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Tunability properties in the paraelectric state of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

$Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics prepared via columbite method exhibit high crystallinity and high density after sintering at 1200 °C. Typical relaxor behavior are demonstrated by the dielectric data. Although showing a diffuse phase transition, at room temperature the system is in its paraelectric state, i.e. the PMN structure is fully cubic. The dc-tunability was investigated above the room temperature, when other field-induced contributions than ferroelectric polarization might cause non-linearity. A random non-interacting dipolar unit in a double well potential was employed to describe the $\varepsilon(E)$ non-linearity. The temperature-dependence of the average polarization corresponding to the polar nanoregions in the paraelectric state of the PMN relaxor was calculated from the $\varepsilon(E)$ data at various temperatures above T_m. A similar trend of decreasing as increasing temperature shows the spin-glass local order parameter determined from the dielectric constant data in the paraelectric state. The local order parameter in the paraelectric state is determined by the nanopolar domains size and correlations.

Keywords: PMN; Relaxor; dc-tunability; Paralectric state; Dipolar units

1.. Introduction

In the last years, electric-field tunable materials have been extensively studied [1–3] due to their potential application as RF and microwave device, phase shifters, filters, and wireless communications. These applications need dielectric materials with high tunability and low losses, non-hysteretic behavior, tailored dielectric constant and thermal stability [4]. Some of these requirements are expected to be obtained in the paraelectric state of ferroelectrics or relaxors [5]. The non-linear properties of the polar systems in their paraelectric state were less investigated in the literature and the origin of the non-linearity $\varepsilon(E)$ without ferroelectric polarization switching is less understood. Among them, relaxors are known to preserve nanoscale polarization islands (polar nanoregions PNR) inside an average cubic matrix at 100 °C above the temperature corresponding to their maximum permittivity [6]. The exceptional properties of relaxors are considered to be determined by the size and dynamics of the PNRs. For such systems, the non-linearity $\varepsilon(E)$ is related to the field-induced re-orientation of PNRs [6,7]. Consequently, the dc-field dependence of the dielectric response can provide very useful information on the basic physics of relaxors.

One of the main investigated relaxors is $Pb(Mg_{1/3}Nb_{2/3}O_3)$ (PMN), a system normally exhibiting very high dielectric constants ($\varepsilon_r > 10{,}000$ at the relaxor–paraelectric transition) and a high electrostrictive coefficient, making the PMN-based ceramics very promising candidates for such applications [8,9]. The main dielectric characteristic of the PMN system is a broad maximum permittivity peak, indicating a diffuse phase transition associated with compositional fluctuations on the B-site sublattice of the perovskite ABO_3 structure [10,11], together with the decrease of the magnitude of the permittivity maximum ε_m, correlated with a shift of its corresponding temperature T_m as the frequency increases.

In the present paper, the temperature dependence of the dc-tunability of $Pb(Mg_{1/3}Nb_{2/3}O_3)$ (PMN) relaxor ceramics in its paraelectric state was investigated. The observed dielectric non-linearity is described by a model of random non-interacting dipolar units in a double well potential free energy [12].

2.. Experimental

The $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics were prepared via columbite method by using $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}4H_2O$

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precursors, as described elsewhere [13,14]. The resulted ceramics exhibit high phase purity, high crystallinity and a good densification (relative density ∼95%) after sintering at 1200 °C/4 h. The phase composition and the structural parameters of the samples were studied by X-ray diffraction (XRD) with a Brucker-AXS D8 diffractometer, using Ni-filtered CuKα radiation. The unit cell parameters were determined by least squares method, based on the position of 9-10 well-defined diffraction lines. For the electrical measurements, the sintered samples were cut in parallel-plate configuration and gold electrodes were applied by rf-sputtering on the polished surfaces. The complex impedance in the frequency domain of (10–10^6) Hz at temperatures of (150–400) K was determined with an impedance analyzer (Solartron, SI 1260). The high voltage dc-tunability measurements were performed above room temperature on the electroded ceramic disks immersed in transformer oil, under high voltages produced by a function generator coupled with a TREK 30/20A-H-CE amplifier [15].

3.. Results and discussion

The X-ray diffraction patterns obtained for the PMN ceramics at 1200 °C/4 h show single-phase compositions (Fig. 1), with a cubic symmetry (unit cell parameter $a = 4.047$ Å). As expected, at room temperature PMN should be in its paraelectric state [16].

The dependence of the real part and imaginary part of permittivity vs. temperature at a few frequencies is shown in Fig. 2. The dielectric properties are very good: high values of the real part of permittivity at room temperature (∼10,000) and at T_m (∼12,000), and dielectric loss: $\tan\delta < 2\%$ in the range (300–450) K and below 10% at T_m were observed. The PMN ceramic shows typical relaxor character, with diffuse phase transition and permittivity dispersion in the kHz range around T_m.

The dc-tunability determined at several temperatures above the room temperature is shown in Fig. 3. In spite of the paraelectric character, a strong non-linearity of the $\varepsilon(E)$ dependence

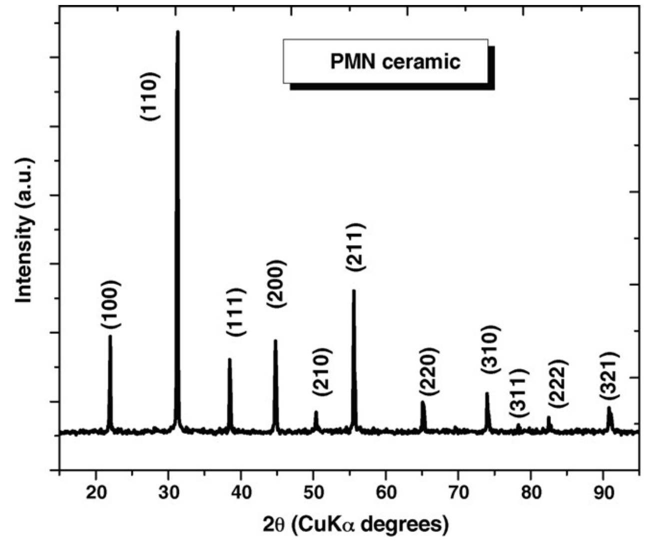

Fig. 1. Room temperature X-ray diffraction pattern of PMN ceramics sintered at 1200 °C/4 h.

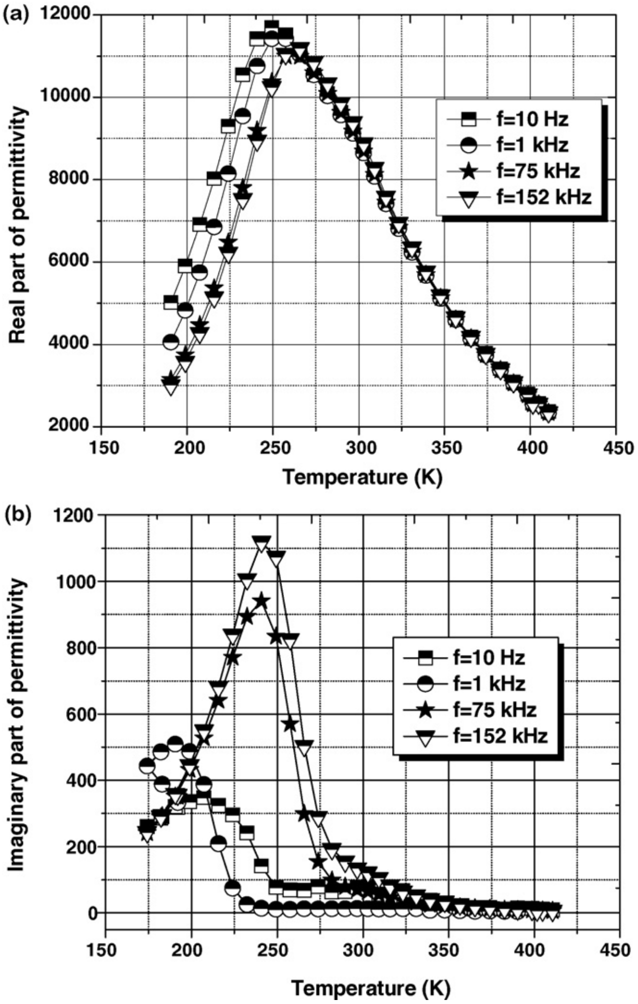

Fig. 2. Real (a) and imaginary (b) part of the permittivity vs. temperature at a few selected frequencies.

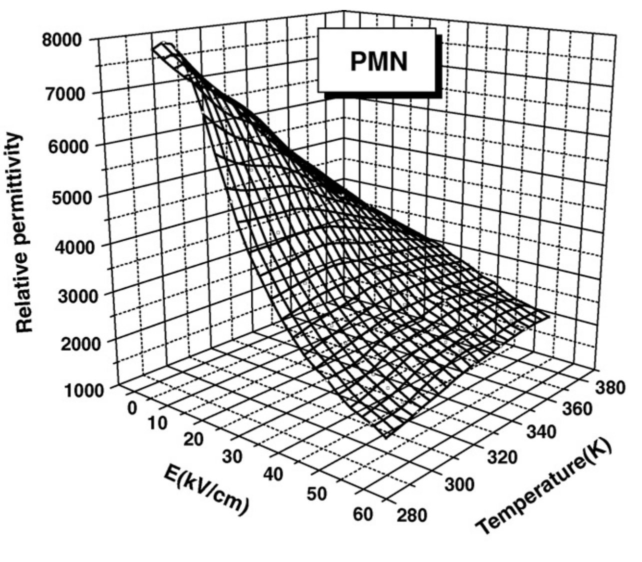

Fig. 3. dc-field and temperature dependence of the real part of permittivity of the PMN ceramic in the paraelectric state.

is still observed, with a tendency towards saturation for high fields of ~60 kV/cm. Therefore, at room temperature, the sample shows high tunability, $n = \varepsilon(0)/\varepsilon(E)$ of ~5 at the maximum applied electric-field. With increasing temperature, the permittivity vs. field strongly decreases, i.e. reduces when the temperature increases ($n = 3.5$ at 321 K and $n = 1.7$ at 383 K, by comparison with $n = 5$ at 293 K). This behavior is most probably due to the fact that at room temperature the sample is still close to its relaxor ferroelectric–paraelectric phase transition, and thus, it is more sensitive to the field variations.

Since the system is in the paraelectric state and is characterized by zero macroscopic polarization, it means that other mechanisms than those ones related to the ferroelectric polarizations are causing the observed non-linearity. For describing the polarization process in such systems, other field-induced polarization mechanisms were proposed [17–19]. For example, a simple model considering random non-interacting dipolar units in a double well potential was considered for explaining the polarization-field dependence in non-ferroelectric pyrochlore bismuth zinc niobate thin films [12]. The same approach is used to discuss the present tunability data. The model considers a dipolar system with the volume V containing identical dipoles of individual moment p_0, characterized by a free energy with two potential minima (1) and (2), separated by an energy barrier. It is worth to mention that this model is valid in the situation when the correlations between the neighboring dipolar units are negligible. This is valid in the present case, since it is known that in the case of relaxors, nanopolar regions with short range order persist far above the maximum permittivity temperatures, but they are uncorrelated [6,7,20]. Only at lower temperatures, under high fields or by forming solid solutions of PMN with ferroelectrics, like in PMN-PT, the degree of correlation will increase and a relaxor–ferroelectric crossover (short range order-to-long range order) takes place [21–23]. Since PMN is at room temperature already with 50 K above its T_m and since the measurements were performed in quasistatic regime, the correlations between the nanopolar dynamic structures can be neglected.

If the total number of dipolar units is $N = N_1 + N_2$, where N_1, N_2 are the number of the occupied wells, the relative population of the double wells under an electric-field E will determine the polarization-field dependence. Thus, the field-induced polarization P at a given temperature depends on the number of not compensated dipoles:

$$P = \frac{p_0 N}{V} \tanh\left(\frac{p_0 E}{kT}\right), \tag{1}$$

and the tunability at a fixed temperature is:

$$n = \cosh^2\left(\frac{p_0 E}{kT}\right). \tag{2}$$

By re-arranging this relationship, another explicit dependence between the applied field and tunability is found:

$$E = \frac{kT}{p_0} \ln \Omega, \quad \text{where } \Omega = \sqrt{n} + \sqrt{n-1}. \tag{3}$$

If the model is well describing the permittivity-field data in the paraelectric state, a linear dependence of the function $E = f(\ln \Omega)$ should be obtained at each temperature. Following this observation, the experimental tunability data for the PMN ceramic were arranged according to Eq. (3), in order to obtain a linear function. Linear fits of these dependences were performed for a few temperatures and they are shown in Fig. 4. For fields below 32 kV/cm, the agreement between Eq. (3) and the experimental data is very good. By linear regression of these dependences, the average value of the dipole moment p_0 vs. temperature was determined (Fig. 5). It is observed that the average dipole moment, which can be interpreted as a local order parameter, is continuously reducing with temperature. This result leads to the idea of size reduction of the nanopolar regions with increasing temperature, as predicted for relaxors [6,19,20]. Values of 4.2–6.4 nm were determined for the present PMN ceramics by these calculations in the range of temperatures of 290 and 380 K.

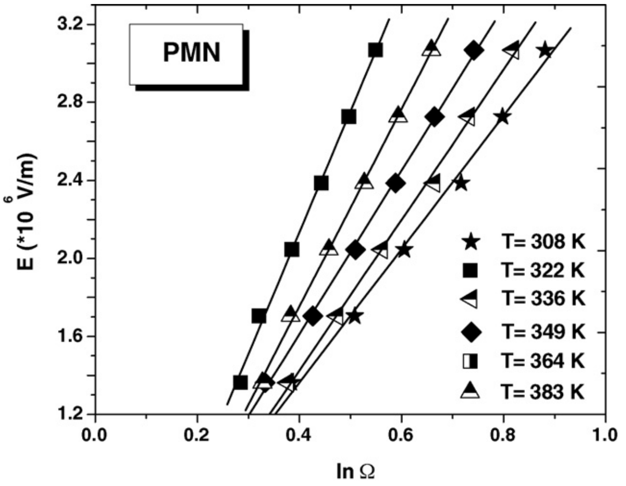

Fig. 4. Experimental linear dependence of the applied dc. field as a function of the logarithm of $\Omega = \sqrt{n} + \sqrt{n-1}$, according to Eq. (3), at a few selected temperatures.

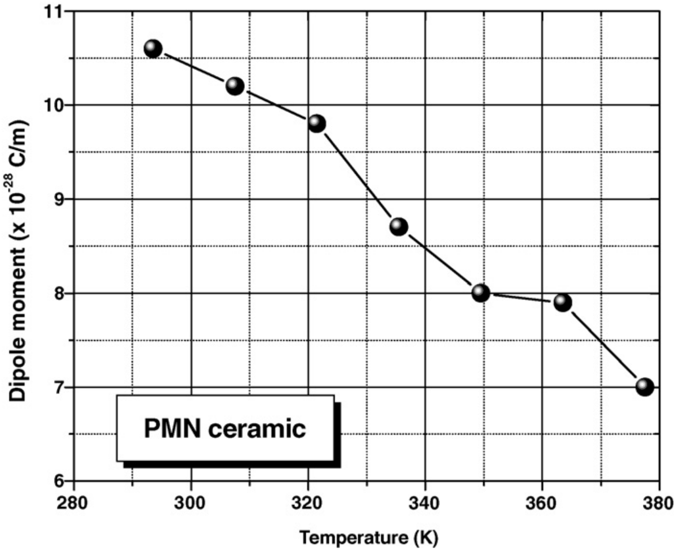

Fig. 5. Computed average dipole moment from the linear fits with Eq. (3), showing a decay with increasing temperature.

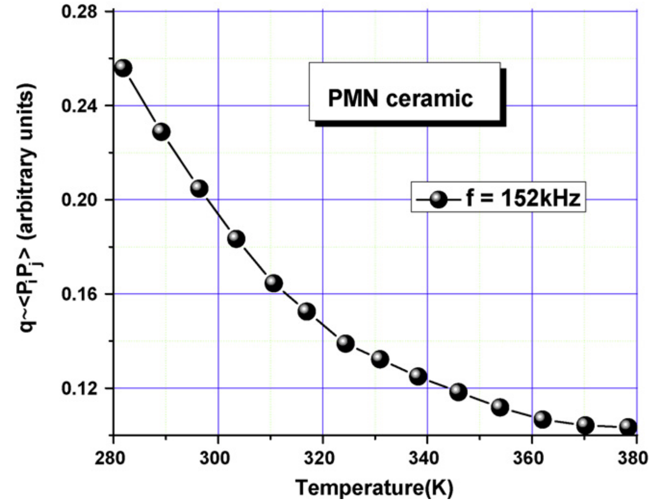

Fig. 6. The temperature dependence of the local order parameter $q(T)$ as determined from the $\varepsilon(T)$ data at f = 152 kHz, according to Eq. (4).

It has long been accepted that the dielectric permittivity of relaxors deviates from the Curie–Weiss behavior over a wide temperature range, in a similar manner with spin-glass systems and this deviation is caused by the correlations between the nanopolar clusters in the paraelectric state [24,25]. Therefore, a local order parameter (Anderson parameter) defined as: $q \propto < P_i P_j >$ can be found from the dielectric data, according to Eq. [26]:

$$\varepsilon = \frac{C(1 - q(T))}{T - \theta(1 - q(T))}, \tag{4}$$

in which C is the Curie constant and θ the Curie–Weiss temperature are fitting constants which are determined at very high temperatures and $q(T)$ the local order parameter. The dielectric data and Eq. (4) allowed to reconstruct the local order parameter and is represented in Fig. 6. Both the temperature dependences of $p_0(T)$ determined from the tunability data (Fig. 5) and $q(T)$ qualitatively show the tendency of the relaxor system to reduce its local order, either by reducing the size of the nanopolar order or their correlation. A further detailed study of tunability in a large range of temperatures coupled with Raman investigations is expected to give more information on the thermal evolution with temperature of the nanopolar domains in the paraelectric state of PMN relaxor ceramics.

4.. Conclusions

$Pb(Mg_{1/3}Nb_{2/3}O_3)$ relaxor ceramics prepared by columbite route using $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}4H_2O$ precursors were investigated by measurements of the dc-tunability at different temperatures. The ceramics show high permittivity (~10,000 at T_m) and loss below 2%. The tunability data in the paraelectric state analyzed using a model of non-interacting dipolar units in a double well potential model allowed to determine the temperature-dependence of the average polarization corresponding to polar nanoregions. This dependence was qualitatively compared with the spin-glass local order parameter decreasing with temperature.

Acknowledgements

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