J Electroceram (2009) 23:387–391
DOI 10.1007/s10832-008-9473-7

Piezoelectric and dielectric characteristics of low-temperature-sintering $Pb(Mg_{1/2}W_{1/2})O_3$–Pb$(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ ceramics according to the amount of PNN substitution

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Received: 23 May 2007 / Accepted: 18 March 2008 / Published online: 17 April 2008

Abstract In this study, in order to develop low-temperature-sintering ceramics for multilayer piezoelectric actuator, Pb $(Mg_{1/2}W_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (abbreviated as PMW–PNN–PZT) ceramics were fabricated using Li_2CO_3 and $CaCO_3$ as sintering aids and their dielectric and piezoelectric properties were investigated with the amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$ (abbreviated as PNN) substitution. PMW–PNN–PZT composition ceramics could be sintered up to 870°C by adding sintering aids. At the sintering temperature of 900°C, electromechanical coupling factor (k_p), piezoelectric constant (d_{33}) and Curie temperature (Tc) in the composition ceramics with 9 mol% PNN substitution showed the optimal value of 0.64 517 pC/N and 317°C, respectively for multilayer actuator application.

Keywords Low-temperature-sintering · Piezoelectric constant · Electromechanical coupling factor (k_p) · Piezoelectric constant (d_{33}) · Curie temperature (Tc) · Sintering aids

1 Introduction

Multilayer ceramic devices such as actuator and piezoelectric transformer require internal electrode with high melting point such as expansive Pd or Pt when they are sintered at temperature more than 1200°C [1, 2]. Ag is an economical material capable of being effectively used as internal electrode of the multilayer ceramic devices which can be sintered at low temperature of about 900°C [3, 4].

Recently, the devices using low temperature co-fired ceramics (LTCC) have been extensively utilized for applications such as multilayer actuator, transformer and capacitor. The reason is that its manufacturing cost and consuming power are sufficiently capable of being reduced because the ceramics can be simultaneously sintered at low temperature of about 900°C with cheap pure Ag internal electrode. Among multilayer LTCC devices, piezoelectric actuators can be used for various applications such as piezoelectric ultrasonic motor, piezoelectric valve and cooling fan etc. The conditions required for application as multilayer piezoelectric actuator are as follows; first of all, a high piezoelectric d constant is required in order to induce a large strain in proportional to applied voltage. And also, a high electromechanical coupling factor (k_p) is necessary in order to increase the energy conversion efficiency. Finally, a high curie temperature (Tc) is also required in order to prevent a thermal de-poling phenomenon of the actuator.

In this paper, from these viewpoints, for searching MPB (morphotrophic phase boundary) region with high electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) values for multilayer actuator application, $Pb(Mg_{1/2}W_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ ceramics, in which $Pb(Mg_{1/2}W_{1/2})O_3$ is added to the $Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ system, were fabricated according to the amount of $Pb(Ni_{1/3}Nb_{2/3})O_3$ substitution, and also Li_2CO_3 and $CaCO_3$ as sintering aids were added to them in order to lower sintering temperature [5, 6]; their piezoelectric and dielectric properties were investigated and evaluated for multilayer piezoelectric actuator application.

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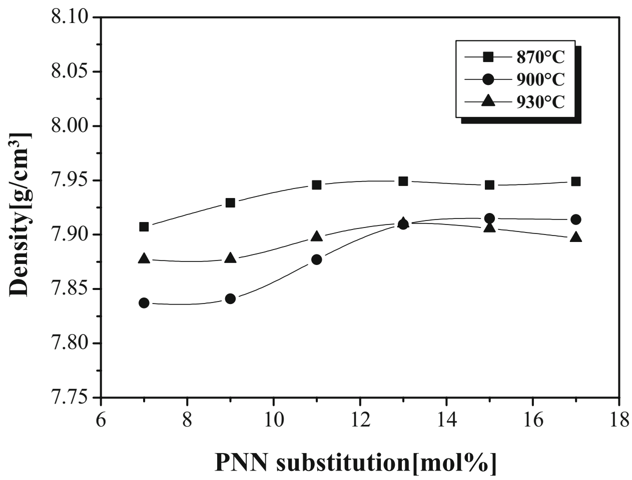

Fig. 1 Density according to the variation of amount of PNN substitution and sintering temperature

2 Experimental

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

$$Pb\left[\left(Mg_{1/2}W_{1/2}\right)_{0.03}\left(Ni_{1/3}Nb_{2/3}\right)_x\left(Zr_{0.50}Ti_{0.50}\right)_{1-0.03-x}\right]O_3$$

$$+ 0.25\ \text{wt.\%}CaCO_3$$

$$+ 0.2\ \text{wt.\%}Li_2CO_3(x = 0.07 \sim 0.17)$$

The raw materials such as PbO, ZrO_2, TiO_2, MgO, WO_3, NiO 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 850°C for 2 h. Thereafter, $CaCO_3$ and Li_2CO_3 were added, ball-milled, and dried again. A polyvinyl alcohol (PVA: 5%) was added to the dried powders. The powders were molded by the

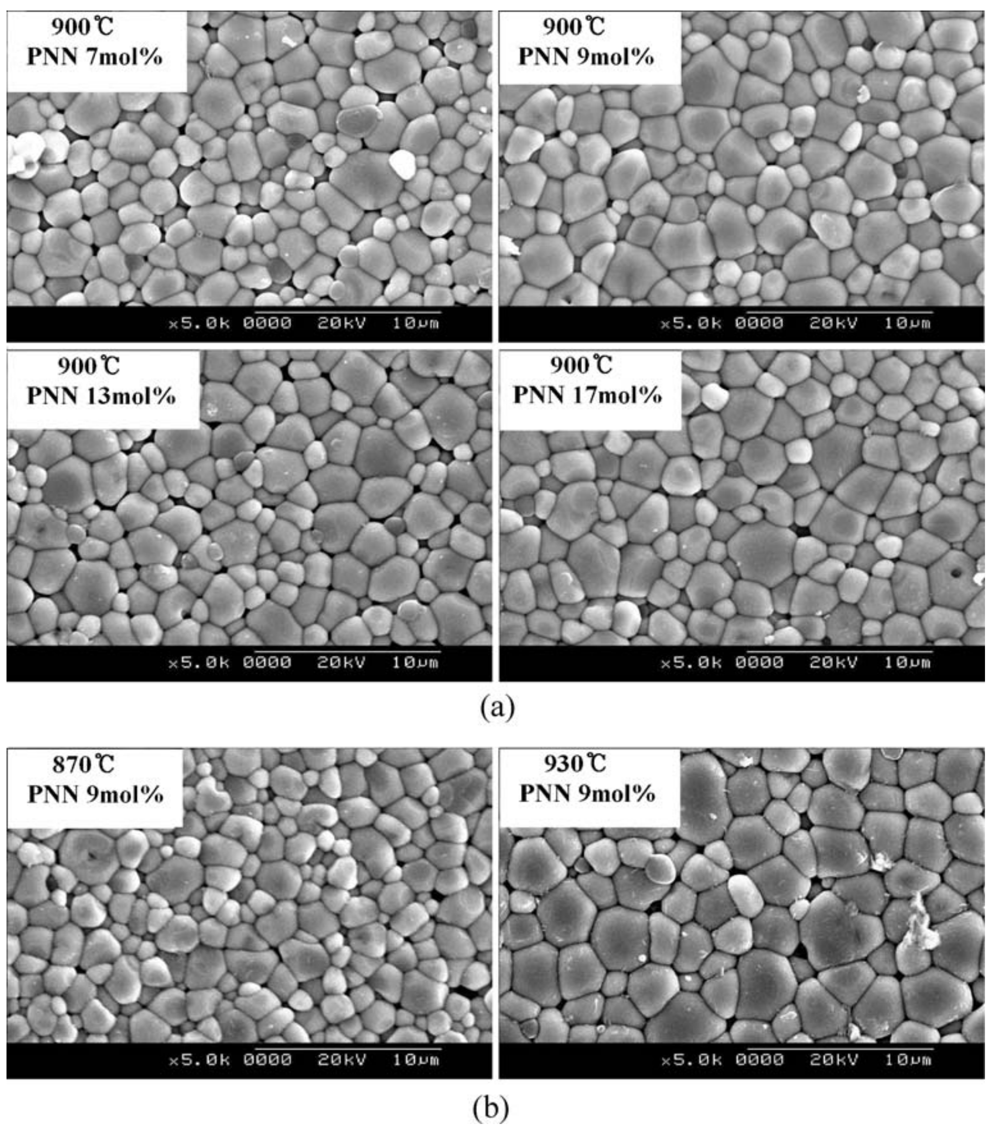

Fig. 2 Microstructure according to the variation of (**a**) amount of PNN substitution and (**b**) sintering temperature

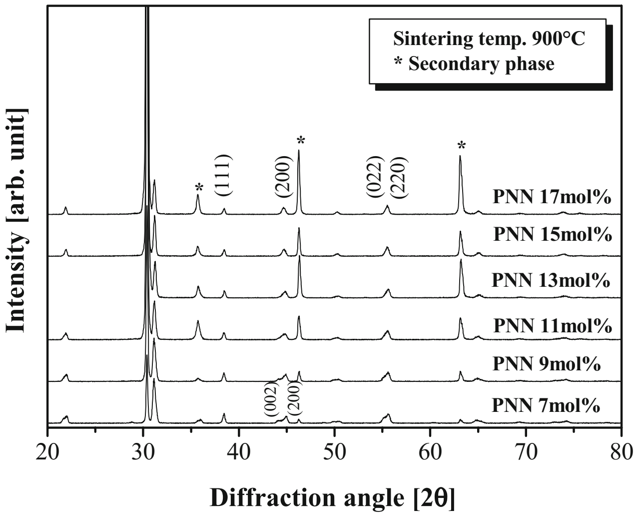

Fig. 3 X-ray diffraction patterns according to the variation of amount of PNN substitution

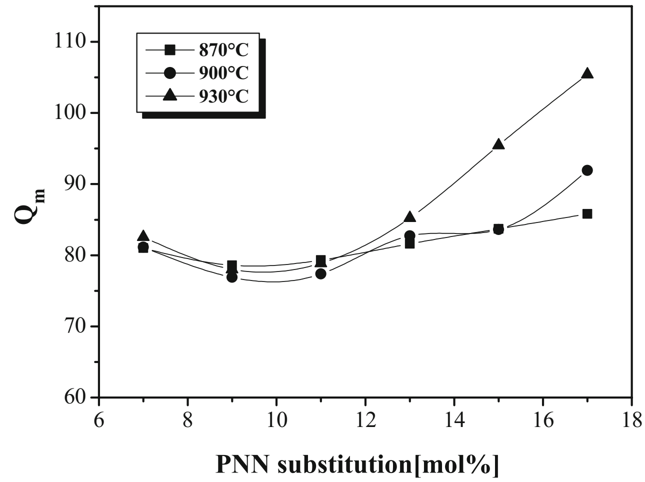

Fig. 5 Mechanical quality factor (Q_m) according to the variation of amount of PNN substitution and sintering temperature

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 870°C, 900°C and 930°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 IRE standard and then the electromechanical coupling factor and mechanical quality factor were calculated.

3 Results and discussion

Figure 1 shows density according to the variation of sintering temperature and the amount of PNN substitution. According to the increase of amount of PNN substitution, density increased and showed the maximum value at each sintering temperature. And then it showed the trend that it was partially decreased by over PNN substitution. The maximum density appeared at 13 mol% PNN substituted specimen at the sintering temperature of 870°C and showed the value of 7.95 g/cm^3. It is considered that the high density at low temperature of 870°C is caused by liquid phase effect of $CaCO_3$–Li_2CO_3 used as sintering aids, which has a eutectic point at 662°C. [5] Thus, it is thought

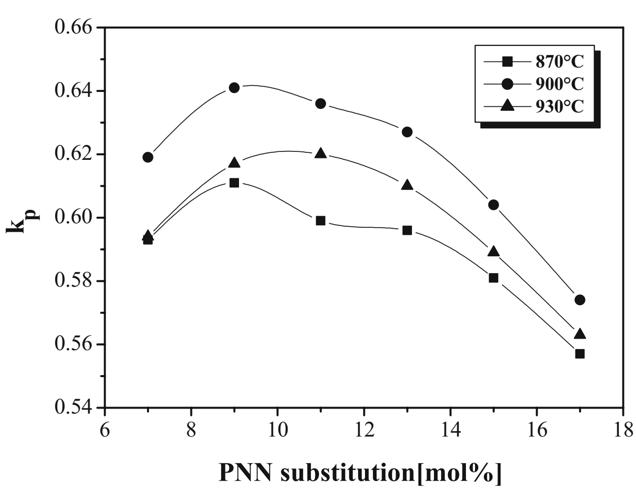

Fig. 4 Electromechanical coupling factor (k_p) according to the variation of amount of PNN substitution and sintering temperature

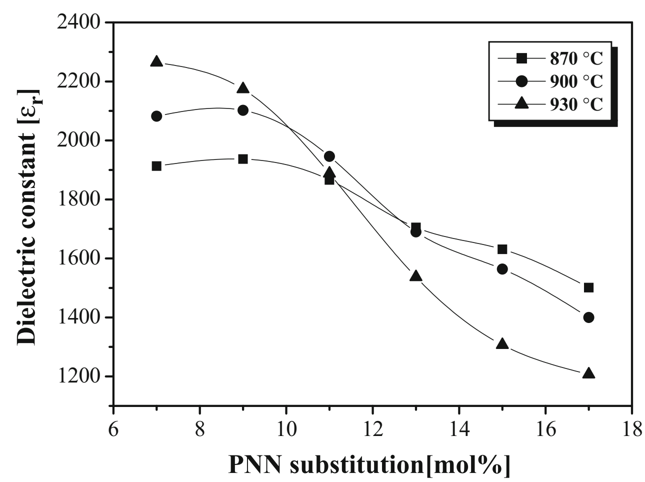

Fig. 6 Dielectric constant (ε_r) according to the variation of amount of PNN substitution and sintering temperature

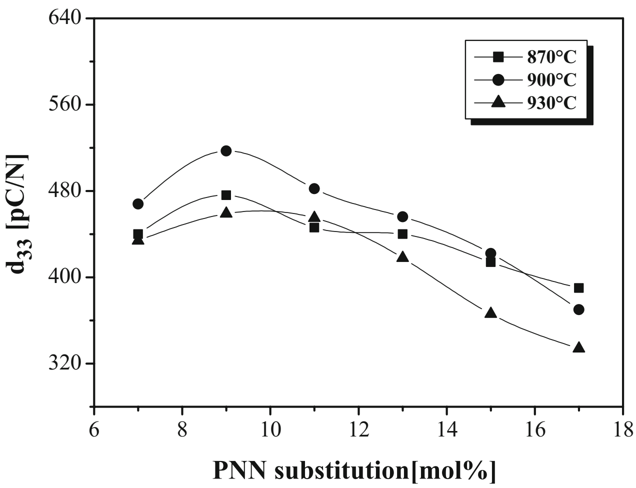

Fig. 7 Piezoelectric constant (d_{33}) according to the variation of amount of PNN substitution and sintering temperature

that the sintering aids with a low melting point such as $CaCO_3$–Li_2CO_3 and Bi_2O_3–Li_2CO_3 can be used in order to increase a densification of specimen at low sintering temperature.

Figure 2 shows the microstructure of specimens according to the variations of (a) amount of PNN substitution at sintering temperature of 900°C and (b) sintering temperature at 9 mol% PNN substitution. As can be seen in Fig. 2(a), the grain size of specimen didn't show nearly any variation. As can be seen in Fig. 2(b), grain size increased according to the increase of sintering temperature and showed the value of 2.40 μm at 930°C.

Figure 3 shows X-ray diffraction pattern of specimens sintered at 900°C according to the variation of amount of PNN substitution. First of all, secondary phase appeared at all specimens, and its intensity increased according to the increase of amount of PNN substitution. Therefore, it seems that PNN could not be substituted at the composition

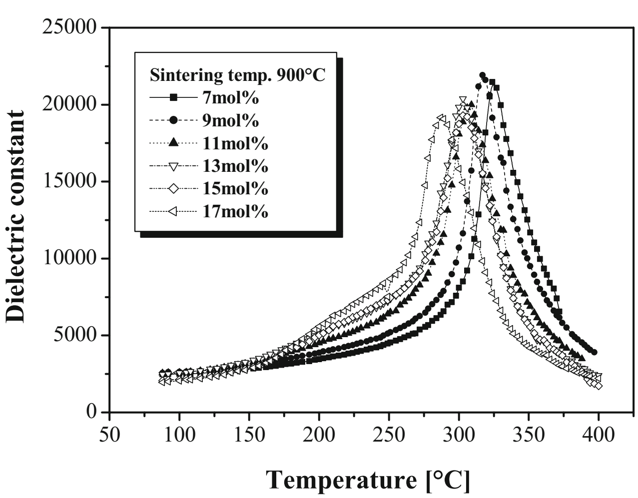

Fig. 8 Temperature dependence of dielectric constant according to the variation of amount of PNN substitution

ceramics completely. As can be seen from (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 9 mol% PNN substitution. Figure 4 shows electromechanical coupling factor (k_p) according to the variation of amount of PNN substitution and sintering temperature. The k_p of specimen at each sintering temperature showed the maximum value at about 9 mol% PNN substitution. Especially, a highest value of k_p=0.64 suitable for actuator application was appeared in 9 mol% PNN substitution composition at sintering temperature of 900°C. 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. 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. That is, this result corresponds with the facts that k_p and Q_m generally show a maximum value and a minimum value at MPB, respectively. [7, 8]

Figure 5 shows mechanical quality factor (Q_m) according to the variation of amount of PNN substitution and sintering temperature. The variation of Q_m showed the opposite properties to k_p, and a minimum value of Q_m appeared at 9 mol% PNN substitution. This result also can be explained by the piezoelectric characteristics at MPB as refer in above k_p analysis.

Figure 6 shows dielectric constant according to the variation of amount of PNN substitution and sintering temperature. The variation of dielectric constant also

Table 1 Physical properties of specimens.

Sintering temperature [°C]	PNN [mol%]	Density [g/cm^3]	Dielectric constant	Grain size [μm]	k_p	Q_m	d_{33} [pC/N]	Tc [°C]
870	7	7.90	1,913	1.71	0.593	71	440	
	9	7.93	1,937		0.611	78	475	
	11	7.94	1,866		0.599	74	446	
	13	7.95	1,705		0.596	81	440	
	15	7.94	1,631		0.581	83	414	
	17	7.94	1,501		0.557	85	390	
900	7	7.83	2,082	1.80	0.619	81	468	327
	9	7.84	2,102	2.01	0.641	76	517	317
	11	7.87	1,946	1.82	0.636	77	482	311
	13	7.90	1,690	1.86	0.627	82	456	306
	15	7.91	1,564	2.09	0.604	83	422	306
	17	7.91	1,400	2.04	0.574	91	370	289
930	7	7.87	2,264	2.40	0.594	82	434	
	9	7.87	2,174		0.617	78	459	
	11	7.89	1,888		0.620	78	455	
	13	7.91	1,537		0.610	85	418	
	15	7.90	1,307		0.589	95	366	
	17	7.89	1,207		0.563	105	334	

coincides with the trend of k_p, and a maximum value of it increased according to the increase of sintering temperature. This result can be explained from the analysis of SEM in Fig. 2, that is, it is caused by the increase of grain size according to the increase of sintering temperature. However, at more than 11 mol% PNN substitution, dielectric constant decreased with the increase of sintering temperature and coincided with the result of density. It can be illustrated by the fact that non-reactant produced by over substitution is evaporated by the increase of sintering temperature, and then porosities with a very low dielectric constant are formed in the evaporated non-reactant position. Thus, the more sintering temperature increased, the more porosity increased, in other words, the more dielectric constant decreased.

Figure 7 shows piezoelectric constant (d_{33}) according to the variation of amount of PNN substitution and sintering temperature. A maximum value of d_{33} appeared at 9 mol% PNN substitution and showed the highest value of 517 pC/N at the sintering temperature of 900°C. This result coincides with the trend of k_p.

Figure 8 shows temperature dependence of dielectric constant according to the variation of amount of PNN substitution at the sintering temperature of 900°C. Curie temperature (Tc) decreased according to the increase of amount of PNN substitution and showed 317°C at 9 mol% PNN substitution with the highest piezoelectric properties. It is considered that the decrease of Tc is caused by PNN substitution with Tc of about −120°C.

Consequently, it was proved that PNN substitution in the PMW– PZT system could densify the specimen and improve the piezoelectric properties such as k_p and d_{33} at low temperature by arriving at MPB region when 9 mol% PNN is substituted. Table 1 shows the physical properties of specimen manufactured according to amount of PNN substitution.

4 Conclusions

In this study, in order to develop low temperature sintering ceramics for multilayer piezoelectric actuator, $Pb(Mg_{1/2}W_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ ceramics were fabricated using Li_2CO_3 and $CaCO_3$ as sintering aids and their dielectric and piezoelectric properties were investigated with the amount of PNN substitution. The results obtained from the experiment are as follows;

1. As amount of PNN substitution increased, crystal structure of specimens changed from tetragonal phase to rhombohedral phase, and MPB (morphotrophic phase boundary) appeared at 9 mol% PNN substitution.
2. Density of specimens was increased by PNN substitution and showed the highest sintering characteristic at 870°C due to the liquid phase effect of $CaCO_3$–Li_2CO_3 used as sintering aids.
3. Curie temperature (Tc) decreased according to amount of PNN substitution.
4. At the sintering temperature of 900°C, electromechanical coupling factor (k_p), piezoelectric constant (d_{33}) and Curie temperature (Tc) in the composition ceramics with 9 mol% PNN substitution showed the optimal value of 0.64, 517 pC/N and 317°C, respectively for multilayer actuator application.

Acknowledgements This work was supported by a KOSEF Grant (No. R01-2006-000-10120-0).

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