Ferroelectricity of Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-BaTiO$_3$-PbTiO$_3$ ceramics in the vicinity of morphotropic phase boundary

W. Z. ZHU, A. KHOLKIN, P. Q. MANTAS, J. L. BAPTISTA
Department of Ceramic and Glass Engineering, University of Aveiro,
UIMC, 3810-193 Aveiro, Portugal
E-mail: weizhong.zhu@pmusa.com

The morphotropic phase boundary (MPB) in the $(0.85 - x)$Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3 - 0.15$BaTiO$_3 - x$PbTiO$_3(0 < x < 0.2)$ ceramic system was delineated by x-ray diffraction analysis. Polarization hysteresis loop measurements at room temperature were performed for compositions in the vicinity of the MPB. Experimental results demonstrate that the MPB, by its definition the rhombohedral and tetragonal phase coexist in the present system, is a broad composition region where the value of x ranges from 0.12 to 0.18. The remanent polarization, P_r, increases with PbTiO$_3$(PT) reaching a maximum value of 18 μC/cm^2 at 15 mol%PT, then decreases remarkably with further PT addition, whereas the variation of coercive field, E_c, with PT content shows the opposite trend. The effect of PT incorporation on P_r is more pronounced than on E_c. Correlation between the degree of lattice distortion, instead of the maximization of the polarization orientations inherent to both phases, and P_r is attained to account for the observed phenomenon. The dependence of E_c upon PT content, however, reflects the transition from typical relaxor ferroelectrics to weak normal ferroelectrics, as confirmed by the results of the dielectric measurement.
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1. Introduction

Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$(abbreviated as PZN) belongs to the family of lead-based relaxor ferroelectrics with complex perovskite structure. It is one of the few compositions with a high Curie temperature of about 140°C at 1 kHz. Preparation of pure PZN in perovskite form using conventional approaches still remains a challenging task, in part due to the inevitable appearance of nonferroelectric phases with pyrochlore-type structure. In the past decade, BaTiO$_3$(BT) was the most widely used additive to stabilize the perovskite phase, and the dielectric and ferroelectric properties of the stabilized system have been extensively investigated [1].

BT-bearing PZN with rhombohedral symmetry in solid solution with tetragonal PbTiO$_3$(PT) exhibits a morphotropic phase boundary (MPB) whose location is dependent upon the BT content. Anomalously high relative dielectric permittivity, electromechanical coupling factor as well as piezoelectric coefficient have been reported for the MPB composition of PZN-PT single crystals [2]. Previous study [3] on the polarization behaviour in the PZN-BT-PT ceramics showed that maximization of the remnant polarization was not found, which was attributed to the possible existence of a nonpolarizable BZN-rich region resulting in the deterioration of the dielectric and ferroelectric properties.

The objective of this paper is to examine the variation of ferroelectric properties with PT content in

PZN-BT-PT system near the MPB region. The variation of two important ferroelectric parameters, remanent polarization, P_r, and coercive field, E_c, is discussed with increasing PT content, as the crystal structure changes from rhombohedral to the region where the rhombohedral and tetragonal phases coexist, since they reflect the switching of ferroelectrically active cations between the two stable off-centered positions of the oxygen octahedra in response to an external electric field.

2. Experimental
2.1. Sample preparation

The columbite precursor approach was adopted to synthesize the PZN-BT-PT samples with different compositions. The mixture of ZnO(99% pure) and Nb$_2$O$_5$ (99.9% pure) in the stoichiometric proportion was first ball-milled, dried and calcined at 1000°C for 4 h to form the single phase ZnNb$_2$O$_6$ for subsequent use. Powders of PbCO$_3$(99% pure), BaTiO$_3$(99.5%), ZnNb$_2$O$_6$ and TiO$_2$(99% pure) were weighed in mole percentage according to the formula: $(0.85 - x)$Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3 - 0.15$BaTiO$_3 - x$PbTiO$_3(0.0 < x < 0.2)$. 10 wt% of excess PbCO$_3$ was added to compensate for the lead vaporization. The mixture was ball-milled, dried and subsequently calcined at 900°C for 5 h in a covered alumina crucible. The remilled and sieved powders were uniaxially

pressed at 100 MPa to form a green body of 10 mm diameter and around 2 mm thick, followed by cold isostatic pressing at 300 MPa. The final sintering was carried out at 1150°C for 1 h using an inverted crucible configuration.

2.2. XRD analysis
As-sintered samples were ground and polished to remove the surface layer, and crushed to powders for x-ray diffraction analysis. Cu K_α radiation with a step of 0.02° was used. The quantitative identification of rhombohedral and tetragonal phases was done by deconvolution of the ensembles of the peaks to determine their angular position and integrated intensities, and calculated using the formula in the literature [4]. The lattice parameters of each phase were calculated by the least-square method.

2.3. Dielectric measurement
Polished specimens with parallel surfaces were electroded using gold sputtering. Air-dried silver paint was also applied to improve the mechanical intensity of the contact. Dielectric measurements were carried out with an automated system, whereby a temperature controller connected with the furnace and a Solartron 1260 impedance/Gain-Phase Analyzer controlled by a desktop computer were employed. Dielectric permittivity and dissipation factor were measured at various frequencies between 0.1 kHz and 100 kHz as the samples were cooled through the transition range at a rate of 1°C/min. No difference between heating and cooling was noted during the measurement.

2.4. Hysteresis loop measurement
The measurement of polarisation versus electric field (P versus E) at room temperature was conducted with samples submerged in silicon oil, using a modified Sawyer-Tower circuit where an alternating electric field of 50 Hz was applied. A maximum field of 1.2 kV/mm was used.

3. Experimental results
XRD diffraction profiles of specimens with various amounts of PT are shown in Fig. 1. Due to the proximity of lattice parameters of rhombohedral and tetragonal phase, their diffraction lines in the coexistence region partially overlap. Therefore the (200) reflection was chosen to study since it splits into two peaks for the tetragonal structure and doesn't split for the rhombohedral one. The broadening of this reflection at 12 mol%PT implies the appearance of the tetragonal phase, therefore, this composition is regarded as the onset of morphotropic phase boundary (MPB). Peak deconvolution and subsequent curve fitting indicate that the coexistence region extends up to 18 mol%PT that can be considered as the end composition of MPB. The PT content dependence of the relative fraction of rhombohedral and tetragonal phases is plotted in Fig. 2. It
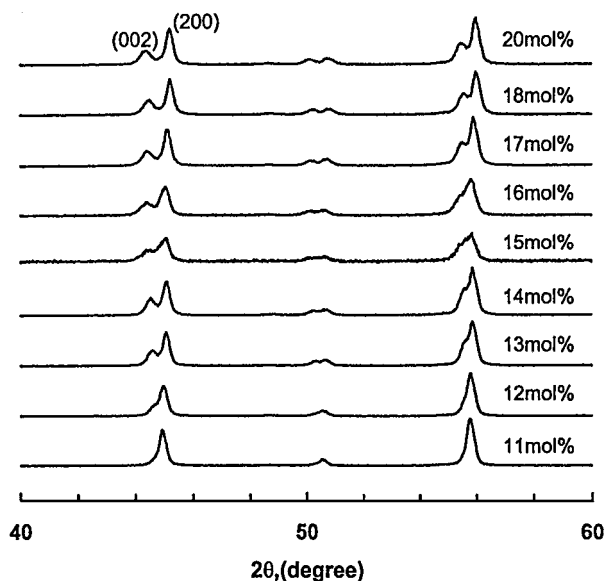

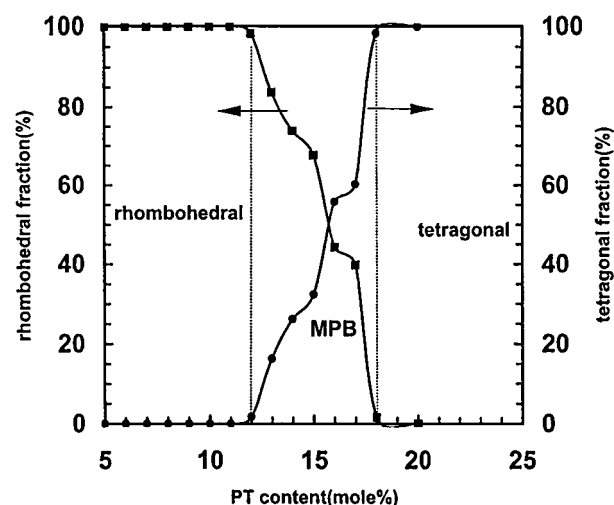*Figure 1* XRD profiles of specimens containing various amounts of PT.

Figure 2 Variation of the volume fraction of the rhombohedral (or tetragonal) phase with PT content.

can be clearly seen that the MPB is a broad composition range rather than a line as observed in PZN-PT single crystals [2]. Moreover, it is displaced toward higher PT content compared with the result of the literature [5] where the content of BT is 10 mol% instead of 15 mol%. This is presumably due to the diluting effect of Ba^{2+} ions since $BaTiO_3$ has been experimentally confirmed to strengthen the relaxor characteristics of PZN [6].

Fig. 3a shows the lattice parameters of the tetragonal phase, a_t and c_t, and that of the rhombohedral one, a_r, as a function of PT content, and Fig. 3b illustrates the change of the rhombohedral lattice distortion angle, α, with PT concentration. For the tetragonal phase, c_t and a_t are merging together with the decrease of Ti content, implying that the structure is approaching the cubic symmetry. For the rhombohedral phase, α is smoothly changing to $\alpha = 90°$, (the limiting case where it should be cubic), with an increase of Ti content. As shown in Fig. 4, for the compositions in the MPB region the tetragonal lattice distortion, c_t/a_t, is gradually decreasing to $c_t/a_t = 1$ (the cubic structure), and the
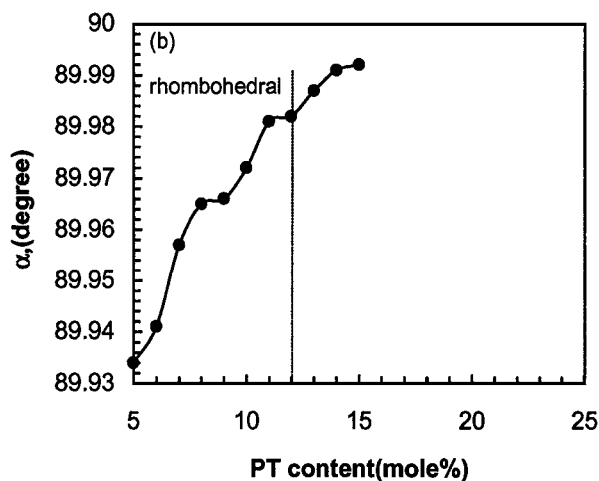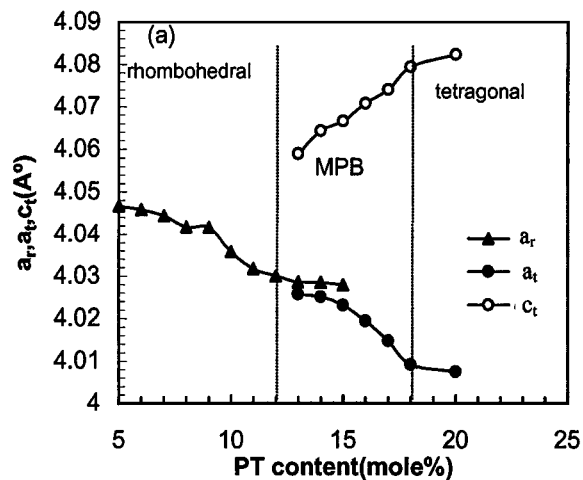
Figure 5 Changes of the relative dielectric permittivity with temperature at 10 kHz measuring frequency for various compositions.

(3) maximization of the dielectric permittivity maximum (ε'_{max}) around the MPB region; (4) for all PT concentrations, the dependence of the dielectric permittivity on temperature at $T > T_{max}$, can be described by the following empirical formula proposed by Uchino et al. [7]

$$1/\varepsilon' = 1/\varepsilon'_{max} + (T - T_{max})^{\gamma}/C', \qquad (1)$$

where C' is a parameter whose magnitude is determined by both the value of ε'_{max} and diffuseness coefficient δ; γ is an exponent whose value decreases from 2 to 1.7 as the PT content is increased, indicating that the dielectric response evolves from typical relaxor ferroelectric to weak normal ferroelectric and the diffuseness of phase transition gradually decreases. In comparison with the results of Kumar et al. [3] for the similar ceramic system, the permittivity maxima obtained in the present experiment are apparently higher, mainly owing to the absence of the nonpolarizable BZN-rich phase. Due to their relatively high dielectric transition temperatures and large dielectric permittivities, they are potential candidates for high temperature capacitor applications. P-E curves for several typical compositions are presented in Fig. 6. Although the hysteresis loops are not well-shaped due to large conduction losses, the overall changing trend with PT content is consistent. The hysteresis loops are slanted and polarization not squared for samples containing low PT. They become slim and much squarer with increasing PT content up to the MPB range. At higher PT concentration, the squareness of the loops decreases and $P(E)$ curves become somewhat slanting again. The remanent polarization, P_r, and coercive field, E_c, of the samples are plotted in Fig. 7. This figure reveals that P_r increases dramatically with PT content, achieving an optimal value of $18\,\mu C/cm^2$ at 15 mole%PT, and then decreases remarkably with further PT addition, whereas the variation of E_c with PT content is just the opposite in spite of its more gradual tendency as compared to that of P_r. The correlation between the remanent polarization and the rhombohedrality for compositions where the rhombohedral phase is predominate, is redrawn as shown

Figure 3 Variations of (a) rhombohedral lattice parameter a_r, and tetragonal lattice parameter a_t and c_t, and (b) lattice distortion angle α of the rhombohedral phase, with PT content.
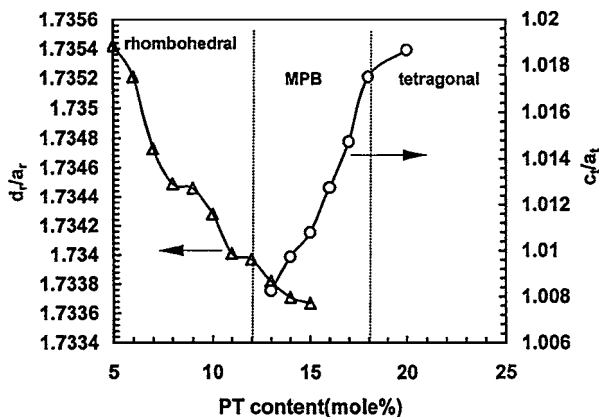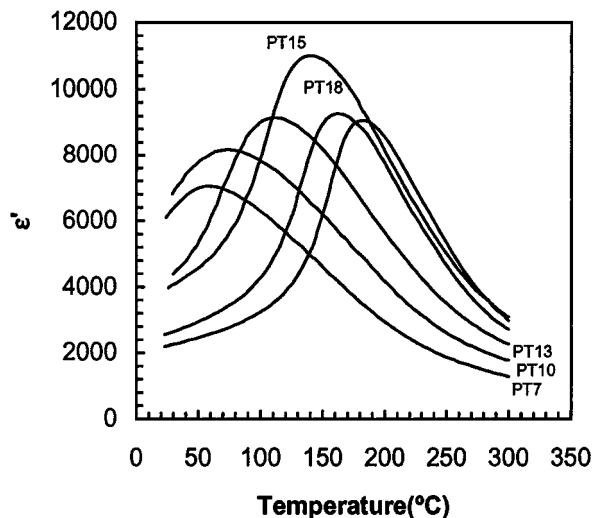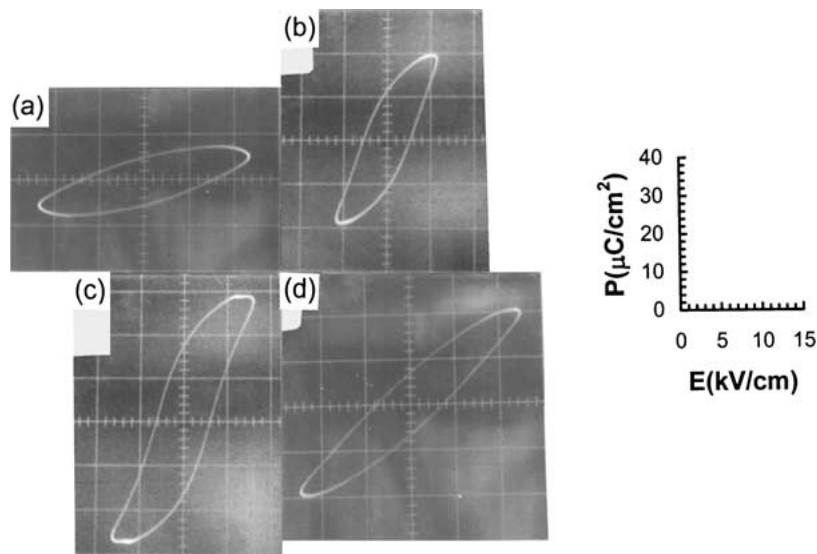

Figure 4 Changes of the lattice distortion of the rhombohedral and the tetragonal phase with PT content.

rhombohedral lattice distortion, d_r/a_r, is scaling down to $d_r/a_r = \sqrt{3}$ (the cubic structure), where d_r is the diagonal of the rhombohedral cell.

Dielectric constant versus temperature curves at 10 kHz for different compositions are shown in Fig. 5, from which the effect of PT addition into the PZN-BT system can be generalized as: (1) shift of the temperature of dielectric permittivity maximum (T_{max}) towards high temperature; (2) reduction of the degree of diffuseness of phase transition with increasing PT content;

Figure 6 Hysteresis loops for several typical compsotions at room temperature (a) PT7; (b) PT13; (c) PT15; (d) PT18.
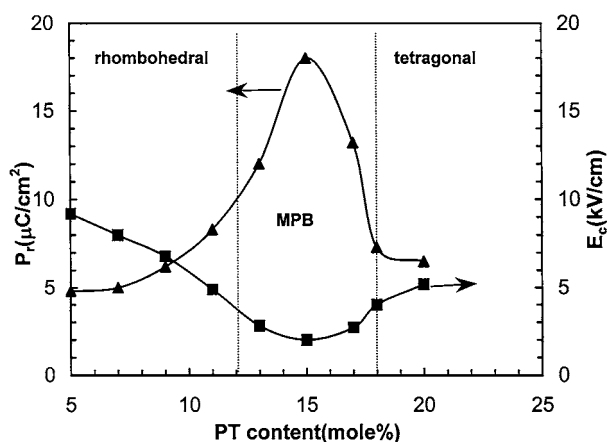

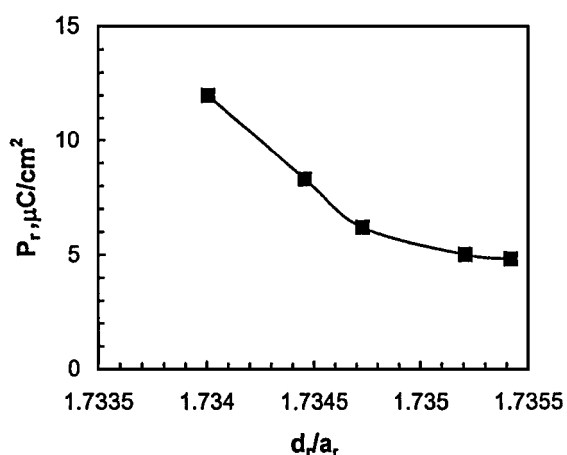*Figure 7* Plots of P_r and E_c against Pt content.

Figure 8 Dependence of the remnant polarization at room temperature on the rhombohedrality for specimens containing less than 13 mole%PT.

in Fig. 8. This figure indicates that enhanced remanent polarization is related to the smaller lattice distortion of the rhombohedral phase, i.e., proximity to cubic structure.

4. Discussion

A large difference is observed between the previous results [3] and the current report. Namely, a maximum in the remanent polarization vs. PT content is found instead of only gradual change for the BT5 system. The coercive field also experiences a progressive drop near the MPB range, and then slightly increases with the increase of tetragonality. The results of current work can be interpreted as follows: In the rhombohedral phase region (where the measurement temperature is close to the permittivity maximum) the sample is in the micropolar(relaxor) state and even with the high electric field it is difficult to induce a long-range ferroelectric order. Therefore, the loops are slanted and P_r is relatively small. In this region, P_r and E_c behaves in an opposing manner with an increase of PT. Since the incorporation of PT into the matrix lattice results in the reduction of the rhombohedrality as shown in Fig. 4, switching of the ferroactive cations between nearby off-centred sites within the same oxygen octahedron becomes relatively easy, contributing to the observed increase in P_r. This increase is, of course, correlated with the degree of lattice distortion at room temperature (Fig. 8). On the other hand, the dielectric response is of typical relaxor ferroelectric as the PT content is below 13 mole%. The vectors of polar nanodomains respond to the applied electric field through polar-vector reorientation mechanism when the measuring temperature is above the freezing temperature. Moreover, the interaction strength among these polar clusters depends upon the size of the polar region, temperature as well as the electric field applied. For compositions with low PT concentration whose Curie regions are close to room temperature, the polar clusters are more independent and disordered so that higher electric field is needed to align the polar vectors. With the increase of PT content, the Curie region is moved to higher temperature, in other words, the temperature for the hysteresis measurement is relatively reduced. The polar clusters in these compositions are more interdependent since their interactions are enhanced, thus, the electric field necessary

to align the polar vectors is decreased. As the composition extends into the MPB region, the stability of ferroelectric phase is apparently increased and the same field can induce ferroelectric state with almost square hysteresis loop (see Fig. 6c). Therefore, the remnant polarization is significantly increased with PT concentration. Normally, a broad maximum is supposed to be observed with further PT addition due to the coexistence of rhombohedral (8 possible polarization directions) and tetragonal phases (6 possible polarization directions). This is true, for example, in the case of the PZT ceramics [8]. However, in our case PT addition and increase of the relative amount of the tetragonal phase results in a obvious decrease of P_r (Fig. 7). This can be related to the high tetragonal distortion of the structure and inability to reverse the polarization with a relatively low electric field ($\sim$7 kV/cm) used in the experiment. Therefore, the loops are quasi-linear with a small hysteresis. This also may account for the slightly increased coercive field when the structure becomes predominantly tetragonal. In the case of PZT ceramics, the increase of the tetragonality for the Ti-rich compositions results in the considerable increase of the coercive field. As pointed out earlier, the dielectric response is of weak normal ferroelectric for the tetragonal-rich compositions, hence, the coercivity behaves somewhat similar to that of PZT. Thus, the composition dependences of remanent polarization and coercive field reflect the transition from micropolar state to a long-range ferroelectric state in PZN-BT-PT system.

5. Conclusions

1. Morphotropic phase boundary (MPB) in PZN-15 mol%BT-PT system was observed in a wide composition range from 12 mol%PT to 18 mol%PT. With an increase of PT content, remanent polarisation first increases then decreases considerably, reaching a maximum value of 18 μC/cm^2 at 15 mole%PT. This can be attributed to the minimisation of lattice distortion. The response of the coercivity to PT incorporation is opposed to that of P_r, but its change is more gradual.

2. Present results have important implication that, at room temperature, the shape of the hysteresis loop for relaxors with rhombohedral or pseudo-cubic symmetry can be tailored: the loop can be rendered slim and square by making the structure more cubic and shifting the Curie range to higher temperature.

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