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Piezoelectric characteristics of low temperature sintering $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{1/2}Ti_{1/2})O_3$ ceramics as a function of $Pb(Mn_{1/3}Sb_{2/3})O_3$ substitution

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Abstract In this study, in order to develop the composition ceramics for multilayer ceramic for ultrasonic nozzle and ultrasonic actuator application, $Pb(Mn_{1/3}Sb_{2/3})O_3$ (abbreviated as PMS) substituted $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (abbreviated as PNN-PZT) ceramics were fabricated using two-stage calcinations method and Li_2CO_3, Na_2CO_3 and ZnO as sintering aids, and their piezoelectric and dielectric characteristics were investigated. With the increase of the amount of PMS substitution, electromechanical coupling factor (k_p), and mechanical quality factor (Q_m) of specimens showed the maximum value at 3 mol% substituted specimen while dielectric constant (ε_r) was decreased. At the sintering temperature of 900 °C, the density, ε_r, k_p, and Q_m of 3 mol% PMS substituted PNN-PZT composition ceramics showed the optimal values of 7.92 [g/cm^3], 959, 0.584, and 1003, respectively, for low loss multilayer piezoelectric actuator application.

Keywords Multilayer ceramic · Ultrasonic nozzle and ultrasonic actuator · Electromechanical coupling factor · Mechanical quality factor · Sintering aids

1 Introduction

In general, PZT system ceramics should be sintered at high temperatures between 1200 and 1300 °C in order to obtain complete densification [1]. Accordingly, environmental pollution due to PbO evaporation under high sintering temperature of the ceramics and the use of expansive Pd rich Ag/Pd internal electrode in the process of manufacturing multilayer ceramic actuator are inevitable [2]. Calcination process in piezoelectric ceramics is one of important process which aids its densification. Calcination process can reduce the shrinkage ratio of the ceramics during sintering process and it cause the densification of ceramic without crack and distortion. And also, repeatable calcinations process such as 2-stage calcinations can improve homogeneity of ceramic composition. In the PZT solid solution system ceramics, $PbTiO_3$(abbreviated as PT) formation is created from 500 °C up to about 800 °C and then it react with ZrO_2 at the temperature above 850~900 °C [3]. However, two-stage calcinations method is able to low sintering temperature of the ceramics, because previously formed B-site reaction materials in the ABO_3 perovskite structured piezoelectric ceramic can directly react with PbO without creation of PT. And also, high diffusion coefficient and tiny particle size of B-site reaction materials help densification of specimens. Piezoelectric actuator requires high electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) in order to induce a large strain in proportional to applied electric field. And also, to prevent its heat generation, when it is driven with high voltage for a long time, high mechanical quality factor (Q_m) is required [4].

$Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ system ceramics show high electromechanical coupling factor(Qm) and excellent temperature stability of resonance frequency nearby MPB (Morphotrophic Phase Boundary) region. Therefore, in this study, in order to develop the composition ceramics for multilayer ceramic for ultrasonic nozzle and ultrasonic actuator application, $Pb(Mn_{1/3}Sb_{2/3})O_3$ substituted $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ ceramics were fabri-

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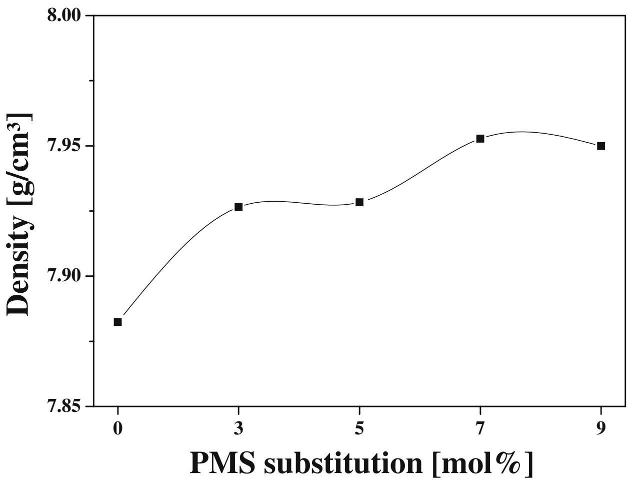


Fig. 1 Density according to the amount of PMS substitution

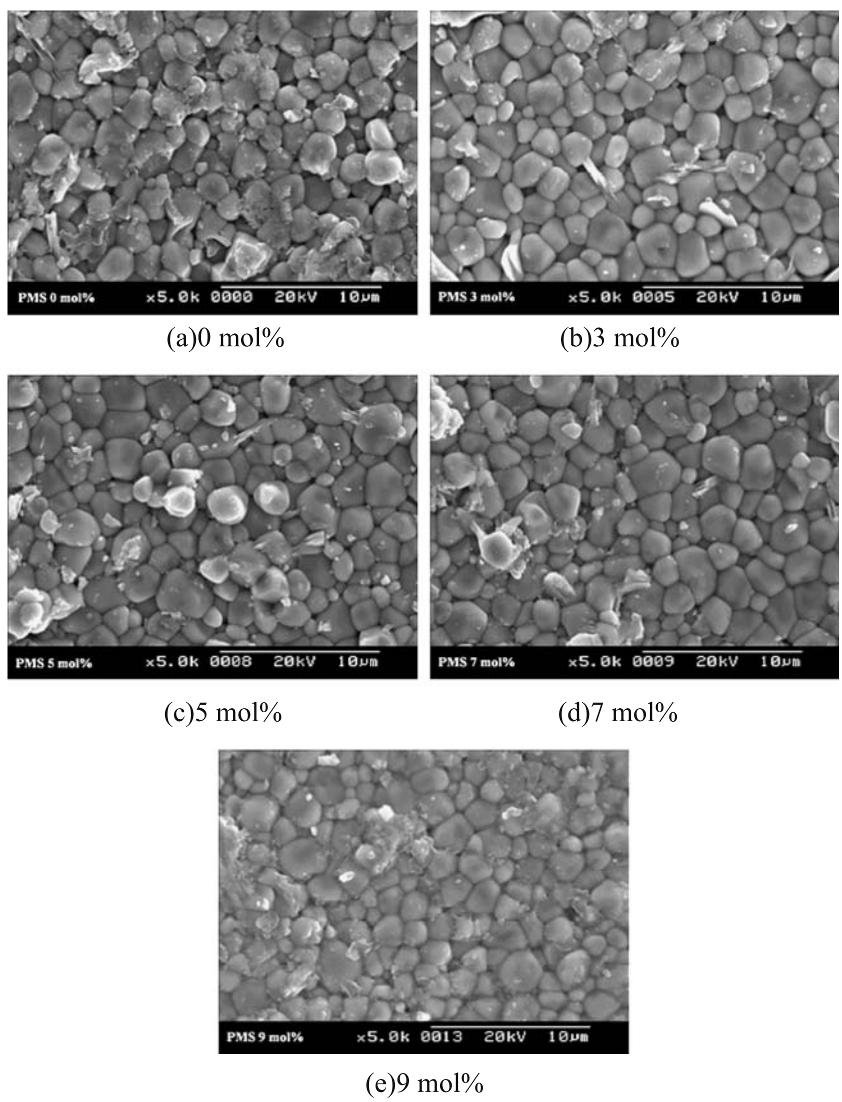
cated using two-stage calcinations method and Li_2CO_3, Na_2CO_3 and ZnO as sintering aids, and their piezoelectric and dielectric characteristics were investigated [4, 5].

2 Experimental

The specimens were manufactured using a conventional mixed oxide process. The compositions used in this study were as follows;

$$\mathrm{Pb}\left(\mathrm{Mn}_{1/3}\mathrm{Sb}_{2/3}\right)_x\left(\mathrm{Ni}_{1/3}\mathrm{Nb}_{2/3}\right)_{0.14-x}(\mathrm{Zr}_{0.50}\mathrm{Ti}_{0.50})_{0.86}\mathrm{O}_3 + 0.1\ \mathrm{wt\%}\ \mathrm{MnO}_2 + 0.2\ \mathrm{wt\%}\ \mathrm{Fe}_2\mathrm{O}_3 + 0.2\ \mathrm{wt\%}\ \mathrm{CuO} + 0.2\ \mathrm{wt\%}\ \mathrm{Na}_2\mathrm{CO}_3 + 0.2\ \mathrm{wt\%}\ \mathrm{Li}_2\mathrm{CO}_3 + 0.4\ \mathrm{wt\%}\ \mathrm{ZnO}(x = 0, 0.03, 0.05, 0.07, 0.09)$$

Fig. 2 Microstructure according to the amount of PMS substitution. (**a**) 0 mol%; (**b**) 3 mol%; (**c**) 5 mol%; (**d**) 7 mol%; (**e**) 9 mol%



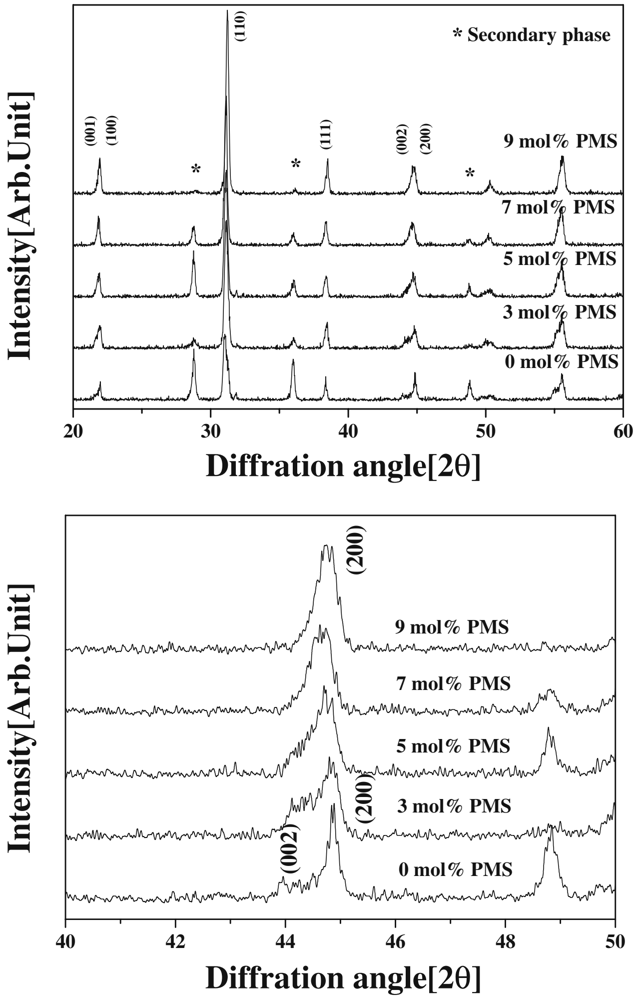


Fig. 3 X-ray diffraction patterns according to the amount of PMS substitution

The raw materials, PbO and sintering aids excepted such as ZrO_2, TiO_2, Sb_2O_5, MnO_2, Fe_2O_3, NiO, CuO and Nb_2O_5 for the given composition were weighted by mole ratio and the powders were ball-milled for 24 h. After drying, they were calcined at 1000 °C for 4 h. Thereafter, PbO was added and ball-milled again. After drying, they were calcined at 750 °C for 2 h. Thereafter, Na_2CO_3, Li_2CO_3 and ZnO were added, ball-milled, and dried again. A polyvinyl alcohol (PVA: 5 wt%) was added to the dried powders. The powders were molded by the pressure of 1,000 kg/cm^2 in a mold which has a diameter of 21 mm, burned out at 600 °C for 3 h, and then sintered at 900 °C for 2 h. For measuring the piezoelectric characteristics, the specimens were polished to 1 mm thickness and then electrodeposited with Ag paste. Poling was carried out at 120 °C in a silicon oil bath by applying fields of 30 kV/cm for 30 min. All samples were aged for 24 h prior to measuring the piezoelectric and dielectric properties. The microstructure and crystal structure of specimens were analyzed through scanning electron microscopy (SEM: Hitachi, S-2400) and X-ray diffraction (XRD: Rigaku, D/MAX-2500H), respectively. For investigating the dielectric properties, capacitance was measured at 1 kHz using an LCR meter (ANDO AG-4034) and dielectric constant was calculated. For investigating the piezoelectric properties, the resonant and anti-resonant frequencies were measured by an Impedance Analyzer (Agilent 4294A) according to IEEE standard and then the electromechanical coupling factor and mechanical quality factor were calculated.

3 Results and discussion

Figure 1 shows density according to the amount of PMS substitution. According to the increase of amount of PMS substitution, density slightly increased up to 7 mol% PMS substitution and then decreased. It is considered that PMS improve sinterability in this composition system. And also, all the specimens showed high densification due to the liquid phase sintering and two-stage calcinations effects. The maximum density value showed 7.95 [g/cm^3] at 7 mol% PMS substitution.

Figure 2 shows the microstructure of specimens according to the amount of PMS substitution at sintering temperature of 900 °C. As can be seen in Fig. 2, grain size slightly increased according to the increase of PMS substitution up to 5 mol% and then decreased. Its results also seem that PMS improve sinterability in this system composition.

Figure 3 shows X-ray diffraction pattern of specimens sintered at 900 °C according to the amount of PMS substitution. First of all, secondary phase appeared at all the specimens, and its intensity decreased according to the increase of amount of PMS substitution. It is clear evidence that PMS enhances sinterability and weakens the secondary phase of the composition ceramics. As can be seen from

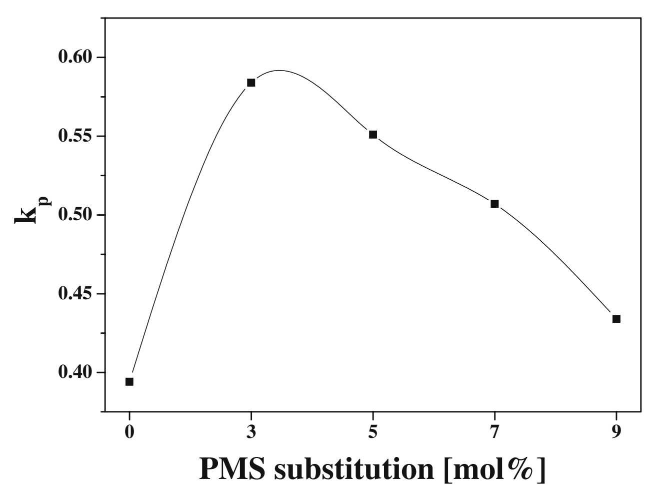


Fig. 4 Electromechanical coupling factor (k_p) according to the amount of PMS substitution

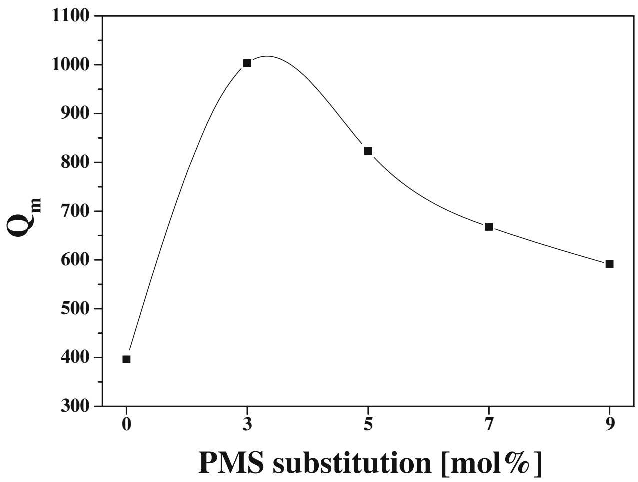


Fig. 5 Mechanical quality factor (Q_m) according to the amount of PMS substitution

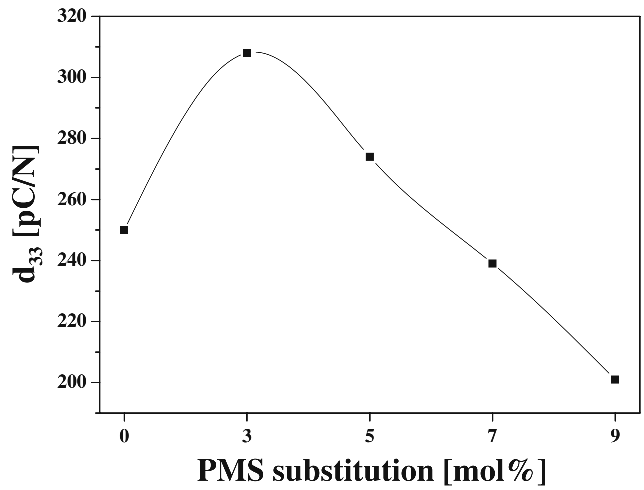


Fig. 7 Piezoelectric constant (d_{33}) according to the amount of PMS substitution

(002) and (200) peaks of X-ray diffraction pattern, it is evident that crystal structure of specimens changes from tetragonal phase to rhombohedral phase, and MPB (Morphotrophic Phase Boundary) appears at 3 mol% PMS substitution.

Figure 4 shows electromechanical coupling factor (k_p) according to the amount of PMS substitution. The k_p of specimen showed the maximum value at about 3 mol% PMS substitution. Especially, a highest value of k_p=0.584 suitable for actuator application was appeared. It is generally known that a magnitude of density is proportional to k_p. However, the variation trend of k_p obtained from this experiment didn't coincide with that of density. High values of k_p in poled ceramics are believed to arise from the easy motion of domain walls under an applied field or a stress. Domain wall motion in the PZT system ceramics can be easily performed through the methods of donor doping and selecting compositions close to the MPB. Therefore, from the analysis of X-ray diffraction pattern, it is evident that a maximum value of k_p has relations with the composition of MPB region [6].

Figure 5 shows mechanical quality factor (Q_m) according to the amount of PMS substitution and sintering temperature. The variation of Q_m showed the coincided value with k_p, and a maximum value of Q_m appeared at 3 mol% PMS substitution. At the 3 mol% PMS substitution, the homogenous grains were uniformly distributed at total microstructure by its sufficient sintering effect. As the result, the smallest intrinsic frictions due to domain wall motion are appeared, and Q_m reaches the maximum value consequently. Hence, it is considered that 3 mol% PMS substitution is optimum condition, in this composition. A highest value of Q_m=1003 suitable for actuator application was appeared.

Figure 6 shows dielectric constant according to the amount of PMS substitution and sintering temperature.

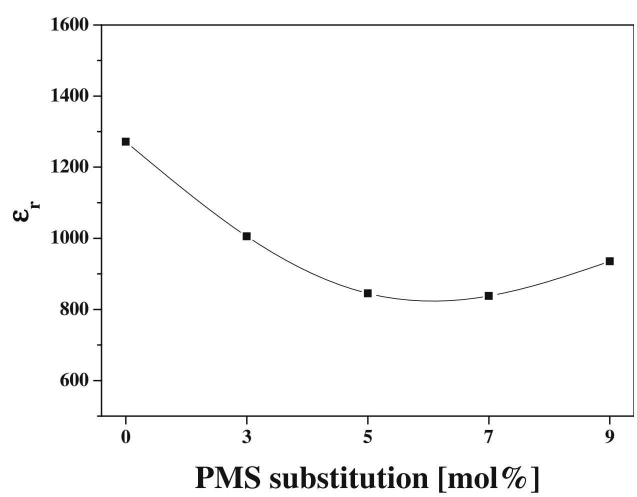


Fig. 6 Dielectric constant (ε_r) according to the amount of PMS substitution

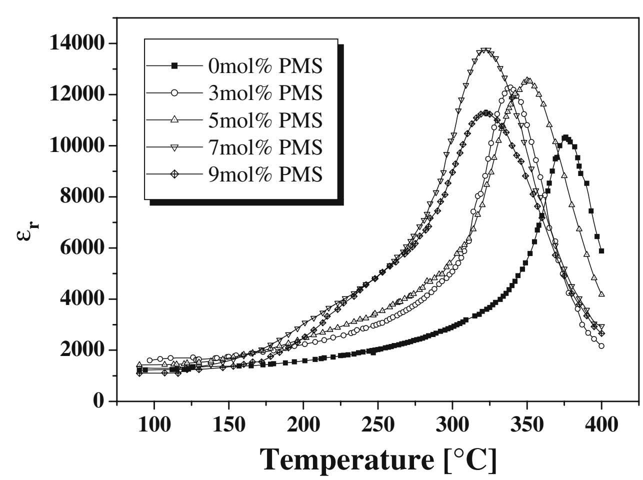


Fig. 8 Temperature dependence of dielectric constant according to the amount of PMS substitution

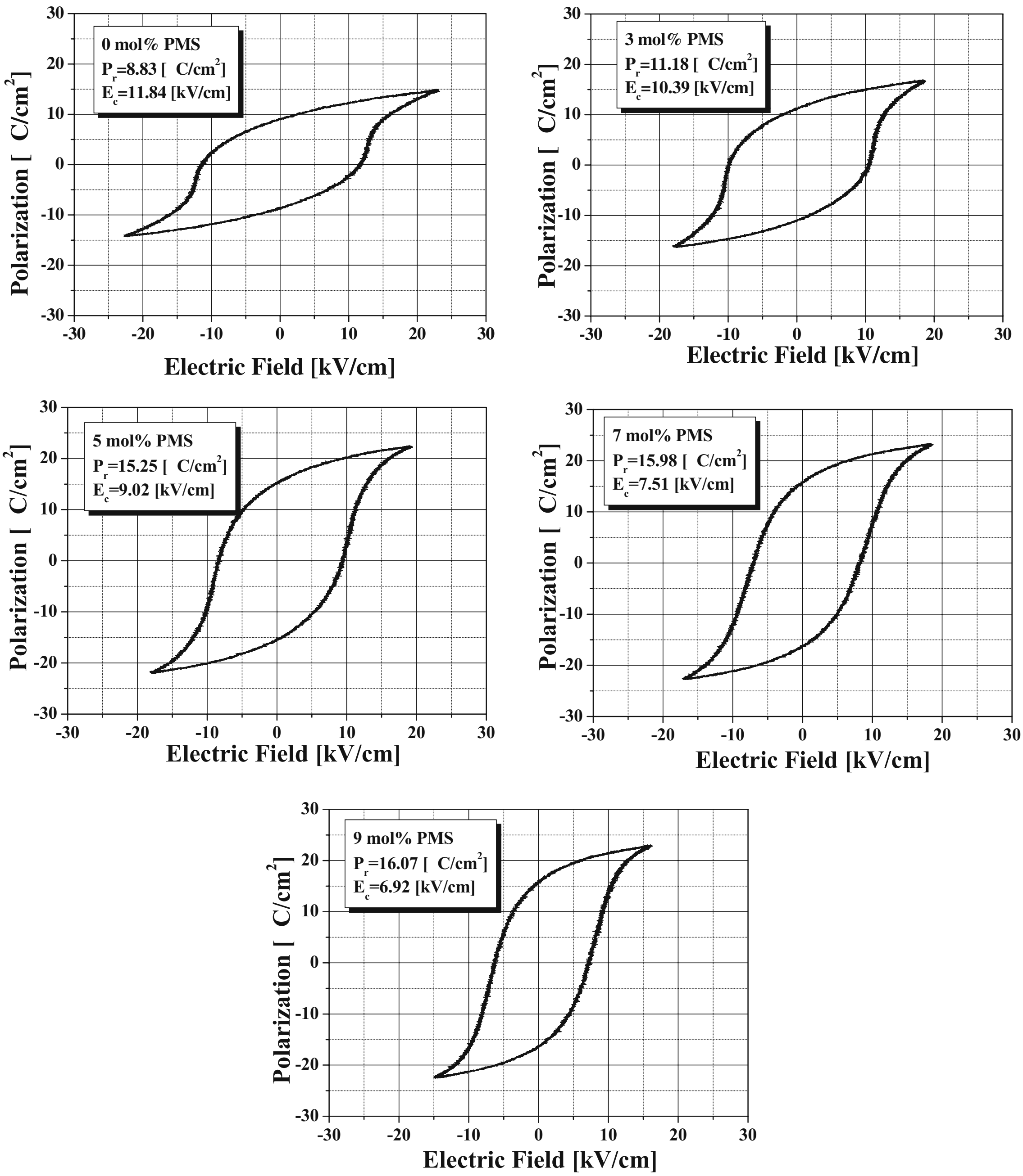


Fig. 9 Hysteresis curve of specimens according to the amount of PMS substitution

Table 1 Physical properties of specimens.

Sintering temp. (°C)	PMS substitution (mol%)	Density (g/cm^3)	ε_r	k_p	Q_m	d_{33} [pC/N]
900	0	7.882	1,271	0.394	396	250
	3	7.926	1,005	0.584	1,003	308
	5	7.928	844	0.551	823	274
	7	7.952	837	0.507	668	239
	9	7.949	935	0.434	591	201

With increasing PMS substitution, dielectric constant decreased at 7 mol% and then slightly increased. Its result is not general dielectric properties of PZT system ceramics. Study of focus on dielectric characteristic in this system is required after.

Figure 7 shows piezoelectric constant (d_{33}) according to the amount of PMS substitution. A maximum value of d_{33} appeared at 3 mol% PMS substitution and showed the highest value of 308pC/N at the sintering temperature of 900 °C. This result coincided with the trend of k_p.

Figure 8 shows temperature dependence of dielectric constant according to the amount of PMS substitution. With increasing PMS substitution, Curie temperature decreased.

Figure 9 shows hysteresis curve of specimens according to the amount of PMS substitution. With increasing PMS substitution, coercive field (Ec) decreased and remanent polarization (Pr) increased due to the decrease of Curie temperature.

Consequently, it was proved that PMS substitution in the PNN-PZT system could densify the specimen and improve the piezoelectric properties such as k_p and Q_m at low sintering temperature. Table 1 shows the physical properties of specimen manufactured according to amount of PMS substitution.

4 Conclusions

In this study, in order to develop the composition ceramics for multilayer ceramic for ultrasonic nozzle and ultrasonic actuator application, $Pb(Mn_{1/3}Sb_{2/3})O_3$ substituted $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ ceramics were fabricated using 2-stage calcinations method and Li_2CO_3, Na_2CO_3 and ZnO as sintering aids, and their piezoelectric and dielectric characteristics were investigated. The results obtained from the experiment are as follows;

1. As the amount of PMS substitution increased, crystal structure of specimens changed from tetragonal phase to rhombohedral phase, and MPB (Morphotrophic Phase Boundary) appeared at 3 mol% PMS substitution.
2. All the specimens were fully densified due to the liquid phase sintering and two-stage calcinations effects.
3. In this system, PMS substitutions improved both k_p and Q_m due to the increase of sinterability.
4. At the sintering temperature of 900 °C, 3 mol% PMS substituted specimen showed a maximum value of density=7.926 g/cm^3, k_p=0.584, d_{33}=308pC/N and Q_m=1003, respectively.

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