J Electroceram (2007) 19:433–435
DOI 10.1007/s10832-007-9061-2

Dielectric spectroscopy and distribution of relaxation times of PMN-PSN ceramics

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Received: 3 March 2006 / Accepted: 21 August 2006 / Published online: 13 March 2007

Abstract The complex dielectric permittivity of 0.05PMN–0.95PSN ceramic was measured in the frequency range from 20 Hz to 3 GHz. Two anomalies of complex dielectric permittivity were observed 398 and 286 K which can be attributed to the ferroelectric and antiferroelectric phase transitions respectively. From frequency dependences of the real and imaginary parts of dielectric permittivity the distribution of relaxation times $f(\tau)$ was calculated. The distribution of relaxation times data together with the dielectric dispersion data shows the competing interactions between these two phase transitions and appearance of the dipolar glass state below the antiferroelectric phase transition.

Keywords Ferroelectric · Antiferroelectric · Phase transition · Dipolar glass · Dielectric dispersion

1 Introduction

Among a variety of ferroelectric materials probably the best known and investigated are materials with $A(B'B'')O_3$ perovskite structure. One of them is lead magnesium niobate $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) which can be called as model relaxor ferroelectric. It is well known that PMN shows broad and diffuse maxima of real and imaginary parts of dielectric permittivity which shifts to higher temperatures when increasing the frequency of measurement. This dielectric anomaly is caused not by any phase transition but only by flipping of polar nano regions because PMN remains cubic down to liquid helium temperatures [1]. $Mg^{2+}$and Nb^{5+}cations in PMN, located at B′ and B″ positions in $A(B'B'')O_3$ frame, produce only short-range local fields and long-range ferroelectric phase can be formed only by applying higher than critical (>1.7 kV/cm) electrical field [2].

Lead scandium niobate $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) is another type of ferroelectric relaxor. This material undergoes the order–disorder transition based on the ordering of $Sc^{3+}$and Nb^{5+}ions near the 1,000 K temperature and the long-range order can be controlled by thermal treatment [3–6]. The disordered PSN displays a diffused relaxor behaviour of dielectric permittivity whereas ordered PSN shows almost a “classical” ferroelectric properties but weak relaxation and deviation from the Curie law was observed [4] It was showed, that disordered PSN undergoes the spontaneous relaxor-ferroelectric phase transition at 373 K [3]. For a partially disordered PSN the two consecutive anomalies were observed at 366 and 345 K, respectively [5]. The coexistence of two phases of disordered and ordered PSN together is supposed.

There were several studies on the dielectric properties of the mixed $(1-x)$PMN$-(x)$PSN ceramics and crystals [7, 8]. The dielectric dispersion of ordered $(1-x)$PMN$-(x)$PSN ceramics, when x varies from 0.2 to 0.9, showed crossover from PMN type behaviour to PSN type one when $x\approx0.5$ however for the disordered samples the relaxor type dielectric dispersion remain even for $x>0.5$ [7]. Because the dielectric permittivity data on composition with $x=0.95$ was not reported until present, we investigated how the

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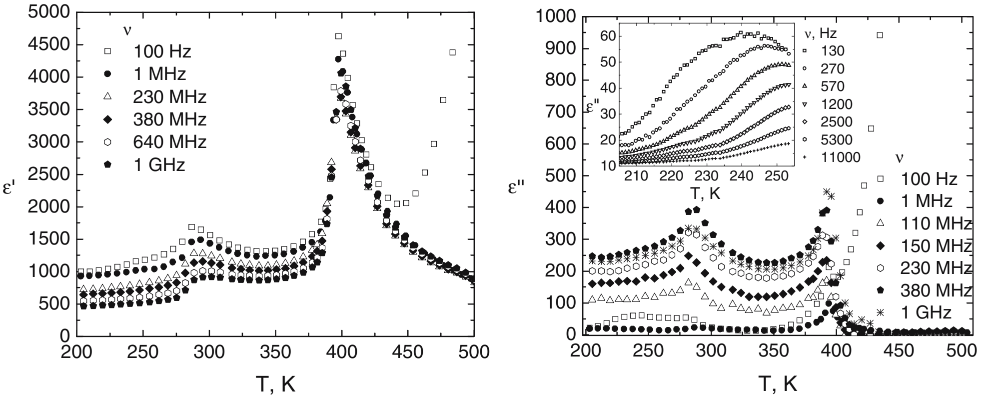

Fig. 1 Temperature dependences of the complex dielectric permittivity of 0.05PMN–0.95PSN ceramic at different frequencies. *Insert* shows the dispersion of imaginary part of complex dielectric permittivity at low temperatures where the dipolar glass interactions are supposing

small amount of PMN can change dielectric properties of ordered PSN ceramics.

2 Experimental procedure

The samples for dielectric measurements were cut from a plate of ceramics. The details of sample preparation and characterization were already presented in [9]. The frequency range from 20 Hz to 3 GHz was covered by using HP 4284 precision LCR meter in low frequency (20 Hz–1 MHz) and Agilent 8714 network analyzer in high frequency (1 MHz–3 GHz) part. The silver electrodes were applied on the each sample to produce good electrical contact and the samples were annealed to 500 K before each measurement to avoid memory effects The measurements were performed in cooling cycle down to 200 K with the temperature change rate 1 K/min. monitored within 0,1 K accuracy with Pt temperature sensor.

3 Results and discussion

Dielectric spectra of 0.05PMN–0.95PSN ceramic are presented in Fig. 1. Two dielectric permittivity anomalies can be seen clearly at 398 K and about 286 K, respectively. The first anomaly is similar to the transition typically observing in ordered PSN except for the transition temperature which, in this case, is about 15 K higher. The second anomaly is a little bit diffused and, according to its behaviour, can be attributed to the antiferroelectric phase transition. At temperatures lower than 250 K the low frequency dispersion region appears as is shown in inserted picture. This dispersion region vanishes with increasing of the frequency and disappears at several kHz. Behaviour of this dispersion region is similar to that typically observed in dipolar glasses [10]. When the temperature is above 400 K the high ionic conductivity can be clearly distinguished at low frequencies. Obviously this conductivity gives contribution to the total dielectric spectrum till about 350 K. Because dielectric dispersion below this temperature not vanishes but some rising of the imaginary part of the dielectric permittivity is observing, so we can conclude that this dispersion is influenced by forming ferroelectric domains which disappears after antiferroelectric phase transition at lower temperatures.

Frequency dependencies of the real and imaginary parts of dielectric permittivity are presented in Figs. 2 and 3 for low temperature and high temperature anomalies respectively. The dielectric dispersion clearly appears in both phases above 100 MHz and extends to the microwave region. A less pronounced dispersion of dielectric permittivity can be seen also below 10 MHz. In contrast to the high temperature dispersion, this dispersion region is

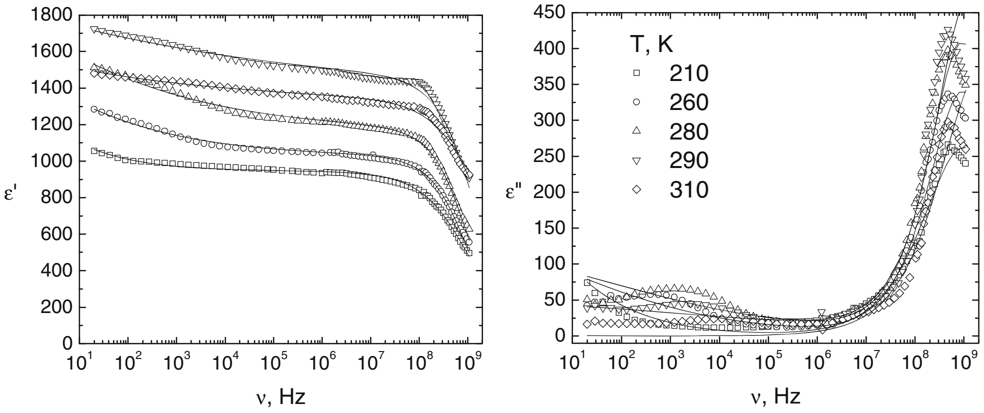

Fig. 2 Frequency dependences of complex dielectric permittivity of 0.05PMN–0.95PSN ceramic in the low temperature anomaly region. The *solid lines* are Cole–Cole fits

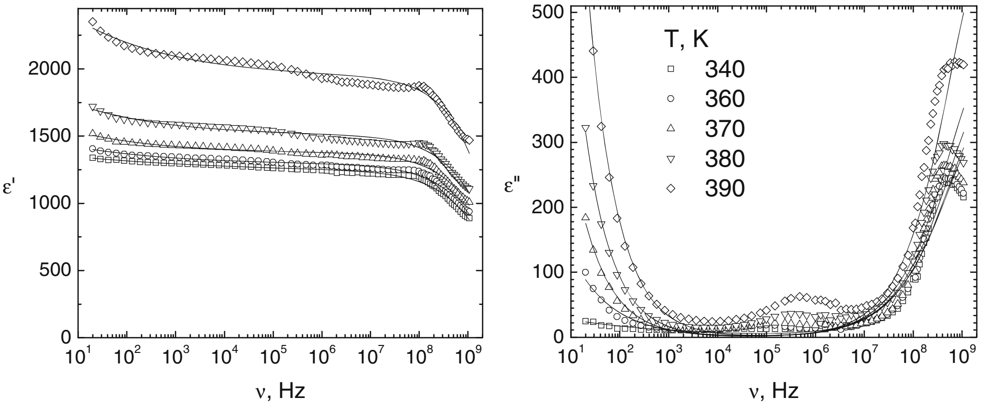

Fig. 3 Frequency dependences of complex dielectric permittivity of 0.05PMN–0.95PSN ceramic in the high temperature anomaly region. The *solid lines* are Cole–Cole fits

temperature dependent and shifts to the lower frequency region with temperature decreasing. The high temperature and low frequency dispersion region, as mentioned above, can be attributed to the ionic conductivity while the monotonically slowing down real part of the dielectric permittivity at intermediate frequencies shows the influence ferroelectric domains as can be seen in Fig. 2 and dipolar glass interactions in Fig. 3.

To get more complete picture about the relaxation processes in 0.05PMN–0.95PSN ceramics we calculated the relaxation time distribution function at different temperatures according to the method described in [10]. Curves of the relaxation time distribution function (Fig. 4) can be separated into two parts. The first part stays stable in 10^{-14}–10^{-8} s region and represents motions of single dipoles. The another part which extends from 10^{-6} s to 10^{2} s shifts to the longer relaxation times with decreasing the temperature and supposing is caused by competing interactions between PSN and PMN in this ceramic, thus producing something like dipolar glass state in this composite.

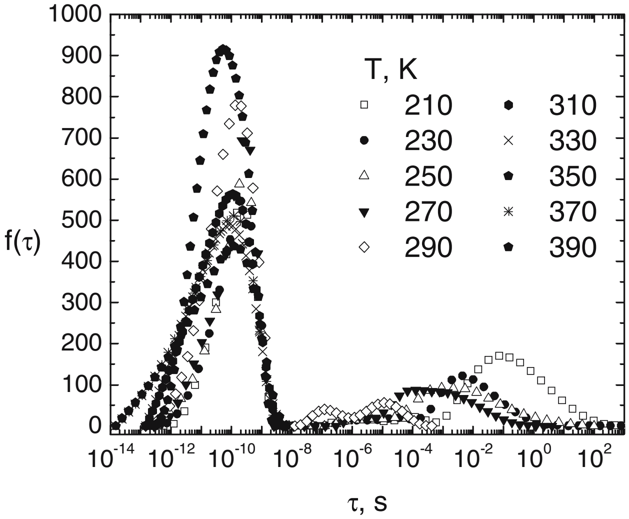

Fig. 4 Relaxation time distribution function *f(τ)* of 0.05PMN–0.95PSN ceramic at different temperatures

4 Conclusions

Our investigations on dielectric properties of 0.05PMN–0.95PSN ceramic revealed an complicated picture of dielectric behaviour of this composite. We observed a typical ferroelectric phase transition at 398 K as in ordered PSN and also antiferroelectric phase transition which was observed by Takesue et al [6] and are clearly shown in dielectric spectra by Perrin et al [5] for a partially disordered PSN. Additionally, the dipolar glass state was observed below the antiferroelectric phase transition. Competing interactions between the ferroelectric and antiferroelectric regions in PSN, as was supposed by Takesue et al [6], can produce dipolar glass state, which cause the relaxor behaviour in PSN if some disorder exists there. In 0.05PMN–0.95PSN composite this disorder is caused by the presence of PMN but there is evidence that 5% of PMN in such composite is not enough to form polar nano regions and induce the relaxor behaviour in 0.05PMN–0.95PSN system.

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