

Role of perovskite PMN in phase formation and electrical properties of high dielectric $\text{Pb}[(\text{Mg}_x, \text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ ceramics

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Abstract

The structural evolution of perovskite phase $\text{Pb}[(\text{Mg}_x, \text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ (abbreviated to PZMN) was found to be highly dependent on its precursors' strong tendency of forming pyrochlore phase in the mixture of raw materials. Three major pyrochlore compositions, $\text{Pb}_2\text{Nb}_2\text{O}_7$, $\text{Pb}_3\text{Nb}_2\text{O}_8$ and $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, were characterized and analyzed to understand their roles in the formation of the perovskite PZMN phase. Based on phase structure evolution, a preparation method for forming high dielectric constant PZMN ceramics without using common stabilizers such as SrTiO_3 was proposed. By using pre-synthesized perovskite PMN, a Zn-rich PZMN composition with an almost 100% perovskite content and a maximum dielectric constant of 22 000 at 1 kHz is obtained. The formation mechanism of PZMN perovskite phase was also reported in this research. The pre-synthesized perovskite PMN acts as stabilizer and nuclei to initiate PZMN perovskite formation through the reaction in the PMN/ZnO interface. A ternary phase diagram of PMN–PZMN– SrTiO_3 was further constructed to investigate the perovskite development and its related electrical properties. © 1998 Elsevier Science S.A.

Keywords: Perovskite PMN; Electrical properties; Ceramics

1. Introduction

The multilayer ceramic capacitor industry is growing rapidly because of the continuing miniaturization of integrated electronic circuits. BaTiO_3 and other titanates have been primarily utilized for multilayer ceramic capacitors [1]. However, such materials usually require high firing temperatures ($> 1300^\circ\text{C}$), making it necessary to use expensive internal electrodes such as Pd. One of the methods to reduce the capacitor cost is to develop new multilayer materials with high dielectric constants and low firing temperatures, allowing the use of less-expensive internal electrodes of Ag/Pd alloys which have made ferroelectric relaxors promising candidate materials for capacitors. It is a well-known fact that the dielectric constant of ceramics and their related electrical properties are highly influenced by the structure of the starting materials present and its ceramic processing. This is especially true for lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (abbreviated to PZN), and lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (abbreviated to PMN), with their perovskite phase exhibiting the largest dielectric constant.

PZN is a relaxor-type ferroelectric material with a partially disordered perovskite structure. It undergoes a diffuse phase transition at about 140°C from rhombohedral (ferroelectric) to cubic (paraelectric) symmetry [1–3]. Single crystal perovskite PZN, synthesized by the PbO flux method, exhibits an unusually large dielectric constant, along with excellent electrostrictive and optical properties [4,5]. It is very difficult, however, to synthesize pure PZN polycrystalline specimens with the perovskite structure by conventional ceramic processes. The structure obtained by solid-state reaction at 1100°C is mainly cubic pyrochlore phase $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, which exhibits inferior dielectric and electrostrictive properties [6].

PMN is the most extensively studied ferroelectric relaxor material because of its relatively large dielectric constant and the broad transition temperature [7–9]. It is also difficult to prepare pure PMN ceramics with the perovskite structure by conventional processes owing to the problem associated with pyrochlore formation. However, this problem can be eliminated effectively by employing the columbite precursor (MgNb_2O_6) method proposed by Swartz and Shrout [6].

Although perovskite phases such as SrTiO_3 , PbTiO_3 , BaTiO_3 or PbZrO_3 are usually used to stabilize perovskite PZN, the dielectric properties of PZN are severely diluted and decreased [8,9]. PMN is one of perovskite phases and

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exhibits similar relaxor characteristics to PZN, which shows an extremely large dielectric constant with a broad transition temperature. One would expect that the addition of perovskite PMN to the $\text{PbO-ZnO-Nb}_2\text{O}_5$ system at above a certain critical concentration could probably eliminate the problem of pyrochlore phase formation and promote the formation of perovskite PZMN phase. Also, it does not inflict an appreciable loss of dielectric properties on perovskite PZN. The concept to use perovskite PMN as a stabilizer for high dielectric $\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ has been confirmed by us [10]. A new material system based on PZMN compositions suitable for the use of low-fire Y5V multilayer ceramic capacitors has been tested in our laboratories. Recently, a similar approach was also reported and confirmed by Jang et al. [11]. Two different types of columbite precursors, $(\text{Mg,Zn})\text{Nb}_2\text{O}_6$ (MZN) and $\text{MgNb}_2\text{O}_6 + \text{ZnNb}_2\text{O}_6$ (MN + ZN), were used. A minimal fraction of PMN needed to effectively stabilize the pyrochlore phases in the PZMN system was approximately 0.4 which was in agreement with our previous report [10]. However, the role of PMN in the perovskite formation of the PZMN system and its effects on the dielectric properties of PZN are still unknown.

In this study we will focus on the perovskite formation and electrical properties of PZMN. Since PMN perovskite ceramics possess the unique dielectric properties, its two major precursor systems, P-Z-M-N and PMN-P-Z-N, were chosen for investigating the effect of the preformed perovskite PMN phase on the dielectric constant of PZMN ceramics. Furthermore, the role of the stabilizer SrTiO_3 was also studied in both mixture systems for comparison.

2. Experimental procedure

Two different types of raw precursors, P-Z-M-N and PMN-P-Z-N, were prepared in accordance with the formula of $\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$. For the P-Z-M-N precursor, raw materials PbO , ZnO , MgO and Nb_2O_5 were weighed in appropriate proportions and mixed together in a polyethylene jar with ZrO_2 as the grinding media and an alcohol solution as the mixing agent. For the PMN-P-Z-N precursor, following the procedure of Swartz and Shrut [6], MgO powder was first mixed with Nb_2O_5 and calcined at 1000°C for 4 h to form columbite MgNb_2O_6 . PbO was then added to the MgNb_2O_6 powder and calcined at 900°C for 4 h to obtain the perovskite PMN. PbO , ZnO and Nb_2O_5 were subsequently mixed with the formed perovskite PMN. Both P-Z-M-N and PMN-P-Z-N precursor systems were calcined at the temperature ranging from 550°C to 950°C for 4 h to study the phase evolution of perovskite PZMN. The effects of stabilizer SrTiO_3 on the phase transformation and electrical properties of the two PZMN systems were also investigated.

The relative amount of the perovskite phase was determined by the XRD patterns with major integrated intensities of (110) for the perovskite phase and (222) for the pyrochlore phases for both calcined and as-sintered samples in

accordance with the method described by Klug and Alexander [12]. The percentage of formed perovskite phase was calculated by the following equation:

$$\% \text{ perovskite} = 100 \times I_{\text{pero}}(110) / [I_{\text{pero}}(110) + I_{\text{pyro}}(222)]$$

where I_{pero} and I_{pyro} represent the intensities of XRD peaks for perovskite and pyrochlore phases, respectively. To identify the reaction sequences of perovskite formation, differential thermal analysis (DTA) was used to examine phase reactions during the calcination. Dielectric measurements were carried out on an automated system, whereby an impedance analyzer (HP 4192A) and a temperature-control box (Delta 9023) were controlled by a desk-top computer system. Dielectric permittivity and dissipation factor ($\tan\delta$) were measured at a frequency of 1 kHz.

3. Results and discussion

3.1. The role of stabilizer SrTiO_3 in PZMN ceramics

It has been known that in pure stoichiometric PZN, its perovskite phase is thermodynamically unstable and only the pyrochlore phase was observed from XRD patterns [5]. Also, polycrystalline PZN ceramics with a perovskite structure could only be synthesized by hot-pressing at elevated temperatures [13]. Thus, stabilizers such as SrTiO_3 were usually added to promote the formation of the PZN perovskite phase [9]. Similar experiments were conducted in $\text{PbO-MgO-ZnO-Nb}_2\text{O}_5$ compositions added with 0.12 mol SrTiO_3 as a stabilizer. XRD patterns reveal that the perovskite $\text{Pb}[(\text{Mg,Zn})\text{Nb}]\text{O}_3$ phase was easily formed without producing other second phases. However, SrTiO_3 addition diluted the dielectric properties. The peak dielectric constant reported was around 6000 (Fig. 1), which is very low compared to the extremely large values observed in perovskite ferroelectric relaxors such as PZN or PMN. The Curie temperature (T_c), however, decreases with the addition of MgO

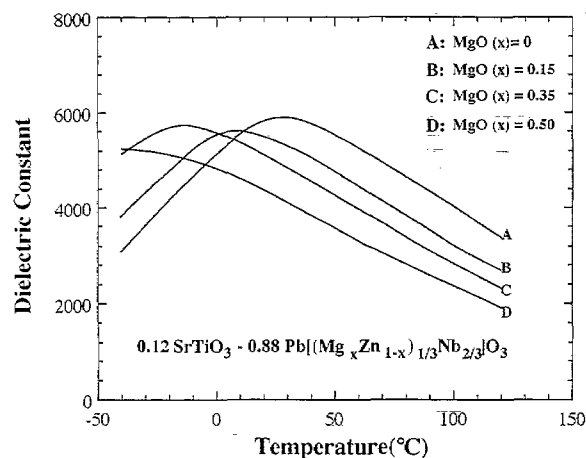


Fig. 1. Dielectric feature of $\text{PbO-MgO-ZnO-Nb}_2\text{O}_5$ mixtures with SrTiO_3 stabilizer.

(x) because PMN perovskite has a lower curie temperature ($T_C = -10^\circ\text{C}$) as compared to the PZN perovskite ($T_C = 140^\circ\text{C}$). The broad temperature dependences of dielectric constant reflect that the peak dielectric constant is independent of the ZnO quantity in the PbO–ZnO–MgO–Nb₂O₅ added with SrTiO₃ systems when enough stabilizer such as SrTiO₃ was used.

In order to clarify the role of stabilizer SrTiO₃ in mixture systems of P–Z–M–N and PMN–P–Z–N, the maximum dielectric properties of these systems were investigated. Fig. 2 shows that the PMN–P–Z–N system exhibits a higher maximum dielectric constant than the P–Z–M–N system when the concentration of stabilizer SrTiO₃ is less than 5 mol%. However, when the concentration of SrTiO₃ increases to more than 10 mol%, no significant difference is observed between these two mixture systems. Note that both systems have not only the same composition but also possess an almost 100% perovskite content.

3.2. The role of perovskite PMN in PZN ceramics

As mentioned earlier, the addition of a common stabilizer of SrTiO₃ usually results in a significant decrease in the dielectric properties of PZN ceramics. To obtain a ferroelectric relaxor material with high dielectric constant and low temperature coefficient of capacitance (TCC), a PMN–PZN binary system was chosen for investigation in this study. X-ray diffraction patterns of Pb[(Mg_{*x*}Zn_{1–*x*})_{1/3}Nb_{2/3}]O₃ (PZMN) specimens calcined at 900°C for 4 h and sintered at 1150°C for 1.5 h were analyzed and shown in Fig. 3. It was found that partial substitution of Zn with Mg atoms in the B-sites stabilizes the perovskite phase in the PMN–PZN pseudobinary system. The minimum amount of Mg needed to stabilize the perovskite phase is dependent on the raw precursors used. For the P–Z–M–N system, where PbO, ZnO, MgO and Nb₂O₅ powders were directly mixed in an appropriate ratio, the minimum required amount (x) of Mg is approximately 0.35 in Pb[(Mg_{*x*}Zn_{1–*x*})_{1/3}Nb_{2/3}]O₃, and the resultant PZMN without SrTiO₃ possesses about 80% perovskite phase. This is in agreement with the report of Jang et al. [11] that the minimum fraction of PMN for stabilized perovskite PZMN is about 0.4. That means that it is impossible to obtain PZMN having an almost 100% perovskite content using a conventional process.

On the contrary, the perovskite PMN in the PMN–P–Z–N system was first synthesized and then mixed with PbO, ZnO and Nb₂O₅ powders in appropriate ratio to form PZMN ceramics. An almost 100% perovskite PZMN was obtained when a minimum amount of 25 mol% of perovskite PMN was added to PZN ceramics. In other words, a Pb[(Mg_{*x*}Zn_{1–*x*})_{1/3}Nb_{2/3}]O₃ with x in the range of 0.25 ~ 1.0 gives rise to a product with a high fraction of perovskite phase (say, > 95%). These different characteristics can be interpreted from XRD, DTA and reaction kinetics.

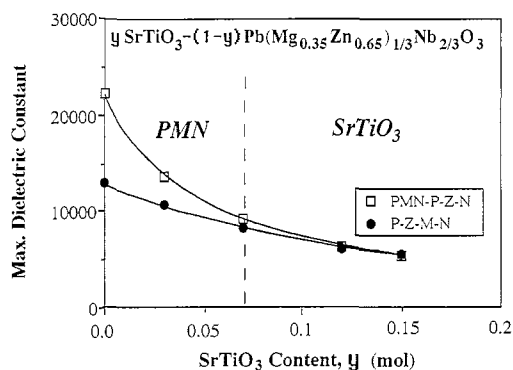


Fig. 2. Effect of SrTiO₃ content on maximum dielectric constant.

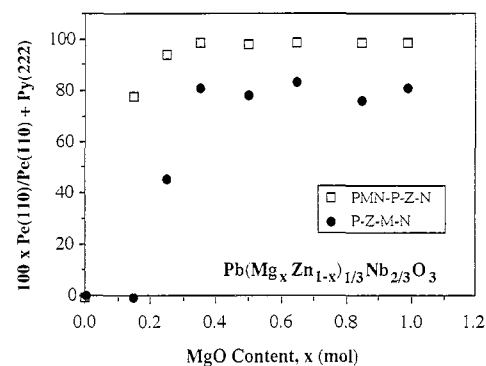


Fig. 3. Relative perovskite phase content for both precursor systems.

3.3. Phase reaction and transformation of PZMN system

The phase formation and reactions in the Pb[(Mg_{*x*}Zn_{1–*x*})_{1/3}Nb_{2/3}]O₃ system with various compositions (x) for the two different types of precursor systems were analyzed by DTA as shown in Fig. 4. In the P–Z–M–N precursor system (Fig. 4(a)), its phase formation sequences similar to those previously reported [14], the Pb₃Nb₄O₁₃ pyrochlore phase was first observed at around 580°C according to the XRD analysis, but it was further transformed into Pb₂Nb₂O₇

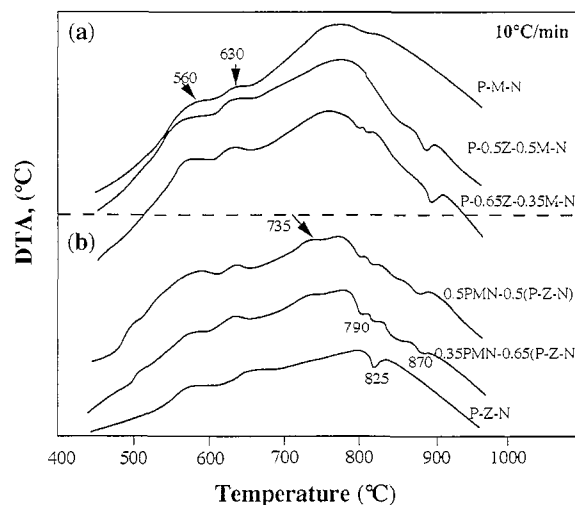


Fig. 4. DTA curves for both (a) P–Z–M–N and (b) PMN–P–Z–N precursor systems.

pyrochlore phase by reacting it with PbO at a calcination temperature of 650–700°C. The several small endothermic peaks found at around 775–850°C are probably caused by chemical reactions between the perovskite Mg-rich PMN and the Zn-rich pyrochlore phase. These findings are consistent with the report of Ling et al. [15] in that several weak X-ray peaks were observed and considered to be the $\text{Pb}(\text{Zn}_x\text{Nb}_{1-x})\text{O}_{0.35-1.5x}$ pyrochlore phase, when the mixture powder of $\text{PbO-ZnO-Nb}_2\text{O}_5$ was calcined at 800°C. These are probably caused by the variation of Zn concentration in the pyrochlore phases. In addition, the extra endothermic peak observed at around 870°C in the P-Z-M-N system, but not in the $\text{PbO-MgO-Nb}_2\text{O}_5$ (P-M-N) and $\text{PbO-ZnO-Nb}_2\text{O}_5$ (P-Z-N) systems, was probably due to the formation reaction of PZMN perovskite phase by the interaction between the Mg-rich perovskite PMN and Zn-rich PZN perovskite formed.

On the contrary, in the PMN-P-Z-N precursor system, three exothermic peaks were observed at 570°C, 625°C and 720°C, corresponding to the formation reactions of the $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, $\text{Pb}_2\text{Nb}_2\text{O}_7$ and $\text{Pb}_3\text{Nb}_2\text{O}_8$ phases, respectively. Those peaks were followed by several small endothermic peaks (as indicated by the arrows in Fig. 4(b)). The phenomenon reflects the fact that some phase transformations occur in the temperature range at 780–870°C. We postulated that those peaks probably result from a slow diffusion reaction of perovskite PMN with refractory ZnO, and cause partial substitution of Mg with Zn atoms in the B-sites of the ABO_3 perovskite structure. Therefore, perovskite PMN act as a nucleus for the perovskite PZMN phase formation in the PMN-P-Z-N system. The pyrochlore/perovskite phase transformation of PZMN occurs via the PMN/ZnO interface.

An isothermal kinetics of perovskite formation for two different types of precursor systems with the composition of $x=0.35$ were evaluated. The samples were quenched from 850°C to room temperature after a variety of annealing time. In the P-Z-M-N system, as shown in Fig. 5, the formation of the perovskite phase (around 20%) was initially rapid and then followed by a slow increase in the fraction of perovskite phase with annealing time. On the contrary, in the PMN-P-Z-N system, the perovskite formation started with the preformed perovskite PMN (or PZMN) and gradually increased with annealing time. The relative fraction of formed perovskite phase was approached to the saturation of about 90% after the samples were annealed longer than 180 min at 850°C. Furthermore, when the annealing temperature was raised to 900°C, the perovskite phase formed rapidly irrespective of precursor systems. However, a formation fraction of 95% perovskite phase cannot be obtained in the P-Z-M-N in contrast to the PMN-P-Z-N precursor systems because of the formation of stable P_3N_4 pyrochlore phase in the former system.

According to the aforementioned observations, a reaction mechanism for perovskite formation (with schematic microstructural evolution) in the PZMN system for two different types of precursor mixtures is summarized in Fig. 6. The

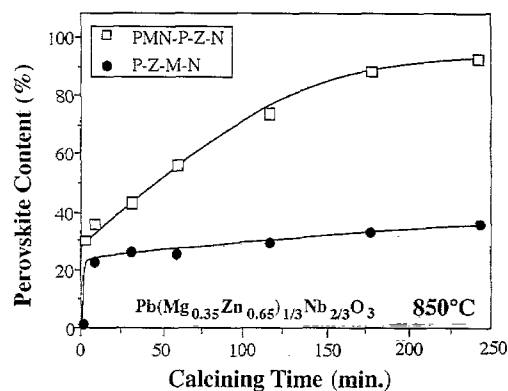


Fig. 5. Influence of calcining time on the perovskite content for both P-Z-M-N and PMN-P-Z-N systems.

pyrochlore phases involved in the PZMN formation reaction are the cubic pyrochlore $3\text{PbO} \cdot 2\text{Nb}_2\text{O}_5$ (herein designated as P_3N_4), rhombohedral pyrochlore $2\text{PbO} \cdot \text{Nb}_2\text{O}_5$ (P_2N_2), and tetragonal pyrochlore $3\text{PbO} \cdot \text{Nb}_2\text{O}_5$ (P_3N_2). It is very important to note that only at the P_3N_2 pyrochlore phase can MgO be easily inserted, because its BO_6 octahedral sublattice is partially vacant. For the P-Z-M-N system, these three pyrochlore phases probably coexist during the calcination. Therefore, it is impossible to form only P_3N_2 initially, then perovskite PMN or PZMN, because P_3N_4 is a very stable pyrochlore phase and tends to retard the formation of PZMN perovskite. The formation of the perovskite phase in the P-Z-M-N system is characterized by two kinetically distinct processes as confirmed from the DTA in Fig. 4. In contrast, for the PMN-P-Z-N system, the PMN perovskite acts as a stabilizer and initiates the formation process of the PZMN perovskite through the reaction between formed perovskite PMN and ZnO. The perovskite phase formation in the PMN-P-Z-N system is characterized by a diffusion-controlled process with preformed PMN as the perovskite nuclei for PZMN. This corresponds to the fact that perovskite phase formation remains continuously raised when the sample was annealed at 850°C, as shown in Fig. 5. As a result, an almost 100% perovskite PZMN can be obtained.

3.4. Electrical properties

The temperature dependence of dielectric constant for both P-Z-M-N and PMN-P-Z-N systems was further examined and is shown in Fig. 7(a) and (b), respectively. The dielectric features exhibit diffuse phase transition (DPT) which indicates a broadened and inhomogeneous microcompositional distribution of the B-site cations in these two systems. The effect of this raw precursor system on the dielectric features was further evaluated by examining the relationship of maximum dielectric constant to the PZMN composition. The maximum dielectric constant attained for the P-Z-M-N system is about 13 000 and is slightly dependent on the $\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ composition with x in the range from 0.35 to 1.0.

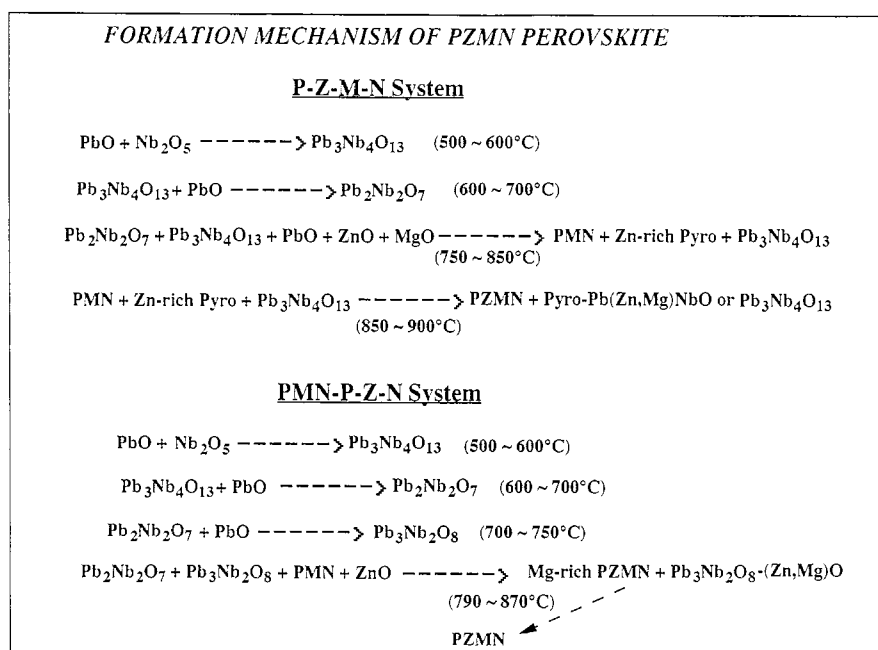


Fig. 6. Reaction mechanisms of PZMN perovskite phase.

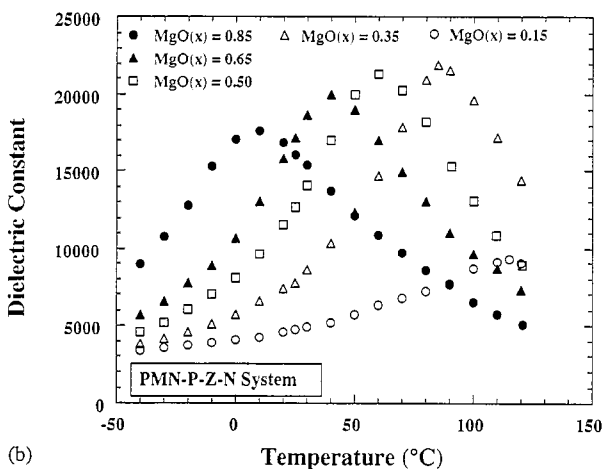
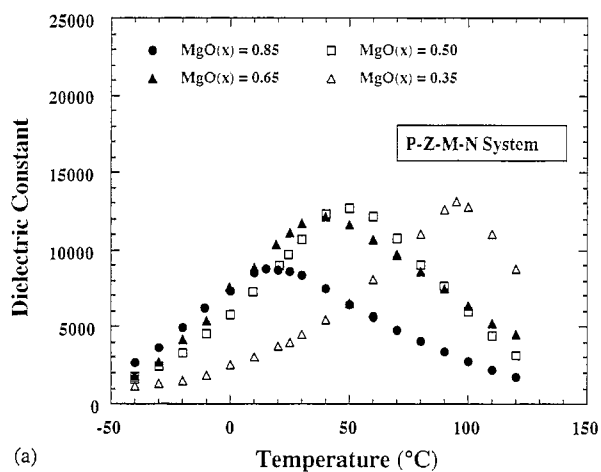


Fig. 7. (a) Temperature dependence of dielectric constant for P-Z-M-N system. (b) Temperature dependence of dielectric constant for PMN-P-Z-N system.

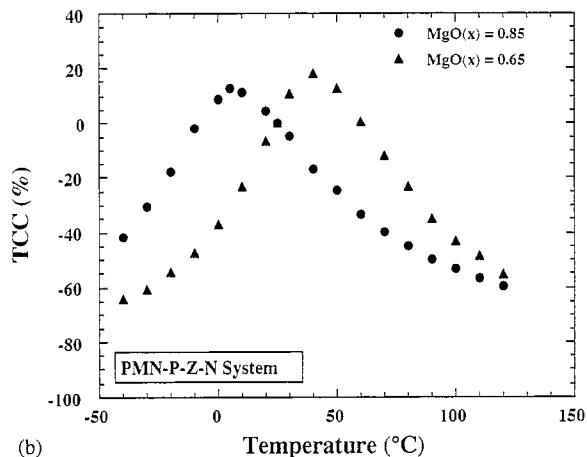
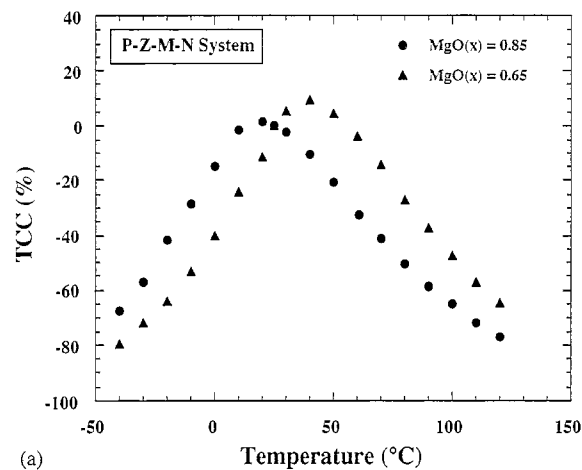


Fig. 8. (a) Temperature coefficient of capacitance (at 1 kHz) of P-Z-M-N system. (b) Temperature coefficient of capacitance (1 kHz) of PMN-P-Z-N system.

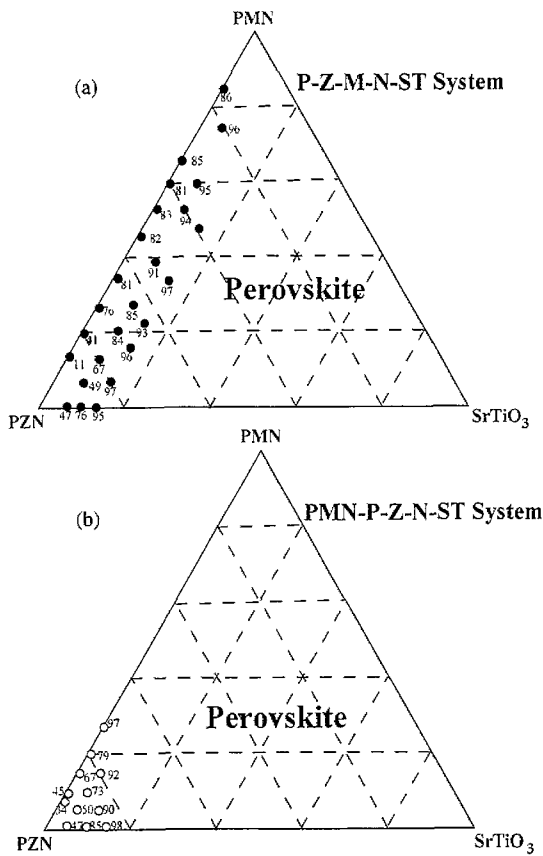


Fig. 9. Relative perovskite content of PMN–PZN–SrTiO₃ ternary phases for (a) P–Z–M–N and (b) PMN–P–Z–N systems. (The number near to the mark indicates the relative perovskite content.)

On the contrary, the maximum dielectric constant attained for the PMN–P–Z–N system is 22 000, which is much higher than that for the P–Z–M–N system (13 000). Such difference can be attributed to the contribution of pre-synthesized perovskite PMN in the formation of the PZMN perovskite phase. In addition, the effect of ZnO content on the T_C of PZMN is also studied. Even though PMN–P–Z–N shows a higher dielectric feature than P–Z–M–N, it was found that the relationship between the ZnO content and the T_C of PZMN was the same for both systems in spite of having different precursor systems.

There is a need for a high dielectric constant capacitor with a low temperature dependence of capacitor (TCC) which is defined as

$$TCC = 100(C_T - C_{25^\circ\text{C}}) / C_{25^\circ\text{C}}$$

The values of TCC for some compositions in both P–Z–M–N and PMN–P–Z–N systems with Curie temperature around room temperature are shown in Fig. 8(a) and (b). The TCC values are within the limits of Z5U and Y5V capacitor specifications. The PZMN compositions with 65 to 85 mol% of PMN are shown to be the potential materials for low-fire high dielectric capacitors.

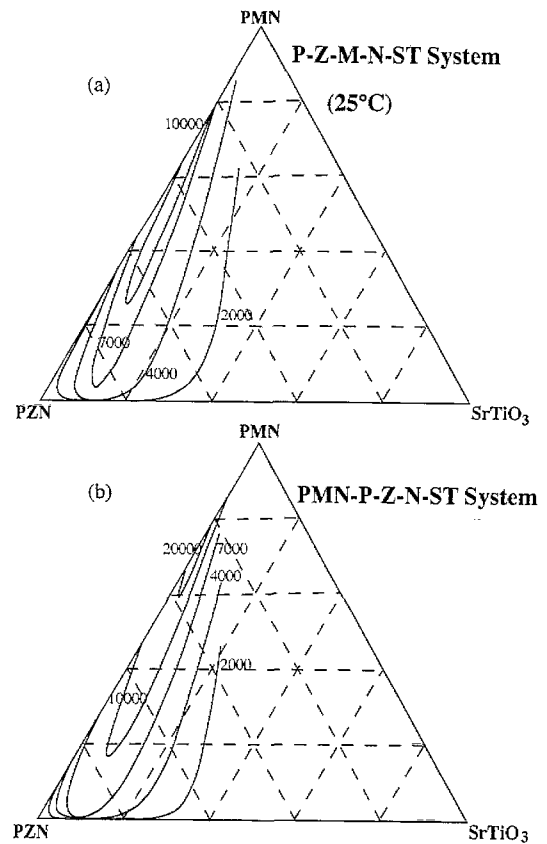


Fig. 10. Dielectric feature of PMN–PZN–SrTiO₃ phase diagram for (a) P–Z–M–N and (b) PMN–P–Z–N raw precursor systems.

3.5. Ternary phase diagram of PMN–PZN–SrTiO₃ ceramics

A ternary phase diagram of SrTiO₃, PMN and PZN was constructed to summarize the effect of stabilizer SrTiO₃ on P–Z–M–N and PMN–P–Z–N mixture systems. Fig. 9 indicates that the perovskite content increases with increasing the amount of both PMN and SrTiO₃. At least 12 mol% SrTiO₃ in pure PZN was needed to obtain an almost 100% perovskite phase. This observation is in agreement with the report made by Furukawa et al. [16], that the formation of the pyrochlore phase in PZN can be suppressed by adding 15 mol% SrTiO₃. Fig. 9 also shows that without the addition of stabilizer SrTiO₃ in the P–Z–M–N system, the maximum obtainable perovskite content is about 80–85% and increases with the addition of SrTiO₃ up to 15 mol%. However, for the PMN–P–Z–N system, 100% perovskite PZMN is easily attained except at the narrow region of PZN-rich compositions. This leads to the postulation that PMN perovskite in the PMN–P–Z–N system shows the characteristics of the stabilizer.

The temperature dependences of dielectric constant (at 1 kHz) for a wide range of compositions of PMN–PZN–SrTiO₃ were measured and analyzed to construct a ternary phase diagram of dielectric properties. As shown in Fig. 10(a) and (b) for both P–Z–M–N and PMN–P–Z–N raw precursor systems, the composition with $x=0.7$ in SrTiO₃ +

$\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ gives a higher dielectric constant because it has a T_C of 25°C and contains a higher perovskite content. Without the addition of stabilizer SrTiO_3 , the PMN–P–Z–N system always gives a higher dielectric constant in contrast to P–Z–M–N because of the higher perovskite content generated by the stabilizer-like PMN perovskite. However, with the addition of 10 mol% SrTiO_3 stabilizer, in spite of the presence of 100% perovskite phase, the dielectric constant of the PMN–P–Z–N system has been decreased remarkably. When the stabilizer SrTiO_3 increased up to 15 mol%, no significant differences in the dielectric features are observed for both systems. This reflects that when a minimum amount of stabilizer was added to both systems, the dominating role of the SrTiO_3 stabilizer is similar and irrespective of the mixture systems as a result of its enhancement of the tolerance factor and the electronegativity difference of PZMN [4].

Regarding the Curie temperature (T_C), it was found that even though PMN–P–Z–N shows a higher dielectric feature, the T_C variation of the final product seems to be independent of the structure of the raw starting materials but is highly dependent on the composition and phase of the final product.

4. Conclusions

1. Three major pyrochlore compositions, $\text{Pb}_2\text{Nb}_2\text{O}_7$, $\text{Pb}_3\text{Nb}_2\text{O}_8$ and $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, were characterized in the formation of the perovskite PZMN phase.
2. The formation of the perovskite PZMN phase in the P–Z–M–N system is characterized by two kinetically distinct processes.
3. Perovskite PMN functions like stabilizer SrTiO_3 in promoting the formation of perovskite phase in the PMN–P–Z–N system.
4. Maximum perovskite content and dielectric constant of the $\text{Pb}[(\text{Mg}_x\text{Zn}_{1-x})_{1/3}\text{Nb}_{2/3}]\text{O}_3$ phase are easily obtained in the PMN–P–Z–N system at an appropriate ratio of $x = 0.7$.
5. Ternary phase diagrams of PMN–PZN– SrTiO_3 for both perovskite content and dielectric constant are established.

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