

The effect of pyrochlore phase on formation mechanism and electrical properties of perovskite PZMN relaxors

San-Yuan Chen^a, Chien-Min Wang^b, Syh-Yyuh Cheng^b

^a Institute of Materials Science and Engineering, National Chiao-Tung University, 1001 Ta-Hsueh, Hsinchu, Taiwan, Republic of China

^b Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015 Taiwan, Republic of China

Received 17 April 1996; revised 18 November 1996; accepted 18 November 1996

Abstract

The reaction mechanism and electrical properties of phase formation of the perovskite $\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3\text{-SrTiO}_3$ (PZMN-ST) were studied. Three major pyrochlore phase types, $\text{Pb}_2\text{Nb}_2\text{O}_7$, $\text{Pb}_3\text{Nb}_2\text{O}_8$ and $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ were characterized and analyzed to understand their roles in the formation of perovskite PMN, PZN and PZMN phases. The formation of a perovskite phase within PMN relaxors requires the presence of either $\text{Pb}_2\text{Nb}_2\text{O}_7$ or $\text{Pb}_3\text{Nb}_2\text{O}_8$ pyrochlore phases in the mixture and is only slightly dependent on the presence of the stabilizer. On the other hand, the formation of a perovskite phase within PZN or PZMN relaxors requires the presence of both $\text{Pb}_3\text{Nb}_2\text{O}_8$ pyrochlore phase and stabilizer. The maximum dielectric constant for PMN, PZN and PZMN systems can be obtained with the $\text{Pb}_3\text{Nb}_2\text{O}_8$ phase present in the starting raw materials because of the benefit of $\text{Pb}_3\text{Nb}_2\text{O}_8$ to perovskite phase formation.

Keywords: Pb-based relaxors; $\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]_3\text{O}_3\text{-SrTiO}_3$; Pyrochlore phase; Perovskite phase; Reaction mechanism

1. Introduction

The Pb-based relaxors, because of their low temperature sinterability, high permittivity and low temperature coefficient of capacitance (TCC), find widespread industrial applications such as multilayer ceramic capacitors and actuators. Currently, most R&D efforts have been concentrated on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), in spite of the fact that $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) ceramic is evaluated as having higher market potential than the PMN owing to its excellent optical and electrostrictive properties [1]. One reason which hampers PZN application is the difficulty to prepare pure PZN or PZN-based ceramics with perovskite structure by conventional processing technique owing to the formation of pyrochlore phases [2], but the problem of pyrochlore formation has been studied extensively in PMN system and can be avoided by pre-reacting MgO with Nb_2O_5 to form MgNb_2O_6 columbite structure [3]. Thus stabilizers such as PbTiO_3 [4], BaTiO_3 [5,6] are usually added to increase the tolerance factor and electronegativity difference in the PZN or PZMN systems [7].

As both PMN and PZN ceramics are lead-based $\text{A}(\text{B}'\text{B}'')\text{O}_3$ type ferroelectric compounds with perovskite structure and are formed from an $\text{XPbO-YNb}_2\text{O}_5$ mixture [7], it is our conviction that the pyrochlore phase sequence present within the $\text{XPbO-YNb}_2\text{O}_5$ mixture during their for-

mation can influence the final perovskite content of the PMN and PZN. The pyrochlore phases [8–10] present in the $\text{PbO-Nb}_2\text{O}_5$ mixture are of three main compositions, namely, rhombohedral pyrochlore $2\text{PbO}\cdot\text{Nb}_2\text{O}_5$ (herein designated P_2N_2), tetragonal pyrochlore $3\text{PbO}\cdot\text{Nb}_2\text{O}_5$ (herein designated P_3N_2) and cubic pyrochlore $3\text{PbO}\cdot 2\text{Nb}_2\text{O}_5$ (herein designated P_3N_4). P_2N_2 is a stoichiometric pyrochlore phase of $\text{A}_2\text{B}_2\text{O}_7$, P_3N_4 is an A-deficient pyrochlore phase, and P_3N_2 is a B-deficient pyrochlore phase [10,11]. Although the formation sequences of perovskite phase in PMN have been reported, the role of the formed pyrochlore compound in the phase formation of PMN or PZN perovskite has not been described [12].

In this paper we shall investigate how these pyrochlore phases within $\text{PbO-Nb}_2\text{O}_5$ mixture influence the perovskite content and their effects on dielectric properties of PMN, PZN and PZMN ceramics. To study the electrical properties in this ST-PZMN system, strontium titanate (ST) [13] was utilized as a stabilizer for PZMN.

2. Experimental procedure

ST-PZMN ceramics with composition $0.12\text{SrTiO}_3\text{-}0.88\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ (ST-PZMN) were chosen for these studies. Raw materials including SrTiO_3 , PbO , ZnO ,

MgO and Nb₂O₅ were weighed in appropriate proportions and mixed together in a polyethylene jar with ZrO₂ as the grinding medium and alcohol solution as the mixing agent. After drying, the mixture was subjected to calcination at temperatures in the range 500–950°C for 4 h. The pre-calcined powder with the formula of Pb_xNb_yO_z pyrochlore phases was first synthesized by reacting PbO with Nb₂O₅ powders at 480–800°C. PZMN–ST ceramics were then fabricated by reacting the constituents with the pyrochlore phases.

The relative amount of pyrochlore phase to perovskite phase was determined by measuring the major integrated intensities of XRD peaks for perovskite (110) and for pyrochlore (222) phases (P₂N₂, P₃N₂, P₃N₄) as described by Klug and Alexander [14]. The percentage of formed perovskite phase was calculated by the following equation:

$$\% \text{perovskite} = 100 \times I_{\text{perov}} / (I_{\text{perov}} + I_{\text{pyro}})$$

where I_{perov} and I_{pyro} represent the intensities of XRD peaks for perovskite and pyrochlore phases, respectively. To determine the reaction sequences of perovskite formation, differential thermal analysis (DTA) was used to examine phase reactions during the calcination. Dielectric measurements were performed on an automated system wherein a temperature box (Delta 9023) and Hp 4192A Impedance analyzer at a frequency of 1 kHz were controlled by a desktop computer.

3. Results

3.1. Pyrochlore phase formation within XPbO–YNb₂O₅ mixtures

The formation reactions of pyrochlore phases for XPbO–YNb₂O₅ mixtures at different calcination temperatures were studied and analyzed with XRD. For the 3PbO–2Nb₂O₅ mixture (Fig. 1), cubic P₃N₄ pyrochlore phase is first formed around 580°C and remains stable throughout the whole range of calcination temperatures. For the 2PbO–Nb₂O₅ mixture (Fig. 2), P₃N₄ is still first observed pyrochlore phase, but it was further transformed into P₂N₂ pyrochlore phase by reaction with PbO at calcination temperature of ≈ 700°C. Similar results were also observed in the 3PbO–Nb₂O₅ mixture (Fig. 3): P₃N₄ was the first formed pyrochlore phase and P₂N₂ phase was subsequently observed with increasing calcination temperature. P₃N₂ phase began to appear at 700°C and become dominant at temperature of 800°C. This change from P₃N₄ to P₂N₂ and finally to P₃N₂ is strongly dependent on PbO amount and phase stability.

The phase formations of the XPbO–YNb₂O₅ mixtures were further confirmed by DTA results as shown in Fig. 4. Only one exothermic peak was observed at around 560°C in the 3PbO–2Nb₂O₅ mixture. The peak corresponds to the formation of P₃N₄ pyrochlore phase according to the XRD analysis. The starting formation temperature was approximately

530°C. In the 2PbO–Nb₂O₅ mixture, corresponding to Fig. 2 of XRD, there is one more exothermic peak around 630°C other than the peak of P₃N₄ formation. The peak at 630°C was believed to correspond to the formation of P₂N₂ phase. Furthermore, as shown in Fig. 4, three exothermic peaks,

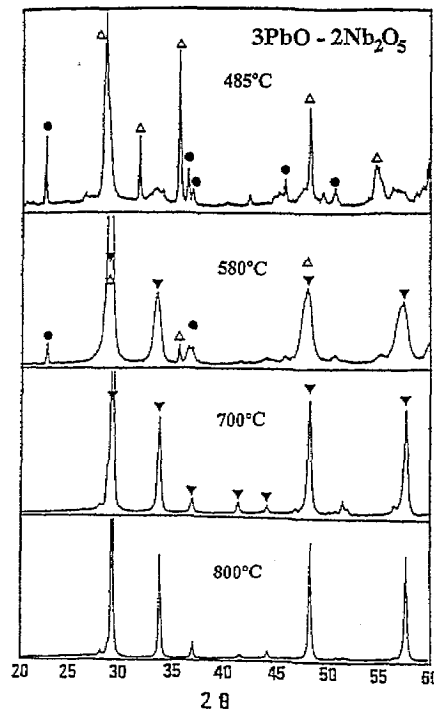


Fig. 1. XRD patterns of calcined 3PbO–2 Nb₂O₅ mixture: Δ, PbO; ▼, Pb₃Nb₄O₁₃; ●, Nb₂O₅.

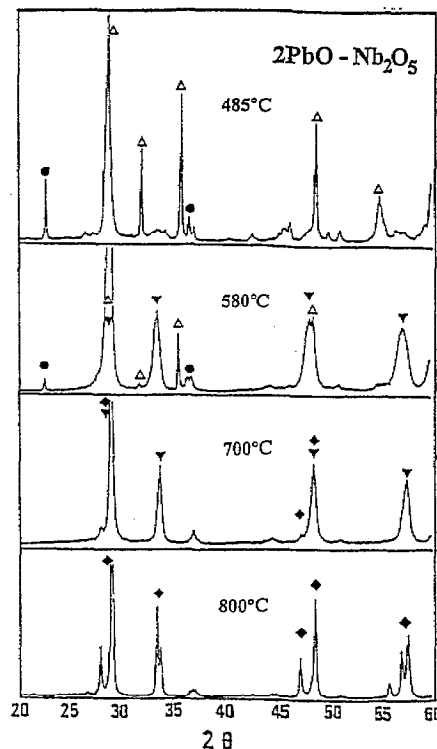


Fig. 2. XRD patterns of calcined 2PbO–Nb₂O₅ mixture: Δ, PbO; ▼, Pb₃Nb₄O₁₃; ●, Nb₂O₅; ◆, Pb₂Nb₂O₇.

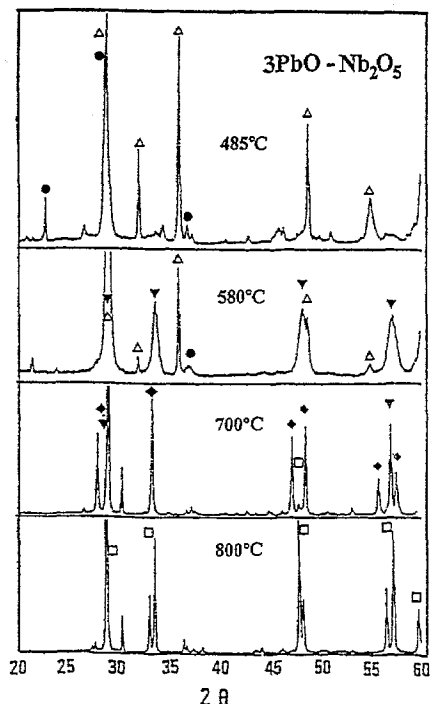


Fig. 3. XRD patterns of calcined 3PbO-Nb₂O₅ mixture: Δ, PbO; ▼, Pb₃Nb₄O₁₃; ●, Nb₂O₅; □, Pb₃Nb₂O₈; ◆, Pb₂Nb₂O₇.

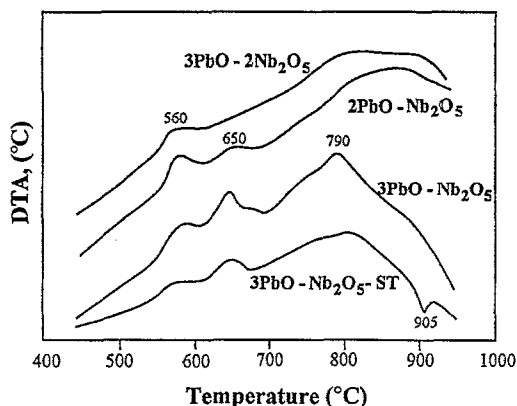


Fig. 4. DTA curves in XPbO-YNb₂O₅ with/SrTiO₃ mixture.

representing the formation of P₃N₄, P₂N₂ and P₃N₂ phases, were found in the 3PbO-Nb₂O₅ mixture.

3.2. Phase evolution of SrTiO₃-Pb[(Mg_xZn_{1-x})_{1/3}Nb_{2/3}]O₃ system

The phase formation and evolution at different calcination temperatures in ST-Pb[(Mg_xZn_{1-x})_{1/3}Nb_{2/3}]O₃ system with various compositions (x) were studied and analyzed by X-ray diffraction patterns. The results were summarized in Table 1. For the composition of ST-PMN ($x=1$), both P₃N₄ and P₂N₂ were considered to be main intermediate pyrochlore phases below 700°C prior to the perovskite PMN phase formation. With increasing calcination temperature (especially above 800°C), the relative amount of P₂N₂ formation decreases sharply with the formation of perovskite PMN

Table 1

Effect of calcination temperature on phase formation in 0.88 Pb[(Mg_xZn_{1-x})_{1/3}Nb_{2/3}]O₃-0.12SrTiO₃ composition

Composition: PZMN-ST	Calcination temperature (°C)	Phases
$x=1$	500–600	P, N, M, P ₃ N ₄ , ST
	600–700	P ₂ N ₂ , P ₃ N ₄ , P, M, ST
	700–800	PMN, P ₂ N ₂ , P ₃ N ₄ , M, ST
	800–900	PMN, P ₃ N ₄ , ST
$x=0.5$	500–600	P, P ₃ N ₄ , M, Z, ST
	600–700	P ₂ N ₂ , P ₃ N ₄ P, Z, M, ST
	700–800	PMN, P ₃ N ₂ , P ₃ N ₄ , Z, ST
	800–900	PZMN, P ₃ N ₄
$x=0$	500–600	P, P ₃ N ₄ , N, Z, ST
	600–700	P ₂ N ₂ , P ₃ N ₄ , P, Z, ST
	700–800	P ₃ N ₂ , P ₃ N ₄ , Z, ST
	800–900	PZN, P ₃ N ₄

P=PbO, N=Nb₂O₅, M=MgO, Z=ZnO, ST=SrTiO₃, PZN=Pb(Zn_{1/3}Nb_{2/3})O₃, PMN=Pb(Mg_{1/3}Nb_{2/3})O₃, P₂N₂=Pb₂Nb₂O₇, P₃N₂=Pb₃Nb₂O₈, P₃N₄=Pb₃Nb₄O₁₃, PZMN-ST=0.88 Pb[(Mg_xZn_{1-x})_{1/3}Nb_{2/3}]O₃-0.12SrTiO₃

while P₃N₄ seems relatively unchanged. On the other hand, in the case of PZN perovskite formation ($x=0$), the pyrochlore phase formation reactions are very similar to those of ST-PMN when the calcination temperature is below 700°C. However, when the calcination temperature increases, e.g. to 750°C, the decrease of P₂N₂ is accompanied by an increase of P₃N₂. Later, both P₃N₂ and SrTiO₃ phases gradually disappear and perovskite PZN forms at temperatures above 800°C. The formation reaction sequences of ST-PZN perovskite indicates that P₃N₂ is the main pyrochlore precursor for PZN perovskite formation in ST-PZN system. For $x=0.5$ of ST-PZMN system, the P₃N₄ is the first observed pyrochlore phase (at 500–600°C), followed by P₂N₂ (at 600–700°C). XRD patterns revealed that a small amount of P₃N₂ phase can be observed at 750°C. P₃N₂ appears together with PMN at the expense of P₂N₂ and the disappearance of MgO. PZMN appears at 800–900°C with the disappearance of P₃N₂, ZnO and stabilizer SrTiO₃.

3.3. The role of pyrochlore phase type in perovskite phase formation of PMN and PZN

Two main different mixture systems were chosen to study the phase evolution and perovskite content for both compositions of PMN ($x=1$) and PZN ($x=0$). In one mixture system, the raw materials used were PbO, Nb₂O₅, ZnO, MgO and SrTiO₃, and in the other system, pyrochlore phases were used instead of PbO and Nb₂O₅ while the other constituents remained the same. For the PMN-ST system (Table 2), perovskite phase still can be produced in the 3PbO-MgO-Nb₂O₅ mixture system without the stabilizer SrTiO₃. That means the stabilizer has little effect on the formation of PMN perovskite. In addition, Table 2 also indicates that the 3PbO-Nb₂O₅-

Table 2
Pyrochlore content and reactions between pyrochlore phases in PbO–Nb₂O₅ system and PbO, MgO, SrTiO₃

Mixture system ^a	Phase (content)
<i>Role of PbO and stabilizer ST</i>	
3PbO–Nb₂O₅–MgO	P ₃ N ₄ (21%), Pero. PMN (79%)
2PbO–Nb ₂ O ₅ –MgO	P ₃ N ₄ (47%), Pero. PMN (53%)
3PbO–Nb₂O₅–MgO–SrTiO₃	P ₃ N ₄ (16%), Pero. PMN (84%)
3PbO–2Nb ₂ O ₅ –MgO	P ₃ N ₄ (96%)
<i>Role of pyrochlore phase</i>	
Pb ₂ Nb ₂ O ₇ –MgO	P ₃ N ₄ (62%), Pero. PMN (38%)
<u>Pb₃Nb₂O₈–MgO</u>	P ₃ N ₄ (24%), Pero. PMN (76%)
Pb₃Nb₄O₁₃–MgO	P₃N₄ (97%)
<i>Enhancing perovskite formation by excess PbO</i>	
Pb ₃ Nb ₄ O ₁₃ –MgO–SrTiO ₃ –3PbO	P ₃ N ₄ and P ₃ N ₂ (22%), Pero. PMN (78%)
Pb ₃ Nb ₄ O ₁₃ –MgO–3PbO	P ₃ N ₄ (29%), Pero. PMN (71%)

^a Calcined at 900°C for 4 h.

MgO mixture system has the higher relative perovskite content than other mixture systems. Similar observation was also found in the mixture system using pyrochlore as raw material. Pb₃Nb₂O₈–MgO gives a higher perovskite content than other pyrochlore phase systems. This further confirms our results that P₃N₂ is more important than P₂N₂ for perovskite formation of PMN phase. Therefore, when the pre-synthesized P₃N₂ phase was used as the starting material, the P₃N₂ phase acts as a nucleation center to form perovskite PMN. Table 2 also indicates that the presence of Pb₃Nb₄O₁₃ (P₃N₄) inhibited perovskite phase formation as found in the Pb₃Nb₄O₁₃–MgO–(SrTiO₃) system. However, the addition of a 3 mol excess of PbO to the Pb₃Nb₄O₁₃–MgO mixture with or without SrTiO₃ can promote the formation of perovskite phase.

For the PbO–ZnO–Nb₂O₅ system, the resulting PZN phases are always pyrochlore, independent of mixture compositions and phases (Table 3). These phenomena are completely different from those of the PbO–MgO–Nb₂O₅ system. However, with the addition of stabilizer SrTiO₃, the situation changes for both 3PbO–Nb₂O₅–ZnO–SrTiO₃ and Pb₃Nb₂O₈–

ZnO–SrTiO₃ mixture systems, showing the possibilities of forming PZN perovskite phase. In other words, no perovskite phase can be observed in Pb₃Nb₄O₁₃–ZnO–SrTiO₃ and Pb₂Nb₂O₇–ZnO–SrTiO₃ mixture systems. Similarly, the addition of a 3 mol excess of PbO to the Pb₃Nb₄O₁₃–ZnO–SrTiO₃ system promotes the formation of perovskite PZN, but without SrTiO₃ stabilizer, the excessive PbO is still not effective for perovskite formation as observed in the Pb₃Nb₄O₁₃–ZnO–3PbO system.

3.4. The effect of preformed pyrochlore phase on PMN, PZN and PZMN system

Experimental results indicate that the preformed pyrochlore phases can exert similar effects to those of pyrochlore phases present in the mixture, with P₃N₂ pyrochlore phase still leading the other two phases in the production of the perovskite content within the final product (see Pb₃Nb₂O₈–MgO mixture system in Table 2 and Pb₃Nb₂O₈–ZnO–SrTiO₃ mixture system in Table 3). Pyrochlore phases are considered

Table 3
Pyrochlore content and reactions between pyrochlore phases in PbO–Nb₂O₅ system and PbO, ZnO, SrTiO₃

Mixture system ^a	Phase (content)
<i>Stabilizer ST is important for Pero. PZN</i>	
3PbO–Nb ₂ O ₅ –ZnO	P ₃ N ₄ , Pyro. PZN
2PbO–Nb ₂ O ₅ –ZnO	P ₃ N ₄ , Pyro. PZN
3PbO–Nb₂O₅–ZnO–SrTiO₃	P ₃ N ₄ (19%), Pero. PZN (81%)
3PbO–2Nb ₂ O ₅ –ZnO	P ₃ N ₄ , Pyro. PZN
<i>Pyrochlore P₃N₂ and ST are required for Pero. PZN</i>	
Pb₃Nb₂O₈–ZnO	P₃N₄, P₃N₂, Pyro. PZN
Pb ₂ Nb ₂ O ₇ –ZnO–SrTiO ₃	P ₃ N ₄ (93%), Pero. PZN (7%)
Pb₃Nb₂O₈–ZnO–SrTiO₃	P ₃ N ₄ (13%), Pero. PZN (87%)
Pb ₃ Nb ₄ O ₁₃ –ZnO–SrTiO ₃	P ₃ N ₄ , Pyro. PZN
<i>Enhancing Pero. PZN in excess PbO</i>	
Pb₃Nb₄O₁₃–ZnO–SrTiO₃–3PbO	P ₃ N ₄ (19%), Pero. PZN (81%)
Pb ₃ Nb ₄ O ₁₃ –ZnO–3PbO	P ₃ N ₄ , Pyro. PZN

^a Calcined at 900°C for 4 h.

to be the intermediate products in the formation of perovskite phase. The effect of P_3N_2 pyrochlore phase raw material on PZMN-ST system is shown in Fig. 5. If the pyrochlore phase P_3N_2 was used as the raw material, the formation behavior of PZMN-ST perovskite phase (labeled as P_3N_2 -Z-M-ST system) is different from that formed by the conventional method (labeled as P-Z-M-N-ST system). As indicated in Fig. 5, the pyrochlore precursor to form perovskite phase is probably P_2N_2 in the P-Z-M-N-ST system but the dominant pyrochlore phase to form perovskite phase is P_3N_2 in the

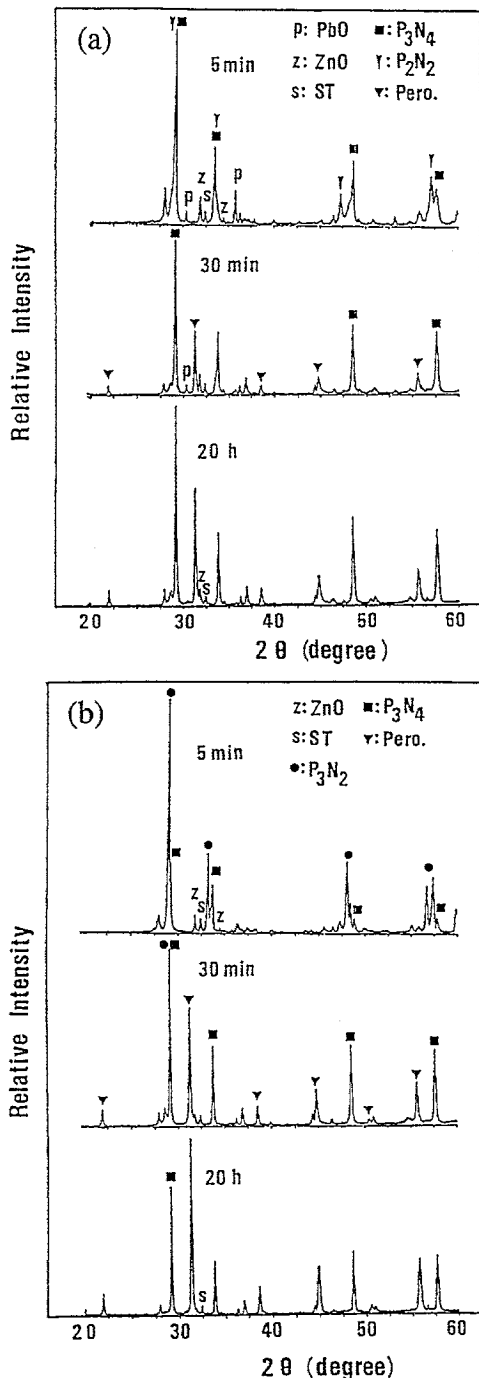
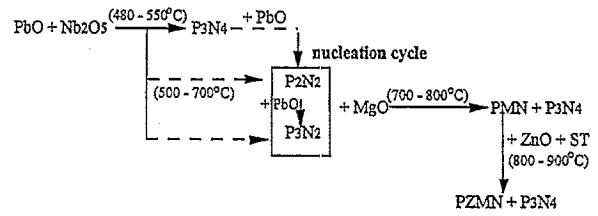


Fig. 5. XRD patterns of (a) P-Z-M-N-ST and (b) P_3N_2 -Z-M-ST with $Mg(x) = 0.35$ systems calcined at 800°C .

Reaction Kinetics of Perovskite Formation

(a) P-Z-M-N-ST System: Constant nucleation rate



(b) P_3N_2 -Z-M-ST System: Fixed number of nuclei

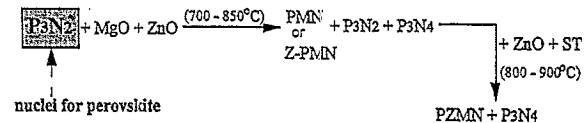


Fig. 6. The overall reaction mechanism of perovskite phase formation in (a) P-Z-M-N-ST and (b) P_3N_2 -Z-M-ST systems.

P_3N_2 -Z-M-ST system, although P_3N_4 phase always remains in both precursor systems. An improvement in perovskite content is observed for the P_3N_2 -Z-M-ST system, and its reaction kinetics for perovskite formation is shown in Fig. 6.

3.5. Electrical properties

Two major compositions, $0.88(\text{Pb}_x\text{Nb}_y\text{O}_z\text{-MgO})\text{-}0.12\text{SrTiO}_3$ and $0.88(\text{Pb}_x\text{Nb}_y\text{O}_z\text{-ZnO})\text{-}0.12\text{SrTiO}_3$, were chosen to study the effect of pyrochlore phase on the electrical properties of SrTiO_3 -PMN and SrTiO_3 -PZN. Figs. 7 and 8

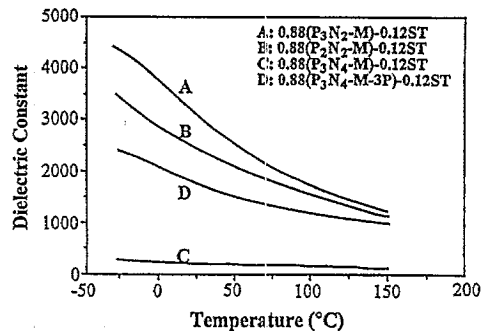


Fig. 7. Temperature dependence of dielectric constant in $\text{Pb}_2\text{Nb}_2\text{O}_7\text{-MgO-SrTiO}_3$ systems.

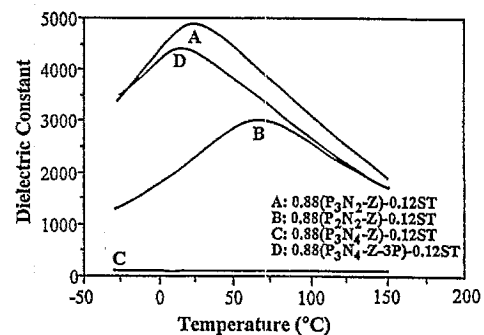


Fig. 8. Temperature dependence of dielectric constant in $\text{Pb}_2\text{Nb}_2\text{O}_7\text{-ZnO-SrTiO}_3$ systems.

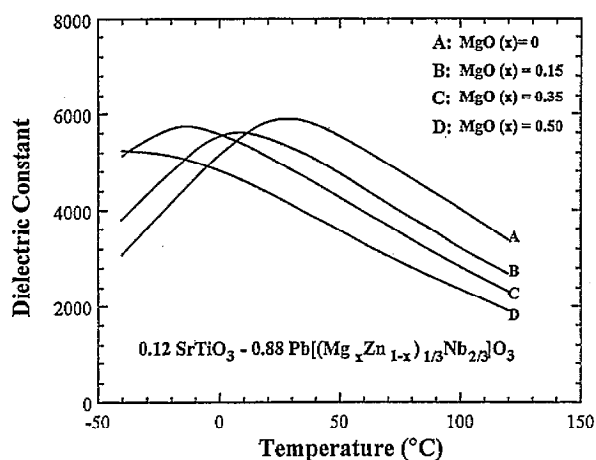


Fig. 9. Dielectric constant vs. temperature for PZMN-ST composition.

show the temperature dependences of dielectric constant at 1 kHz for the three main pyrochlore phase systems containing MgO and ZnO, respectively. The maximum attainable dielectric constant was found in P_3N_2 pyrochlore-containing system but a flat curve with low dielectric constant was observed in the P_3N_4 pyrochlore phase-containing system. The dielectric constant of either P_3N_4 -MgO-ST or P_3N_4 -ZnO-ST systems still can be modified and enhanced by adding a 3 mol excess of PbO. These phenomena can possibly be explained via P_3N_2 formation as shown in the following reactions: $P_3N_4 + P \rightarrow 2(P_2N_2)$ and $P_2N_2 + P \rightarrow P_3N_2$. In order to compare with P_3N_4 -ZnO-ST system, the temperature dependence of dielectric constant of P-Z-M-N-ST system was studied as shown in Fig. 9. It was found that the dielectric properties are comparable for the same composition such as 0.12ST-0.88PZN in these two systems $0.88(Pb_3Nb_2O_8-ZnO)-0.12SrTiO_3$ (curve A, Fig. 8) and $0.88Pb(Zn_{1/3}Nb_{2/3}O_3)-0.12ST$ (curve A in Fig. 9).

4. Discussion

4.1. The effect of PbO and Nb₂O₅ contents on pyrochlore phase within XPbO-YNb₂O₅ mixture

Three main pyrochlore phases, namely, rhombohedral P_2N_2 , tetragonal P_3N_2 and cubic P_3N_4 have been considered to play important roles in perovskite formation of Pb-based relaxors [8–10]. Experimental results of this study [XRD (Figs. 1–3) and DTA (Fig. 4)] indicate that P_3N_4 is the first formed pyrochlore phase within the XPbO-YNb₂O₅ mixture; the formation of P_2N_2 and P_3N_2 pyrochlore phases will depend on the contents of PbO and Nb₂O₅ as well as the calcination temperature. P_2N_2 starts to appear at 2PbO-Nb₂O₅ mixture and at 3PbO-Nb₂O₅ mixture at $\approx 700^\circ\text{C}$. These are mixtures with lower Nb₂O₅ content than the 3PbO-2Nb₂O₅ mixture where only the P_3N_4 pyrochlore phase exists regardless of calcination temperature. P_3N_2 starts to appear at 800°C for the 3PbO-Nb₂O₅ mixture where the Nb₂O₅ content still remains low but the PbO content is higher than that

for the 2PbO-Nb₂O₅ mixture. The phase formation sequences for these mixtures were further confirmed by DTA and the results are shown in Fig. 4. These results indicate that higher Nb₂O₅ content does not favor P_2N_2 and P_3N_2 formation; also the changes in pyrochlore phase sequence within the mixture from P_3N_4 to P_2N_2 and finally to P_3N_2 are strongly dependent on the PbO content. Excess PbO, besides favoring the formation of P_3N_2 within the mixture, also promotes the formation of perovskite phase within the PMN and PZN system. A similar observation was also reported and confirmed by Lejeune et al. [15]. The latter was confirmed in this study by adding a 3 mol excess of PbO to $Pb_3Nb_4O_{13}$ -MgO (Table 2) and $Pb_3Nb_4O_{13}$ -ZnO-SrTiO₃ mixtures (Table 3) exhibiting only P_3N_4 , perovskite PMN and perovskite PZN were formed, respectively. These observations are in agreement with the report that perovskite phase content increases with excess PbO [16].

4.2. The effect of mixture pyrochlore phase on the perovskite phase of PMN, PZN and PZMN

The pyrochlore phases present in the XPbO-YNb₂O₅ mixtures can influence the final phases of the PMN, PZN and PZMN. Their effects on each of these systems are as shown below.

4.2.1. PMN system

Perovskite PMN phase is easily attained in XPbO-YNb₂O₅-MgO mixture provided no excess of Nb₂O₅ is present as in 3PbO-2Nb₂O₅-MgO mixture which exhibits only P_3N_4 phase (Table 2). The latter's situation can be altered with the addition of a 3 mol excess of PbO. The mixture composition which exhibits the most perovskite PMN is 3PbO-Nb₂O₅-MgO. As this composition favors the formation of P_3N_2 phase, we conclude that P_3N_2 phase is important for the formation of perovskite PMN. In fact a complete conversion to perovskite PMN from an equimolar mixture of $Pb_3Nb_2O_8$ and MgO was also reported by Guha and Anderson [17].

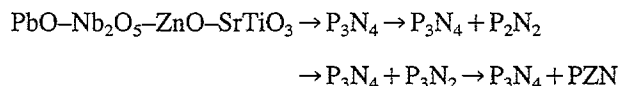
The role of P_3N_2 in the perovskite phase formation was in good agreement with the opinion of Lejune and Boilot [8] and that of Villegas et al. [11] for the PMN-PZT system. It was reported that the decomposition of columbite $MgNb_2O_6$ to react with PbO was followed by the formation of P_3N_2 which, having a partially vacant BO_6 octahedral sublattice, would easily accommodate the MgO to form a B-deficient pyrochlore structure with the formula of $Pb_2(Nb_{1.33}Mg_{0.17})O_{5.5}$ whose subsequent reaction with MgO and PZT yielded PMN-PZT perovskite phase. The effect of raw precursor type on the formation mechanism of perovskite phase was also examined by Jang et al. [18] using two different types of columbite precursor, $(Mg,Zn)Nb_2O_6$ and $MgNb_2O_6 + ZnNb_2O_6$.

The fact that the X-ray peak of the stabilizer SrTiO₃ was still clearly observed at the higher calcination temperatures such as 900°C leads to the postulation that the stabilizer

SrTiO₃ has no effect on the content of perovskite PMN, but it influences its intermediate pyrochlore phase. For in PMN–ST system (Table 1), no P₃N₂ phase existed during its formation. PMN synthesized with 3PbO–Nb₂O₅ mixture having P₃N₂ phase exhibits higher perovskite PMN content than the 2PbO–Nb₂O₅ mixture which shows only P₂N₂ phase. Since preferred phase formation of either P₂N₂ or P₃N₂ pyrochlore type is strongly influenced by PbO content, we conclude that the formation of perovskite PMN requires the presence of either P₂N₂ or P₃N₂ phase with P₃N₂ phase being the preferred phase for PMN. Furthermore, both P₃N₂ and PMN phase formation probably occur immediately and simultaneously.

4.2.2. PZN system

The formation of perovskite PZN requires the presence of stabilizer (see Table 3). Without any stabilizer, the final phase of PZN will be pyrochlore, regardless of the mixture's composition and phase condition. Besides stabilizer, the existence of P₃N₂ pyrochlore phase in the mixture is another prerequisite for the formation of perovskite PZN. For 2PbO–Nb₂O₅–ZnO–SrTiO₃ system, the mixture exhibits only limited amount of perovskite PZN (7%) which may be negligible owing to experimental error. All these are further confirmed by the phase sequences exhibiting in the formation of PZN–ST (Table 1). They are as follows:



Comparing ST–PMN ($x=1$) with ST–PZN ($x=0$) revealed that P₃N₂ phase plays a dominating role in the formation of PZN perovskite and a stabilizer such as SrTiO₃ is needed for such reactions, although the SrTiO₃ stabilizer is less important for perovskite PMN formation. In addition, P₃N₂ phase seems to react with ZnO under the influence of SrTiO₃ stabilizer to form PZN perovskite at above 850°C.

4.3. Effect of raw material phase on formation mechanism of PZMN–ST perovskite phase

Although the usage of preformed P₃N₂ pyrochlore phase as starting raw material in the formation of PMN and PZN does not increase the perovskite content of the final product as compared with that of using raw material mixture, its usage in the formation of PZMN–ST shows a complete different mechanism as shown in Fig. 5.

XRD results indicate that the first major formed perovskite is PMN phase because the maximum content of perovskite phase obtainable corresponds to the disappearance of MgO content at the temperatures below 850°C. In other words, the relative XRD peak intensities of ZnO to perovskite phase are almost constant up to 800°C as shown in Fig. 5(a). The dissolution of ZnO into the perovskite phase seems to be initiated only beyond 800°C. Moreover, it was found that the effect of stabilizer SrTiO₃ on the formation of PMN or PMN-rich perovskite phase is negligible. On the other hand,

(Fig. 5(b)) in P₃N₂–Z–M–ST system, the formation of perovskite phase was accompanied by the gradual disappearance of ZnO peak with increasing calcination time at 800°C (Fig. 5(b)). It is believed that ZnO may react with P₃N₂ or the formed PMN phase to form Zn-rich PZMN perovskite even the temperatures below 850°C.

These phenomena are further confirmed by the DTA analysis shown in Fig. 10. The first endothermic peak around 838°C was observed especially for Zn-rich ST–PZMN or pure PZN compositions in both P₃N₂–Z–M–ST and P–Z–M–N–ST systems. As no obvious endothermic peak was observed in the composition of $x=0$, i.e. for the P₃N₂–M–ST system, this peak is probably caused by the ZnO dissolving into the lead-rich P₃N₂ phase, forming the liquid phase. In the literature, several new but weak X-ray peaks have been reported for the Pb(Zn_xNb_{1-x})O_{0.35-1.5x} pyrochlore phase when the powder mixture of PbO–ZnO–Nb₂O₅ was calcined at 800°C, [9] and they are probably caused by the variation of Zn concentration in the pyrochlore phases. However, the other endothermic peak at 900°C which was observed in the ST–PZMN system, but not in ST–PMN and PbO–ZnO–Nb₂O₅ systems, was the result of the formation reaction of PZMN perovskite phase under the catalysis of stabilizer SrTiO₃. From the above-mentioned results, we may conclude that the P₃N₂ phase is required for perovskite PZMN phase formation. The overall reaction mechanism of perovskite phase formation can be summarized as in Fig. 6.

In P–Z–M–N–ST system, pyrochlore phases (P₂N₂ and P₃N₂) which are believed to be the nucleation centers for perovskite phase formation are constantly produced through the reaction of preformed P₃N₄ with unreacted PbO. The structure of the perovskite phase is mainly PMN at temperatures below 850°C and is attained through diffusion and reaction between P₃N₂ or P₂N₂ phases and MgO [17,19]. The stabilizer SrTiO₃ plays its role only when the temperature is higher than 850°C, and the perovskite phase is almost completely formed at a temperature above 900°C.

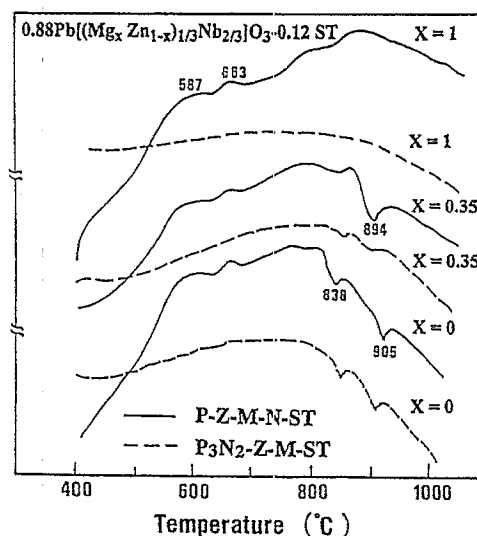


Fig. 10. DTA results for both P–Z–M–N–ST and P₃N₂–Z–M–ST systems.

On the other hand, in the P_3N_2 -Z-M-ST system, P_3N_2 dominates the formation of PMN or Zn-containing PMN by reacting with MgO and ZnO phases at calcination temperatures below 850°C. Formation of perovskite PZMN is nearly complete when the temperature is higher than 900°C. However, P_3N_4 once formed remained unchanged throughout these reactions.

4.4. Pyrochlore phase versus electrical properties

As shown in Figs. 7 and 8, PMN and PZN compounds formed with P_3N_2 mixtures exhibited the highest dielectric constant while those from P_3N_4 mixtures showed the lowest dielectric constant. Although the addition of a 3 mol excess PbO to P_3N_4 mixtures can boost the dielectric constant values, still they cannot exceed those obtained from P_3N_2 mixtures. These delineate once more the importance of having P_3N_2 pyrochlore phase in the system for obtaining a final product with a high dielectric constant.

The fact that there is not much difference in dielectric constant for PZN of composition 0.12ST–0.88PZN obtained either via PbO–Nb₂O₅ mixture (curve A in Fig. 9) or via preformed P_3N_2 pyrochlore phase (curve A in Fig. 8) confirms once more that pyrochlore phase is the major factor in determining the electrical properties of the system regardless of the mean of obtaining it.

5. Conclusions

1. The formation of perovskite phase within PMN relaxors requires the presence of either P_2N_2 or P_3N_2 pyrochlore phases in the mixture and is only slightly dependent on the presence of the stabilizer.
2. The formation of perovskite phase within PZN or PZMN relaxors require the presence of both P_3N_2 pyrochlore phase and stabilizer.
3. Excess PbO can be used to modify the pyrochlore phase present in the mixture and promote perovskite formation through the pyrochlore reaction of $P_3N_4 + P \rightarrow 2(P_2N_2)$; $P_2N_2 + P \rightarrow P_3N_2$

4. Maximum dielectric constant for PMN, PZN and PZMN systems can be obtained with the P_3N_2 phase present in the starting raw materials.

Acknowledgements

The authors are thankful to Ms. Kathy Hu for helpful suggestions. This work was made possible by the financial support from The Ministry of Economic Affairs of The Republic of China.

References

- [1] J. Kuwata, K. Uchino and S. Nomura, *Ferroelectrics*, 22 (1979) 863–867.
- [2] O. Furukawa, Y. Yamashita, M. Harata, T. Takahashi and K. Inagaki, *Jpn. J. Appl. Phys.*, 24 (Suppl. 24-3) (1985) 96–99.
- [3] S.L. Swartz and T.R. Shrout, *Mater. Res. Bull.*, 17 (10) (1982) 1245–1250.
- [4] J. Kuwata, K. Uchino and S. Nomura, *Ferroelectrics*, 37 (1981) 579–587.
- [5] S.Y. Chen, S.Y. Cheng and C.M. Wang, *J. Am. Ceram. Soc.*, 74 (2) (1991) 400–405.
- [6] A. Halliyal, U. Kumar, R.E. Newnham and L.E. Cross, *Am. Ceram. Soc. Bull.*, 66 (4) (1987) 671–676.
- [7] T.R. Shrout and A. Halliyal, *Am. Ceram. Soc. Bull.*, 66 (4) (1987) 704–711.
- [8] M. Lejeune and J.P. Boilot, *Ceram. Int.*, 8 (3) (1982) 99–105.
- [9] H.C. Ling, M.F. Yan and W.W. Rhodes, *J. Mater. Sci.*, 24 (1989) 541.
- [10] F. Chaput, J.P. Boilot, M. Lejeune, R. Papiernik and L.H. Pfalzgraf, *J. Am. Ceram. Soc.*, 72 (8) (1989) 1355–1357.
- [11] M. Villegas, J.R. Jurado, C. Moure and P. Duran, *J. Mater. Sci.*, 30 (1995) 1391–1396.
- [12] M. Inada, *Jpn. Natl. Tech. Rep. (Matsushita Elect. Ind. Co.)*, 27 (1) (1977) 95.
- [13] J.R. Belsick, A. Halliyal, U. Kumar and R.E. Newnham, *Am. Ceram. Soc. Bull.*, 66 (4) (1987) 66467.
- [14] H.P. Klug and L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York, 1974, pp. 411–415.
- [15] M. Lejeune and J.P. Boilot, *Ferroelectrics*, 54 (1982) 191.
- [16] M. Lejeune and J.P. Boilot, *Mater. Res. Bull.*, 20 (1985) 493–499.
- [17] J.P. Guha and U.U. Anderson, *J. Am. Ceram. Soc.*, 69 (1986) C-287.
- [18] H.M. Jang, S.R. Cho and K.-M. Lee, *J. Am. Ceram. Soc.*, 78 (2) (1995) 297–304.
- [19] S.Y. Chen, C.M. Wang and S.Y. Cheng, *J. Am. Ceram. Soc.*, 74 (10) (1991) 2506–2512.