

Double hysteresis loops induced by Mn doping in $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{O}_3$ ferroelectric ceramics

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ABSTRACT

$\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{O}_3$ (PNZT95/5) ceramics with 1 mol% and without Mn doping were prepared via conventional solid state reaction process. X-ray diffraction patterns show that the PNZT95/5 and Mn-doped PNZT95/5 (PNZTM95/5) ceramics, with composition near the boundary of the ferroelectric phase (FE)/antiferroelectric phase (AFE), have a rhombohedral perovskite structure. The ferroelectric behavior of PNZT95/5 ceramics is strongly affected by Mn doping. Without any aging process the PNZTM95/5 ceramics possess double hysteresis loops (P - E loops), whereas the PNZT95/5 ceramics possess normal single hysteresis loops. Due to the defect dipoles formed by effectively negatively charged Mn^{3+} dopants and positively charged O^{2-} vacancies, the PNZTM95/5 ceramics exhibit the double P - E loops. The defect dipole effect has been proved by investigating the P - E loops under different external fields. As a result, the PNZTM95/5 ceramics become “hardened”, exhibiting a high mechanical quality factor (1300).

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1. Introduction

Double hysteresis loops (P - E loops) are an exceptional phenomenon in ferroelectrics (FE), which are often observed in antiferroelectric (AFE) materials such as the Zr-rich $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) ceramics because of the neighboring lines polarized in antiparallel directions [1–5]. In the Zr-rich family, $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ (PZT95/5) near the boundary of FE/AFE is of technological importance due to its wide applications in micro-electromechanical systems and energy storage devices [1–4]. Then, a particularly interesting member in the PZT95/5 family is the $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{O}_3$ (PNZT95/5). A small amount of Nb substitution can stabilize the FE phase and reduce the dielectric losses [2]. And it is also a mature material for studying the FE/AFE phase transition. As a matter of fact, in the acceptor doped ferroelectric materials (mainly in BaTiO_3) double hysteresis loops can also be observed [6–11]. Based on the symmetry-conforming principle of point defects, the domain stabilization is a volume effect in the ferroelectrics [12]. This theory could well explain the differences of the P - E loops between the acceptor doped ferroelectric and the normal ferroelectric [5,12,13]. Ren et al. has suggested that in the acceptor element

Mn doped BaTiO_3 , the defect ions Mn^{3+} and the O^{2-} vacancies form defect dipoles to pin the migration of ferroelectric dipoles and induce double hysteresis loops [6,12]. Although the defect dipoles induced double loops are often observed in the conventional ferroelectrics like BaTiO_3 , there is little work about similar characteristics in the PZT family, especially near the FE/AFE boundary. In this work, we report the observation of double loop phenomenon in 1 mol% Mn-doped PNZT95/5 (denoted as PNZTM95/5) ceramics and the resulting effects on the electromechanical and dielectric properties of the ceramics.

2. Experimental procedure

The PNZT95/5 and PNZTM95/5 ceramics, respectively, were synthesized by a solid-state reaction process using metal oxides or carbonate powders: PbO (99%), ZrO_2 (99%), Nb_2O_5 (99.5%), TiO_2 (99%), and MnCO_3 (98%). Raw materials with the proper ratio were mixed by ball milling in ethanol with zirconium media for 24 h, and then calcined at 850 °C in air for 3 h to synthesize the powders. With a little organic binder polyvinyl alcohol (PVA), the powder was pressed into pellets with 1 mm in thickness and 10 mm in diameter under 20 MPa. The compacts were sintered at 1250–1300 °C for 2 h in the PbO atmosphere. Silver paste was sintered on both sides of the samples at 700 °C for 10 min to form the electrodes for electrical measurements.

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X-ray diffraction (XRD) analysis was examined using Philips X'Pert Pro X-ray diffractometer with Cu K_{α} radiation. The polarization versus electric field (P - E) hysteresis loops of the ceramics were measured using a Radiant Precision Workstation (USA). The ceramic samples were poled in a 120 °C silicon oil bath by applying the direct current (dc) electric field of 60 kV/cm for 1 h. The piezoelectric properties, such as electromechanical coupling factor (k_p) and mechanical quality factor (Q_m), and dielectric properties, such as dielectric permittivity (ϵ_r), of the ceramics were measured with an Agilent 4294A Precision Impedance Analyzer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the PNZT95/5 and PNZTM95/5 ceramics, respectively. Both ceramics exhibit rhombohedral perovskite structure, and the lattice parameters are shown in Table 1. A small change in their lattice parameters is found; the lattice volume of PNZTM95/5 is smaller than that of PNZT95/5. It suggests that Mn has diffused into the PNZT95/5 lattice. From the enlarged XRD patterns of the ceramics in the 2θ range of 37.5–38.5°, 53.5–55.5°, and 62.5–64.5°, there are two splitting peaks in the PNZT95/5 ceramics. However, the two splitting peaks are incorporated in the PNZTM95/5 ceramics. Being very near to the FE/AFE phase boundary, PNZT95/5 has been known to be in the ferroelectric phase at room temperature [5]. It is reasonable to speculate that the PNZT95/5 and PNZTM95/5 ceramics belong to the ferroelectric phase at room temperature.

Fig. 2 shows the P - E loops of the PNZT95/5 and PNZTM95/5 ceramics, measured at 10 Hz and room temperature. The two P - E loops are obviously different, as shown in the figure. The PNZT95/5 ceramics possess a relatively large P_r (31 $\mu\text{C}/\text{cm}^2$) and low coercive field E_c (10.4 kV/cm), and show a normal single loop. Coherent with the XRD patterns, the single loop of PNZT95/5 provides an additional evidence for the conclusion that PNZT95/5 belongs to ferroelectric phase. However, the P - E loop of PNZTM95/5 shows a double loop character. The P_r (2.48 $\mu\text{C}/\text{cm}^2$) of the PNZTM95/5 is relatively lower. As mentioned above, the double hysteresis loop of PNZTM95/5 can not be interpreted by the antiferroelectric mechanism; the second possible reason is the acceptor doping induced defect dipoles in ferroelectrics [8]. In fact, recent electron paramagnetic resonance measurements revealed that even with Nb doping, Mn^{2+} and Mn^{4+} exist at very low concentration, thus Mn^{3+} predominates [14]. Similar to the Mn-doped BaTiO_3 ceramics, it is obvious that the electrovalence of the Mn^{3+} dopant ions is lower than that of the B-site ions Zr/ Ti^{4+} . The non-centric distribution of dopant ions form defect dipoles (effectively positively charged O^{2-} vacancies and negatively charged dopant ions, Mn^{3+} substituted for Zr/ Ti^{4+}), and based on the symmetry-conforming principle of point defects, defect dipoles tend to align along the spontaneous polarization direction [6]. Because of the low migration rate of defects, the defect dipoles remain in the original orientation during the P - E loop measurement, which provides a restoring force to reverse the switched polarization and, thus, induces the constricted loops [6,7,11,12].

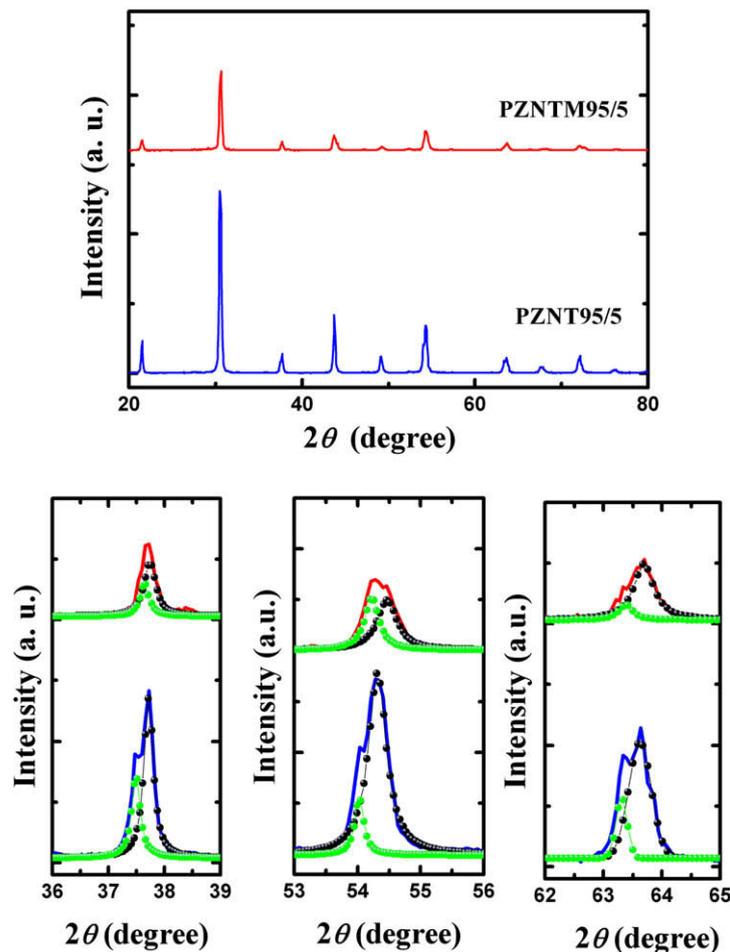


Fig. 1. RD patterns of PNZT95/5 and PNZTM95/5 ceramics, and the corresponding expanded XRD patterns in the 2θ range of 36–39°, 53–56°, and 62–65°.

Table 1
Piezoelectric and dielectric coefficients and lattice parameters of PNZT95/5 and PNZTM95/5 ceramics.

	Piezoelectric constant (d_{33} : pC/N)	Mechanical quality factor (Q_m)	Relative permittivity (ϵ_r)	a (nm)	b (nm)	c (nm)
PNZT95/5	60	354	400	0.42696	0.46474	0.44852
PNZTM95/5	55	1300	209	0.42615	0.46423	0.44961

To provide additional evidence for the point-defect-mediated reversible domain switching effect, the evolution of P - E loops under different external fields has been determined. Fig. 3 shows the variation in the P - E loops of PNZTM95/5 with the measurement frequency. As presented above, the PNZTM95/5 ceramic exhibits double-like loops at 10 Hz. However, with the frequency decreasing, the constricted loops become “fat” gradually at $E = 0$ kV/cm. The same phenomenon can be observed as the measuring temperature is increased. The P - E loops measured at 10 Hz and different temperatures are shown in Fig. 4. With the temperature increasing, the constricted double loops gradually open and fully open at 120 °C. In order to know the influence of bias electric field on the defect dipoles, the P_r/P_s ratio is calculated as a function of the applied electric field and shown in Fig. 5. As shown in Fig. 5, the P_r/P_s ratio increases with increasing the bias electric field and the P - E loops exhibit the normal single loop behavior under high bias electric fields; however, the P_r (17.6 $\mu\text{C}/\text{cm}^2$) is still lower than that obtained in the PNZT95/5 ceramics (31 $\mu\text{C}/\text{cm}^2$).

These experimental results reveal that the migrating behaviors of defect dipoles can be strongly affected by external fields. In the high-frequency P - E loop measurements, the polarization is switched abruptly by the bias electric field. Probably due to the insufficient time for the defect dipoles to migrate, they remain in their original orientation, thereby providing a restoring force to reverse the switched polarization upon removal of the external electric field. Therefore, the P - E loops show a double loop response. On the contrary, at low frequencies, the defect dipoles may have enough time to migrate. Accordingly, the defect dipoles rotate with the polarization (but probably at a lower rate), the restoring force decreases, and the reversal degree of the switched polarization can be lowered as compared with the high-frequency measurements [11]. Therefore, the double-like P - E loops have been gradually transformed to the normal single loops with decreasing the frequency. On the other hand, the high external fields (including temperature and bias electric field) can stimulate the switching process of defect dipoles, following the ferroelectric polarization. As a result, even at high frequencies (e.g. 10 Hz), the defect dipoles can respond to the bias electric field in a very short time, and the restoring force cannot be reached to reverse the switched polariza-

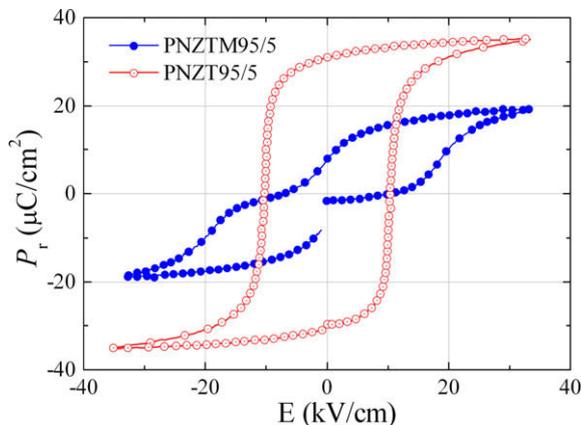


Fig. 2. P - E loops of PNZT95/5 and PNZTM95/5, respectively, measured at a frequency of 10 Hz and at room temperature.

tion completely. Therefore, the P - E loops also exhibit the single loop character under relatively strong external fields, i.e., relatively high temperature and large bias electric field. Nonetheless, because the reversal of the switched polarization induced by defect dipoles cannot be absolutely avoided, the P_r is still comparatively lower.

Unlike BaTiO₃, the double loops can be detected in “unaged” PNZTM95/5. This is probably attributed to their different phase transition temperatures. It is well known that the FE-PE (paraelectric) transition temperature of BaTiO₃ is about only 128 °C [7]. In the symmetry-conforming principle of point defects, the defect symmetry should follow the crystal symmetry. The low phase transition temperature in BaTiO₃, however, makes the ferroelectric phase not stable. The distribution of the charged defects remains in the cubic symmetry even though the crystal has transformed

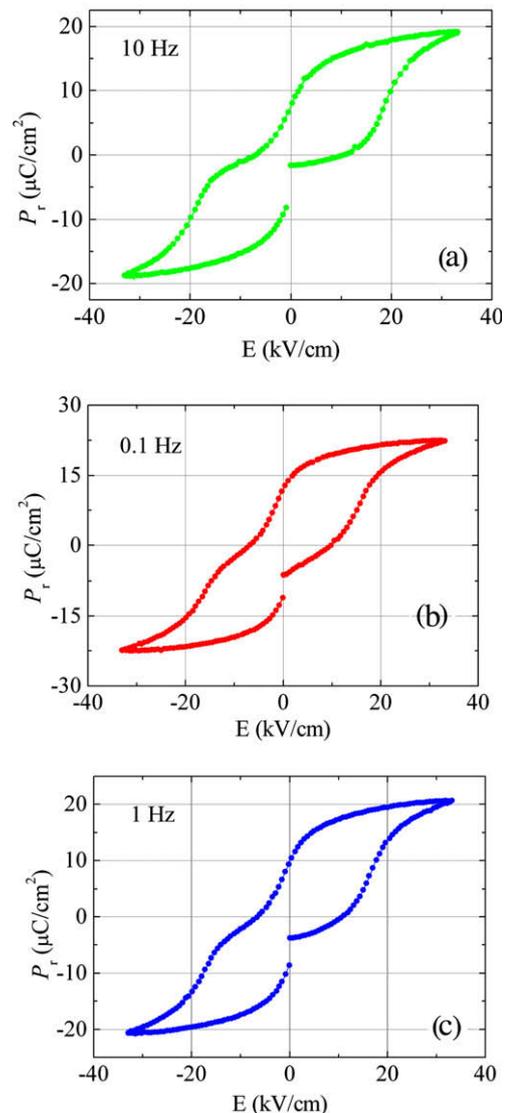


Fig. 3. P - E loops of PNZTM95/5 at (a) 10, (b) 1 and (c) 0.1 Hz, all of which were measured at room temperature.

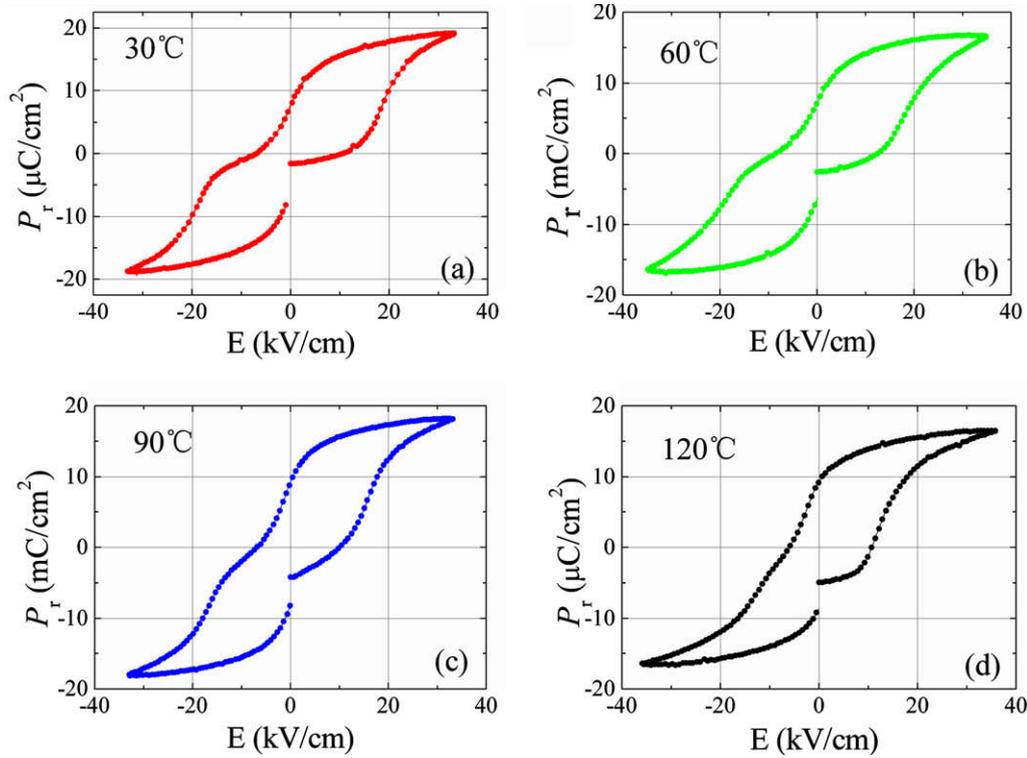


Fig. 4. P - E loops at 10 Hz for PNZTM95/5, measured at (a) 30 °C, (b) 60 °C, (c) 90 °C, and (d) 120 °C.

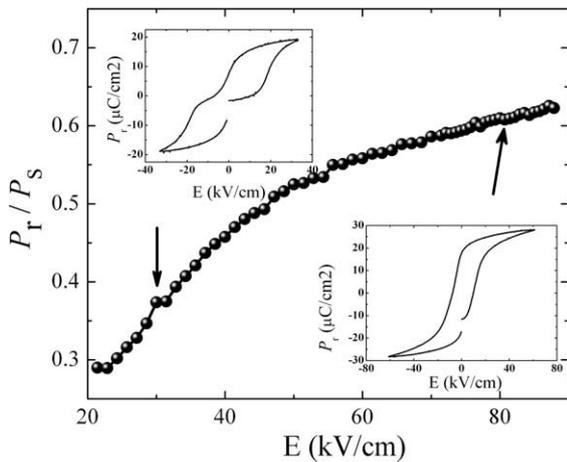


Fig. 5. P_r/P_s ratio as a function of the applied electric field for PNZTM95/5, measured at room temperature and at 10 Hz. The two insets show P - E loops, respectively, under low and high bias electric fields, displaying different characters.

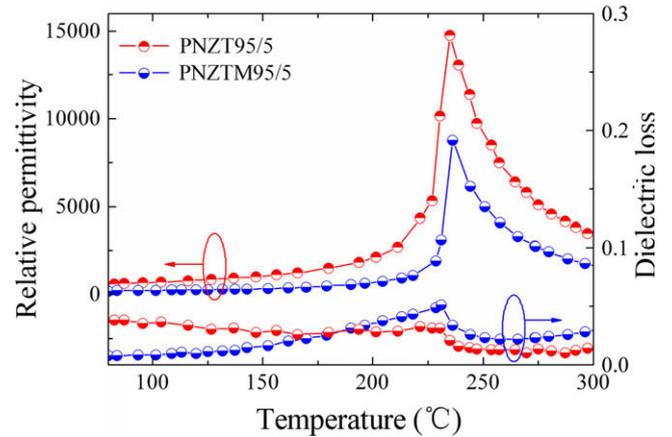


Fig. 6. Relative dielectric permittivity (ϵ_r) and dielectric loss ($\tan\delta$) of PNZTM95/5 over the temperature range of 80–300 °C.

to a tetragonal symmetry. It takes some time (called aging) for the defect symmetry to correct into a polar tetragonal symmetry [12]. Fig. 6 shows the relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) at 10 kHz as a function of the temperature in the range of 80–300 °C. It can be seen that the PNZTM95/5 undergoes the FE–PE transition at about 260 °C. In this case, the large temperature interval between the relatively high transition temperature and room temperature makes a sufficient migration of ions/vacancies possible during the slow cooling process for preparation of the ceramic samples, which enables the defect symmetry to follow the rhombohedral crystal symmetry. Accordingly, aging is not required for the PNZTM95/5 ceramics.

It should be pointed out that an extraordinarily high mechanical quality factor ($Q_m = 1300$) is obtained in the PNZTM95/5 ceramics,

as presented in Table 1, which is far larger than that of the PNZT95/5 ($Q_m = 354$). It was measured after poling with applying a direct current electric field (60 kV/cm) for 1 h at 120 °C. The dc poling at 120 °C ensures that the defect dipoles have been migrated and formed along the direction of the aligned polarization after poling. Similar to the polarization switching process, the defect dipoles provide restoring forces to the deformed polarization during the piezoelectric activities and the local domain–wall motion can also be restricted by such a volume effect [11,12]; hence, the loss of energy for hard migrating dipoles in the alternating current field is very low, and the Q_m reaches as high as 1300. Meanwhile, a low piezoelectric constant ($d_{33} = 55$ pC/N) and a low relative permittivity ($\epsilon_r = 209$) can also be detected for PNZTM95/5. Consequently,

compared to PNZT95/5, the PNZTM95/5 ceramics become “hardened”.

4. Conclusions

Double P - E loops have been observed in 1 mol% Mn-doped $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{O}_3$ (PNZTM95/5) ceramics. From the comparison of XRD results between PNZT95/5 and PNZTM95/5, it is confirmed that the PNZTM95/5 ceramics belong to a rhombohedral structure. Due to the defect symmetry-conforming property, the effectively negatively charged acceptor dopant ions Mn^{3+} and positively charged O^{2-} vacancies form defect dipoles along the polarization direction, providing a restoring force to reverse the switched polarization and thus inducing a double-like loop behavior. This unusual behavior induced by defect dipoles can be strongly affected by applying external fields, such as a high temperature and a high bias electric field. The defect dipoles also provide a similar volume “pinning” effect in the normal piezoelectric activities. As a result, the PNZTM95/5 ceramics exhibit “hardened” characteristics, and Q_m reaches as high as 1300.

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