# CHAPTER 4

# INFLUENCE OF PROCESSING CONDITIONS ON THE PHASE TRANSITION AND FERROELECTRIC PROPERTIES OF $x\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$–$(1\text{-}x)\mathrm{Pb(Zr_{1/2}Ti_{1/2})O_3}$ CERAMICS

***Overview*** – 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 was no significant difference in $P_r$ across the composition range. However, the coercive field $E_c$ was shown to exhibit a strong compositional dependence. 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 the columbite method. However, this transformation was obscured in the ceramics prepared with the mixed oxide method. It is proposed that compositional heterogeneities were responsible for these experimental investigations.

## 4.1 Introduction

Ferroelectric materials are widely used for various devices, including multilayer capacitors, sensors, and actuators. By the 1950's, the piezoelectric solid solution $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) was found to host exceptionally high dielectric and piezoelectric properties for compositions close to the morphotropic phase boundary (MPB).[2] This MPB is located around $PbTiO_3$:$PbZrO_3$ ~ 1:1 and separates the Ti-rich tetragonal phase from the Zr-rich rhombohedral phase.[13] Most commercial PZT ceramics are thus designed in the vicinity of the MPB with various dopings in order to achieve high properties.

$Pb(Zn_{1/3}Nb_{2/3})O_3$ (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.[21] Extensive research has been carried on PZN single crystals because of their excellent dielectric, electrostrictive, and optical properties.[25] Although single crystals of PZN can routinely be grown by the flux method[47], 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.[16] Attempts to synthesize perovskite PZN ceramics invariably results in the formation of pyrochlore phase with inferior dielectric and piezoelectric properties. The columbite method, as suggested by Swartz and Shrout[20] for the preparation of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramic, is not effective in suppressing pyrochlore phase formation in PZN ceramics.[16] Hot isostatic pressing was reported to be able to produce phase-pure perovskite PZN ceramics.[48] 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.*[18] 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[49] 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[24] 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.

## 4.2 Experimental procedure

For the conventional method, regent grade oxides of PbO, ZnO, $ZrO_2$, $TiO_2$ and $Nb_2O_5$ were mixed in the required stoichiometric ratios for the general composition $x$PZN–$(1-x)$PZT where $x = 0.1, 0.2, 0.3, 0.4$, and $0.5$. After ball milling for 24 hours and drying at 120°C, the mixture was calcined at temperatures between 750 to 950°C for 4 hours in a double crucible configuration.[50] A heating rate of 20°C/min was selected for all of the compositions in this system.[50] For the columbite method, the columbite precursor $ZnNb_2O_6$ was prepared from the reaction between ZnO (99.9%) and $Nb_2O_5$ (99.9%) at 975°C for 4 hours. The wolframite precursor $ZrTiO_4$ was formed by reacting $ZrO_2$ (99.9%) with $TiO_2$ (99.9%) at 1400°C for 4 hours.[51] The precursors $ZnNb_2O_6$, $ZrTiO_4$ were then subsequently mixed with PbO (99.9%) (with 2 mole% excess PbO[50]) and milled, dried, and calcined under the same conditions as the powder prepared by conventional method. The calcined powders of both methods were cold isostatically pressed into pellets at a pressure of 80 MPa.

Five sintering conditions were selected to be used with both methods ranging 1175°C, 1200°C, 1225°C, 1250°C, and 1,275°C dwell 2 hours. 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 and peak deconvolution was done with JADE v.6. The relative amounts of perovskite and pyrochlore phases were approximated by calculating the ratio of the major XRD peak intensities of the perovskite and pyrochlore phase using the equation (3.1)

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 hours 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.

## 4.3 Results and discussion

### 4.3.1 Perovskite phase formation and the MPB

Powder XRD patterns of the calcined *0.3*PZN-*0.7*PZT powders at different calcination temperatures for both methods are shown in Fig. 4.1(a) and (b). The XRD results show that the pyrochlore phase $Pb_{1.88}(Zn_{0.3}Nb_{1.25})O_{5.305}$ (JCPDS No.25-0446) was dominant at calcination temperatures of 750°C and below for all of the columbite-derived powders. The precursor phases PbO, $ZrTiO_4$, $ZnNb_2O_6$ were also detected by XRD at below 800°C. No evidence of the precursor phase $ZrO_2$, $TiO_2$,

$Nb_2O_5$ or ZnO was detected by XRD for conventional preparation. Moreover, the pyrochlore phase was only observed in the conventional method-derived powders for compositions with a high concentration of lead zinc niobate. It is assumed that the columbite phase $ZnNb_2O_6$ decomposed via reaction with PbO at low temperatures to form the pyrochlore phase $Pb_{1.88}(Zn_{0.3}Nb_{1.25})O_{5.305}$.

For the conventional method, $Pb_xNb_yO_z$ pyrochlore phases were found at calcination temperatures below 800°C for $x > 0.3$. Swartz & Shrout[20] reported that in PMN, no reaction occurs between the individual raw oxides until 700°C. Only cubic pyrochlore was detected at 700°C. Only cubic pyrochlore was detected at 700°C. The pyrochlore phase reacted with PbO and MgO at 850-900°C to form a mixture of perovskite and cubic pyrochlore phases. They reported that this discrepant from earlier studies was due to different experimental parameters such as surface area of raw materials and heating rate. In their work, 100% perovskite PMN could not be formed by conventional mixed oxide processing. In the work by Chen *et.al.*[52] it was reported that in the lead-niobium pyrochlore system the cubic $Pb_3Nb_4O_{13}$, pyrochlore phase (JCPDS No. 25-443) forms first around 580°C. At higher temperatures, it transforms to $Pb_2Nb_2O_7$, (JCPDS No. 40-828) and finally to $Pb_3Nb_2O_8$, (JCPDS No. 30-712) with increased calcination temperatures. At 800°C, the pyrochlore phase began to decrease and disappeared completely at 850°C for powder prepared by conventional method and at 900°C for the columbite method. The optimum calcination temperature for the formation of phase pure perovskite was found to be about 850°C for the conventional method and 900°C for the columbite method.

The perovskite phase formation for both processing methods at various calcination temperatures is shown in Fig. 4.2(a) and 4.2(b) respectively. All the compositions from both methods in the present work showed pyrochlore-free XRD scans at calcination temperatures at above 900°C. These experiments indicate that for both methods as the concentration of the PZN phase increased the calcination temperature must be increased in order to obtain phase-pure perovskite. Most processing procedures for PZN-based ceramics make use of calcination temperatures in excess of 900°C. The experiments in this study suggest that the conventional method helps to stabilize the perovskite phase compared with the columbite method.

Moreover the perovskite formation temperature for the conventional method was significantly lower than that of the columbite method. The difference in the formation temperatures was presumably due to a different reaction path to the formation of the perovskite phase for the two methods. However, any technique which would improve the reactivity of the B-site constituent oxide or of the whole mixture would lead to improved perovskite yield. One such technique is to optimizing the firing schedule; perovskite yield was also found increase in PMN case. For example, a fast rate of 170°C/min resulted in 49 % perovskite phase and a relative permittivity of 313 while a slow rate of 5°C/min. resulted in a 79 % perovskite yield with an improved relative permittivity of 5,050. Lejeune *et.al*[30] attributed this large variation in perovskite yield to the sluggishness of the kinetics causing incomplete reaction for the fast heating rate.

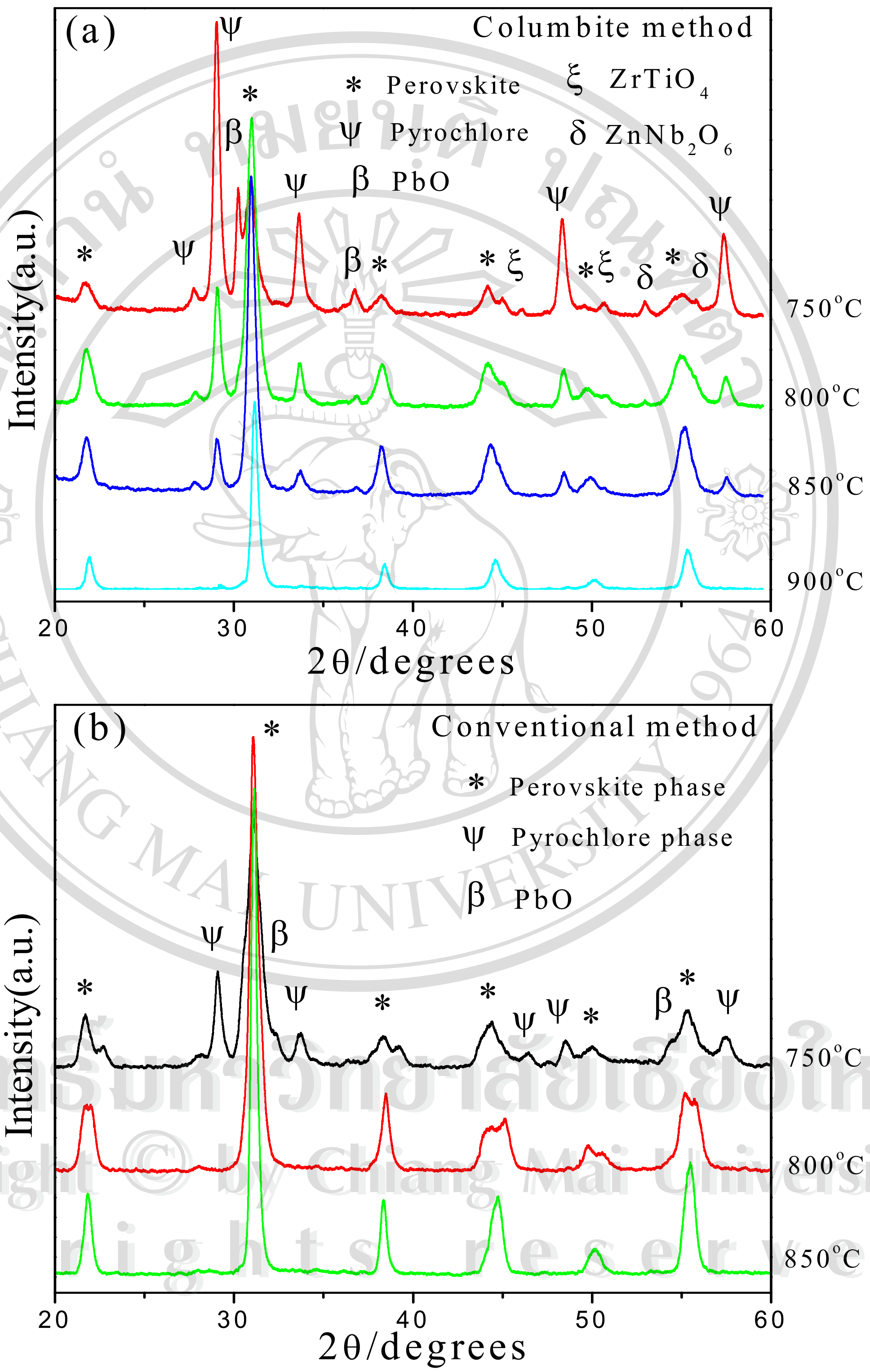

**Figure 4.1** XRD patterns for *0.3*PZN – *0.7*PZT ceramics calcined at varies temperatures for 4 hours. (a) columbite method ; (b) conventional method.

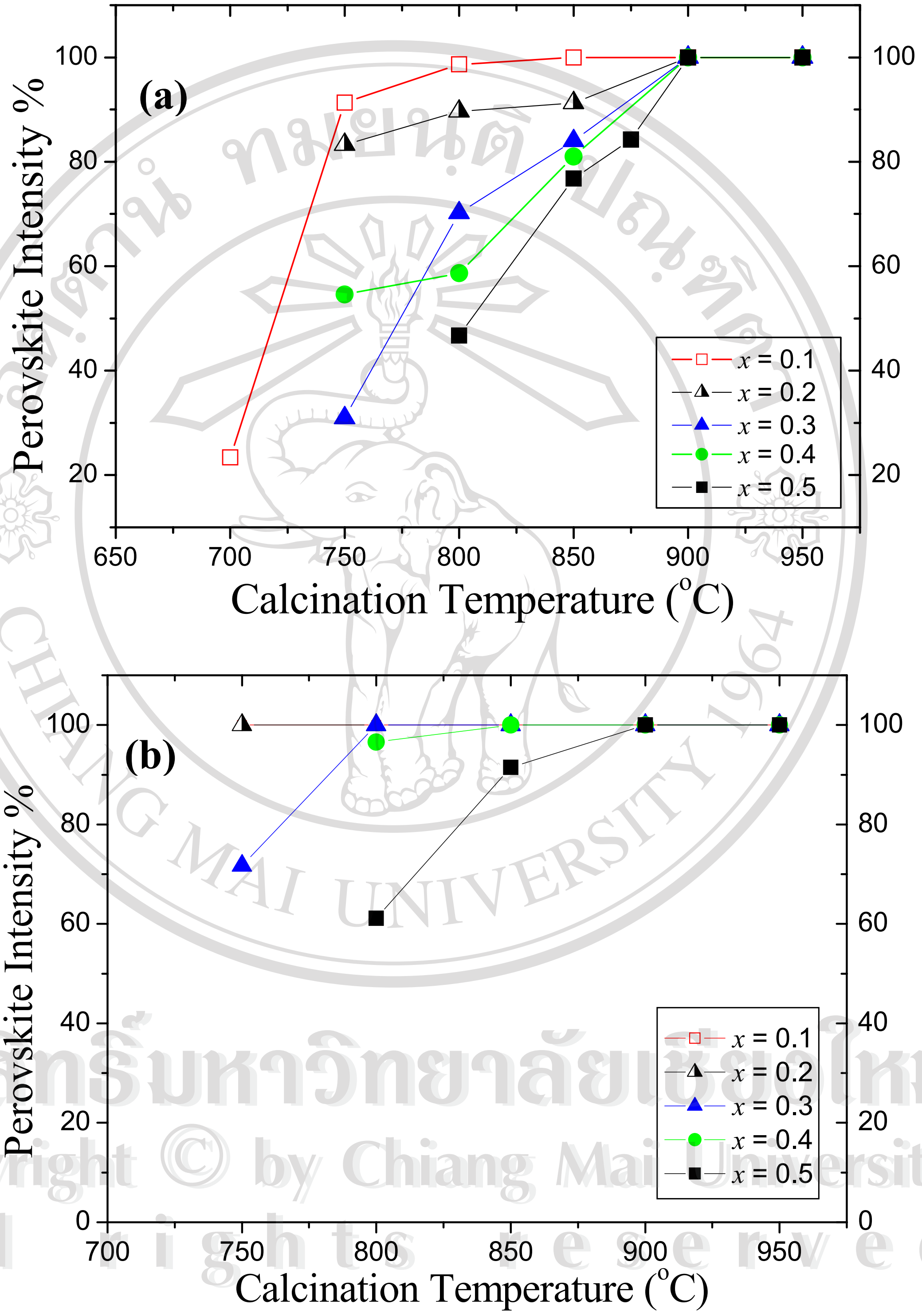

**Figure 4.2** Percentage of perovskite phase as a function of calcination temperature for *x*PZN – *(1-x)*PZT ceramics: (a) columbite method; (b) conventional method.

Fig. 4.3 shows the XRD patterns of $x$PZN–$(1-x)$PZT ceramics sintered at 1200°C for 2 hours to illustrate the change in crystal structure as a function of composition for both processing methods. The results indicate that, for the same composition, different processing methods may develop a perovskite structure with different symmetries. Fig. 4.4 shows the evolution of the (200) peak as a function of composition and processing method. The $PbZrO_3$–$PbTiO_3$ phase diagram predicts that at room temperature $Pb(Zr_{1/2}Ti_{1/2})O_3$ falls within the tetragonal phase field near the MPB.[2] The XRD patterns with low PZN concentration show strong (200) peak splitting which is indicative of the tetragonal phase.

As the PZN concentration increased, for both processing methods the (200) transformed to a single peak which suggests rhombohedral symmetry. Fig. 4.5(a)-(d) show the XRD patterns for both processing methods in the vicinity of the MPB at $x = 0.2$ and $0.3$ over the range $2\theta = 43 - 45.5$. The data shows the appearance of a triplet peak due to the superposition of the tetragonal and rhombohedral (200) peaks. The columbite prepared samples show a relatively sharp transition between the tetragonal phase at $x = 0.2$ to the rhombohedral phase at $x = 0.3$. In the conventional prepared samples, while the $x = 0.2$ samples shows the presence of the tetragonal phase there is a strong co-existence of both phases for the $x = 0.3$ pattern.

While Fan and Kim[24] reported a phase boundary in the same PZN-PZT system at the composition $x = 0.5$, there are no prior reports of the phase boundary observed in this work between $x = 0.2$ to $0.3$.

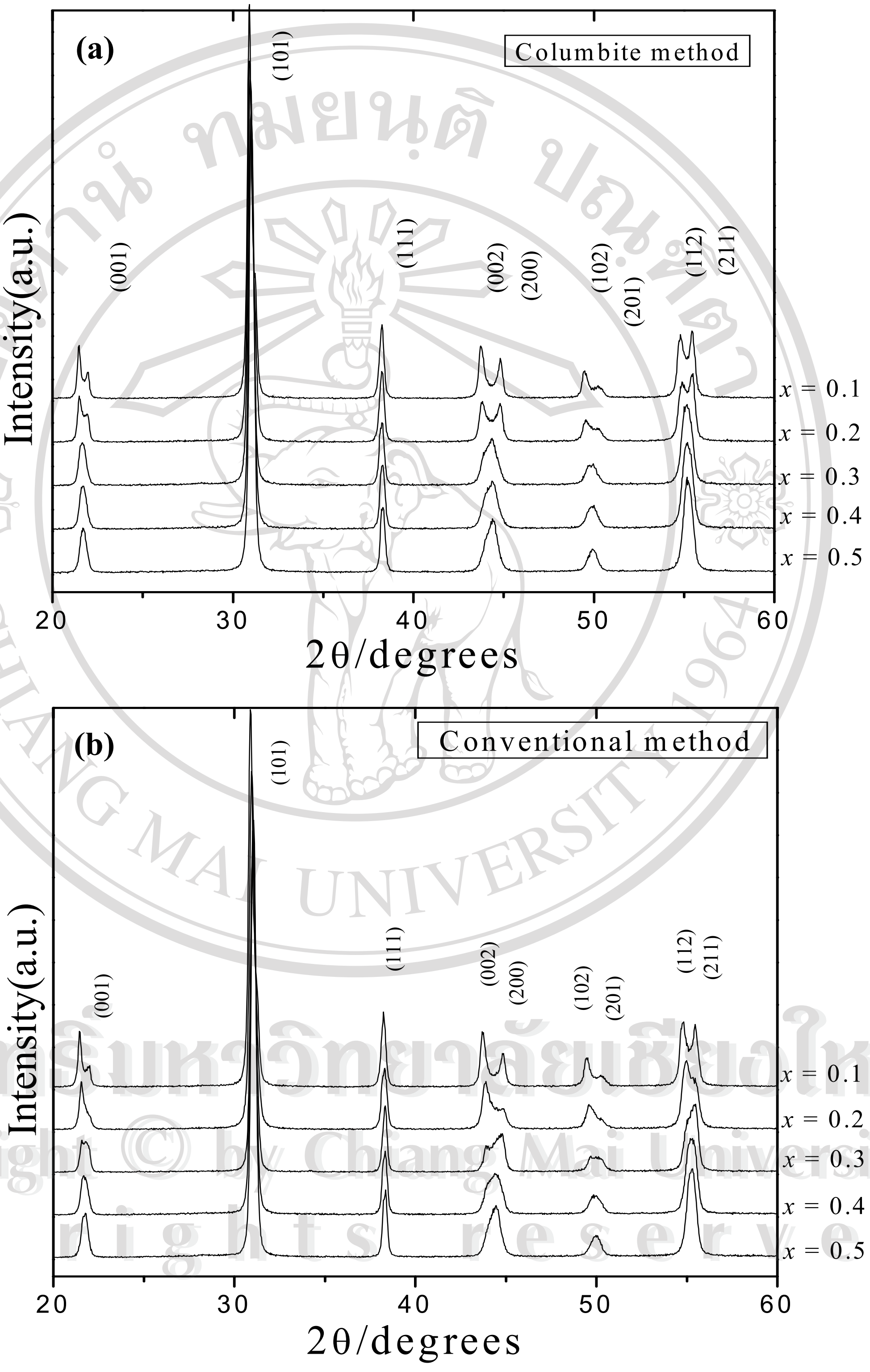

**Figure 4.3** XRD patterns for $x$PZN – $(1-x)$PZT ceramics sintered at 1200°C for 2 hours : (a) columbite method ; (b) conventional method.

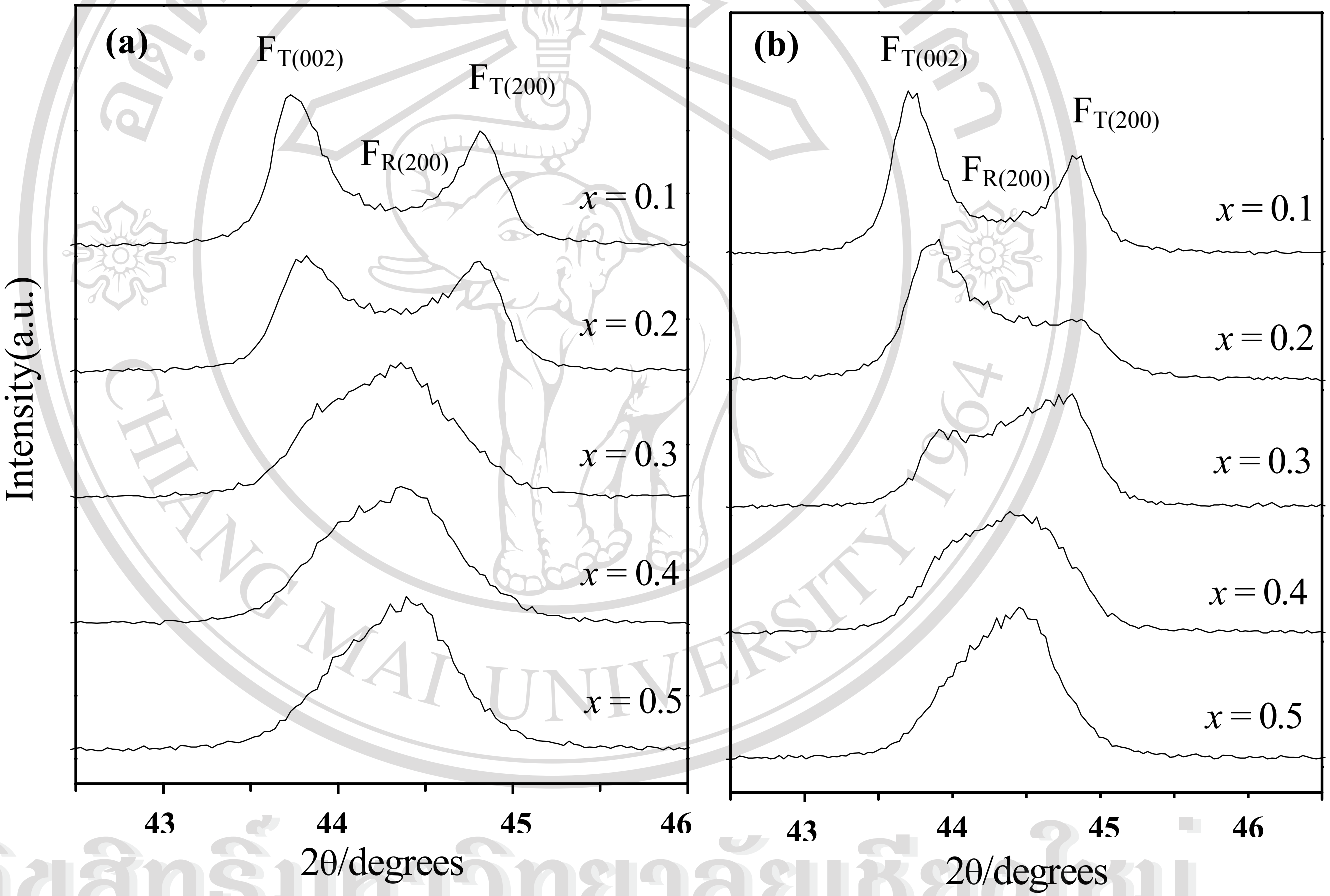

**Figure 4.4** Close examination of the (002) peaks shown in Fig. 4.2(a) columbite method; (b) conventional method.

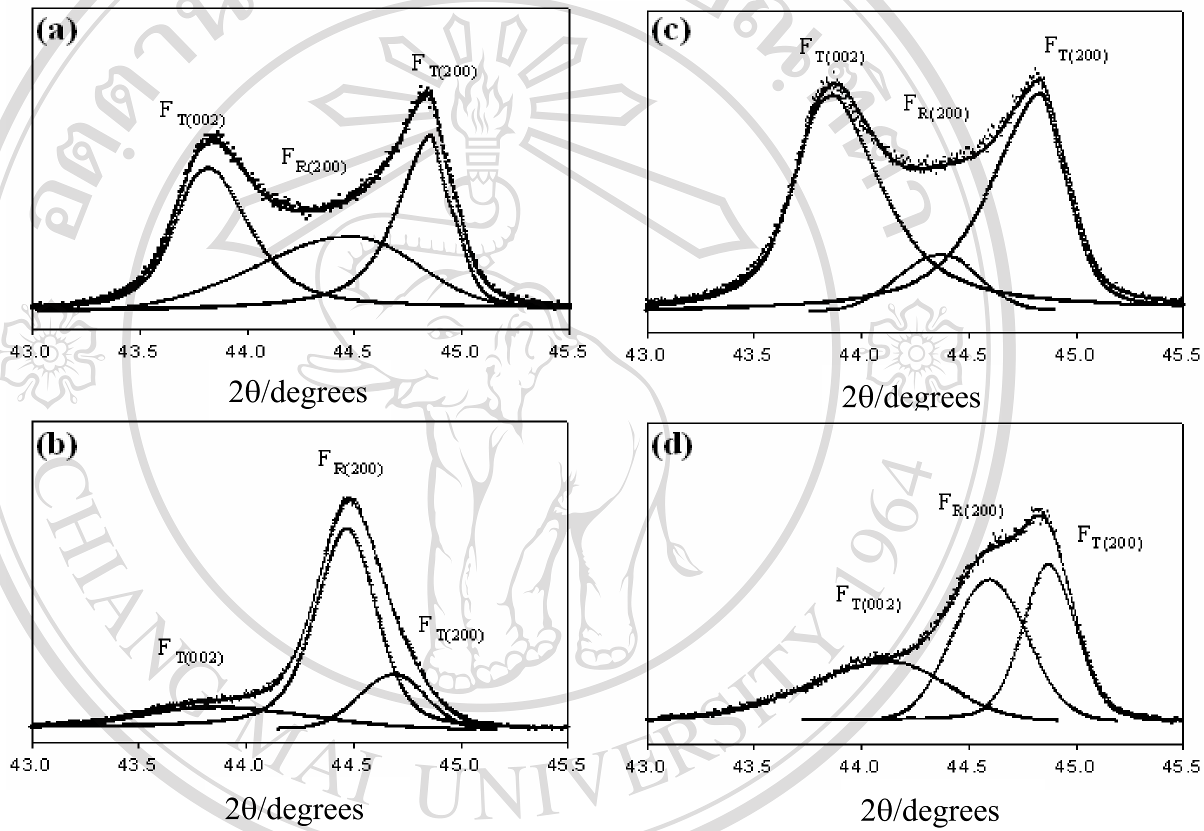

**Figure 4.5** Individual x-ray diffraction (002) peak for the tetragonal ($F_{T(002)}$ , $F_{T(200)}$) and Rhombohedral($F_{R(200)}$) phase for difference methods,

(a) *0.2*PZN-*0.8*PZT prepared by columbite method, (b) *0.3*PZN-*0.7*PZT prepared by columbite method,

(c) *0.2*PZN-*0.8*PZT prepared by conventional method, (d) *0.3*PZN-*0.7*PZT prepared by conventional method.

## 4.3.2. Effect of sintering temperature and post-sinter annealing

The effect of sintering temperature on the properties was assessed by the polarization–field (P/E) measurements. Fig. 4.6 shows the results for the composition of $x = 0.2$ for both methods at different sintering temperatures. Ceramics from both methods showed normal ferroelectric behavior with a rectangular loop. The remanent polarization, $P_r$, was observed to increase with increasing sintering temperature. This is probably due to the smaller grain size at low sintering temperature. This may result in a smaller domain size, and furthermore domain wall motion in smaller grains is subject to stricter constraints.[13] Strong internal stresses are expected in fine-grained specimens and polarization switching is thus greatly suppressed. This was accompanied by the decrease in the coercive field with increasing sintering temperature.[53] For compositions with $x > 0.3$, the $P_r$ decreased at high sintering temperatures. For the composition of $x = 0.1$, rectangular hysteresis loops were not observed even at a sintering temperature of 1250°C, as shown in Fig.. 4.7. It has been reported that post-sinter annealing is effective in improving the dielectric and ferroelectric properties of lead-based ceramics.[39] Specimens for each composition sintered at the lowest temperature (1175°C) were annealed at 1250°C for 6 hours. Indeed, significant improvements of the ferroelectric properties were demonstrated (see Fig. 4.7 for the 0.1PZN–0.9PZT). The results on other compositions are listed Table 4.1. Very limited improvements were observed for the $x = 0.5$ composition because the higher PZN content required lower sintering temperatures, thus limiting the efficacy of the annealing step. It has been suggested that PZT ceramics should be sintered at temperatures above 1200°C[16,28] and PZN-based ceramics should be sintered below this temperature[16] to achieve the best combination of density and properties.

This explains the results in our present study where increasing molar fraction of PZN directly led to a lower sintering temperature. Therefore, post-sinter heat treatment is not necessary for ceramics with high PZN content. Based on these ferroelectric measurements, the optimum sintering conditions for compositions of $x = 0.3$, $0.4$, and $0.5$ is 1200°C for 2 hours. The sintering process was not completed at these sintering conditions for compositions of $x = 0.1$ and $0.2$ and therefore post-sinter annealing at 1250°C for 6 hours is necessary for improvement of ferroelectric properties. Further characterization techniques and comparisons, which are described in the following section, were made on these as-sintered specimens (for $x = 0.3$, $0.4$, $0.5$) and annealed specimens (for $x = 0.1$, $0.2$) because they were found to have the optimum ferroelectric properties.

**Table 4.1** Post-sinter annealing effects on the remanent polarization $P_r$ and saturation polarization $P_s$ in $x$PZN–$(1-x)$PZT ceramics sintered at 1175°C for 2 hours and annealed at 1250°C for 6 hours.

| $x$ | $x$PZN–$(1-x)$PZT | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Columbite method | | | | Conventional method | | | |
| | $P_r$ (μC/cm$^2$) | | $P_s$ (μC/cm$^2$) | | $P_r$ (μC/cm$^2$) | | $P_s$ (μC/cm$^2$) | |
| | sintered | annealed | sintered | annealed | sintered | annealed | sintered | annealed |
| *0.1* | 7.6 | 37.1 | 15.8 | 42.9 | 9.4 | 34 | 19.0 | 39.2 |
| *0.2* | 14.6 | 36.1 | 20.6 | 38.9 | 13.8 | 31.5 | 21.4 | 35.0 |
| *0.3* | 31.9 | 30.4 | 37.2 | 33.5 | 23.8 | 20.0 | 27.9 | 23.2 |
| *0.4* | 32.3 | 30.6 | 35.8 | 34.5 | 30.5 | 23.2 | 35.0 | 28.7 |
| *0.5* | 35.6 | 36.4 | 40.4 | 42.1 | 29.4 | 29.5 | 34.5 | 34.9 |

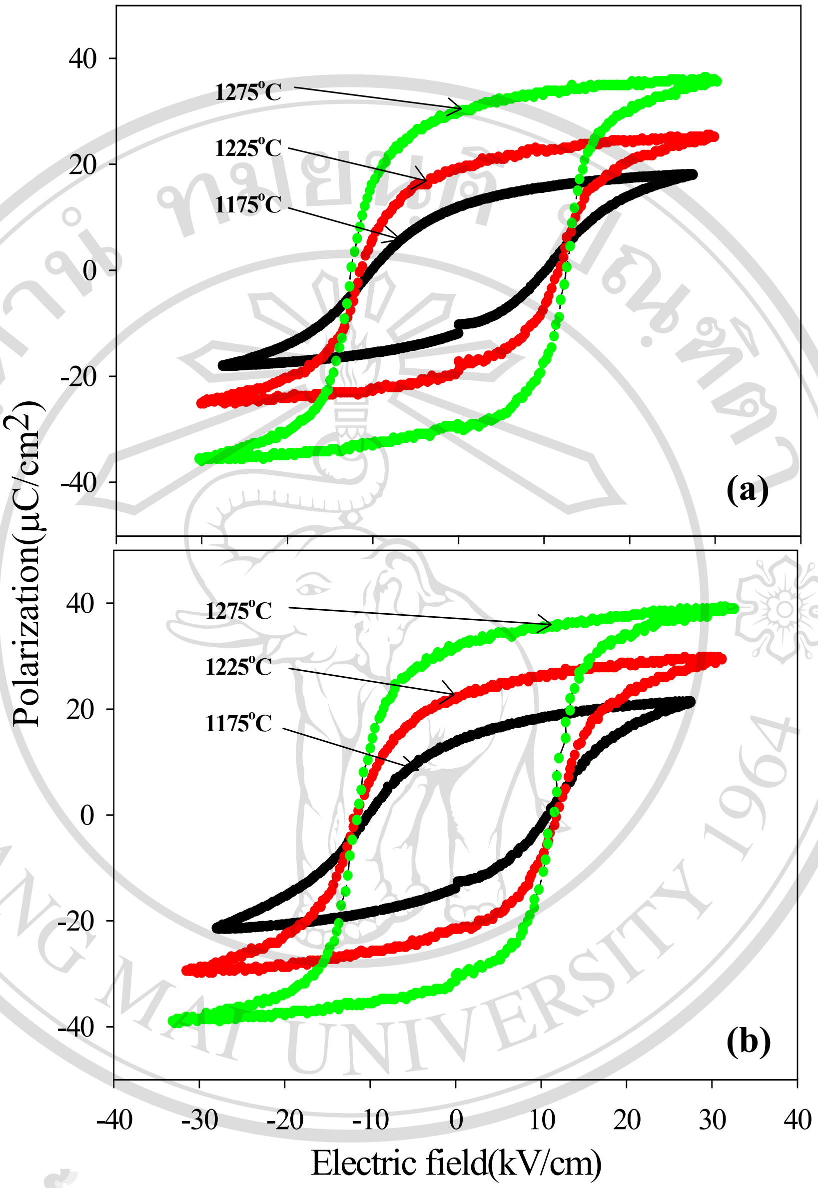

**Figure 4.6** Room temperature P-E hysteresis as a function of sintering temperature for *0.2*PZN – *0.8*PZT: (a) columbite method; (b) conventional method.

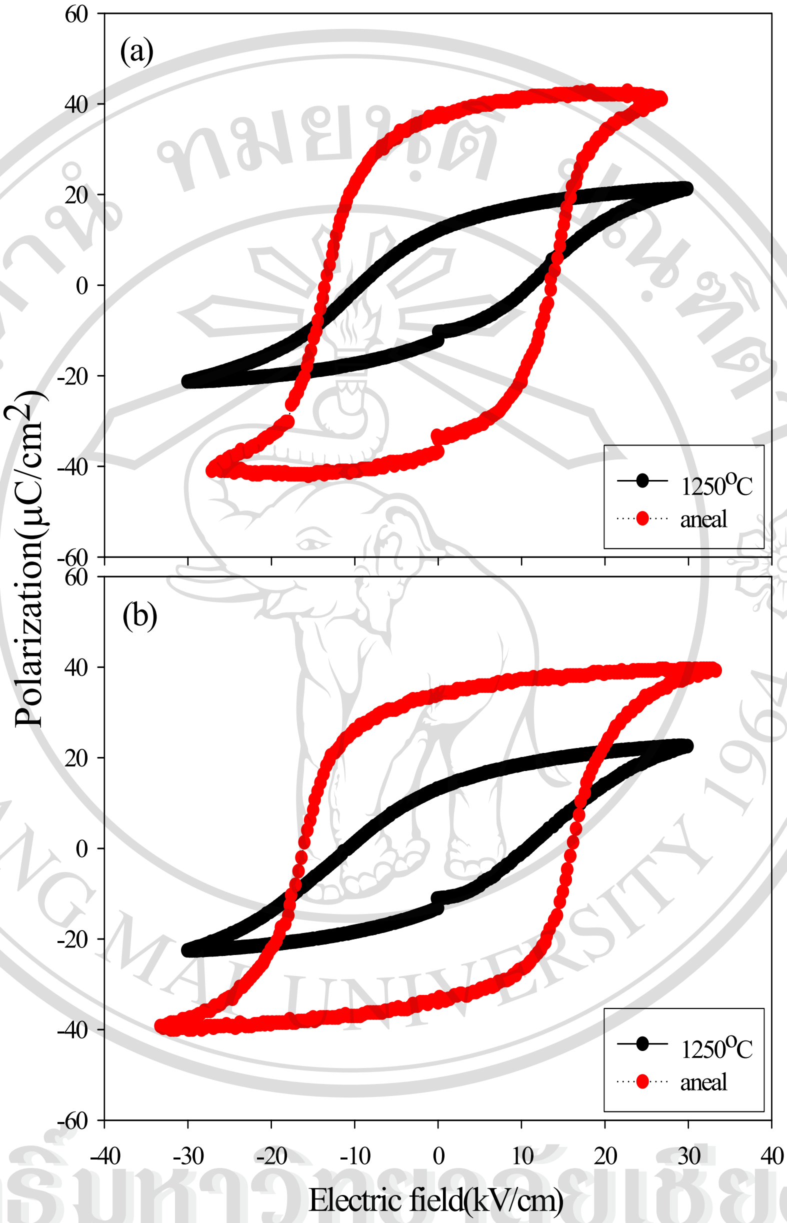

**Figure 4.7** Effect of post-sinter annealing on the P-E hysteresis for *0.1*PZN – *0.9*PZT ceramics: (●) sintered at 1250°C, (o) sintered at 1175°C and annealed at 1250°C for 6 hours: (a) columbite method, (b) conventional method.

## 4.3.3. Effect of processing method on the phase transformation

The P–E ferroelectric property measurements for the specimens processed at optimum conditions are summarized in Fig. 4.8. 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 Fig. 4.9. 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, as indicated in Fig. 4.9(b). Combined with the XRD examination described in section 4.3.1, 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.

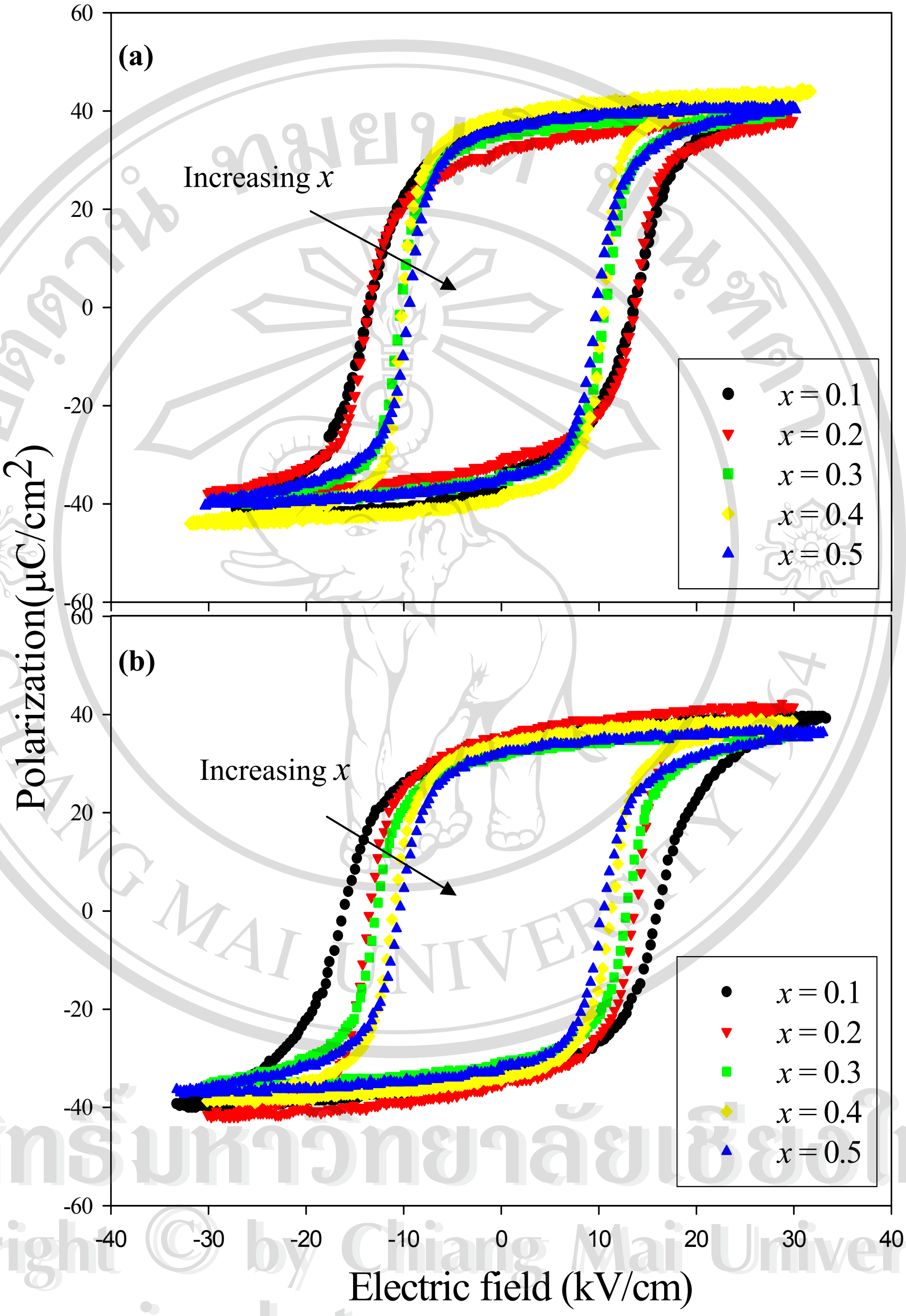

**Figure 4.8** Effect of composition ($x$) on the P-E hysteresis loops for $x$ PZN − *(1-x)* PZT processed at the optimum processing conditions: (a) columbite method;(b) conventional method.

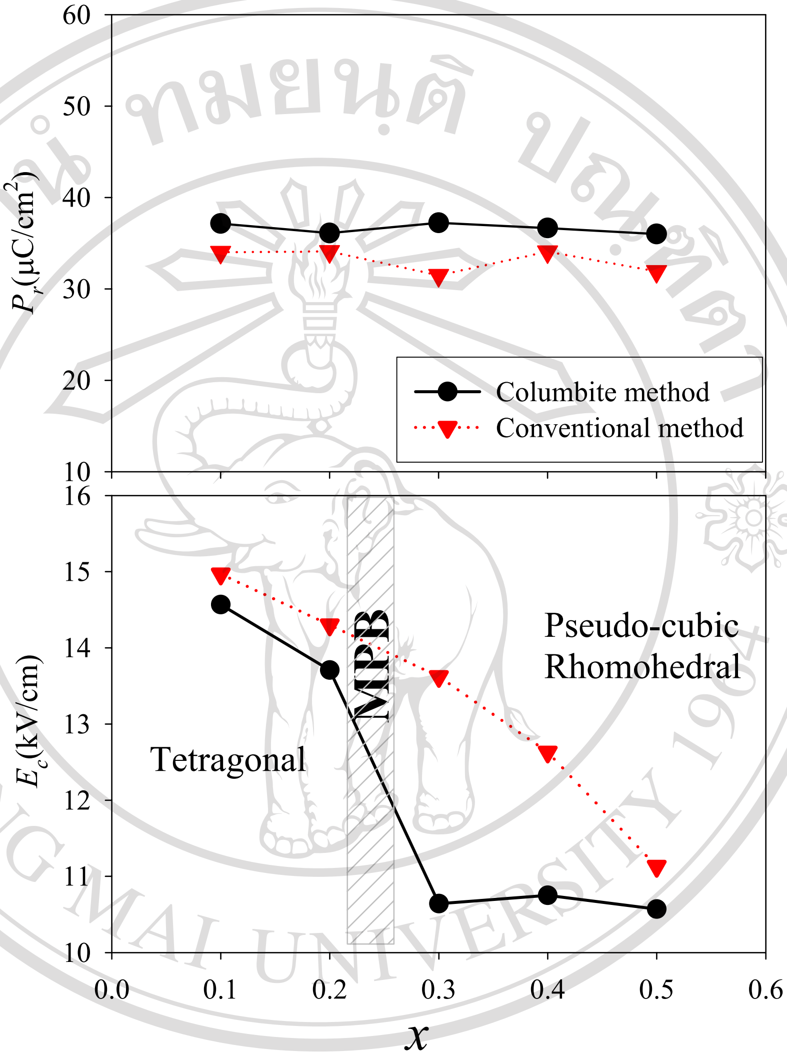

**Figure 4.9** Variation of remanent polarization $P_r$ and coercive field $E_c$ with composition for $x$ PZN – $(1-x)$PZT ceramics: (a) remanent polarization; (b) coercive field.

## 4.4 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−$(1\text{-}x)$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 calcination 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 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 diffuse in ceramics prepared by 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. Lower sintering temperatures were required for compositions with an increasing molar fraction of PZN. For the $x = 0.1$ and $0.2$ compositions, sintering at 1250°C for 2 hours was observed to produce inferior ferroelectric properties and post-sinter annealing was required to achieve excellent ferroelectric properties.
5. 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.