J Electroceram (2008) 21:279–282
DOI 10.1007/s10832-007-9150-2

Dielectric loss anomalies of 0.68PMN–0.32PT single crystal and ceramics at cryogenic temperature

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Published online: 1 May 2007

Abstract The temperature dependence of dielectric constant and loss were investigated for poled and unpoled [001]-oriented 0.68PMN–0.32PT single crystal and ceramics at cryogenic temperature. Two abnormal loss peaks, which are frequency dependent, are presented for all the samples. One of abnormal loss peaks locates in the range from 50 to 80 K and the other was observed in the range from 200 to 300 K. The difference of the abnormal loss between the single crystal and ceramics were compared. It is assumed that the dielectric loss anomalies at cryogenic temperature are related to the change of domain structure and phase structure parameter induced by temperature.

Keywords Dielectric loss · Cryogenic temperature · PMN–PT · MPB

1 Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$(PMN) is a typical relaxor ferroelectrics. The existence of a morphotropic phase boundary (MPB) is an important feature of the solid solution between typical relaxor ferroelectrics and normal ferroelectrics $PbTiO_3$ (PT). For $(1-x)$PMN–xPT system, the MPB exist at x= 0.30∼0.35 [1]. MPB is thought a phase boundary separating rhombohedral (R) phase and tetragonal phases (T). Recently monoclinic (M) and orthorhombic (O) have also been reported in PMN–PT single crystal with MPB compositions [2, 3]. Noheda et al. [4] reported the stability region of monoclinic or orthorhombic phase by synchrotron X-ray powder diffraction, which extends from x=31% to x=37% at 20 K in PMN–xPT system. This observation shows that the MPB of the PMN–PT system is characterized by multiphase components and complex phase behavior.

It is well know that the study of dielectric spectra is a powerful tool in determining various dielectric peaks as well as dielectric relaxation behavior, which is critical in understanding the dielectric polarization mechanisms. Because the phase transition temperatures for MPB compositions in PMN–PT system are higher than room temperature, most work on dielectric properties for PMN–PT system was carried out above or a little below room temperature. Dielectric spectra at lower temperature, especially below liquid nitrogen temperature, are rarely reported. Recently, the dielectric anomalies at low temperature in PZN–PT and PMN–PT system were reported [5–8]. In this work, the dielectric spectra at cryogenic temperature were investigated for 0.68PMN–0.32PT single crystal and ceramics. The abnormal dielectric losses for these materials at cryogenic temperature were presented and discussed.

2 Experimental procedures

The 0.68PMN–0.32PT single crystal and ceramics were prepared as described in literature [9]. The [001]-oriented single crystal of size of $5\times5\times0.8$ mm^3 and the ceramics with about 12 mm in diameter and 1 mm in thickness were used for dielectric measurements.

For dielectric property measurements, gold electrodes were sputtered on both sides of the samples and data were collected using an HP 4284A LCR meter in conjunction

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with a cryostat and furnace for low and high temperature experiments, respectively. The poled electric field was 2 kV/mm for poling the samples. Data were collected at 1 k, 10 k and 100 kHz, in the temperature range of 10 to 300 K and room temperature to 500 K with a heating rate of 3 K/min.

3 Results and discussion

Figure 1(a) and (b) show the temperature dependence of dielectric constant (ε_r) and dissipation factor (tan δ) as a function of frequency for unpoled and poled [001]-oriented 0.68PMN–0.32PT single crystal, respectively. The inset in Fig. 1(a) shows the measurements at high temperature. It can be seen that ε_r has sharp peaks near T_m=420 K for ferroelectric–paraelectric phase transition. The shoulders around ~350 K are attributed to a rhombohedral to tetragonal phase transition. The phase transition behavior of the sample is similar to other MPB samples in PMN–PT system [1]. In ε_r-T curve of Fig. 1(a), from 10 to 300 K, dielectric constant (ε_r) rises up gradually with increasing temperature, and obvious frequency dependence is shown above 150 K. In tan δ-T curve of Fig. 1(a), there are two dielectric loss anomalies. One strong peak in tan δ (noted as peak A) was observed near ~50 K and the other tan δ peak (noted as peak B) was around ~220 K. $T_{m,100\ kHz}$ and $T_{m,1\ kHz}$ are the temperature of maximum tan δ at 100 kHz and 1 kHz, respectively. ΔT ($=T_{m,\ 100\ kHz}-T_{m,\ 1\ kHz}$) for peak A and B is 11.2 and 22.7 K, respectively, which implies strongly frequency dependent of tan δ. The tan δ peak value for peak B is higher than that for peak A. For poled sample, in Fig. 1(b), two dielectric loss anomalies were also observed. With increasing temperature, one broad tan δ peaks (peak A) locate around ~65 K, which is strongly frequency dependent, and then tan δ keeps near flat from 120 to 240 K and decreases quickly above 240 K. The peak B around 220 K is strongly frequency dependent also. From Fig. 1, it was found that two dielectric loss anomalies exist below 300 K for unpoled and poled single crystal. However, no dielectric constant anomalies were observed in this temperature range. Comparing dielectric loss anomalies between unpoled and poled samples, T_m of tan δ in poled sample is higher by about 10 K than that for unpoled sample for peak A and the tan δ peak value in poled sample is lower than that in unpoled sample for peak B. It implies that poling of sample has effects on dielectric loss anomalies. Normally, the poled sample should have better ferroelectric domains because of effects of poling electric field on domains. However, the poled sample has a higher peak of loss in peak A. Therefore, dielectric anomalies cannot be only attributed to the domain structure.

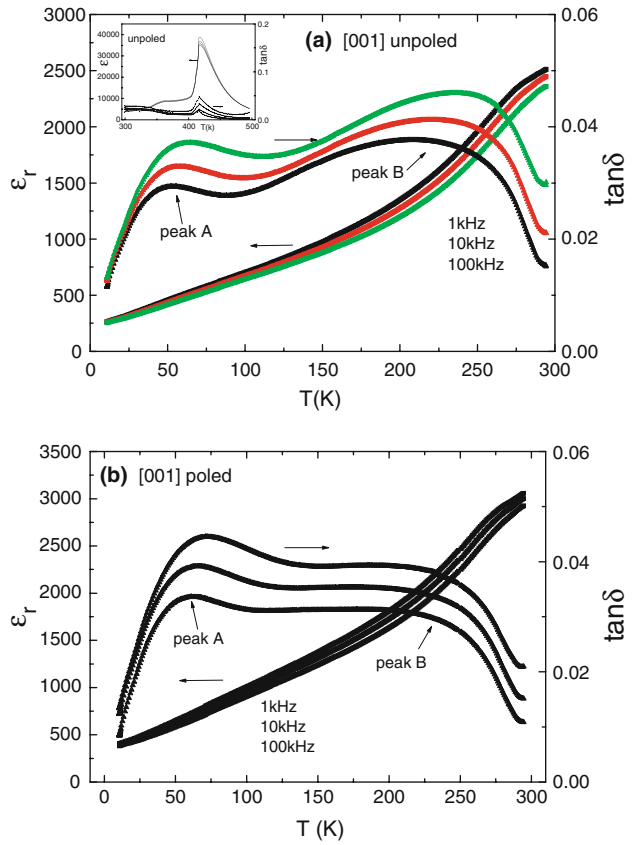

Fig. 1 Temperature dependence of dielectric properties for (**a**) unpoled and (**b**) poled 0.68PMN–0.32PT single crystal

Figure 2(a) and (b) show temperature dependence of dielectric properties for unpoled and poled 0.68PMN–0.32PT ceramics. The inset in Fig. 2(a) shows the measurements at high temperature. There are two dielectric loss anomalies, which are similar to 0.68PMN–0.32PT single crystal (in Fig. 1). One broad loss (tan δ) peaks (peak A) locate around 55 and 75 K (at 10 kHz) and ΔT of the loss peaks is 7.1 and 9.7 K for unpoled and poled ceramics, respectively. Other loss anomalies (peak B) are around 220 and 250 K for unpoled and poled ceramics, respectively. The dielectric loss anomalies are strongly frequency dependent. No dielectric constant anomalies were observed in this temperature range. Compared with the unpoled ceramics, the poled ceramics has a lower and less frequency dispersion of the dielectric loss in the measuring temperature range.

Comparing Fig. 1 with Fig. 2, although the dielectric loss value of single crystal is lower than that of the ceramics, the dielectric loss anomalies of single crystal are similar to that of ceramics. Dielectric loss in ferroelectrics is generally attributed to domain-wall contributions. Arlt and Herbiet et al. observed one low temperature relaxational behavior below 300 K in PZT ceramics. A phenomenological model of a vibrating 90°-domain wall in an electric and mechanic stress field was built. The pronounced low temperature relaxation was attributed to domain wall

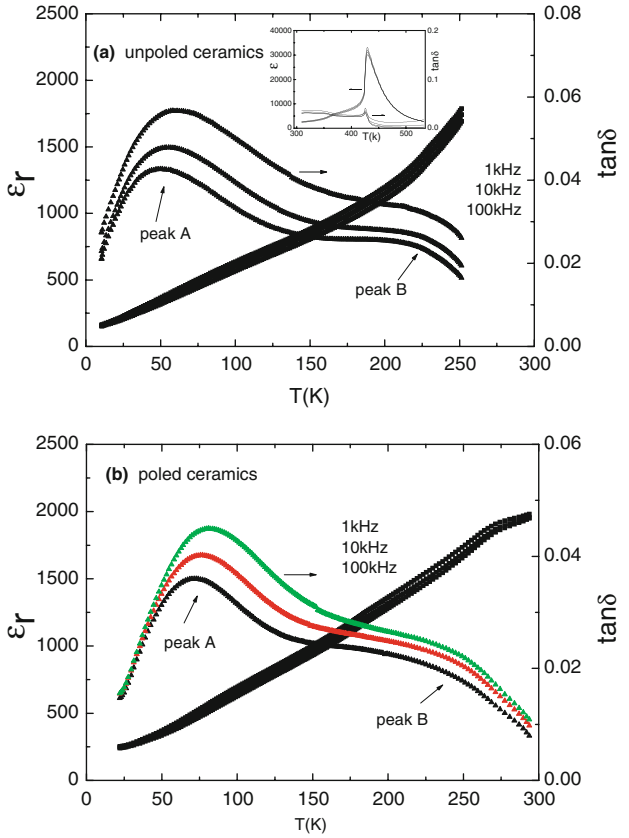

Fig. 2 Temperature dependence of dielectric properties for (**a**) unpoled and (**b**) poled 0.68PMN–0.32PT ceramics

vibration [10, 11]. Recently, the unexpected frequency dependent dielectric anomalies at low temperature have also been reported in some relaxor system. Two dielectric relaxation processes were presented from 12 to 300 K in PZN4.5PT single crystal [5]. One is around 100 K, which attribute to the domain-wall motion and the other is around 250 K, which is related to a more intrinsic behavior. Dielectric relaxation in PZN9PT single crystal below 180 K was also observed. The relaxation process can be attributed to the freezing of ferroelectric macrodomain walls induced by the pinning of point defects [6]. Priya et al. [7] have also observed a strong peak in loss near 75 K, which was frequency dependent, in PMN–PT single crystal. It is thought that the losses are dominated by structure irregularities (or fractal clusters of low symmetry) inside of normal micro-sized domain, rather than the motion of domain walls. Lente et al. [8] investigated the dielectric property of $(1-x)$PMN–xPT ceramics for $0.10 \leq \times \leq 0.40$ from 15 to 600 K. The results reveal remarkable dielectric anomalies with frequency dispersion at cryogenic temperatures over the all investigated composition ranges. That is to say, the dielectric relaxation is independent of whether the composition presents a normal or relaxor characteristics. The low temperature relaxation in PZT ceramics, which are normal ferroelectrics, is also supported this suggestion [10, 11]. Therefore, the mechanism related to this low temperature dielectric relaxation process in ferroelectrics system is complicated and indefinite.

It has been reported that ferroelectric domains in some ferroelectric materials normally froze at low temperature [12]. To observe the domain structure in samples at cryogenic temperature is helpful for understanding the dielectric anomalies. The domain structures of ceramics with the MPB composition $0.68Pb(Fe_{2/3}W_{1/3})O_3$–$0.32PbTiO_3$ (PFW–PT) were analyzed in situ by TEM as a function of temperature from 16 to 300 K [13]. With increasing temperature, a macrodomain with lamellar structure throughout the grain at 16 K was gradually changed into core-shell structure, which the central region still contained strain contrast from the domain walls and the exterior or shell of the grains was free from domain wall contrast. At the same time, the phase structure parameter was being adjusted from low temperature to 300 K, however there is no phase transition during this temperature range. It is interesting that the dielectric loss anomalies below 150 K were observed in PFW–PT system also. Although the evolution of domain structure with temperature for different system is different, the results indicated that the change of domain structure and phase structure could be induced by rising temperature even if at cryogenic temperature. Noheda's results showed the phase coexistence (R+Mc, T+Mc or T+Mc+O) could remain in MPB composition for PMN–PT system until 20 K [4]. This observation shows that the MPB is characterized by multiphase components and complex phase behavior. According to the results in PFW–PT ceramics, we assume that the dielectric loss anomalies at cryogenic temperature are related to the change of domain structure and phase structure induced by rising temperature. Recently, it's found that the dielectric loss anomalies in $Pb(Zn_{1/3}Ta_{2/3})O_3$–$PbTiO_3$ system at cryogenic temperature [14]. So it seems that the dielectric anomalies at low temperature are common phenomena in ferroelectric system. A clear understanding of the anomalies needs further study.

4 Conclusion

The temperature dependence of dielectric constant and loss were investigated for poled and unpoled [001]-oriented 0.68PMN–0.32PT single crystal and ceramics from 10 to 300 K. Two dielectric loss anomalies were observed for all the samples, which are strong frequency dependent. One of abnormal loss peaks locate in the range from 50 to 80 K and the other is observed in the range from 200 to 300 K. These results indicate that complicated polarization mechanisms at cryogenic temperature are in MPB samples. We assume that the dielectric loss anomalies at cryogenic

temperature are related to the change of domain structure and phase structure induced by rising temperature.

Acknowledgments The first author would like to thank Dr. A. Wu for her help in measurements and helpful discussion. This work was supported by the Ministry of Sciences and Technology of China through 973-project under grant No. 2002CB613304 and No. 2002CB613307 and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (2005).

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