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Study of the Electrical Properties of $Pb(Mg,Ni)_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ System Across the Morphotropic Phase Boundary

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Abstract. Phase transitional behavior and electrical properties of $(1-x)Pb(Mg,Ni)_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ ceramics (PMNN-PT with Mg/Ni = 1:1, $x = 0.20$–0.40) across the morphotropic phase boundary (MPB) were examined. X-ray diffraction and dielectric measurement reveal that two phases, pseudocubic and tetragonal phases, coexist in the composition range $x = 0.30$–0.36. The maximum d_{33} (about 570 pC/N) was observed at the composition $x = 0.32$–0.34. Dielectric and ferroelectric properties exhibit abnormal high near the MPB. An unusual peak shoulder occurred in the dielectric measurement upon thermal cycling for poled samples. This phenomenon was considered to be associated with the "macro to micro domain" transition and depolarization.

Keywords: morphotropic phase boundary, dielectric properties, relaxor ferroelectrics, ferroelectric domain

1. Introduction

Relaxor ferroelectrics of $Pb(Zr,Ti)O_3$ (PZT) [1], $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) [2] and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) [3] are attracted much attention for the application of multiplayer capacitors, piezoelectric actuator and other devices, as well as for an understanding of fundamental physics of the type materials. It has been found that there is a morphotrophic phase boundary (MPB) which separates the pseudocubic and tetragonal phases of these systems. The discovery of extraordinarily high piezoelectric and dielectric properties near the MPB of these materials stimulates many researchers to investigate the essential of the MPB in more detail.

The solid solution of lead nickel niobate $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) with PT is also a relaxor-type ferroelectrics, which has drawn much interest in recent years for its excellent dielectric properties. It has been reported that the MPB in $(1-x)$PNN-xPT system lies in the composition range of $x = 0.34$–0.38 [4]. Many researches have been carried out on the ternary ferroelectric system in order to obtain the better properties. But so far, we hardly find the study on the MPB and electrical properties of the PMN-PNN-PT system.

In this work, the structure and electrical properties of $(1-x)Pb(Mg,Ni)_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ (PMNN-PT with Mg/Ni = 1:1) with the composition range of $x = 0.20$–0.40 were investigated. Particularly the dielectric and ferroelectric as well as piezoelectric behaviors of the MPB of this system were examined and discussed.

2. Experimental Procedure

The compositions used for this study were $(1-x)$ PMNN-xPT with x changing as 0.20, 0.22, 0.24, 0.26, 0.28, 0.30, 0.32, 0.34, 0.36, 0.38 and 0.40 (hereafter named as PMNNT1 to PMNNT11). The perovskite-phase powders were synthesized using columbite precursor method in order to avoid the formation of a pyrochlore phase [5]. $NiNb_2O_6$ and $MgNb_2O_6$ were first formed at 1000°C and 1100°C for 6 h respectively, and then the powders of $NiNb_2O_6$, $MgNb_2O_6$, PbO (with an excess content of 3 mol%), TiO_2 were weighed and mixed by ball milling with zirconia balls in alcohol

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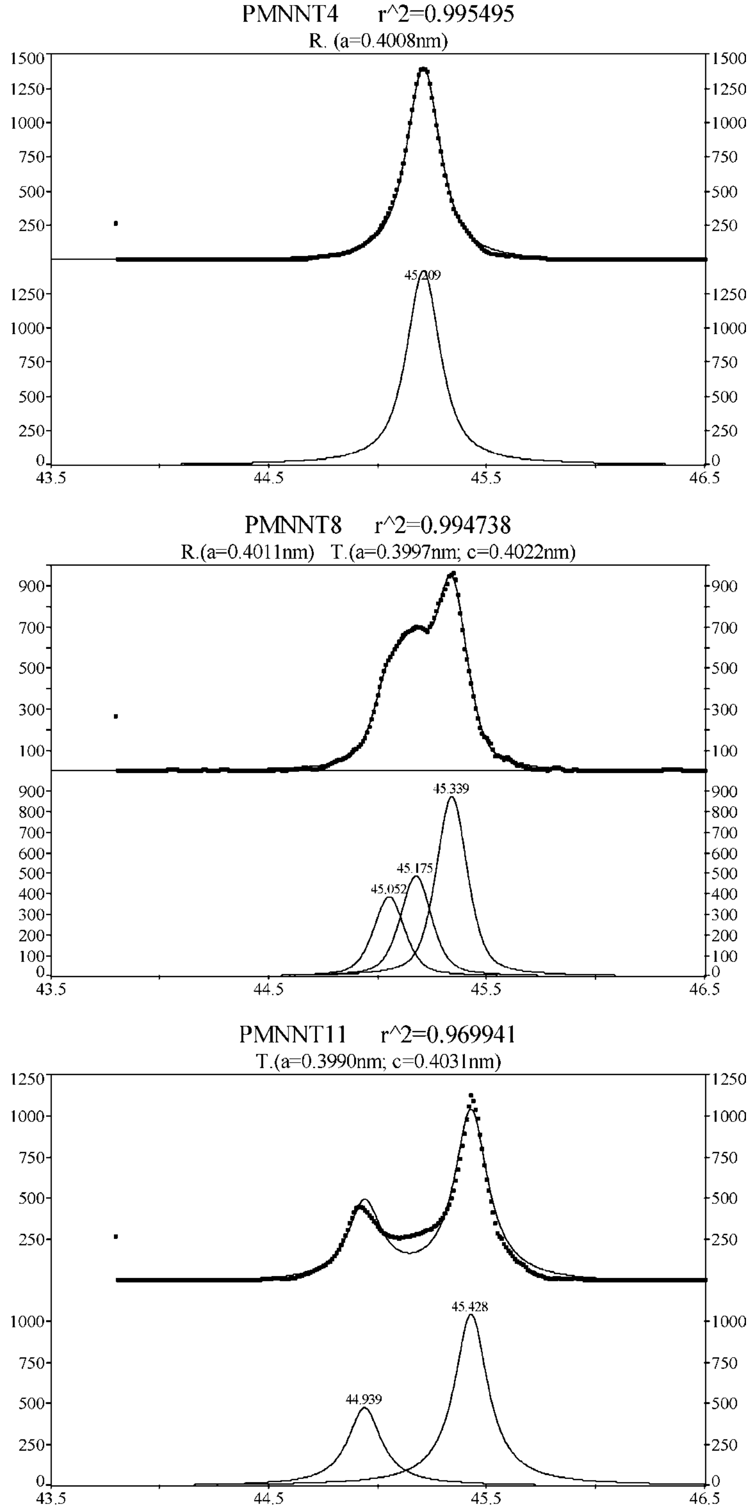

Fig. 1. XRD patterns around $2\theta = 45^{\circ}$ for PMNNT4, PMNNT8 and PMNNT11 ceramics, together with their fitting results (Dotted curve—experimental results; Full curve—fitting results R.—Pseudocubic phase; T.—Tetragonal phase).

for 12 h. After drying, the PMNN-PT powders were obtained by calcining at 850°C for 2 h. Then after remilling, drying and sieving, the various powders were cold pressed into disks with 10 mm in diameter and then sintered at 1150°C for 2 h in sealed alumina crucibles. To limit the loss of PbO, the disks were covered with $PbZrO_3$ powder.

To investigate the electrical properties, both sides of the sintered pellets were covered with silver and fired at 500°C for 20 min. The poling was carried in a silicone oil bath at room temperature by applying 20 kV/cm for 30 min. Dielectric measurements were operated using an impedance analyzer (HP4192A Precision LCR meter), The frequencies used were 1,10,100 kHz and the temperature range were −40°–200° with a heating rate of 2°/min. The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, ZJ-2).

3. Results and Discussion

3.1. The Phase Transition of (1−x)PMNN-xPT Ceramics

The {111} and {200} diffraction lines for all of the samples were measured carefully. Figure 1 shows some typical XRD profiles around $2\theta = 45°$. Peakfit v4 software was used to separate the overlapped lines. It was showed that there are two phases coexistence in the sample PMNNT8 and the MPB was identified to lie between the composition range $x = 0.30$–0.36. More detailed analysis of the XRD results as well as the phase transition across the MPB will be published in Ref. 6.

Figure 2 shows the morphology of fractured surface of different ceramic samples. The average grain size is about 3–5 μm.

3.2. Dielectric Behavior of the PMNN-PT System

The temperature dependencies of the dielectric constant for all of the poled and unpoled PMNN-PT ceramics were measured at different frequencies (1,10, 100 kHz). Figure 3 shows the variation of dielectric constant with temperature for unpoled samples at 1 kHz. It was found that the dielectric constants for the most of samples are higher than 30000 and the highest dielectric constant (36370) was obtained when PT content is 0.30.

In order to obtain the normalized relative permittivities, the relative permittivities ε of the unpoled samples were divided by their experimental values of maximum relative permittivities ε_m respectively, which

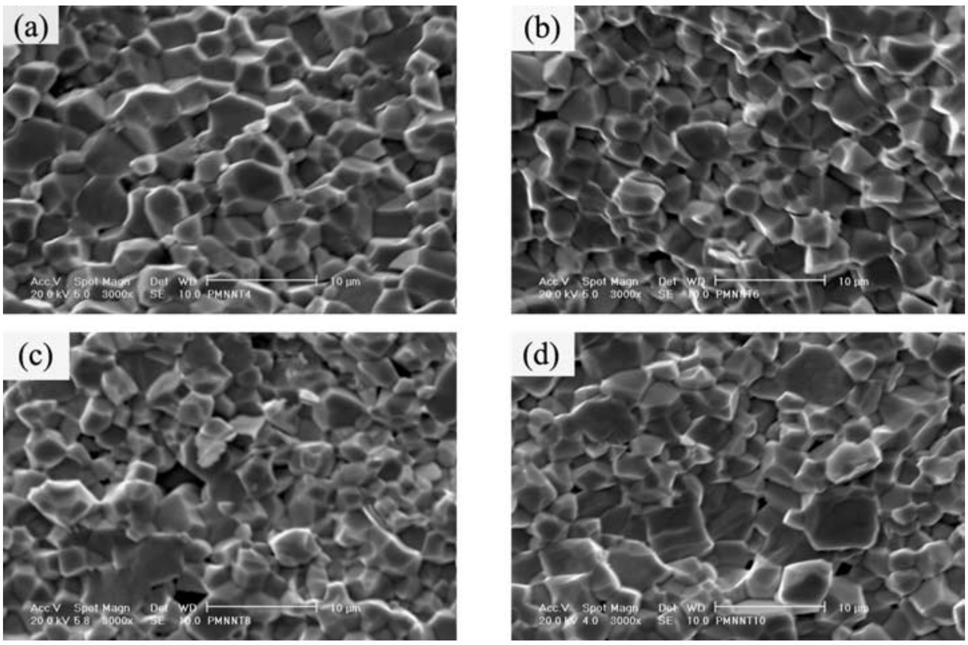

Fig. 2. Morphology of fractured surfaces of different samples. (a) PMNNT4, (b) PMNNT6, (c) PMNNT8 and (d) PMNNT10.

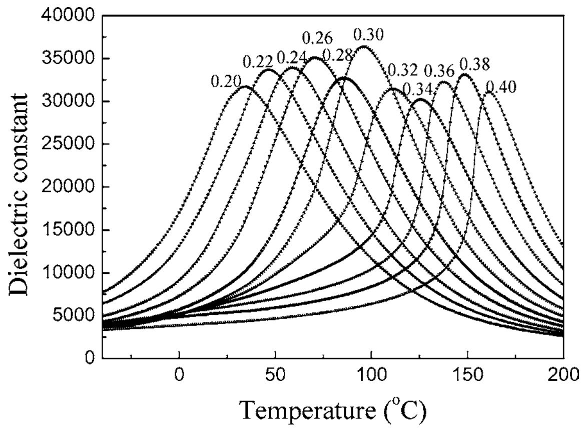

Fig. 3. Temperature dependence of dielectric constants for the unpoled PMNN-PT ceramics at 1 kHz.

were plotted as function of $T - T_m$ (see Fig. 4(a)). The dependence of normalized dielectric constant versus $(T - T_m)$ for the eleven PMNN-PT samples was compared with the Curie-Weiss law. In the side of $T - T_m > 0$, it reveals to gradually approach the Curie-Weiss law with the PT content increasing (see Fig. 4(b)), indicating that the PMNN-PT ceramics continuously transform from relaxor to normal ferroelectric behavior with PT content increasing.

When the poled ceramics were surveyed for dielectric behaviour, it is interesting to find from Fig. 5 that PMNNT4 and PMNNT5 reveal an obvious frequency dispersion behavior when the temperature is higher than 30°C and 40°C respectively. It means there is a "macro to micro domain" transition occurred, which is similar to a previous report about poled lead lanthanum zirconate titanate (PLZT) [7] and a recent report in poled PMN-PT single crystal [8]. It is well known that the polar nanometric regions (micro domains) with short range ordering (SRO) exist in relaxor ferroelectrics. But it has been verified that a macrodomain state with long range ordering (LRO) can be metastably locked in by poling field [9]. And it is believed that upon thermal cycling, if the temperature is high enough to destroy the metastable LRO state, the microdomains will be recovered again. The nonexistence of the "macro to micro domain" transition in PMNNT1–PMNNT3 probably demonstrates that the external electric field was not as strong as to transform the SRO state of microdomain for these relaxor ferroelectrics with lower content of PT.

While in samples PMNNT6–PMNNT8, a small peak-shoulder appeared at about 60°C. This dielectric

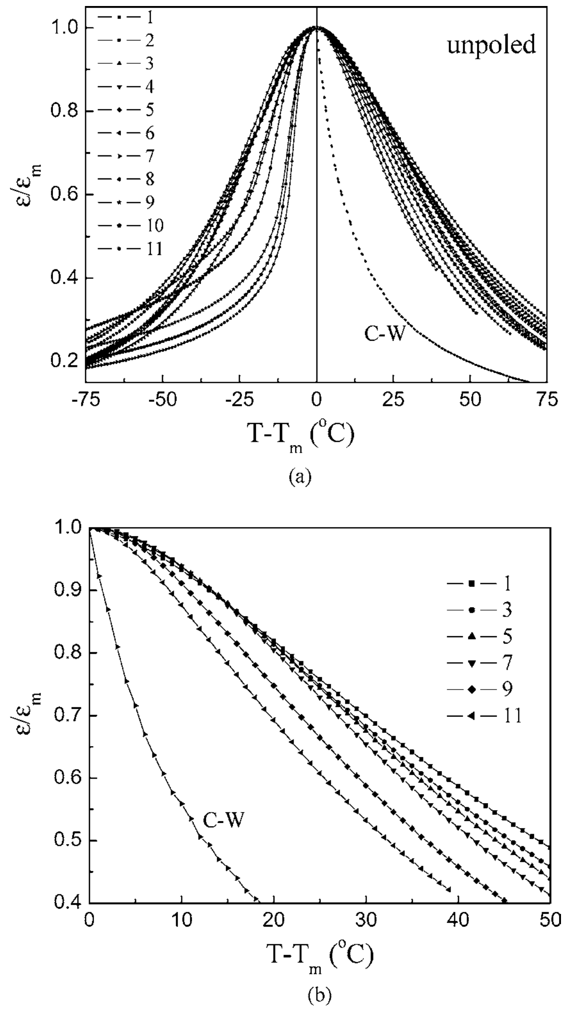

Fig. 4. (a) Normalized real part of dielectric constant as function of $T - T_m$ for PMNN-PT ceramics. (b) Amplified part in the range of $T - T_m > 0$ for Fig. 4(a).

anomaly lies also in the MPB region and probably is associated with depolarization. It is recently reported that a "electric field induced phase transition" can occur in this two-phase zone composition [10], and a model to explain the essential of the MPB was proposed as well [11]. It is suggested that in a very limited region the free energy for both pseudocubic and tetragonal phase is almost equal, consequently both the two phases could coexist in this limited region and their sensitive lattice symmetry is easily affected by external influence [12, 13]. An external electric field can promote a phase transition from pseudocubic to tetragonal phase, or perhaps to an orthorhombic symmetry

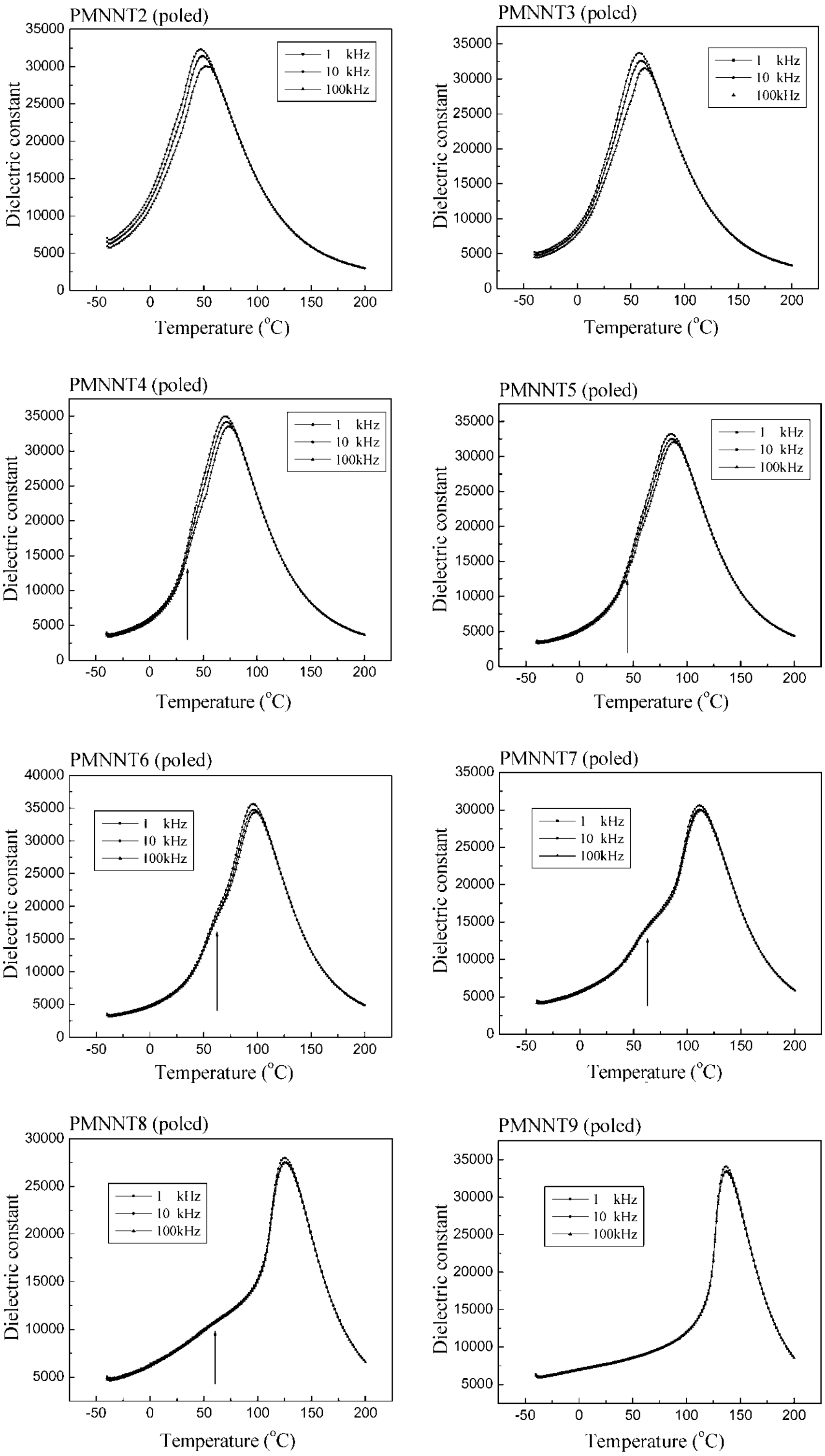

Fig. 5. Temperature and frequency dependence of dielectric constant for PMNN-PT ceramics (poled under 20 kV/cm for 30 min at room temperature).

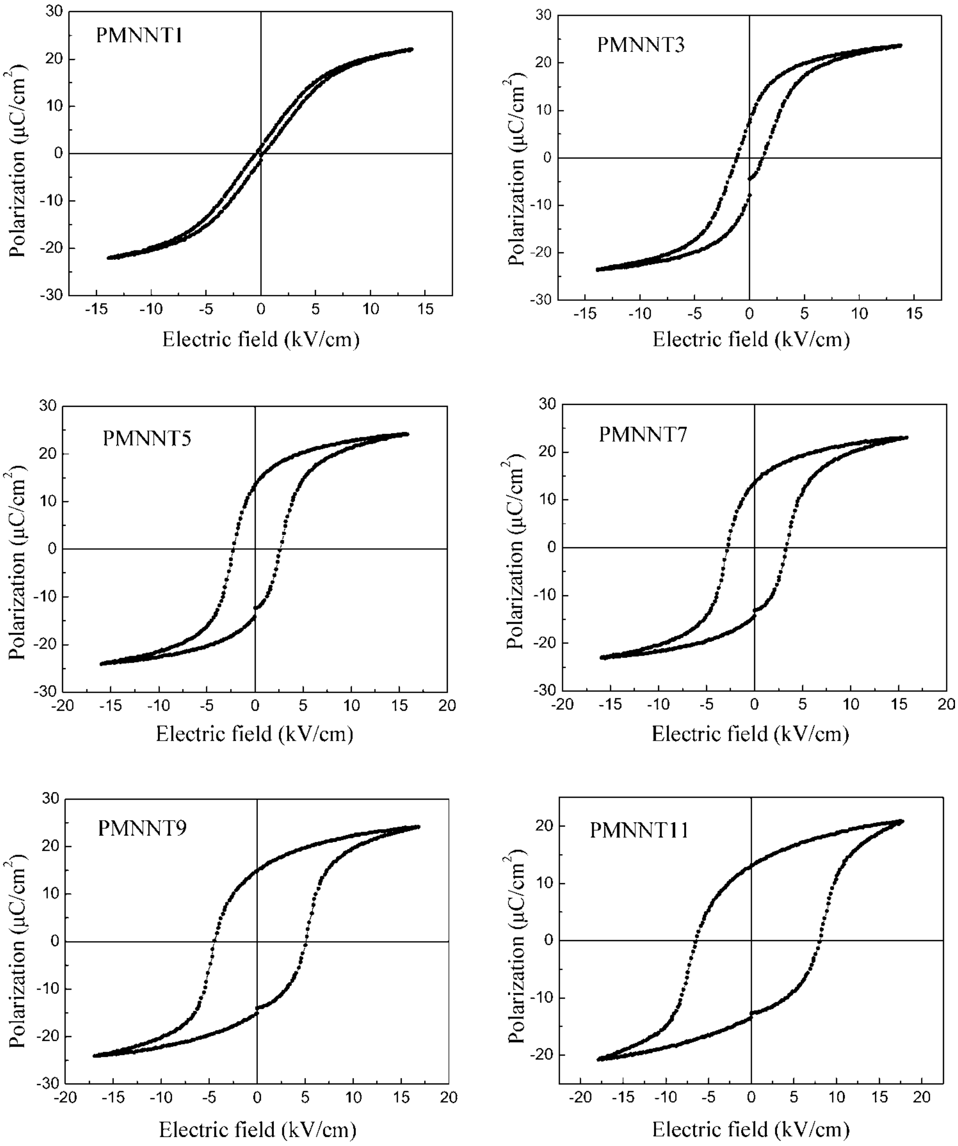

Fig. 6. Polarization hysteresis loops of PMNN-PT ceramics.

[14], and then the field-induced phase was destroyed by temperature increasing. The absence of the small peak-shoulder in PMNNT9 may be due to the relatively little amount of the pseudocubic phase (about 23%), so the field-induced phase transition is feeble and PMNNT9 was hardly affected by external electric field. When PMNNT-PT system enters the pure tetragonal symmetry zone, the dielectric anomaly definitely does not occur. It seems that the exact mechanism of this phenomenon is not yet established in detail and more research is required.

3.3. Ferroelectric and Piezoelectric Properties of the PMNN-PT System

The P-E hysteresis loops for the samples with different PT content are shown in Fig. 6, and the dependences of coercive field and remnant polarization for all of the eleven samples with PT content increasing are also depicted in Fig. 7. It was found that the enhancement of the coercive field in the relaxor phase region (PMNNT1–PMNNT6) is relatively slow, compared with that in samples PMNNT7–PMNNT11. The

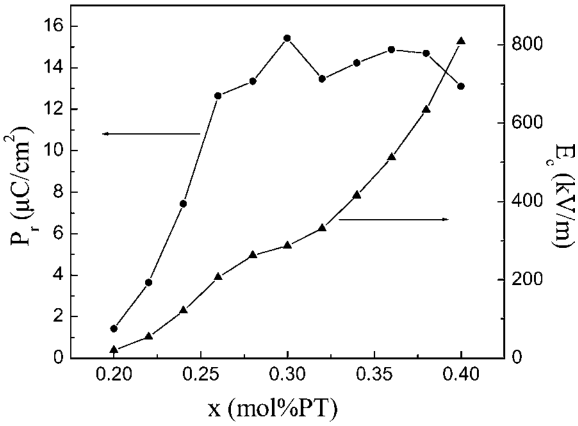

Fig. 7. Dependence of P_r and E_c with PT content for $(1-x)$PMNN-xPT ceramics ($x = 0.20$–0.40).

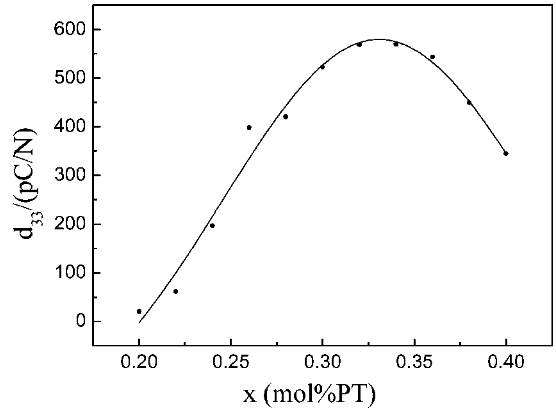

Fig. 8. Dependence of d_{33} with PT content for $(1-x)$PMNN-xPT ceramics ($x = 0.20$–0.40).

phenomenon can be interpreted in terms of polarization mechanism. Since the samples PMNNT1–PMNNT6 are mainly pseudocubic phase with relaxor behavior, the reorientation of microdomains can not contribute much to E_c during the polarization, and their lower coercive fields may be attributed to electrostriction, induced mainly by dipolar and ionic polarization [15]. Whereas in PMNNT7–PMNNT11 samples, the content of tetragonal phase increases with addition of PT, which results in a decreasing contribution from electrostriction, and the 90° domain reorientation gradually exerts the primary influence during polarization. The remnant polarization reach maximum at $x = 0.30$, this composition lying the region of the MPB.

As shown in Fig. 8, the piezoelectric d_{33} constant is also quite high near the MPB, and it reaches maximum at the composition of $x = 0.32$–0.34.

4. Summary

$(1 - x)$PMNN-xPT($x = 0.20$–0.40) relaxor ferroelectrics were synthesized by two-step method and investigated in this study. A morphotropic phase boundary with both pseudocubic and tetragonal phase coexisting has been identified to lie in the composition range of $x = 0.30$–0.36. High dielectric constant occurs near the MPB, and the ferroelectric and piezoelectric properties also reach maximum in the region of the MPB. The dielectric anomaly for poled samples has been detected and may be associated with the "macro to micro domain" transition and depolarization.

Acknowledgments

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