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Perovskite Phase Formation, Phase Transition and Ferroelectric Properties of PZN-based Ceramics

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ABSTRACT

Ceramics solid solutions within the binary system of $x\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$–$(1\text{-}x)\mathrm{Pb(Zr_{1/2}Ti_{1/2})O_3}$ with $x = 0.1 - 0.5$ were synthesized via the mixed oxide method and the columbite method. Phase development of calcined powders and the crystal structure of sintered ceramics were analyzed by X-ray diffraction. Ferroelectric properties were measured to elucidate the phase transformation and identify the impact of the processing conditions. It is shown that there is no significant difference in P_r across the composition range. However, the coercive field E_c is well dispersed over the compositions. Compared with ceramics prepared by the columbite method, ceramics prepared by the mixed oxide method showed a lower remanent polarization P_r and a higher coercive field E_c. In addition, both X-ray diffraction and ferroelectric measurements indicated a phase transformation from a tetragonal to a pseudo-cubic rhombohedral phase when the fraction of PZN was increased. The morphotropic phase boundary (MPB) is located between $x = 0.2$ and 0.3 according to observations made on ceramics prepared with both method.

Keywords: phase formation, phase transition, ferroelectric, columbite, PZN.

INTRODUCTION

Ferroelectric materials are widely used for various devices, including multilayer capacitors, sensors, and actuators. By the 1950's, the piezoelectric solid solution $\mathrm{Pb(Zr_{1\text{-}x}Ti_x)O_3}$ (PZT) was found to host exceptionally high dielectric and piezoelectric properties for compositions close to the morphotropic phase boundary (MPB). This MPB is located around $\mathrm{PbTiO_3{:}PbZrO_3} \sim 1{:}1$ and separates the Ti-rich tetragonal phase from the Zr-rich rhombohedral phase (Alberta and Bhalla, 2001). Most commercial PZT ceramics are thus designed in the vicinity of the MPB with various dopings in order to achieve high properties.

$\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$ (PZN) is an important relaxor ferroelectric material with the rhombohedral structure at room temperature. A diffuse phase transition from the paraelectric state to a ferroelectric polar state occurs at 140°C (Kuwata *et al.*, 1981). Extensive research has been carried on PZN single crystals because of their excellent dielectric, electrostrictive, and optical properties (Kuwata *et al.*, 1981). Although single crystals of PZN can routinely be grown by the flux method, (Kuwata *et al.*, 1981) it is known that perovskite PZN ceramics cannot be synthesized by the conventional mixed-oxide method without doping. This is because PZN has a low tolerance factor and small electronegativity difference between the cations and the pyrochlore phase appears to be more thermodynamically stable than the perovskite phase (Shrout and Halliyal, 1987). Hot isostatic pressing was reported to be able to produce phase-pure perovskite PZN ceramics (Matsuo *et al.*, 1969). However, relatively poor piezoelectric properties were measured in the as-pressed ceramic. Various chemical additives, such as $Ba(Zn_{1/3}Nb_{2/3})O_3$, $BaTiO_3$, and $SrTiO_3$ have thus been explored in an attempt to stabilize the perovskite PZN ceramic and retain the excellent piezoelectric properties. Halliyal et al.(1987) prepared $BaTiO_3$-stabilized PZN ceramics using $BaCO_3$, PbO, ZnO, Nb_2O_5, and TiO_2 as the starting materials. Marina and his co-workers (Villegas *et al.* 2000) incorporated $BaTiO_3$ and $Pb(Zr_{0.4}Ti_{0.6})O_3$ into PZN to produce the ternary system with the perovskite structure from $ZnNb_2O_6$ powder. However, a trade-off was made with these additives which yielded reduced dielectric constants and piezoelectric coefficients. Therefore, there is significant interest in finding a method to stabilize the perovskite phase in PZN without sacrificing the excellent dielectric and piezoelectric properties.

Since both PZT and PZN have perovskite structure and are known to have excellent dielectric and piezoelectric properties, it is suggested to alloy PZN with PZT to stabilize and optimize the PZN ceramics. Recent work by Fan and Kim (2002) has shown promise in producing phase-pure perovskite PZN–PZT ceramics with the conventional mixed-oxide method. The present work aims to provide a comprehensive study on the process-property relationships in the binary system of PZN–PZT with a wide composition range. Both the conventional mixed-oxide method and the columbite precursor method have been used in synthesizing the PZN–PZT ceramics. The conventional method utilized a one-step reaction with all of starting materials whereas the columbite method was used an initial step of preparing columbite precursor ($ZnNb_2O_6$) and wolframite precursor ($ZrTiO_4$) followed by a reaction with PbO to form the PZN-PZT ceramics. Finally, a comparison of the important ferroelectric properties was made to identify the optimum processing conditions.

EXPERIMENTAL PROCEDURE

For the conventional method, reagent grade oxides of PbO, ZnO, ZrO_2, TiO_2 and Nb_2O_5 were mixed in the required stoichiometric ratios for the general composition xPZN–$(1-x)$PZT where $x = 0.1$, 0.2, 0.3, 0.4 and 0.5. After ball milling for 24 h and drying at 120°C, the mixture was calcined at temperatures between 750 to 950°C for 4 h in a double crucible configuration (Vittayakorn *et al.*, 2003). A heating rate of 20°C/min was selected for all of the compositions in this system (Vittayakorn *et al.*, 2003). For the columbite method, the columbite precursor $ZnNb_2O_6$ was prepared from the reaction between ZnO (Fluka, 99.9%) and Nb_2O_5 (Aldrich, 99.9%) at 975°C for 4 h. The wolframite precursor $ZrTiO_4$ was formed by reacting ZrO_2 (Aldrich, 99.9%) with TiO_2 (Aldrich, 99.9%) at 1400°C for 4 h. The precursors $ZnNb_2O_6$, $ZrTiO_4$ were then subsequently mixed with PbO (Fluka, 99.9%), with 2 mole% excess PbO (Vittayakorn *et al.*, 2003) and milled, dried, and calcined under the same conditions as the powder prepared by the conventional method. The calcined powders of both methods were cold isostatically pressed into pellets at a pressure of 150 MPa. Five sintering conditions were selected to be used with both methods ranging 1175°C, 1200°C, 1225°C, 1250°C, and 1275°C with dwell time of 2 h. To prevent PbO volatilization from the pellets, a PbO atmosphere was controlled with a bed of $PbZrO_3$ powder placed in the vicinity of the pellets. The calcined powder and sintered pellets were checked for perovskite phase formation by X-ray diffraction (XRD). Data collection was performed in the 2θ range of 20°–60° with a step scan with a step size of 0.02° and counting time of 2s/step. For profile fitting, a step scan with step size of 0.004° was used with a counting time of 5s/step. The relative amounts of perovskite and pyrochlore phase were determined by measuring the major XRD peak intensities of the perovskite and pyrochlore phase. The percentage of perovskite phase was estimated by the following equation:

$$\%\ \text{perovskite phase} = \left(\frac{I_{perov}}{I_{perov} + I_{pyro} + I_{PbO}} \right) \times 100$$

This equation is the well-know equation widely employed in connection with the preparation of complex perovskite structure materials (Vittayakorn *et al.* 2003; Vittayakorn *et al.* 2004). Here I_{perov}, I_{pyro}, and I_{PbO} refer to the intensity of the (110) perovskite peak, (222) pyrochlore peak, and the intensity of the highest lead oxide peak, respectively

To investigate the influence of post-sintering heat treatments, specimens from both methods which had been sintered at 1175°C were annealed at 1250°C for a dwell time of 6 h in a closed Al_2O_3 crucible with PbO-rich atmosphere. The specimens were polished and electroded via gold sputtering, over which a layer of air-dry silver paint was applied to enhance the electrical contact. The ferroelectric polarization *vs.* electric field (P-E) measurements was made using an RT66A standard ferroelectric test system.

RESULTS AND DISCUSSION

A. Perovskite phase formation and the MPB

Powder XRD was extensively used to monitor the phase development at each step during ceramic preparation to ensure the phase purity. Phase-pure precursors $ZnNb_2O_6$ and $ZrTiO_4$ were obtained using the calcination conditions described previously. The calcined powders for the perovskite solid solutions were also examined by XRD and the results are exemplified by the powders of 0.5PZN–0.5PZT. Similar trends were apparent for both the conventional method and the columbite method as higher calcination temperatures led to higher perovskite phase purity. At 900°C, the pyrochlore phase disappeared below the resolution limits of X-ray diffraction. Figure 1 showed the percent perovskite phase of 0.5PZN-0.5PZT as a function of calcinations temperature for conventional and columbite methods. The increase in the phase purity with increasing calcination temperature for both methods is evident. It is noted in Figure 1 that the conventional method showed a higher amount of the perovskite phase than the columbite method below 900°C. Presumably the difference is due to the different reaction paths between the two methods. After sintering of the powders calcined at 900°C, the perovskite phase was preserved as evidenced by XRD with one exception. At the highest PZN concentration of x = 0.6, a small amount of pyrochlore phase was detected though the sample remained approximately 98.5% perovskite.

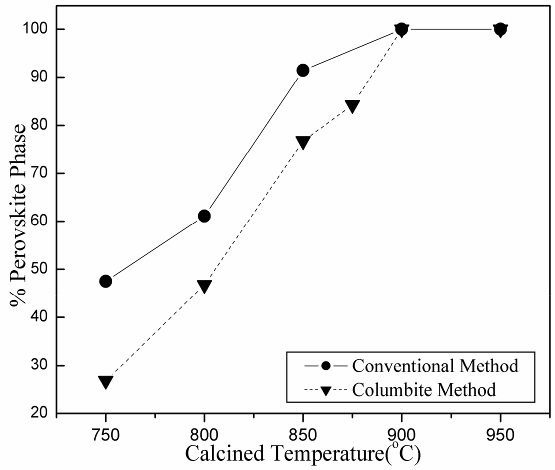

Figure 1 Perovskite phase content in 0.5PZN–0.5PZT powders calcined at different temperatures.

Figure 2(a) and 2(b) show the XRD patterns of xPZN–$(1\text{-}x)$PZT ceramics sintered at 1200°C for 2 h to illustrate the crystal structure change as a function of compositions for both methods. Ceramic specimens from both methods with the compositions closed to PZT (x = 0.1) were observed to be tetragonal as evidenced by the splitting of the (002) and (200) peaks (Figure 3). The results indicate that, for the same composition, different processing methods may develop a perovskite structure with different symmetries. The crystal symmetry of PZN at room temperature was determined to be rhombohedral space group *R3m*. As is well know, the variations in composition may lead to a diffuse MPB between the tetragonal and rhombohedral PZT phase. According to the $PbZrO_3$–$PbTiO_3$ phase diagram, at room temperature $Pb(Zr_{1/2}Ti_{1/2})O_3$ is within the tetragonal phase field near the MPB region. The most obvious different between the patterns for tetragonal and rhombohedral PZT phase concerns the presence of a splitting of (002) and (200) peak at $2\theta \sim 45^{o}$. Since the lattice parameters of (200) and (020) in tetragonal structure are the same but have a little difference with (002), which makes the diffraction peaks of (200) and (020) pile up with the intensity twice over that of the (002). While in rhomohedral structure all the faces of {200} share the same lattice parameters and the XRD profiles of {200} should show only a single peak.

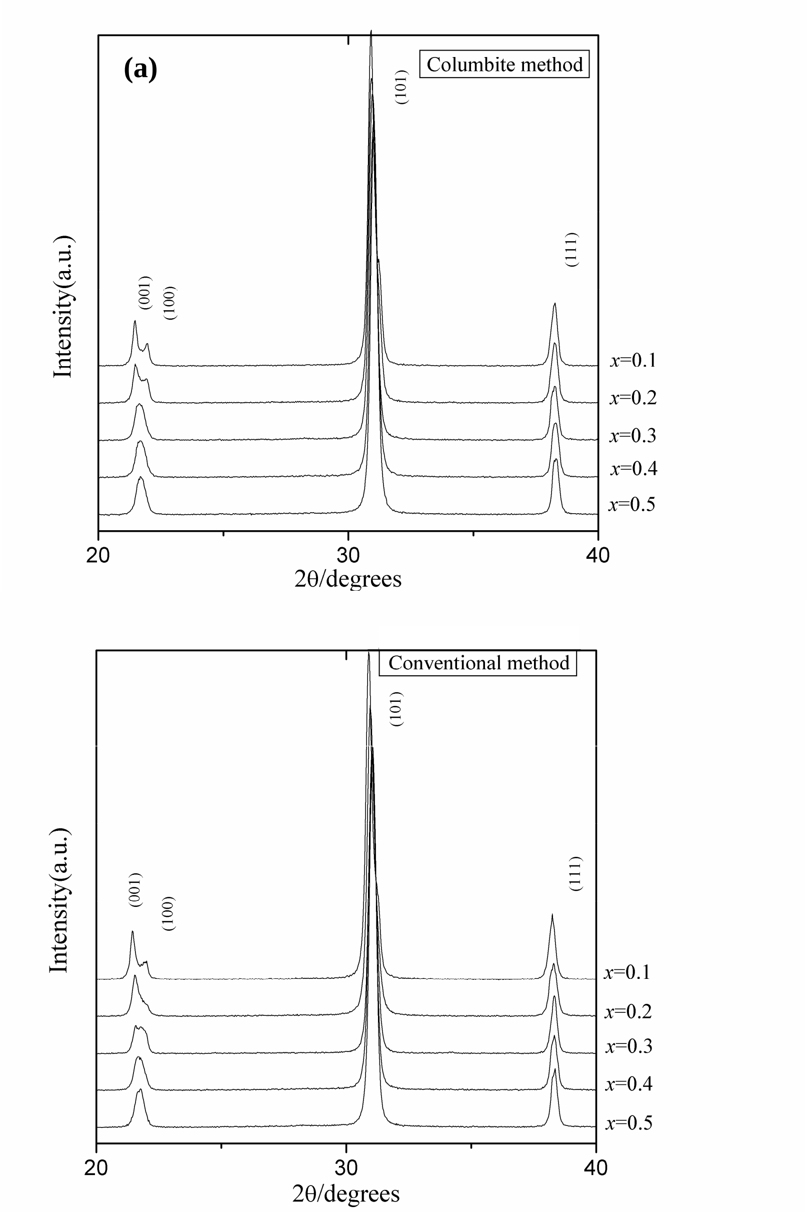

Figure 2 XRD patterns for xPZN – $(1-x)$PZT ceramics sintered at 1200°C for 2 h : (a) columbite method ; (b) conventional method.

Moreover with increase in PZN concentration the crystal structure changes from tetragonal to rhombohedral across the morphotropic phase boundary for both methods (Figure 3).The XRD pattern is dominated by the superposition of (200) and (002) tetragonal peak. The pattern is not very sharp because of the diffraction in the co-existence region incompletely overlaps. The results shows that both the tetragonal and the rhombohedral phases coexist in between the composition of $x = 0.2$ to $x = 0.3$. Moreover at high PZN concentration ($x = 0.5$) no splitting of (002) and (200) peaks was observed. However Figure 3 shows the rhomobohedral (200) peak as a broad peak, indicating the overlapping of the peaks. The overlapping of peaks in the composition $x = 0.5$ is consistent with the observation by Fan and Kim (2002).

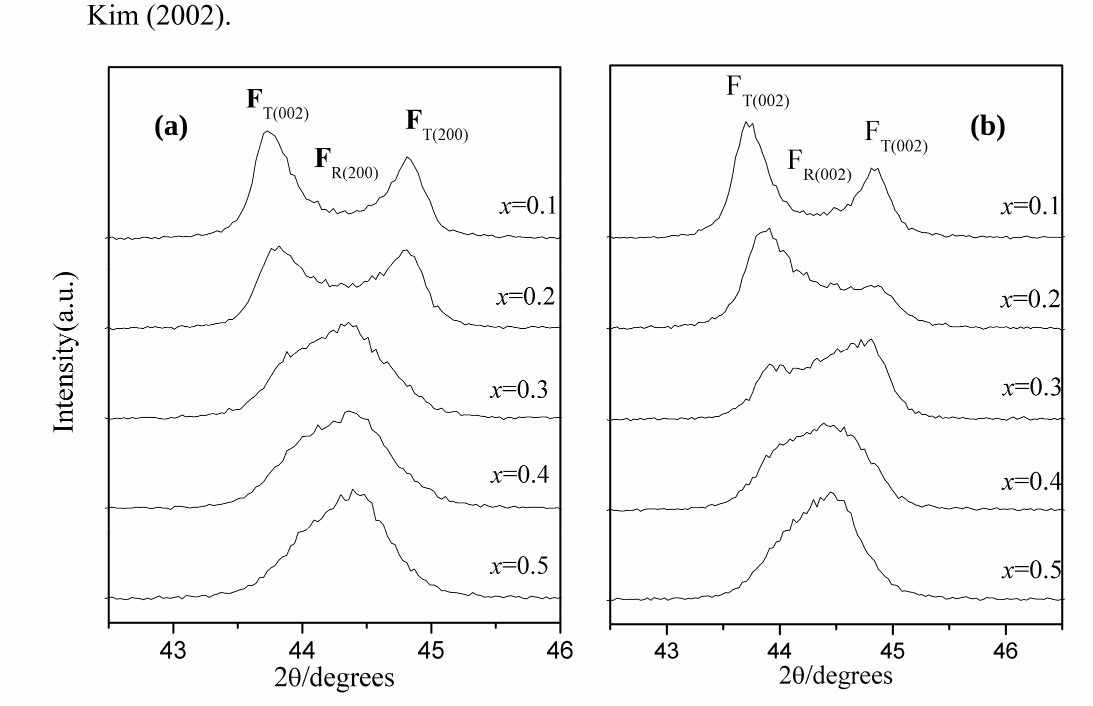

Figure 3 XRD patterns of xPZN – $(1\text{-}x)$PZT with close examination of the (002) peaks shown in Figure 2 (a) columbite method and (b) conventional method.

However, There is no report of phase transformation in this system between $x = 0.2$ to 0.3 from that study. It is also of interest to point out that another MPB compositions between the tetragonal and rhombohedral phases are found at approximately the composition of PZN of $x = 0.25$. The sintered pellets appeared to be dense and the grain size was in the range of 1~5 μm, as shown in Figure 4. The comparison between Figure 4(a) and 4(b) indicates that the conventional method produces ceramics with slightly coarser grains.

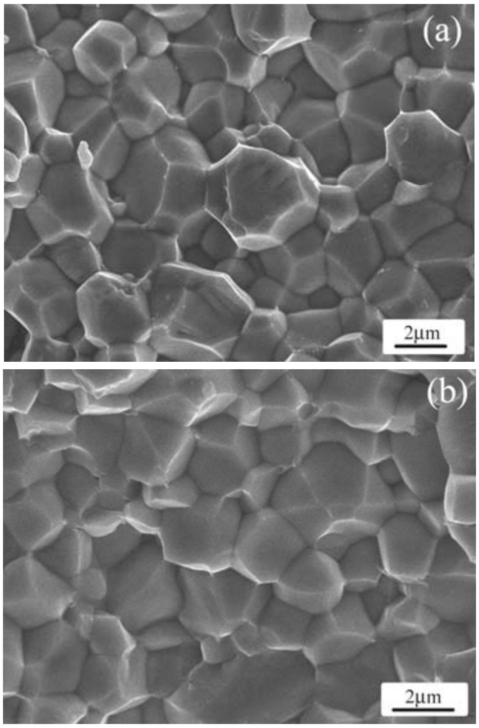

Figure 4 SEM examination of the grain morphology in 0.5PZN–0.5PZT ceramics sintered at 1225°C for 2 h : (a) conventional method and (b) columbite method.

B. Effect of processing method on the phase transformation

The P–E ferroelectric property measurements for the specimens processed at optimum conditions are summarized in Figure 5. It is shown that there is no significant difference in P_r across the composition range. However, the coercive field E_c is well dispersed over the compositions. This is further illustrated in Figure 5. Compared to the conventional method, columbite method produces a slightly higher remanent polarization P_r as well as a lower coercive field E_c. Both methods show a considerable decrease in E_c with increasing molar fraction of PZN. However, the variation in ceramics prepared by conventional method is gradual and continuous, while an abrupt change in E_c occurs in ceramics processed by the columbite method. Combined with the XRD examination described in section A, the change in E_c clearly indicates a phase transformation over that compositional range. Therefore, an MPB separating the tetragonal phase (PZT-rich) from the pseudo-cubic rhombohedral phase (PZN-rich) exists between x = 0.2 and 0.3. Also consistent with the XRD data, the phase transformation in ceramics prepared by the conventional method is smeared out due probably to the chemical heterogeneities. These results lead to the conclusion that the columbite method produces ceramics with better ferroelectric properties even though this method seems initially be prone to form pyrochlore phase. These results underscore the important role that B-site ordering plays in determining the thermodynamic stability and electrical properties of perovskite ferroelectrics.

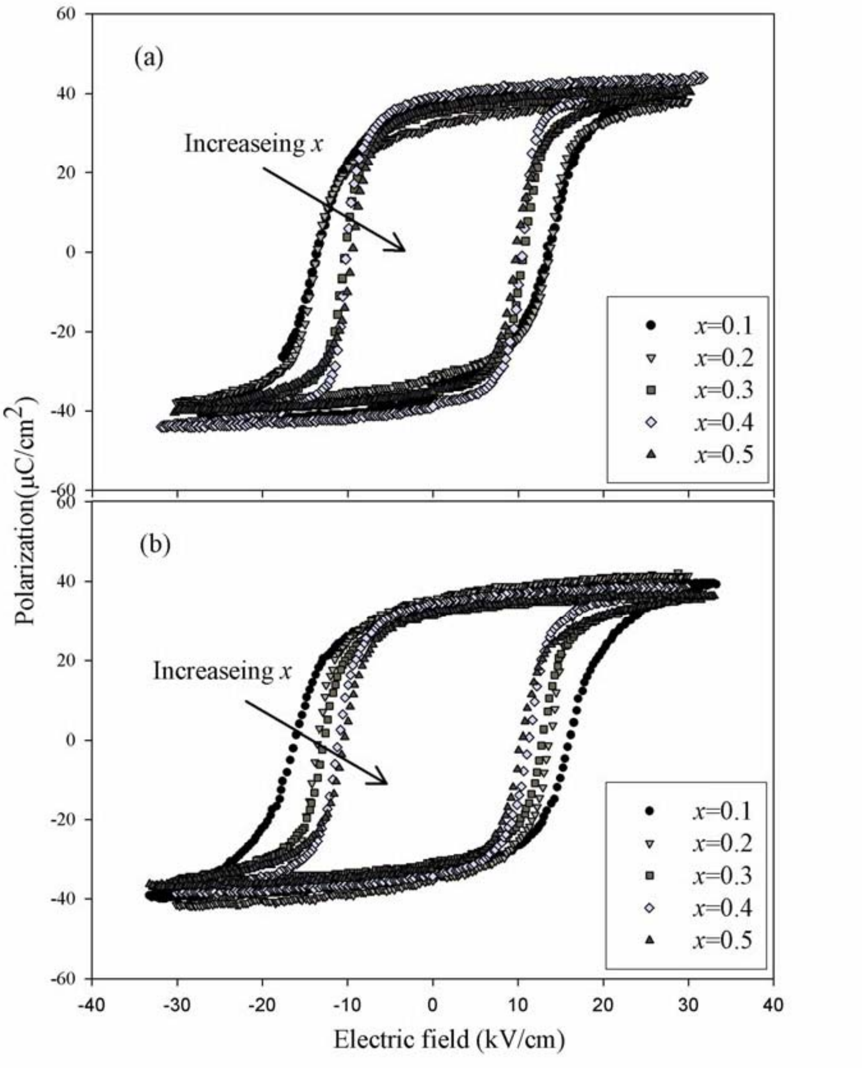

Figure 5 Effect of composition (*x*) on the P-E hysteresis loops for *x* PZN – (*1-x)* PZT processed at the optimum processing conditions: (a) columbite method and (b) conventional method.

C. Piezoelectric properties

The effect of sintering temperature on the piezoelectric coefficient d_{33} of PZN-PZT ceramics prepared via columbite method is illustrated in Figure 6. The coefficient d_{33} increases with increasing sintering temperature up to 1225°C and then decreases for all compositions. It is clearly apparent that the optimum processing condition is sintering at 1225 °C for 2 h. The lower d_{33} values in ceramics sintered at 1250 °C are presumably due to the PbO loss during the sintering process. Also evident in Figure 6 is that the composition 0.3PZN–0.7PZT exhibits the highest piezoelectric coefficient d_{33} among the compositions. The observation is consistent with other relaxor-normal ferroelectric solid solution systems, such as the $Pb(Mg_{1/3}Nb_{2/3})$–$PbTiO_3$ and the $Pb(Zn_{1/3}Nb_{2/3})$–$PbTiO_3$ systems, where ultrahigh piezoelectric properties were found in the rhombohedral phase close to the MPB (Uchino, 2000).

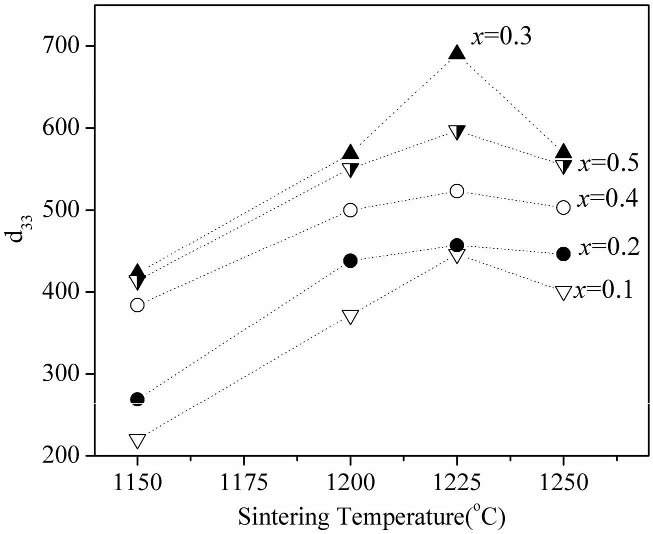

Figure 6 Piezoelectric coefficient d_{33} as a function of sintering temperature for *x*PZN–(*1*-*x*) PZT ceramics prepared via columbite method.

The piezoelectric coefficient d_{33} of the ceramics synthesized via the columbite method sintered at optimum conditions is replotted against the composition parameter *x* in Figure 7, together with the electromechanical coupling factor k_p. High coupling factor values are noted in compositions of $x = 0.3$, 0.4 and 0.5, among which the composition 0.3PZN–0.7PZT displays the highest values. In Table 1, the piezoelectric properties observed in this study are compared with a previous study where the conventional mixed-oxide method was utilized. It is clear that ceramics with excellent piezoelectric properties can be produced in the *x*PZN–(*1*-*x*) PZT pseudo-binary system.

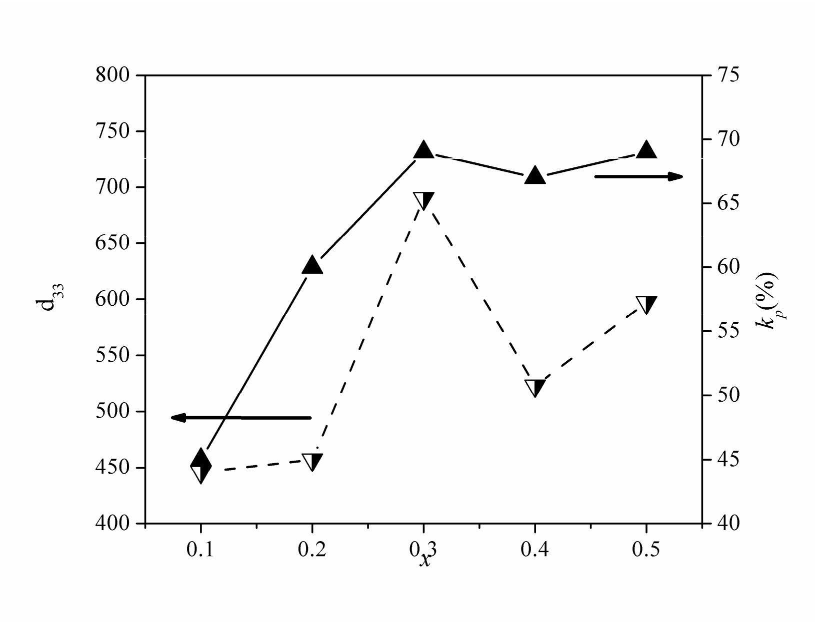

Figure 7 Piezoelectric properties of d_{33} and k_p in ceramics prepared with optimized Processing conditions.

Table 1 Comparison of the piezoelectric properties observed in this study with previous studies.

Ceramics	k_p (%)	d_{33}	References
$Pb(Zr_{0.53}Ti_{0.47})O_3$	52	220	(Jaffe and Cook 1971)
$0.5PZN–0.5Pb(Zr_{0.47}Ti_{0.53})O_3$	67	430	(Fan and Kim 2002)
$0.5PZN–0.5Pb(Zr_{0.5}Ti_{0.5})O_3$	67	600	Present study
$0.3PZN–0.7Pb(Zr_{0.5}Ti_{0.5})O_3$	70	690	Present study

CONCLUSIONS

A comparison between the conventional method and the columbite method was made in the preparation of ceramics within the solid solution of *x*PZN–(*1-x)*PZT over a wide range in composition ($x = 0.1 \sim 0.5$). The optimum processing conditions for excellent ferroelectric properties were identified. Based on the X-ray structural analysis and ferroelectric property measurements, the following conclusions can be drawn:

1. Compared to the columbite method, the conventional method requires lower calcinations temperature to eliminate the pyrochlore phase formation. Increasing in the molar fraction of PZN requires increased calcination

temperatures in order to achieve phase-pure perovskite. At 900°C, all the compositions for both methods can be converted to single-phase perovskite.

2. In ceramics sintered from columbite method as prepared powders, a sharp transition from tetragonal to pseudo-cubic rhombohedral phase was evidenced by the XRD analysis. Thus, an MPB exists between $x = 0.2$ and 0.3. However, such a phase transformation is diffused in ceramics as prepared to the conventional method.
3. The results from XRD analysis are consistent with the ferroelectric property measurements. An abrupt change in coercive field, E_c, was observed in ceramics prepared by the columbite method at the same composition range of $x = 0.2 \sim 0.3$. In contrast, gradual change was found in ceramics prepared by the conventional method.
4. For both methods, no considerable variation of the remanent polarization with compositions was observed. However, the coercive field was observed to decrease with increasing amount of PZN. The columbite method was found to produce ceramics with better ferroelectric properties with higher remanent polarization and lower coercive field.

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