes: (i) a quasi-static (at high temperatures), and (ii) a frequency dispersive (at low temperatures).[10]

The behavior observed for the non-linear dielectric permittivity (quasi-static regime, at high temperatures, and a frequency

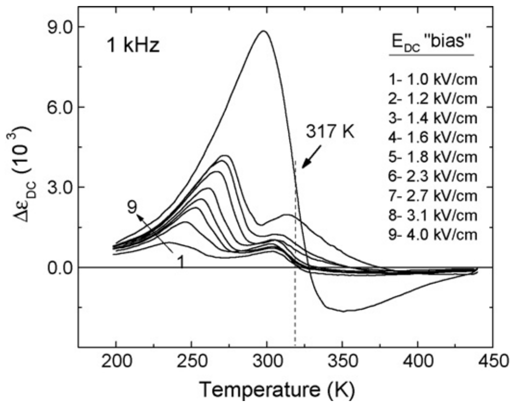

Fig. 2. Temperature dependence of the non-linear component of the dielectric permittivity for the PMN–0.1PT ceramics, as a function of the dc "bias" electric field, measured at 1 kHz.

dispersive, at low temperatures) might be satisfactorily interpreted in the framework of the so-called "breathing" model[10] (PRBV), in which a crossover of the dynamics of polar region boundaries is expected.

The model supposes that the motion of the inter-phase boundaries between the polar regions and the non-polar matrix looks like breathing of the polar regions under the applied ac field. According to the "breathing" model, the ergodic phase (at high temperatures) is treated as a structurally inhomogeneous phase consisting of Nb-rich polar regions (PRs) or polar clusters (PCs) embedded in a non-polar paraelectric matrix. They are elongated along the direction of the local spontaneous polarization, P_s (the shape of which minimizes the effect of the depolarizing field), which can by oriented in one of the eight $\langle 1\,1\,1 \rangle$ pseudo-cubic directions allowed by the rhombohedral symmetry of the polar phase.[11] The orientation does not change under the thermal agitation. The polar region pattern is determined by the spatial distribution of internal random fields (RFs) induced by the charge disorder and chemical inhomogeneities, which act as pinning centers. The non-polar paraelectric matrix may be considered as a quasiregular array of chemically ordered 1:1 (Mg:Nb) regions, which originates the so-called chemical clusters (CCs). The polar clusters have typically the size of a few nanometers and are reorientable, and are thus responsible for the observed dielectric behavior. In contrast, the chemical clusters, or chemical defects, are essentially static and are thus intense sources of the random electric fields. Thus, these RFs are basically originated by the chemical heterogeneity of the crystalline sites related to the charge disorder, ionic radius and compositional fluctuations.

Due to the random distribution of the random fields, the inter-phase boundary of a polar region and a non-polar matrix will not stay flat. Instead, it will become "rough" with a short scale characteristic length, L_c, which is determined by the spatial distribution of the random fields and the elastic characteristics of the inter-phase boundary. If the short scale characteristic length is smaller than the total length of the polar region, the boundary will not be able to move as a whole. At low temperatures (in the dispersive regime), the dielectric response is controlled by the field-induced vibration of the polar regions boundaries on a scale smaller than the size of the polar regions. On the other hand, at high temperatures (in the quasi-static regime), the dielectric response is controlled by the field-induced breathing of the polar region as a whole.

If only a signal ac field is applied, the dielectric response is isotropic because the polar regions are randomly oriented in the volume of the grain. However, the applied bias field changes the profile of the random fields and, thus changes the position of the inter-phase boundaries. The dc field also forces the polar region to reorient in the direction parallel to the field and provides a coalescence of neighboring regions, resulting in a relative diminishing in the total area of the boundaries in the field direction. Consequently, the dielectric permittivity decreases.[10]

On the other hand, as can be seen in the same Fig. 2 for a moderate dc bias field level (up to $E_{dc} = 3.1$ kV/cm), a dielectric anomaly (two peaks) was observed for the NL dielectric permittivity, while only a sharp peak was found for the highest level of the applied dc electric field (4.0 kV/cm). This behavior may be attributed to an electric field-induced transition from relaxor to a ferroelectric state, according to the spherical random bond-random field model (SRB-RF).[5] It is correlated with the fact that the linear dielectric response in ferroelectric materials may be associated to existence of the random fields.[5] It has been reported that some relaxors become ferroelectric upon cooling under strong dc bias,[12] therefore, our results are in agreement with the current literature. The obtained anomalies for moderate dc bias field levels suggest, therefore, the coexistence of a glass state concomitant to a ferroelectric state in the PMN–0.1PT. With the increase of the E_{dc}, the glass state is overlapped with the ferroelectric state leading to a disappearing of the observed anomalies.

Fig. 3 shows the non-linear component of the dielectric permittivity versus the square of the dc bias electric field for the PMN–0.1PT ceramic. The circle and up triangle symbols show the experimental data at 1 kHz for two selected temperatures below (300 K) and above (325 K) the maximum of dielectric permittivity. The lines correspond to the linear fitting. It is verified that for the studied PMN–0.1PT ceramics, in the relaxor state, the dc bias field effect is well described by a quadratic function of the non-linear dielectric permittivity ($\Delta\varepsilon_{dc}$–E_{dc}^2),

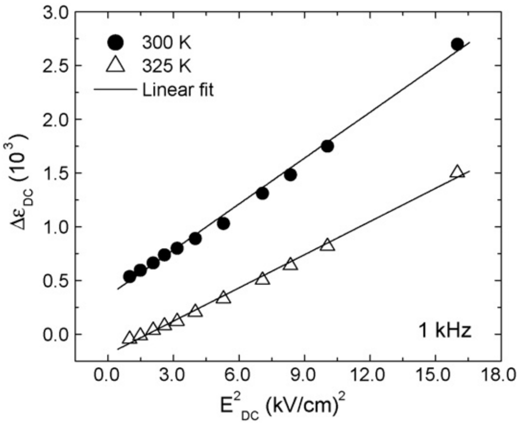

Fig. 3. Non-linear component of the dielectric permittivity of the PMN–0.1PT ceramics, against the square of the dc "bias" electric field.

which is a fundamental characteristic in crystals whose macroscopic structure has a center of symmetry,[13] as in the case of the PMN–0.1PT system. This behavior is in agreement with the obtained results for PMN single crystal materials.[14]

4. Conclusions

In summary, the mechanism of dielectric response of PMN–PT relaxor has been analyzed using the experimental results obtained from the non-linear dielectric response. Studying the influence of the effect of the dc bias field on the dielectric properties, it was observed that, like in the linear dielectric permittivity, the NL component has two regimes: a quasi-static and a frequency dispersive one. On the other hand, it was found that the dielectric relaxation may be related to the motion of the inter-phase boundaries of polar regions, and at the same time, it seems to be hardly influenced by the coexistence of a glass state concomitant to the ferroelectric state in PMN–PT relaxors.

Acknowledgments

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