CHAPTER 8
CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

8.1.1 PZN-PZT system

The conventional mixed oxide method and the columbite-(wolframite) precursor method were successfully used to synthesize phase pure perovskite *x*PZN-(*1-x*)PZT $x = 0.1\text{-}0.5$ ceramics. Phase pure perovskite was obtained at lower calcination temperatures using the conventional method compared to the columbite method. The columbite method required calcination temperatures as much as 150°C higher for some PZN-PZT compositions. It should be noted that the combination of using a double crucible, excess PbO (2 mol%), and a fast heating/cooling rate (20^{o}C/min) were shown to be effective in reducing the total amount of pyrochlore phase in PZN-PZT system. The optimal calcination conditions and optimal sintering conditions for single phase PZN-PZT are shown in Table 8.1. Based on these ferroelectric measurements, the sintering process was not entire completed under these sintering conditions for compositions of $x = 0.1$ and 0.2 and therefore post-sinter annealing at 1250°C for 6 hours was necessary for improvement of ferroelectric properties. This explains the results from our present study where increasing the 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. Compared to the conventional method, ceramics sintered from the columbite method prepared

powders exhibited a sharp transition from a tetragonal to a pseudo-cubic rhombohedral phase as evidenced by the XRD analysis. Thus, an MPB clearly exists between $x = 0.2$ and 0.3.

However, such a phase transformation was diffuse in ceramics prepared by the conventional method. The results from XRD analysis were 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, a gradual change was observed in ceramics prepared by the conventional method. 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. Although the transition temperature of ceramics from both methods varied linearly with composition, the relative permittivity and piezoelectric properties did not. The columbite method was found to produce ceramics with enhanced ferroelectric properties with a higher remanent polarization and lower coercive field.

Investigations on the structure and properties of the $x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$–$(1-x)\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ system over the range $x = 0.1 – 0.6$ have revealed a well-defined MPB around $x = 0.25$, separating a tetragonal phase from a rhombohedral phase. A normal ferroelectric to relaxor ferroelectric transition is also observed around $x = 0.5$ to 0.6.

Table 8.1 Optimal calcinations temperature of *x*PZN-(*1-x*)PZT

Composition *x*	Calcination temperature*		Sintering temperature	
	Conventional method	Columbite method	Conventional method	Columbite method
x = 0.1	750°C	850°C	1150°C 2 h /1250°C 6 h	1150°C 2 h / 1250°C 6 h
x = 0.2	750°C	850°C	1150°C 2 h /1250°C 6 h	1150°C 2 h / 1250°C 6 h
x = 0.3	800°C	900°C	1200°C 2 h	1200°C 2 h
x = 0.4	850°C	900°C	1200°C 2 h	1200°C 2 h
x = 0.5	900°C	900°C	1200°C 2 h	1200°C 2 h

* dwell 4 hours with heating/cooling rates of 20°C/min

The maximum values occurred for the *0.2*PZN-*0.8*PZT composition prepared by columbite method. The maximum permittivity at the transition temperature was 25,800, with a room temperature relative permittivity of 1,150 being obtained. The maximum piezoelectric coefficients occurred in the *0.3*PZN-*0.7*PZT composition. The piezoelectric coefficients obtained were d_{33} = 650 pC/N and k_p = 0.70. In fact the composition between x = *0.2-0.3* was found to have the optimum properties of all of the PZN-PZT compositions studied. These values are comparable or better than those in soft PZT ceramic near the MPB, which exhibits a room temperature relative permittivity of 1,700 at 1kHz and piezoelectric coefficients of d_{33} = 374 pC/N and k_p= 0.60. Moreover, with increasing PZN concentrations a transition between normal ferroelectric to relaxor ferroelectric was observed in composition x = *0.5* for both methods.

8.1.2 PNN-PZT system

The columbite-(wolframite) precursor method was successfully used to synthesize phase-pure perovskite ceramic of *x*PZT-(*1-x*)PNN; x = *0.4-0.9*. The crystal structure data obtained from XRD indicates that the solid solution *x*PZT-(*1-x*)PNN, where x = *0.4-0.9*, successively transforms from pseudo-cubic to rhombohedral to tetragonal symmetry with an increase in PZT concentration. There is a good linear relationship between T_{max} and x, indicating that this system is a well behaved complete solid solution. The relative permittivity was found to improve nearly linearly, until approximately 10%PNN. From the results in the PNN-PZT system the conclusion from chapter 6, that the phase boundary occurs between x = *0.2-0.3*, was supported. In fact the composition *0.2*PNN-*0.8*PZT was found to have the optimum

properties of all of the PNN-PZT compositions studied. The maximum values occurred in the *0.2*PNN-*0.8*PZT composition. The maximum permittivity at the transition temperature was 36,000, at room temperature the relative permittivity of 835 was obtained. A smooth transition from relaxor to normal ferroelectric behavior is observed with increasing mole percent of PZT from $x = 0.7$ to 0.9. Furthermore, the relaxor–normal transformation is very clearly observed with increased PZT concentrations above $x = 0.7$. Both the diffuseness parameter δ_γ and the parameter γ decreased with an increase in the mole fraction of PZT.

8.1.3 PNN-PZN-PZT system

Some general trends were found in these systems. The MPB compositions investigated in this thesis follow the general trend of decreasing piezoelectric coefficient and relative permittivity with increasing Curie temperature. The effect of the transition temperature (T_m) on the piezoelectric properties and relative permittivity are clearly evident in Fig. 8.1 and 8.2. The *0.3*PZN-*0.7*PZT and *0.5*PZN-*0.5*PZT compositions both possessed high piezoelectric coefficients and significantly high transition temperatures. Both compositions are excellent candidates for high-bandwidth medical ultrasound devices because of the low mechanical quality factors and large coupling coefficients. It is noted that the materials used in the ultrasonic imaging industry have a transition ~ 210^{o}C owing to the material having a relatively high dielectric constant and large coupling coefficients with good temperature stability. Moreover, the *0.2*PZN-*0.8*PZT composition showed a large polarization and high transition temperature which also makes them attractive for high-performance actuators.

The MPB compositions investigated in the PZN-PZT system follow the trend of decreasing tolerance factor with increasing transition temperature as shown in Fig. 8.3. It is well known that the transition temperatures of the MPB compositions were found to increase with decreasing tolerance factor in the work of Eitel *et al.*[78] In their work they have shown that the transition temperature of MPB composition is inversely proportional to the tolerance factor of the relaxor end-member. Because of this relationship, the tolerance factor is a useful tool for predicting the transition temperature at the MPB. However, it is not as useful in predicting the exact composition of the MPB for a given system.[79] The average value of the B-site ionic radius shown by Yamashita and Ichinose[23] can be used to predict the value of the electromechanical coupling factor, k_p. In this paper they predicted that large value of k_p would be found for average radii of between 0.785 and 0.81. This prediction has been confirmed using the data collected in our work and as shown in Fig. 8.4.

An interesting combination of dielectric, x-ray data, piezoelectric and hysteresis properties were found in this system. The PZN-PZT system and PNN-PZT system showed micro- to nano-domain switching that resulted in the appearance of a ferroelectric phase in PZT-rich compositions.

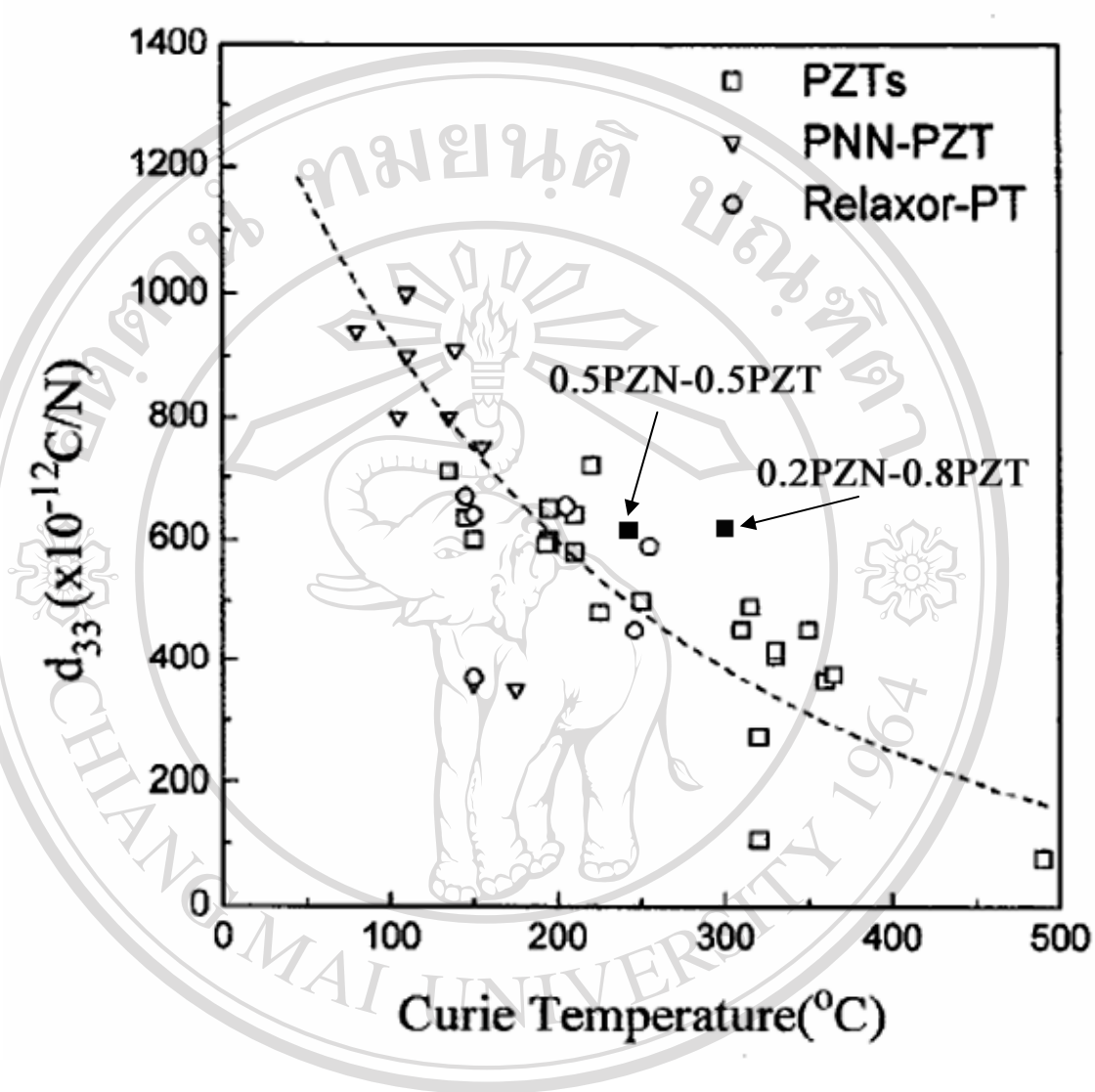


Figure 8.1 Schematic representation of piezoelectric coefficient (d_{33}) as a function of transition temperature for this study compared with other piezoelectric materials. Modified from Seung-Eek Park and Thomas R.Throut.[80]

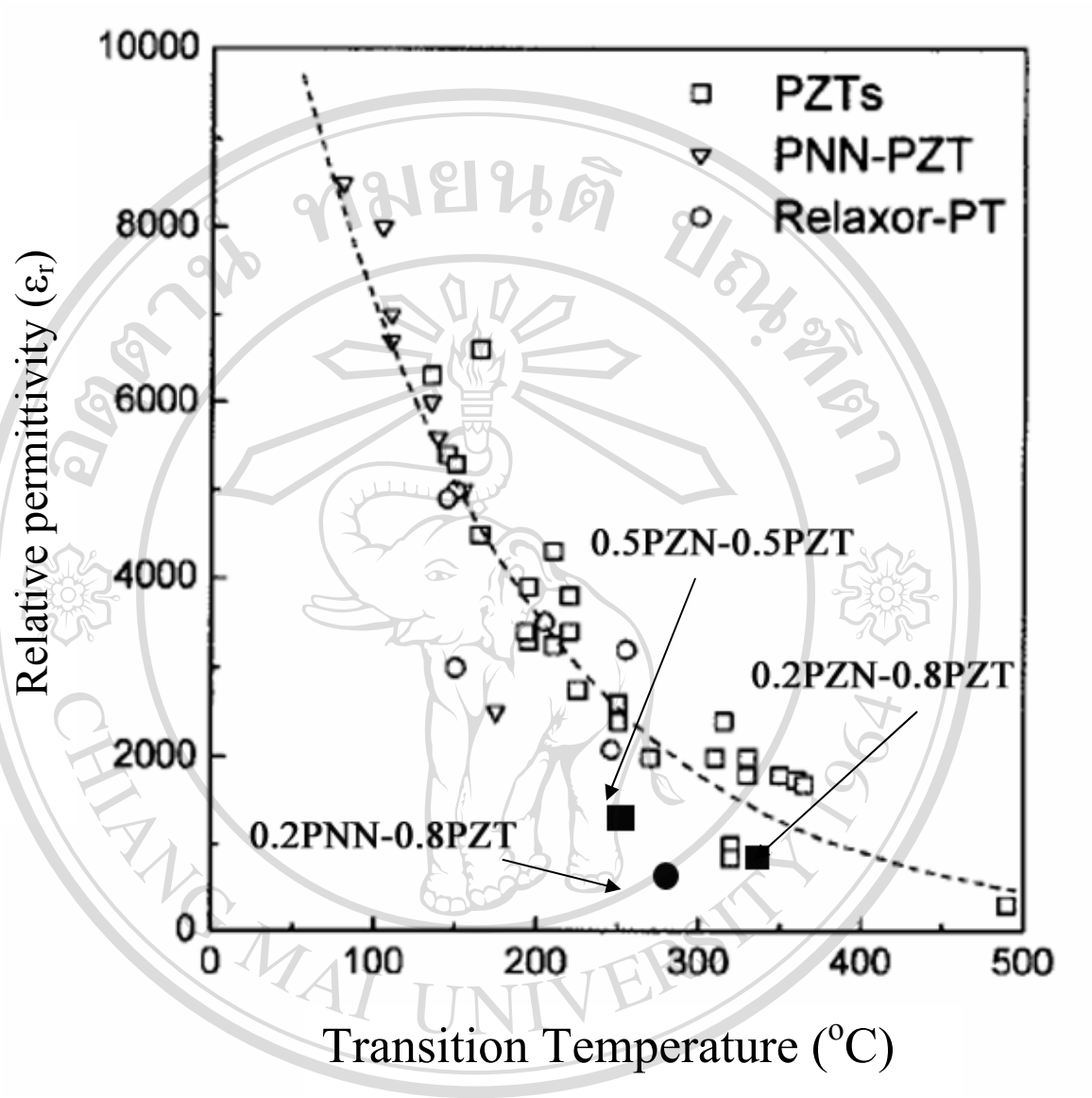


Figure 8.2 Relative permittivity as a function of transition temperature (T_m) for this study compared with other piezoelectric ceramics. Modified from Seung-Eek Park and Thomas R.Throut.[80]

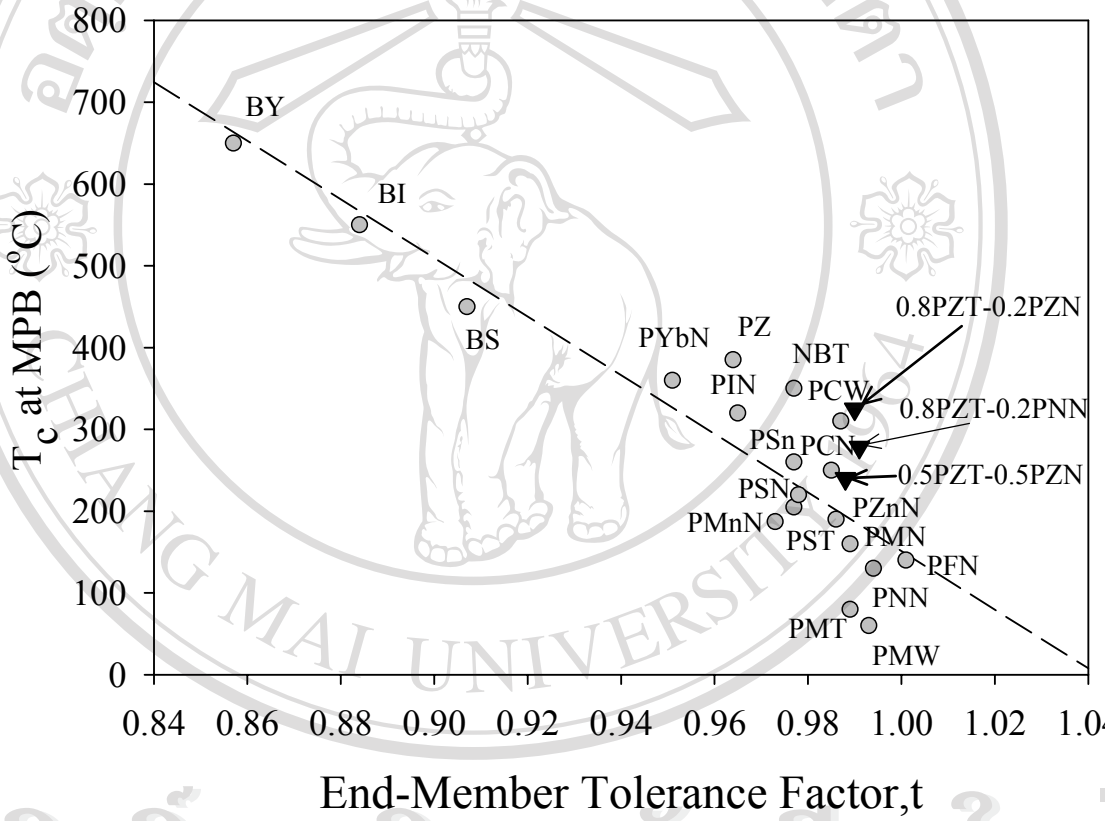


Figure 8.3 Transition temperatures as a function of the perovskite tolerance factors of the MPB composition in this system compared with other MPB composition. Modified from Eitel *et.al.*[78]

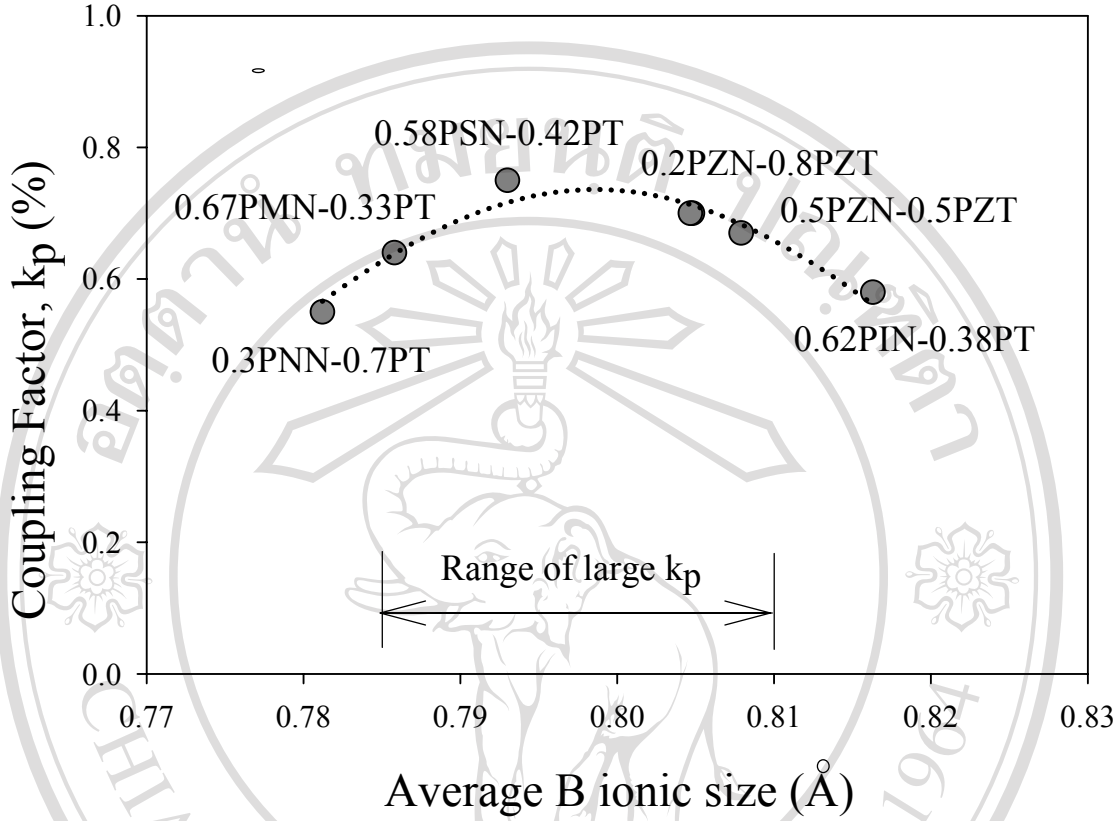


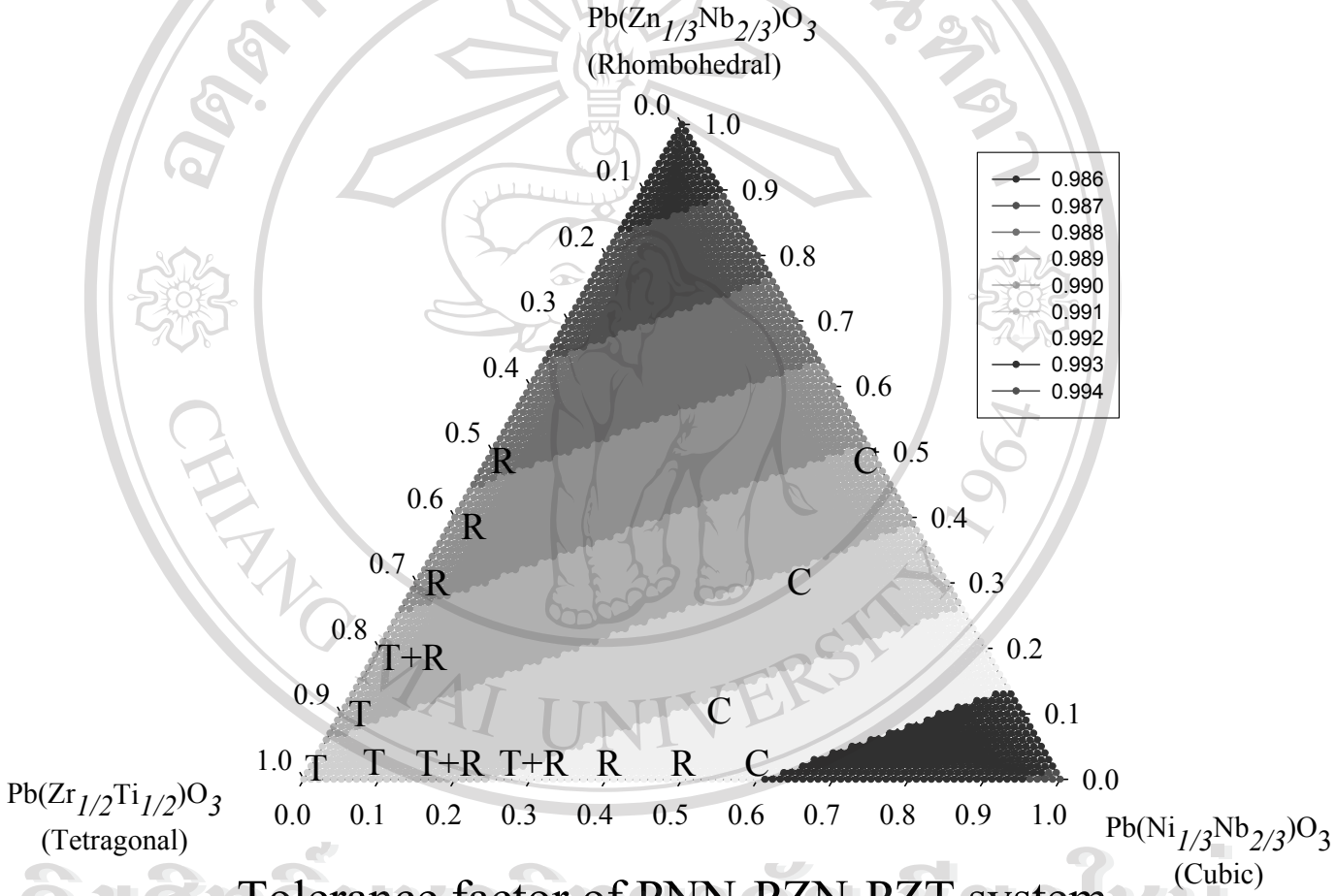
Figure 8.4 Electromechanical coupling factors, k_p, versus the average B-site ionic size of the MPB composition. Modified from Yamashita and Ichinose.[23]

8.2 Future work

The results of this work support the fact that PNN-PZN-PZT ceramics could be alternative materials to PZT for piezoelectric applications. However, the optimum properties in the PNN-PZN-PZT system have not yet been reached. Because of the broad range of compositions investigated in this study, many compositions close to the MPB have not been investigated. Moreover there are several compositions in the PNN-PZN-PZT system which may be utilized as high temperature piezoelectric materials. To predict a new MPB in this system, the crystal structure versus composition has been plotted with the tolerance factor. The location of the MPB

compositions in the ternary systems PNN-PZN-PZT should be determined and dopant modifications in all of the systems studied should also be used to further optimize properties. Fig. 8.5 shows crystal structure of this system versus compositions which have studied in this thesis. It can be seem that the new MPB compositions in this system exist between $0.0<x<0.2$ and $0.0<y<0.2$ in $(0.8-x-y)$PZT-xPZN-yPNN composition. In this thesis, only the conventional technique and columbite-wolframite precursor technique were optimized to obtain pervoskite phase purity. Further study of alternative processing techniques such as sol-gel, molten-salt and various chemistry-based approaches could be used to obtain a high degree of homogeneity and therefore enhance reaction kinetics. Crystal growth and thin film deposition would also offer alternative methods to study these systems.

The effects of annealing time and annealing temperature should also be investigated. Many researchers reported that for further improvements in piezoelectric properties, many samples were thermally treated in a flowing O_2 or air. As a result of this improvement in structure, the dielectric constant (ε_r), the piezoelectric coefficient (d_{33}), and the electromechanical coupling factor (k_p), were enhanced markedly after thermal annealing. The search for higher T_c materials is yet certainly not limited to relaxor-PT systems. It is also important to point out that to date, no relaxor-PT MPB system exhibits a higher T_c than PZT (390^{o}C), nor does any type of MPB piezoelectric material offer significant advantages in overall performance.



Tolerance factor of PNN-PZN-PZT system

Figure 8.5 Tolerance factor and crystal structure in PNN-PZN-PZT system.

Although MPB systems outside the perovskite family are found in the tungsten bronze family and high T_c piezoelectrics, including modified $PbTiO_3$ (T_c = 470°C), $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (T_c = 600°C), and $(Pb,Ba)Nb_2O_6$ (T_c= 400°C), their level of piezoelectric activity is far inferior to that of the PZT-based systems.

A number of other related materials such as the Bi*Me*O_3-PT system (*Me* = Ga, Sc, Yb, Y, etc), for example, offer the hope of transition temperatures as high as 600°C. In the future, it may be useful to fabricate optimum compositions of $BiMeO_3$-$Pb(B'B'')O_3$.

Alternative fabrication methods for new complex perovskite such as $Pb(Lu_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ $Pb(Al_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ or difficult to fabricate materials, such as $Pb(In_{1/2}Ta_{1/2})O_3$, $Pb(Ni_{1/3}Ta_{2/3})O_3$, $Pb(Ga_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ and $Pb(Y_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ should also be investigated. Many synthesis methods could be used to obtain phase pure perovskites. Based on the molecular-mass model proposed by Yamashita[59], two possible new high electromechanical coupling factor perovskite compounds are predicted. One is an aluminum-containing lead-perovskite, $Pb(Al_{1/2}Nb_{1/2})O_3$-$PbTiO_3$, which may provide larger electromechanical coupling factor than PZT 53/47 or PSNT 58/42, if a perfect compound near the MPB can be successfully synthesized. The other candidate material is $Pb(Ga_{1/2}Nb_{1/2})O_3$-$PbTiO_3$. Thus, the combination of both the bulk and single crystal forms of these compounds could yield a number of excellent of materials offering unique, high-performance alternatives for many future piezoelectric components.

Recently, materials with low lead concentrations or lead-free compositions, for example lead free solder, are preferred from the view point of environment impact. These demands may be increasingly important to piezoelectric ceramics as

well. The development of lead free piezoelectric materials as an alternative to PZT-based materials is expected in the near future. A number of other piezoelectric materials such as bismuth layer structure oxides, tetragonal tungsten bronze oxides or hexagonal tungsten bronze oxides may be utilized as high temperature piezoelectric materials.