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The influence of the morphotropic phase boundary on the dielectric and piezoelectric properties of the PNN–PZ–PT ternary system

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The influence of the morphotropic phase boundary (MPB) on the dielectric and piezoelectric properties of $PbNi_{1/3}Nb_{2/3}O_3$–$PbZrO_3$–$PbTiO_3$ (PNN–PZ–PT) ternary system were systematically investigated. The results showed that the piezoelectric constant d_{31} and plane coupling factor k_p reached a maximum in the vicinity of morphotropic phase boundary. The highest value of the piezoelectric constant d_{31} was 260×10^{-12} C/N. The Curie temperature T_c decreased rapidly with increasing content of PNN. The lattice parameters a increased and c decreased with increasing PNN content and the Zr/Zr + Ti ratio as a result of the crystal structural transformation from tetragonal to rhombohedral phases.

1. Introduction

In recent years, electromechanical devices utilizing piezoelectric effects have found many applications in displacement transducers, precision micropositioners and actuators [1]. In order to further improve the dielectric and piezoelectric properties of lead zirconate titanate (PZT), much attention has been focused on the pseudoternary solid solution compounds with perovskite structure containing PZT. Since the lattice parameters of $PbA_{1/3}B_{2/3}O_3$-type compounds (e.g. $PbNi_{1/3}Nb_{2/3}O_3$, or PNN) are very close to those of PZT, it is found that solid solutions are readily formed. Here, A denotes a divalent cation (such as Ni^{2+}) and B a pentavalent cation (such as Nb^{5+}). Therefore, special attention has been given to $Pb(A_{1/3}B_{2/3})$-O_3–PZ–PT type solid solutions [2, 3]. Ko *et al.* [4] reported that the compositions near the MPB in the system $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ (PMN–PZ–PT) had high dielectric constant and radial coupling coefficient. Moon *et al.* [5] found that the densification of the $PbNi_{1/3}Nb_{2/3}O_3$–$PbZrO_3$–$PbTiO_3$ (PNN–PZ–PT) polycrystalline specimens was enhanced by increasing the partial pressure of O_2 in the sintering atmosphere. This was attributed to the increase in the internal pressure of closed pore due to the thermal decomposition of PbO at low partial pressure of O_2. In order to fabricate the piezoelectric ceramic actuators with high displacement characteristics, some attempt has been made to obtain materials with high values of piezoelectric modulus d_{31} and relatively high coercive field E_c in the PNN–PZ–PT ternary system [6], and also the effects of some additives on the dielectric and piezoelectric properties of this ternary system were reported by Kitamura *et al.* [7].

However, there are few papers on the influence of the MPB on the dielectric and piezoelectric properties of the PNN–PZ–PT ternary system. In view of the foregoing discussion, the purpose of this investigation was to study the detailed influence of the MPB on the electrical properties of the PNN–PZ–PT ternary system, which is one of the prime candidates for ceramic microactuator materials.

2. Experimental procedure

The selected compositions in this study were xPNN–$(1-x)Pb(Zr_\sigma Ti_{1-\sigma})O_3$ ($0.2 \leqslant x \leqslant 0.6$, $0.2 \leqslant \sigma \leqslant 0.5$) shown in Fig. 1, which were near the MPB. The oxide powders of PbO, TiO_2, ZrO_2, NiO and Nb_2O_5(> 99.5% purity) were prepared. First, the precursor of $NiNb_2O_6$ powder was synthesized from powders of NiO and Nb_2O_5 by calcinating at 900°C for 2 h. Next the powders of PbO, TiO_2, ZrO_2 and $NiNb_2O_6$ were weighed and mixed according to the above compositions, and 2 wt % Bi_2O_3 of the mixture was added to the above compositions as additive and 3 wt % excess PbO added to compensate the loss of PbO during the sintering process. The mixture was calcinated at 860 °C for 3 h, and then ball-milled to

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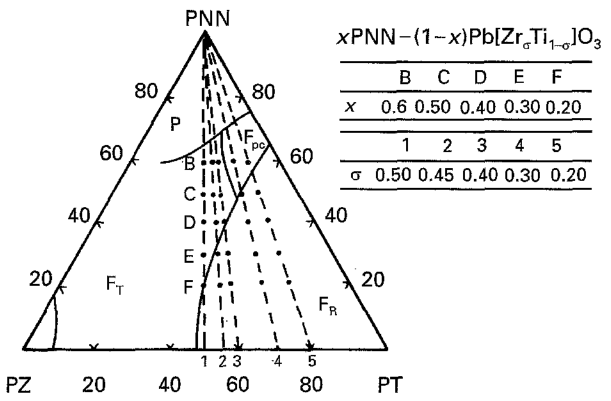

Figure 1 The selected compositions used in this study and their positions in the phase diagram of the PNN–PZ–PT ternary system. (F_R: ferroelectric rhombohedral, F_T: ferroelectric tetragonal, F_{pc}: pseudocubic, P: paraelectric).

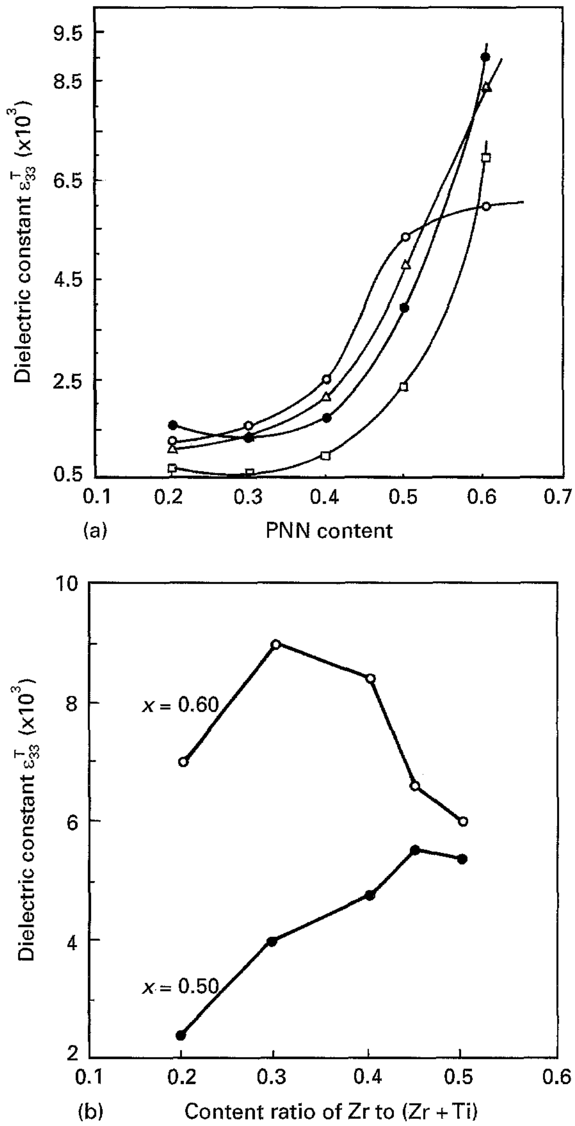

Figure 2 The dielectric constant ε^T_{33} ($f = 1$ kHz) versus PNN content and σ in the xPNN–(1–x)Pb(Zr$_\sigma$Ti$_{1-\sigma}$)O$_3$ ternary ceramic system at room temperature. Key: □ $\sigma = 0.20$; ● $\sigma = 0.30$; △$\sigma = 0.40$; ○ $\sigma = 0.50$.

fine powders, dried and pressed into pellets of 12 mm diameter. Disc samples were sintered at 1250 ~1300 °C for 1 h. Microstructure and crystalline phase identification of the sintered pellets were conducted by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

The silver-coated specimens were poled by applying a d.c. electric field of 2~3 kV mm^{-1}. Dielectric properties were measured with HP 4252A multi-frequency LCR meter. The Curie temperature was determined from the temperature dependence of the dielectric constant measured at 1 kHz. Electromechanical coupling factor was measured at room temperature by using the resonance–antiresonance method. The piezoelectric modulus d_{31} was calculated according to IRE standards on piezoelectric crystals [8].

3. Results and discussion

3.1. Dielectric properties

The dielectric constant at room temperature ($f = 1$ kHz) for the compositions xPNN–(1–x) Pb(Zr$_\sigma$Ti$_{1-\sigma}$)O$_3$ ($0.2 \leqslant x \leqslant 0.6$, $0.2 \leqslant \sigma \leqslant 0.5$) versus x and the Zr/Zr + Ti ratio (σ) is shown in Fig. 2. Fig. 2a revealed that the dielectric constant ε^T_{33} increased monotonically with increasing PNN content when the Zr/Zr + Ti ratio was constant, and that the incrementary ratio of the dielectric constant ε^T_{33} increased with decreasing Zr/Zr + Ti ratio as compared with the dielectric constant ε^T_{33} of xPNN–(1–x)Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ with that of xPNN–(1–x)Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ compositions. It can be interpreted that the Curie temperature moves toward room temperature and consequently the peak dielectric constant corresponding to the Curie temperature becomes close to the value for room temperature, and also that the MPB shifts to a Ti-rich region when PNN is added to the PZ–PT system. The curve of the dielectric constant ε^T_{33} versus the Zr/Zr + Ti ratio exhibits a peak when the PNN content is constant. Furthermore the Zr/Zr + Ti ratio corresponding to the dielectric peak was reduced with increasing PNN content. The dielectric constants occur at a maximum along the MPB. At the same time, Fig. 2b indicates that the MPB shifts to a Ti-rich region when PNN is incorporated into Pb(Zr,Ti)O$_3$.

3.2. Curie temperature

The Curie temperature for the compositions xPNN–(1–x)Pb(Zr$_\sigma$Ti$_{1-\sigma}$)O$_3$ versus x and the Zr/Zr + Ti is shown in Fig. 3. Transition temperatures of PNN, PT and PZ are -120 °C, 490 °C and 230 °C, respectively. The Curie temperature is expected to vary with the compositions. When the PNN content is constant, the Curie temperature decreases smoothly with increasing content ratio of Zr to Zr + Ti. This resulted from the Curie temperature of PZ being lower than that of PT. It is obvious that the Curie temperature is rapidly shifted to a lower temperature with increasing PNN content since the content ratio of Zr to Zr + Ti is constant. By adjusting the values of x and the Zr/Zr + Ti ratio, the required Curie temperature for the xPNN–(1–x)Pb(Zr$_\sigma$Ti$_{1-\sigma}$)O$_3$ can be obtained. It is very useful to achieve the inverse

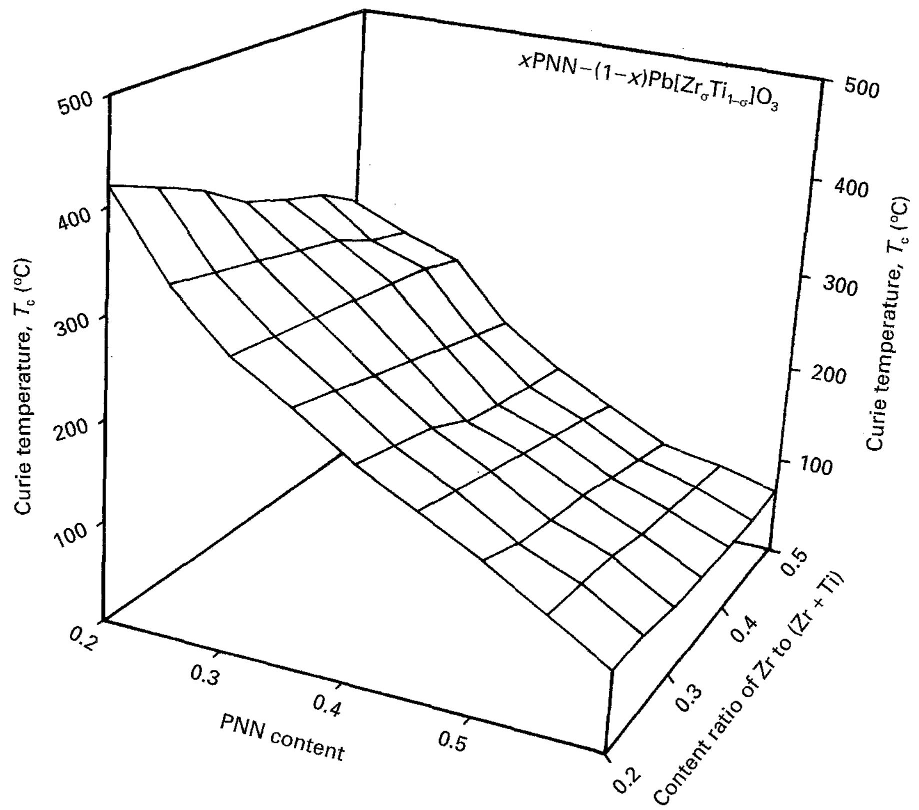

Figure 3 The Curie temperature T_c versus PNN content and σ in xPNN–(1–x)Pb($Zr_\sigma Ti_{1-\sigma}$)O_3 ternary ceramic system.

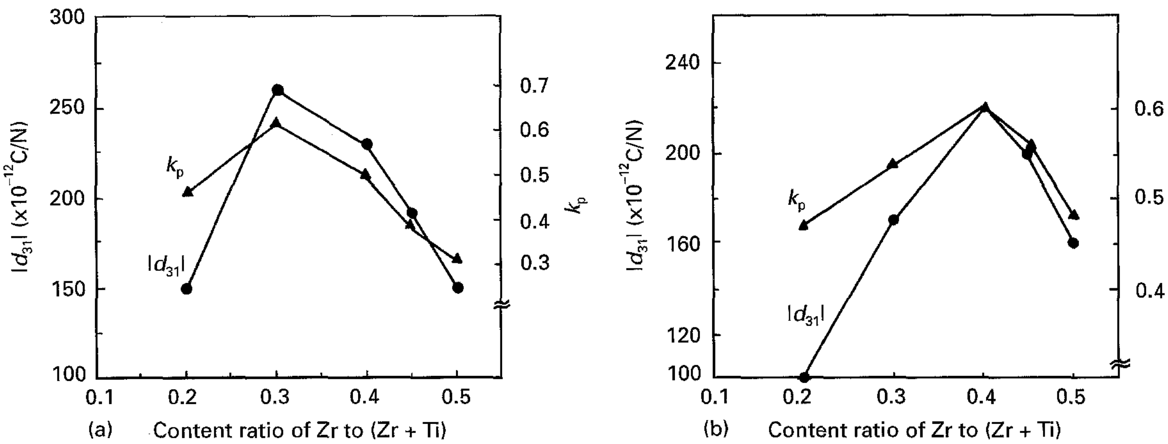

Figure 4 Piezoelectric modulus d_{31} and coupling factor k_p versus the content ratio of Zr to (Zr + Ti) in the xPNN–(1–x)Pb($Zr_\sigma Ti_{1-\sigma}$)O_3 ternary ceramic system ((a) $x = 0.5$; (b) $x = 0.4$).

design procedure for materials from known properties to the required compositions.

3.3. Piezoelectrical properties

The piezoelectric modulus d_{31} and plane coupling factor k_p versus the content ratio of the Zr/Zr + Ti ratio in this system is shown in Fig. 4, which illustrates that the Zr/Zr + Ti ratio value corresponding to the d_{31} peak shifts to a lower value with increasing PNN content. This phenomenon is similar to that of the dielectric constant ε_{33}^T, which can be ascribed to the Curie temperature-shifting effect and to MPB shifting to a Ti-rich region. Of course the high piezoelectric activity compositions lie near the MPB. Similar phenomena have also been found in the PMN–PZ–PT and PCN–PZ–PT systems [4, 9]. The structural activity for the compositions near MPB is much higher, and the structure is easy to transform. MPB for the PNN–PT–PZ ternary system is a mixed phase region of a coexisting ferroelectric tetragonal phase (F_T) and rhombohedral phase (F_R) rather than a critical line. For the compositions near MPB, the two ferroelectric phases coexist and their structural energies are nearly equal. Their crystal structures can be transformed from rhombohedral phase to tetragonal phase when electric field or force is applied, and vice versa. This is the benefit of the mobility and polarization of ferroelectric active ions. Therefore in such structural states, the piezoelectric activity was enhanced by

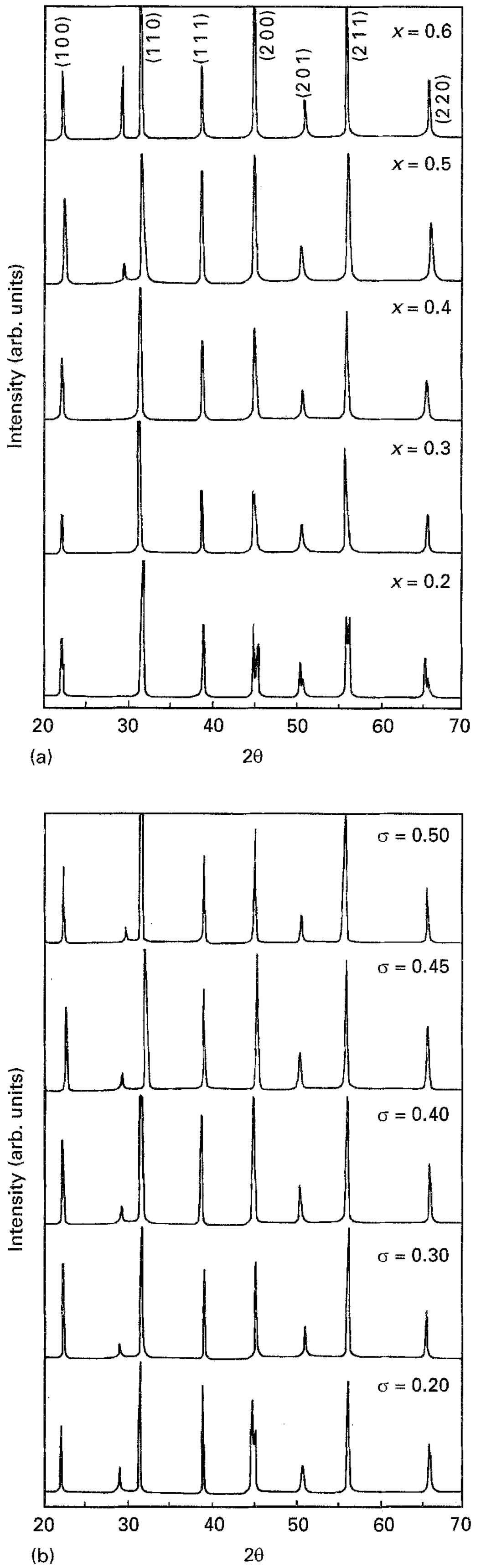

Figure 5 (a) XRD patterns for the compositions of xPNN–(1–x) $Pb(Zr_{0.4}Ti_{0.6})O_3$. (b) XRD patterns for the compositions of $0.5PNN–0.5Pb(Zr_{\sigma}Ti_{1-\sigma})O_3$.

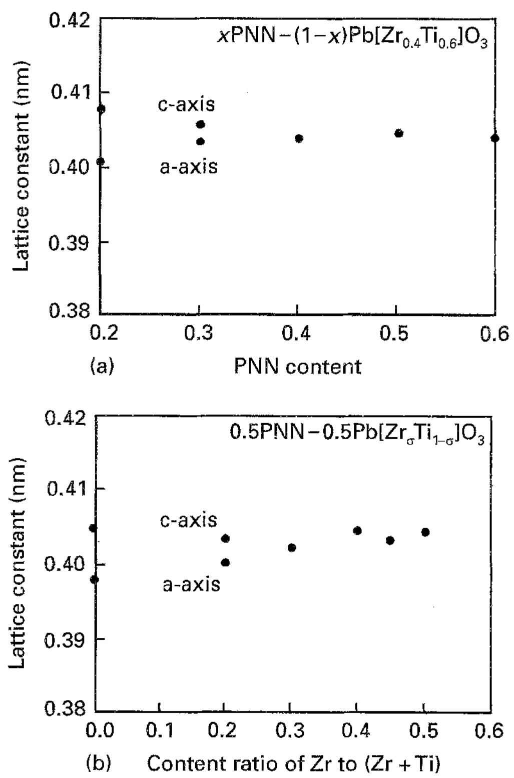

Figure 6 Lattice parameters of the xPNN–(1–x)$Pb(Zr_{\sigma}Ti_{1-\sigma})O_3$ ternary ceramic system versus PNN content and σ ((a) σ = 0.40; (b) x = 0.50).

oscillations of boundaries between coexisting rhombohedral and tetragonal regions, and the plane coupling factor became higher.

3.4. Lattice parameters

The XRD patterns for the compositions 0.5PNN–$0.5Pb(Zr_{\sigma}Ti_{1-\sigma})O_3$ ($0.2 \leqslant \sigma \leqslant 0.5$) and xPNN–(1–x) $Pb(Zr_{0.4}Ti_{0.6})O_3$ ($0.2 \leqslant x \leqslant 0.6$) are shown in Fig. 5. The lattice parameters a and c determined by XRD patterns are shown in Fig. 6. The lattice parameter of the a-axis increased with increasing PNN content and content ratio of Zr to Zr + Ti; however, the lattice parameter of the c-axis decreased. The reason for this discrepancy is that the crystal structure transformation from tetragonal to rhombohedral phase was induced during increasing PNN content and Zr/Zr + Ti ratio.

4. Conclusions

The influence of MPB on the dielectric and piezoelectric properties in the PNN–PZ–PT system were systematically investigated. The compositions around MPB were found to exhibit high dielectric and piezoelectric properties, which were contributed to the oscillations of boundaries between coexisting rhombohedral and tetragonal regions. The Curie temperature T_c decreased rapidly with increasing PNN content while it decreased smoothly with increasing Zr/Zr + Ti ratio. The variations of the lattice parameters a and c versus PNN content and Zr/Zr + Ti ratio were determined.

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