Study of the electrical properties of $Pb(Zn,Ni)_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ ceramics across the morphotropic phase boundary

Jing-Song Pan · Xiao-Wen Zhang · Ke-Pi Chen

Abstract Structure and electrical properties of $(1-x)Pb$ $(Zn_{0.2}Ni_{0.8})_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ ceramics with $x=0.24$–0.38 were examined in detail. X-ray diffraction measurements reveal that all samples are in pure perovskite phase, and most of them lie within the morphotropic phase boundary (MPB) region. The dielectric behaviors of all compositions are characterized with diffuse phase transition and frequency dispersion. The variable power law and the Vogel–Fulcher relation have been used to describe such dielectric behaviors. The highest dielectric constant and the largest piezoelectric coefficient are simultaneously observed when $x=0.30$. The variation of the ferroelectric property with PT content is also discussed.

Keywords Morphotropic phase boundary · Perovskite phase · Electrical properties · Relaxor ferroelectrics

1 Introduction

The morphotropic phase boundary (MPB) of solid solutions between $Pb(B'B'')O_3$-type relaxors and $PbTiO_3$ (PT)

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becomes a popular research subject in recent years. It has been found that many binary systems such as $Pb(Mg_{1/3}Nb_{2/3})$ O_3–$PbTiO_3$ (PMN–PT), $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PNN–PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) exhibit anomalous electrical properties near the MPB [1, 2]. Hence this kind of materials attracts much attention for their potential applications in electronics and microelectronics.

So far, the study on the MPB of the PZN–PNN–PT system has seldom been reported. In this work, the structure and electrical properties of $(1-x)Pb(Zn_{0.2}Ni_{0.8})_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ (PZNN–PT with Zn/Ni=1:4) ceramics with the composition range of $x=0.24$–0.38 were investigated. The results indicate that most of the selected compositions are within the MPB region. In addition, excellent electrical properties have been revealed in this ternary system near the MPB.

2 Experimental procedure

The selected compositions in this study are $(1-x)$PZNN–xPT with x changing as 0.24, 0.26, 0.28, 0.30, 0.32, 0.34, 0.36 and 0.38. Ceramic pellets of such compositions were prepared using the columbite precursor method as Swartz and Shrout described [3]. XRD experiments were performed on a Rigaku D/max–3B diffractometer using Cu Kα radiation, 35 kV, 30 mA. Dielectric constant with respect to temperature at different frequencies was measured on heating using a HP4192A Precision LCR meter connected to a computer for automatic measurement. The P–E hysteresis loops were measured by RT6000HVS (Radiant Technologies). The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, ZJ-2).
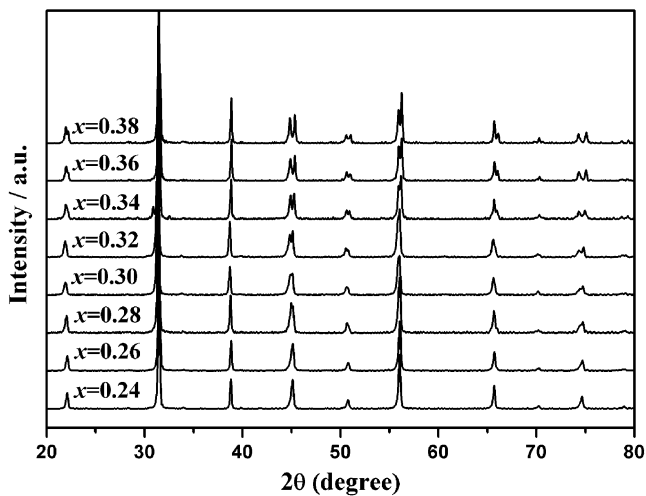
Fig. 1 X-ray diffraction patterns of $(1-x)$PZNN–xPT ceramics

3 Results and discussion

3.1 The structure of $(1-x)$PZNN–xPT ceramics

Figure 1 shows the XRD profiles for all samples. It is observed that all the selected compositions are in the pure perovskite structure. Although phase-pure perovskite PZN ceramic is accepted to be thermodynamically unstable over a wide range of temperature and is easy to yield pyrochlore phase and PbO as the decomposition products [4], it is confirmed from Fig. 1 that introducing a little amount of PZN into PNN-PT will not change the perovskite structure of the system.
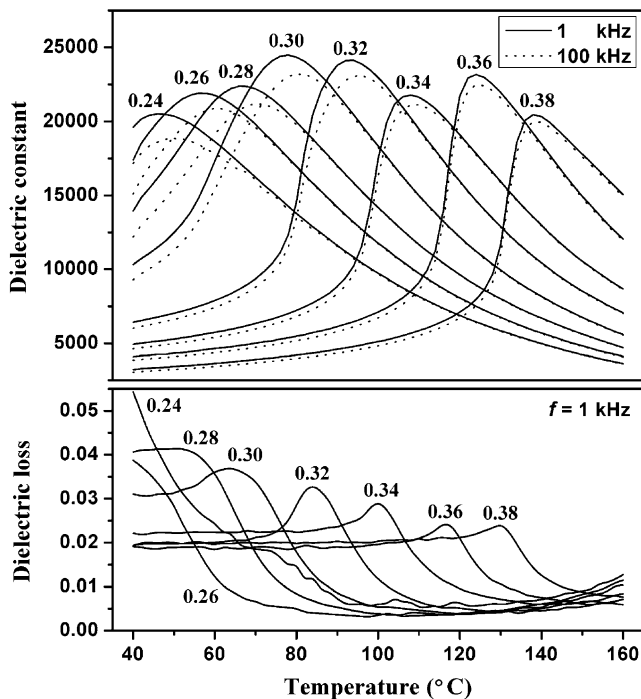

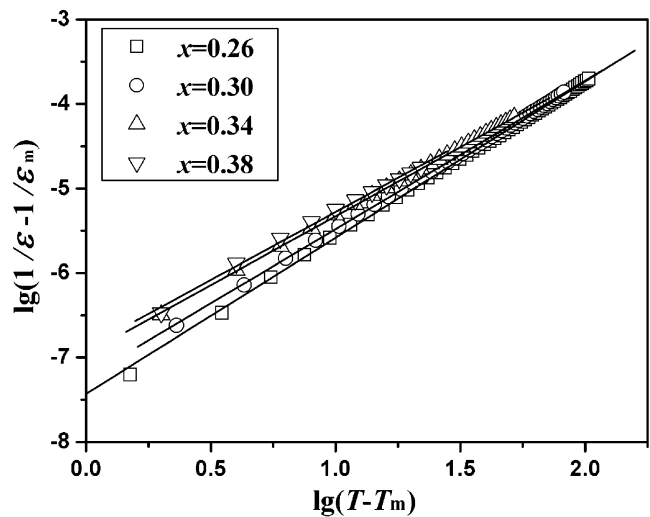**Fig. 2** Temperature dependencies of dielectric constant and dielectric loss for $(1-x)$PZNN–xPT ceramics

Fig. 3 Dependence of $\lg(1/\varepsilon - 1/\varepsilon_{\mathrm{m}})$ with $\lg(T-T_{\mathrm{m}})$ at 1 kHz for some $(1-x)$PZNN–xPT ceramics. *Symbols* are the experimental data and the *solid lines* are the results of the linear fits

It is also shown that the XRD profiles of {200}, which are around $2\theta=45°$, change from a single peak to two peaks with the increasing of PT content. This indicates that a phase transition from the pseudocubic symmetry to the tetragonal symmetry occurs. As the composition with $x=0.24$ shows a narrow single peak of {200}, we deduce that it is in the pure pseudocubic phase. Although compositions with $x=0.26$–0.30 also show no peak splitting, their {200} reflection lines become broadened, indicating that such compositions must lie within the MPB region. The peak splitting appears to be distinct when x increases to 0.32. However, even the composition with $x=0.38$ does not enter the pure tetragonal symmetry zone because the intensity heights of the split peaks, (002) and (200), are almost equal, suggesting that it is still within the MPB region.
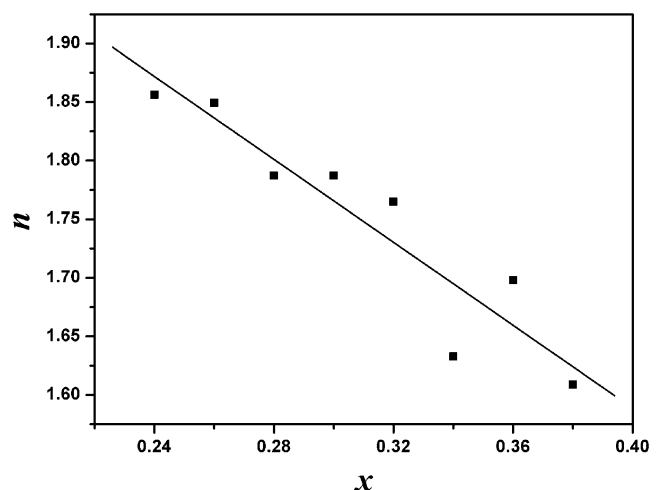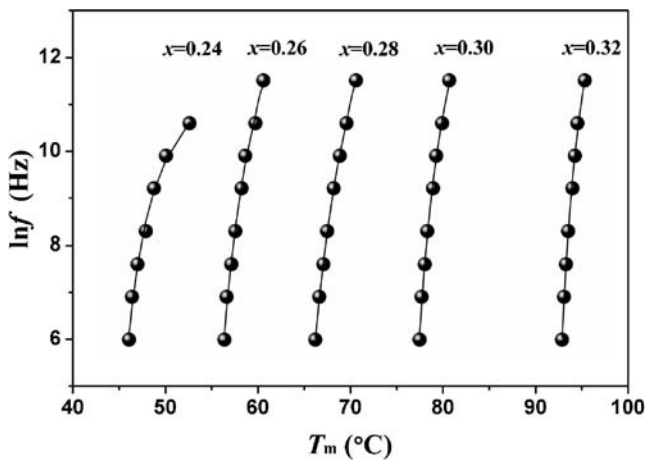

Fig. 4 Dependence of n value on PT content for $(1-x)$PZNN–xPT ceramics

Fig. 5 Plot of ln$f$ as a function of T_m for some $(1-x)$PZNN–xPT ceramics. (The *symbols*: experimental data; the *solid curve*: fitting to the Vogel–Fulcher relation.)

3.2 Electrical properties of $(1-x)$PZNN–xPT ceramics

The temperature dependencies of the dielectric constant and the dielectric loss for all samples are shown in Fig. 2. It is found that the Curie temperature increases with the increasing of PT content. All peak dielectric constants at 1 kHz are found larger than 20000 and the highest one (>24000) is obtained when PT content is 0.30, indicating that the dielectric properties of this ternary system are excellent near the MPB.

Differing from normal ferroelectrics with a sharp phase transition, all the compositions in our study reveal dielectric relaxation behaviors around their respective Curie temperatures. To estimate the degree of the diffuseness phase transition (DPT), here the variable power law developed by Uchino et al. [5] is adopted. That is, when T is above the peak temperature T_m, the dielectric constant ε can be expressed as:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^n}{C} \tag{1}$$

where ε_m is the peak dielectric constant, n and C are both material constants depending on the composition of the samples. It is known that Eq. (1) corresponds to perfect relaxor ferroelectrics when $n=2$, while $n=1$ is equal to Curie–Weiss equation which well describes the dielectric

**Table 1** Best fitting parameters to the Vogel–Fulcher relations.

Sample	lnf_0 (Hz)	E_0 (K)	T_f (K)
x=0.24	12.94	22.88	315.88
x=0.26	17.38	53.71	324.76
x=0.28	19.27	83.40	333.06
x=0.30	18.29	50.02	346.49
x=0.32	17.85	33.21	363.21
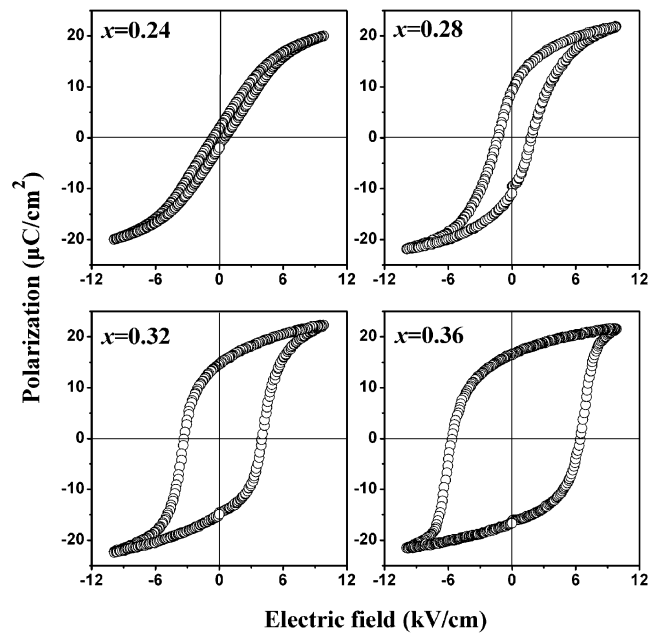
Fig. 6 Polarization hysteresis loops of some $(1-x)$PZNN–xPT ceramics

behavior of normal ferroelectrics above T_m. Therefore, n represents the degree of relaxor behavior. Figure 3 shows the plot of lg($1/\varepsilon - 1/\varepsilon_m$) versus lg($T - T_m$) for compositions with x=0.26, 0.30, 0.34 and 0.38 at 1 kHz. According to Eq. (1), the values of n can be calculated from the slopes after linear fitting. Figure 4 shows the almost linear decreasing of n with PT content, suggesting that the relaxor behaviors of all samples are gradually weakened across the MPB with the increasing of PT content.

It also can be observed from Fig. 2 that T_m strongly depends on frequency f for compositions with $x \leq 0.32$. The frequency dispersions (FD), $\Delta T_m = T_m$ (100 kHz)$-T_m$ (1 kHz), for such compositions are larger than 2 K. However, the value of ΔT_m decreases to below 1 K when x increases to 0.34, suggesting that the addition of PT can
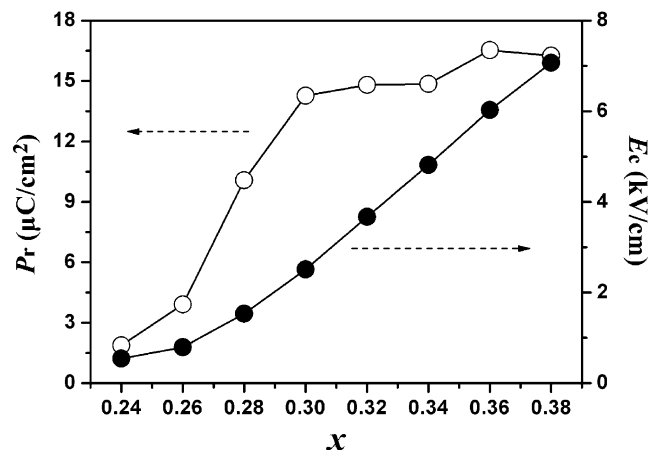
Fig. 7 Dependence of P_r and E_c with PT content for $(1-x)$PZNN–xPT ceramics

suppress the FD behavior of PZNN-PT ceramics. The dependence of T_m on $\ln f$ for $x \leq 0.32$ is plotted in Fig. 5. In order to analyze their relaxation features, all the data in Fig. 5 were fitted using the empirical Vogel–Fulcher relation [6]

$$f = f_0 \exp\left(\frac{-E_0}{T_m - T_f}\right) \qquad (2)$$

where f_0 is the testing frequency, E_0 is the activation energy and T_f the freezing temperature. The best fitting parameters are listed in Table 1. It should be noted that the values of E_0 in our study are obviously smaller than those of some reported systems [6, 7]. This can be attributed to the degraded random electric field in this ternary system near the MPB that forms a lower potential barrier and makes the reversal of the polar domains easier.

Figure 6 shows the P–E hysteresis loops at room temperature with the driving electric field at 10 kV/cm for compositions with $x=0.24$, 0.28, 0.32 and 0.36. The dependences of coercive field (E_c) and remnant polarization (P_r) with PT content for all samples are illustrated in Fig. 7. In the range of $x \leq 0.26$, it is found from Fig. 7 that not only the value of E_c itself is small, but also the enhancement of E_c is slow because it is only the existence of electrostriction, induced mostly by dipolar and ionic polarization [8], that contributes much to E_c of compositions mainly in the pseudocubic phase during polarization. However, as the content of tetragonal phase increases rapidly with the addition of PT for compositions within the MPB region, the 90° domain reorientation, which is by far slower than electrostriction in keeping up with the alternation of external electric field, gradually exerts the primary influence during polarization, resulting in the rapid linear increase of E_c in the range of $x=0.28$–0.38 compared with that of $x \leq 0.26$.

The piezoelectric properties of all samples were also investigated. It is found that the compositions with $x=0.24$ and 0.26 have low d_{33} values (<60 pC/N) while other compositions have by far higher ones (>350 pC/N). The composition with $x=0.30$ has the largest value of d_{33} (~730 pC/N), superior to many reported relaxor-PT systems.

4 Summary

(1−x)PZNN–xPT ceramics with $x=0.24$–0.38 were synthesized by the columbite precursor method and investigated in this study. Most of the samples are found lying within the MPB region with excellent electrical properties. Their DPT and FD behaviors have also been discussed. The composition with $x=0.30$ has the highest values of ε_m (>24000) and d_{33} (~730 pC/N), superior to many reported relaxor-PT systems.

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