Relaxor behavior in nanostructured Pb(Zn$_{1/3}$Nb$_{2/3}$)$_2$O$_3$–Pb(Fe$_{1/2}$Nb$_{1/2}$)$_2$O$_3$–PbTiO$_3$ ceramics

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There is controversy about the persistence or not of the relaxor state in the nanoscale. We report here the dielectric properties of nanostructured ceramics of the Pb(Zn$_{1/3}$Nb$_{2/3}$)$_2$O$_3$–Pb(Fe$_{1/2}$Nb$_{1/2}$)$_2$O$_3$–PbTiO$_3$ ternary system with an average grain size of 20 nm, which clearly indicate that it persists as long as correlations among polar nanoregions are possible across grain boundaries. Two independent Vogel–Fulcher type relaxations are found in the materials that have a non-negligible width of the size distribution, which are proposed to be associated with intra- and intergranular correlations that show freezing at different temperatures. © 2009 American Institute of Physics. [DOI: 10.1063/1.3118527]

Ferroelectric (FE) nanostructures are attracting a lot of attention from the microelectronic industry due to their potential applications in piezoelectric microelectromechanical systems and also for implementing sensing and actuation in nanoelectromechanical devices. The feasibility of using FE systems and also for implementing sensing and actuation in potential applications in piezoelectric microelectromechanical systems, particularly in perovskite-grain size reduction on the macroscopic properties. Particu-
larly, in perovskite (Pe) relaxor-FE solid solutions with mor-
photropic phase boundary. Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$–PbTiO$_3$ (PMN-PT) is one of these systems, for which an evolution from FE to relaxor-type behavior with decreasing grain size has been described. In relaxor PMN, the disappearance of the dielectric relaxation below a critical grain size of 30 nm has been reported. Pb(Zn$_{1/3}$Nb$_{2/3}$)$_2$O$_3$–PbTiO$_3$ (PZN-PT) is another example of such systems, which present the highest known piezoelectric coefficients. However, Pe phase powders have only been obtained by high pressure synthesis or by mechanochemical activation. Moreover, the processing of high-quality ceramics has not been accomplished due to the thermal decomposition of the Pe into a pyrochlore (Py) phase.

We recently succeeded in processing nanostructured ceramics of 0.92PZN-0.08PT with an average grain size of 20 nm by spark plasma sintering (SPS) of a powder obtained by mechanochemical activation. SPS technique allows to obtain dense ceramics at moderate temperatures and short times, thus limiting grain growth. In the case of PZN-PT, this is also advantageous for minimizing Pe thermal decomposition, and ceramics were obtained at 873 K. However, materials presented traces of Py due to the onset of Pe decomposition at 823 K. This prevented the temperature of the SPS to be further increased. The electrical properties of the nanostructured material were characterized and relaxor-type behavior was found.

In this work, we present results on the dielectric properties of similarly nanostructured materials with decreasing Py content up to its disappearance. This was achieved by adding Pb(Fe$_{1/2}$Nb$_{1/2}$)$_2$O$_3$ (PFN) to the binary system, which enhanced the stability of the Pe phase. Results on samples with different PFN contents and Py phase allow to deepen the study of the relaxor state in these nanostructured materials.

Nanostructured ceramics of selected compositions, namely (0.92–x)PZN-xPFN-0.08PT with x = 0.1, 0.2, and 0.4, were processed by SPS (2080 Sumitomo apparatus) of nanocrystalline powder obtained by mechanochemical activation. The powder presented an average particle size of ~12 nm with standard deviation (SD) of 5 nm.

Figure 1 shows the x-ray diffraction patterns (Siemens D500 and Cu Kα radiation) of ceramics processed by SPS at 873 K. Residual Py phase is still present in the sample with composition x = 0.1 and a Py free ceramic was obtained for the composition with x = 0.4. Densification levels of ~80% of the theoretical density were achieved for all samples. A transmission electron microscopy (TEM) image (Philips CM20 microscope) of the sample with composition x = 0.4 and its grain size distribution (obtained by measuring the Feret’s diameter of more than 300 grains) are shown in Fig. 2 as example. The size distributions for all samples showed a lognormal character with an average size of ~20 nm and SD of 8 nm.

Electrical characterization was carried out on ceramic disks on which Pt/Au electrodes were deposited by sputtering and annealed at 673 K in air. Dielectric permittivity and losses were dynamically measured from 77 to 500 K at

FIG. 1. XRD patterns of nanostructured ceramics processed by SPS at 873 K: (a) 0.92PZN-0.08PT, (b) 0.82PZN-0.1PFN-0.08PT, and (c) 0.52PZN-0.4PFN-0.08PT. Py: pyrochlore.
1.5 K min\(^{-1}\) with a HP4284A precision LCR meter in the frequency range from 100 Hz to 1 MHz. Measurements were carried out in vacuum using a Cryostat Janis VPF 700 coupled to a temperature controller Lakeshore 331.

Figure 3 shows the temperature dependence of the real \(K'\) and the imaginary \(K''\) components of the relative permittivity at several frequencies for the nanostructured ceramics. In all cases, a very broad maximum that moves toward higher temperatures on increasing frequency is found for both \(K'\) (between 200 and 300 K) and \(K''\) (between 80 and 120 K). Around the maximum, \(K'\) decreases and \(K''\) increases when frequency is increased. This is a typical dielectric behavior of relaxor-type FE materials such as prototype PMN, which is associated with the dynamics of polar nanoregions (PNRs). The dielectric relaxations are present in materials with compositions \(x=0\) and 0.1 and without Py (for \(x=0.4\)) so it is a phenomenon associated with the Fe phase. The only role of Py is to reduce permittivity.

For 0.92PZN-0.08PT single crystals, the relaxor state does exist at high temperature and evolves to a FE state at \(-440\) K. The relaxor to FE transition has associated a sharp increase of the permittivity that is not observed for the nanostructured materials in all the temperature ranges down to 77 K, suggesting that the transition might disappear as a size effect, in good agreement with the results reported for PMN-PT. Nevertheless, the relaxor state was proposed to vanish below a critical grain size of 30 nm in Ref. 2, whereas our study reveals relaxor-type behavior for PZN-PFN-PT with an average grain size of 20 nm.

Analysis of the dielectric relaxations suggests that there are more than one dipolar process in the nanostructured ceramics. For the 0.92PZN-0.08PT ceramic, \(K'\) presents a main relaxor-type maximum at temperatures between 220 and 250 K. Also, a second anomaly can be observed at \(-320\) K in the same temperature range at which the relaxor maximum is present for the 0.82PZN-0.1PFN-0.08PT sample [see the vertical arrow in Fig. 3(a)]. This second anomaly is likely associated with the partial incorporation of Fe contamination from the milling media into the PZN-PT Pe, and its effect in the PNR dynamics. The relaxor maximum in \(K'\) is shifted to \(-280\) K for the 0.52PZN-0.4PFN-0.08PT sample. On the other side, all samples present a main relaxor-type maximum in \(K''\) between 90 and 120 K. Also, a second anomaly can be observed in \(K''\) at the same temperature at which the relaxor maximum is present in \(K'\) [see the arrow in Fig. 3(b)].

In order to investigate the origins of these relaxations, we have used the well-known Vogel–Fulcher (VF) law to fit the frequency dependence of the temperature of maximum permittivity \(T_m\), which is usually applied to relaxor FE,10,12

\[
\omega = \omega_o \exp\left[-\frac{E_a}{k(T_m - T_f)}\right],
\]

where \(\omega_o\) is a pre-exponential factor, typically \(-10^{13}\) Hz, \(E_a\) is the activation energy, \(T_f\) is the freezing temperature, and \(k\) is the Boltzmann constant.

The frequency dependence of \(T_m\) for the maxima of \(K'\) and \(K''\) were fitted to VF relationships for all materials (\(R^2 > 0.999\) in all cases), and the characteristics \(T_f\) and \(E_a\) of the relaxor state are summarized in Table I. Two independent relaxations can be identified from the dielectric data and the VF fitting parameters. For 0.92PZN-0.08PT, \(T_f\) and \(E_a\) values of 178 K and 90 meV, respectively, are obtained for the

<table>
<thead>
<tr>
<th>(K')</th>
<th>(T_f) (K)</th>
<th>(E_a) (meV)</th>
<th>(\omega_o) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x=0)</td>
<td>178 ± 5</td>
<td>90</td>
<td>(1.8 \times 10^{13})</td>
</tr>
<tr>
<td>(x=0.1)</td>
<td>296 ± 1</td>
<td>26</td>
<td>(3.2 \times 10^{12})</td>
</tr>
<tr>
<td>(x=0.4)</td>
<td>247 ± 1</td>
<td>34</td>
<td>(2.1 \times 10^{12})</td>
</tr>
<tr>
<td>(x=0)</td>
<td>50 ± 1</td>
<td>(K'')</td>
<td>7.6 \times 10^{10}</td>
</tr>
<tr>
<td>(x=0.1)</td>
<td>58 ± 1</td>
<td>44</td>
<td>(3.5 \times 10^{10})</td>
</tr>
<tr>
<td>(x=0.4)</td>
<td>60 ± 1</td>
<td>40</td>
<td>(3.4 \times 10^{10})</td>
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main relaxation of $K'$. Note that $T_f$ is lower than that obtained for single crystals, which might be associated with a modification of the dynamics of the relaxor state at the nanoscale, an effect described for 0.8PMN-0.2PT. For the ceramics with compositions $x=0.1$ and 0.4, $T_f$ of 296 and 247 K, and $E_a$ of 26 and 34 meV were obtained, respectively. We believe that these differences reflect a complex role of Fe in B-site on the dynamics of the relaxor state.

A similar effect of the PFN content is not found in the relaxation of $K''$ for which similar VF parameters are obtained. Also, figures are very different to those obtained for relaxation in $K'$, which strongly indicates that they are associated with a second, independent process. Although $T_f$ obtained from $K''$ in relaxors may be slightly smaller than that derived from $K'$, this does not seem to be the case here because of the large difference in $T_f$ of $>100$ K.

In relaxors, PNRs nucleate and grow slowly on cooling, increasing, and broadening the distribution of correlation length in an environment of random local fields. A size effect can be expected in their dynamics when the grain size approaches the characteristic size of the PNRs, which has been shown to be $\sim 10$ nm for PZN-PT single crystals at 300 K. The two independent relaxations observed in the nanostructured ceramics under study can be explained by considering different types of correlations among interacting PNRs.

For the nanostructured ceramics reported here, though the average grain size is 20 nm, its lognormal distribution spreads from 10 nm up to 50 nm in such a way that half of the volume of the material is formed by grains with a size above 32 nm. Several units of interacting PNRs can exist in grains of this size, yet their dynamics are altered in relation to that of PNRs in single crystals by the low number of interactions (random bonds) and by the presence of the grain boundary. Modification of the relaxor state at the grain boundary of submicron grain-sized PMN ceramics was proposed by Papet et al. and also by Carreau et al. For the PZN-PFN-PT nanostructured ceramics, this is most probably the phenomenon responsible of the main relaxation in $K''$, and also of the anomalously low values of permittivities of the materials as compared with those of coarse grained ceramics. In relaxors, the main contribution to permittivity stems from the PNR dynamics, e.g., cluster flipping, which is dramatically reduced at the grain boundary.

The origin of the second, independent low temperature VF phenomenon in $K''$ could be a correlation among PNRs of different grains. This mechanism is probably present in coarse grained materials, yet its contribution to permittivity is negligible as compared with that of the correlations within a grain. In the nanostructured ceramics, however, there is a significant fraction of material with grain size similar to that of a single PNR and for which correlations across the grain boundaries are the only ones possible. This mechanism requires pores-free nanostructured materials with perfectly bounded grains and clean boundaries, which are very difficult to process. In our ceramics, the microstructure presented large inhomogeneities with regions of very high densification, as shown by the scanning electron microscopy (SEM) image (Nova™ NanoSEM 230 microscope) in Fig. 4(a). In these regions, the intergranular correlations among PNRs are possible and result in a relaxation, as discussed above. However, correlations must be weaker than those among PNRs within a grain and freezing is more difficult, which explains the low temperature at which it takes place. Figure 4(b) shows a schematic representation of PNRs with intra- and intergranular (weaker) correlations in a nanostructured relaxor material.

In summary, nanostructured ceramics of PZN-PFN-PT with an average grain size of 20 nm present relaxor-type behavior down to 77 K and two independent VF processes that are probably associated with correlations among PNRs within a grain and across the grain boundaries, respectively. This indicates that the transition from the relaxor to FE phase might disappear as a size effect in the nanoscale. It also suggests that the relaxor phase does not disappear when the grain size approaches the typical size of PNRs, provided that correlations across the grain boundaries are possible.

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