Piezoelectric and Dielectric Properties of Low Temperature Sintering $Pb(Zn_{1/2}W_{1/2})O_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ Ceramics

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In this study, in order to develop the composition ceramics for low loss multilayer piezoelectric actuator application, $Pb(Zn_{1/2}W_{1/2})O_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ (abbreviated as PZW-PMN-PZT)ceramics according to the amount of MnO_2 addition were fabricated using two-stage calcinations method. And also, their dielectric and piezoelectric properties were investigated. At the 0.2 wt% MnO_2 added PZW-PMN-PZT ceramics sintered at 930 °C, density, electromechanical coupling factor k_p, dielectric constant ε_r, piezoelectric d_{33} constant and mechanical quality factor Q_m showed the optimum value of 7.84 g/cm^3, 0.543, 1,392, 318.7 pC/N, 1,536, respectively for low loss multilayer ceramics actuator application.

Keywords : Two-stage calcinations method, Low temperature sintering, Piezoelectric constant, Electromechanical coupling factor

1. INTRODUCTION

$Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ system ceramics have been widely used as composition ceramics for piezoelectric transformer and ultrasonic motor applications because they relatively have high electromechanical coupling factor (kp)and mechanical quality factor(Qm) in comparison with other lead-based materials[1-4]. However, high sintering temperature more than 1200 °C induces evaporation of PbO during sintering process. Accordingly, sintering of the ceramics at the temperature less than 1000 °C is necessary. The method can inhibit evaporation of PbO[5].

Piezoelectric actuators and transformers require multilayer structure in order to increase displacement and output power, respectively. These devices also require co-firing with Ag/Pd internal electrode. The ratio of expensive Pd in Ag/Pd internal electrode must be increased when multilayer structured piezoelectric ceramics are co-fired with internal electrode since the sintering temperature of $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ system ceramics is higher than 1,200 °C. And also, high sintering temperature can deteriorate the stability of the piezoelectric properties and particularly mechanical quality factor(Qm), due to the formation of interfacial micro-defects and internal electrode loss[6,7]. In order to solve above problems, low temperature sintering of the ceramics is essential. In addition, decreasing sintering temperature can also afford the advantages of suppressing the compositional change, reducing the energy consumption and preventing the environmental pollution.

In this study, in order to develop composition ceramics capable of being sintered at the low temperature for multilayer piezoelectric actuator application, $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(ZrTi)O_3$ ceramics, which is substituted as $Pb(Zn_{1/2}W_{1/2})O_3$ for enhancing its low temperature sintering effect, were fabricated using two-stage calcination method and the amount of MnO_2 addition, And their dielectric and piezoelectric properties were investigated.

2. EXPERIMENTAL

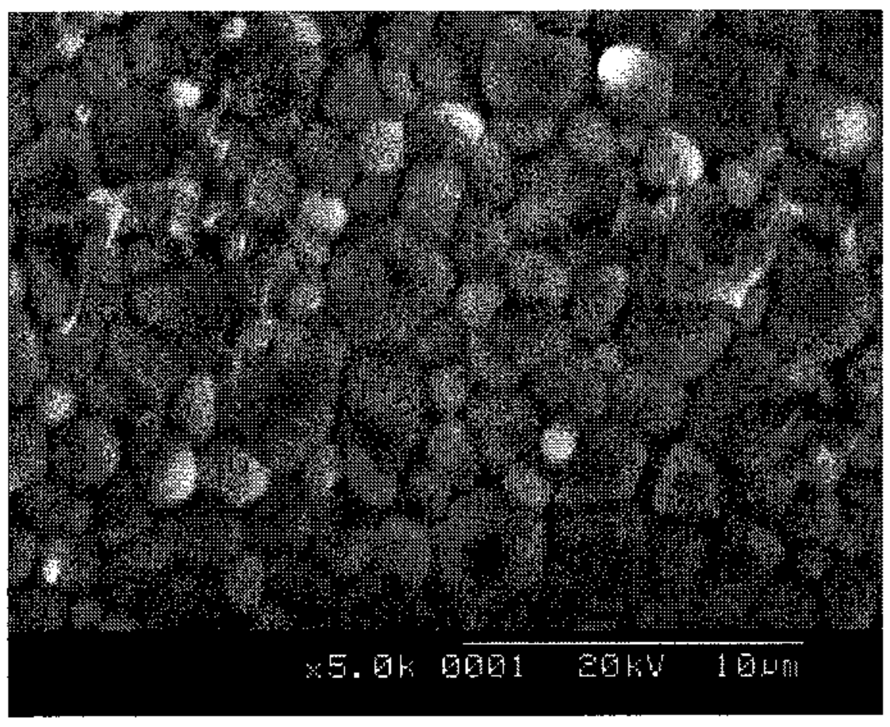
The specimens were manufactured using a conventional mixed oxide process. The compositions used in this study were as follows;

$$Pb(Zn_{1/2}W_{1/2})_{0.02}(Mn_{1/3}Nb_{2/3})_{0.07}(Zr_{0.48}Ti_{0.52})_{0.91}O_3$$
$$+Xwt\%MnO_2\text{+ Sintering aids } (Li_2CO_3, Bi_2O_3, \text{ and } CuO)$$
$$X = 0, 0.1, 0.2, 0.3, 0.4$$

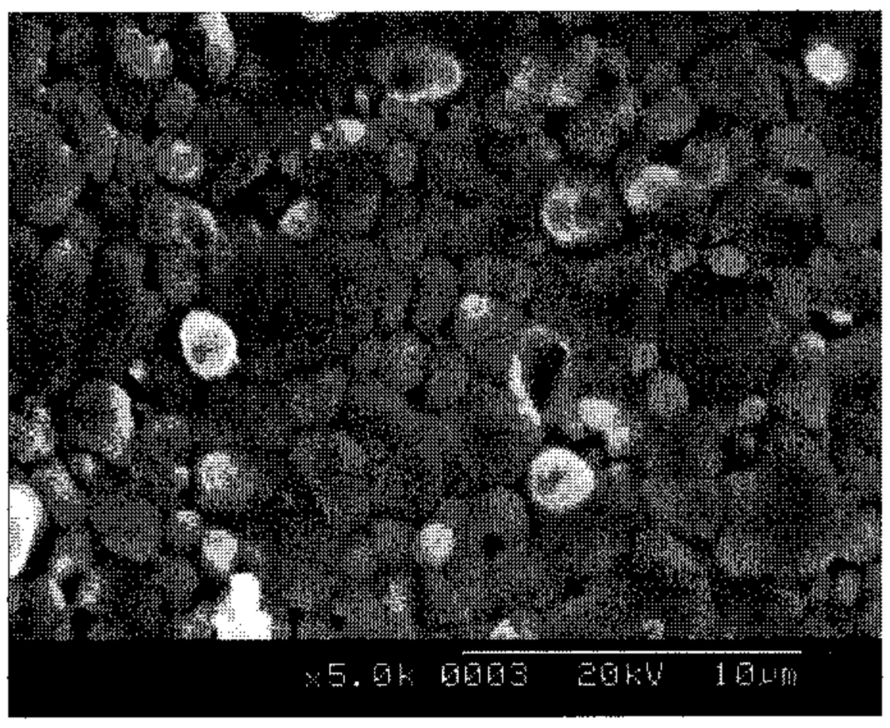
The specimens were fabricated using two-stage calcinations method. In the first stage, PbO and sintering aids excepted such as ZrO_2, TiO, MnO_2, Nb_2O_5, WO_3 and ZnO for the given composition were weighted by mole ratio and the powders were ball-milled for 24 h. They were calcined at 1,100 °C for 4 h. In the second stage, PbO was added ball-milled again. They were calcined 750 °C for 2 h. Thereafter, Li_2CO_3, Bi_2O_3 and CuO were added, ball-milled again. A polyvinyl alcohol (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 and 930 °C for 2 h. For measuring the piezoelectric properties, the specimens were polished to 1 mm thickness and then electro-deposited 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. The microstructure and crystal structure of specimen were analyzed through SEM and XRD. 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) and then the electromechanical coupling factor and mechanical quality factor were calculated, and piezoelectric constant was measured using d_{33}-meter.

3. RESULTS AND DISCUSSION

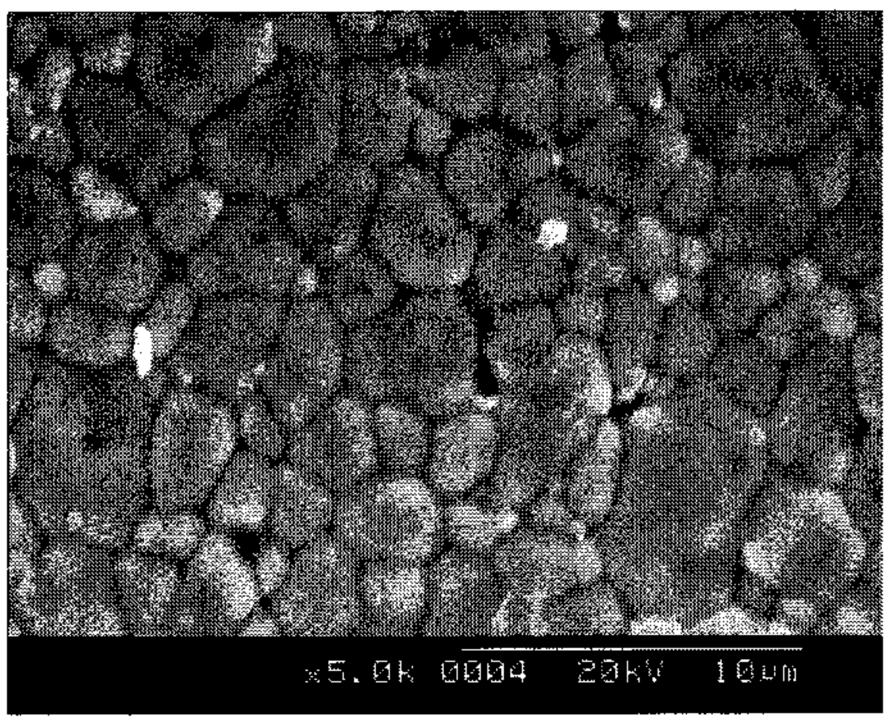
Figure 1 shows the microstructure of specimens with the amount of MnO_2 addition at the sintering temperature of 930 °C. The grain size increased with increasing amount of MnO_2 addition. The specimen doped with 0.3 wt% MnO_2 exhibited the largest grain size of about 3.08 μm. However, further increasing amount of MnO_2 above 0.3 wt% gradually reduced the grain size and MnO_2 additive can inhibit the grain growth due to accumulation of manganese ion at the grain boundary.



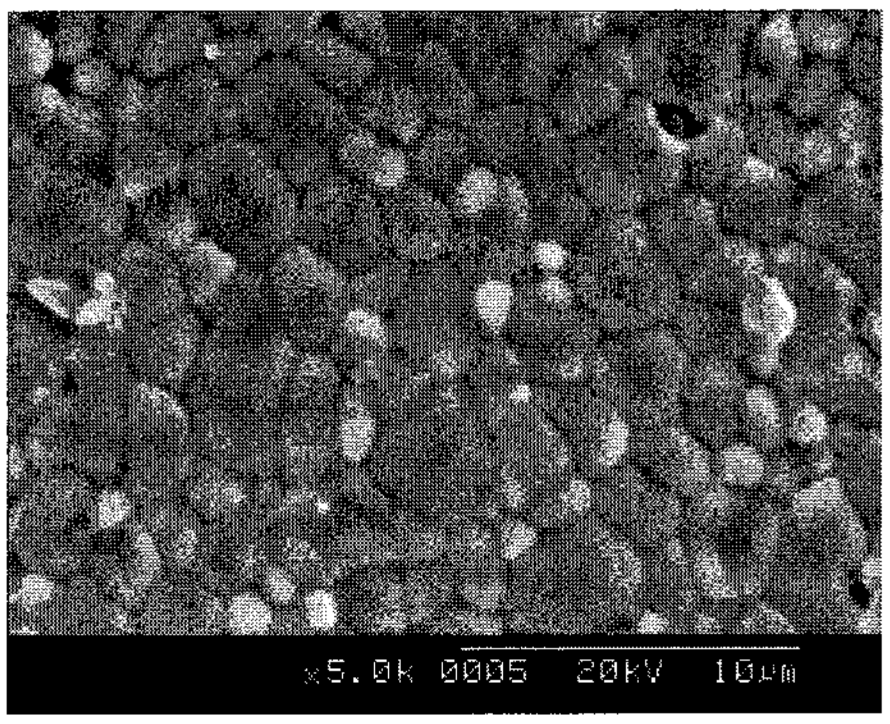
(a) 0 wt% MnO_2



(b) 0.2 wt% MnO_2



(c) 0.3 wt%MnO_2



(d) 0.4 wt% MnO_2

Fig. 1. Microstructure of specimen with the amount of MnO_2 addition at the sintering temperature of 930 °C.

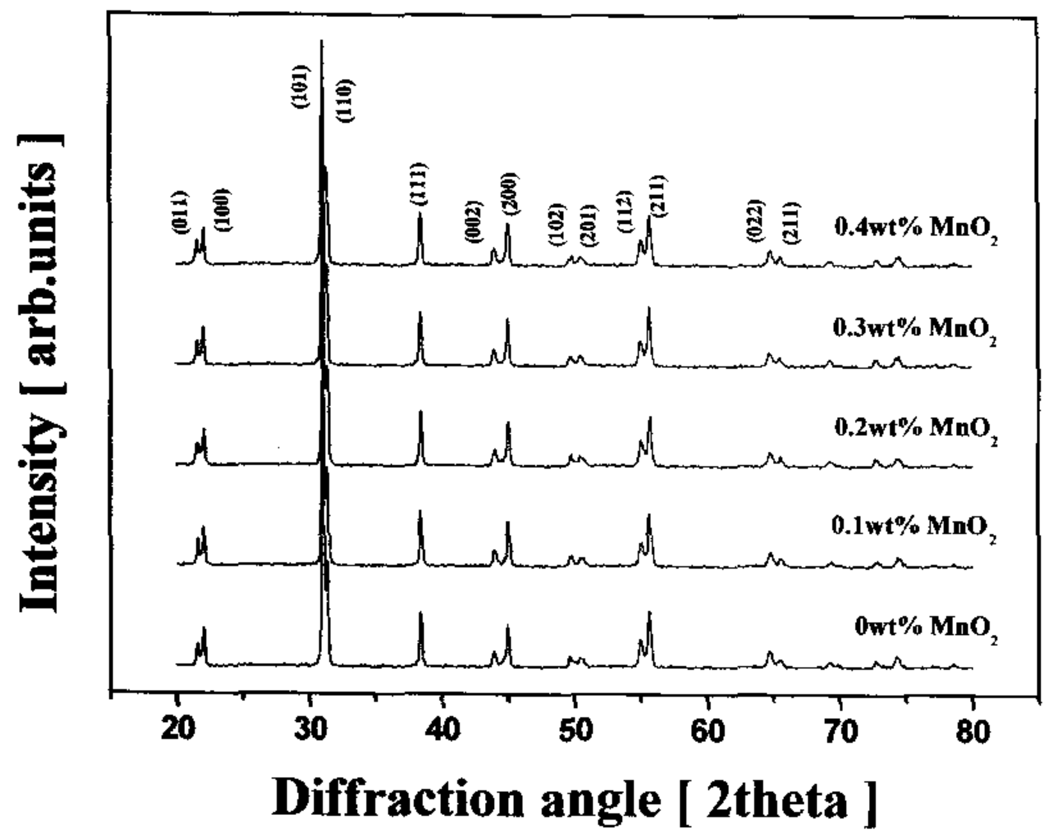


Fig. 2. X-ray diffraction pattern of specimen with the amount of MnO_2 addition at the sintering temperature of 930 °C.

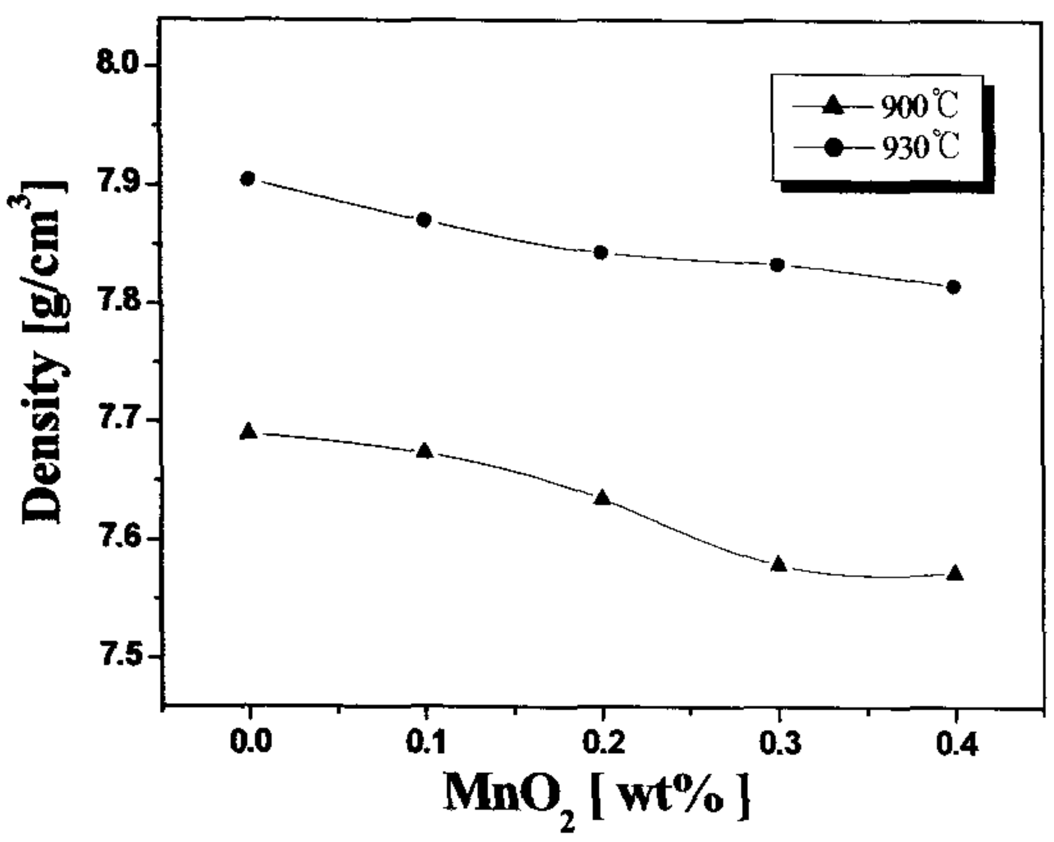


Fig. 3. Density according to the amount of MnO_2 addition.

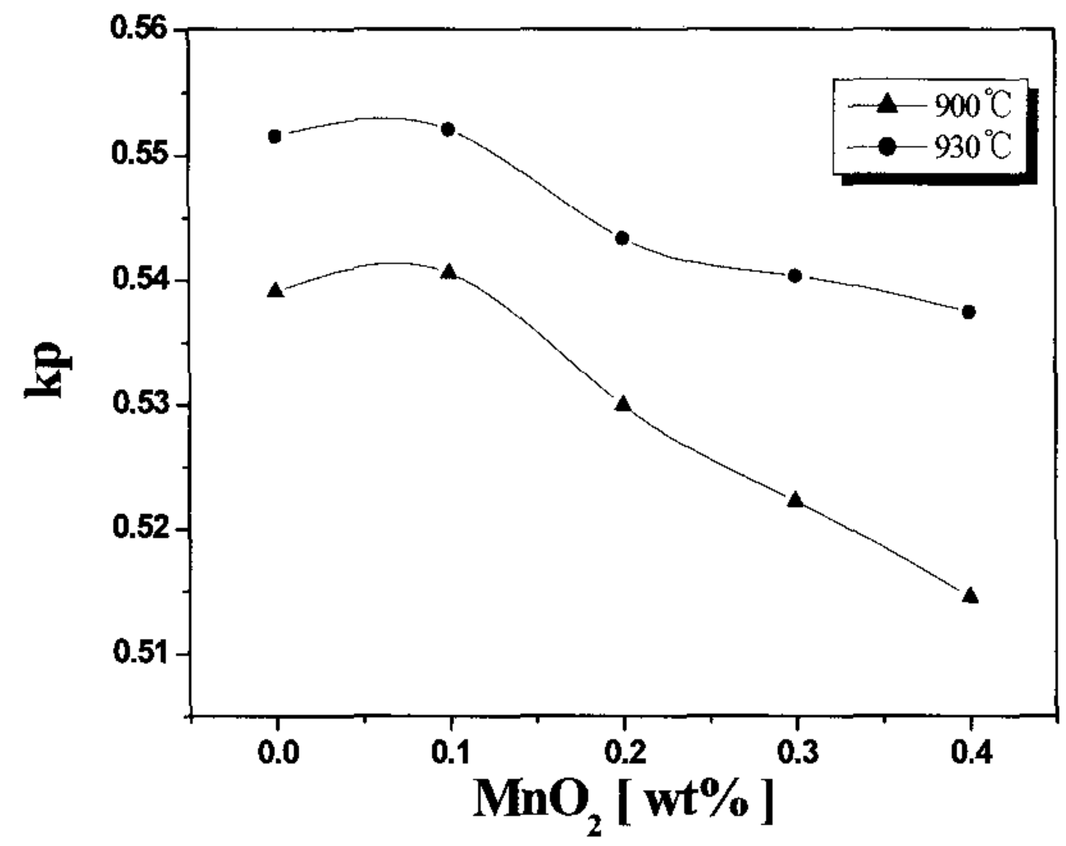


Fig. 4. Electromechanical coupling factor (kp) according to the amount of MnO_2 addition.

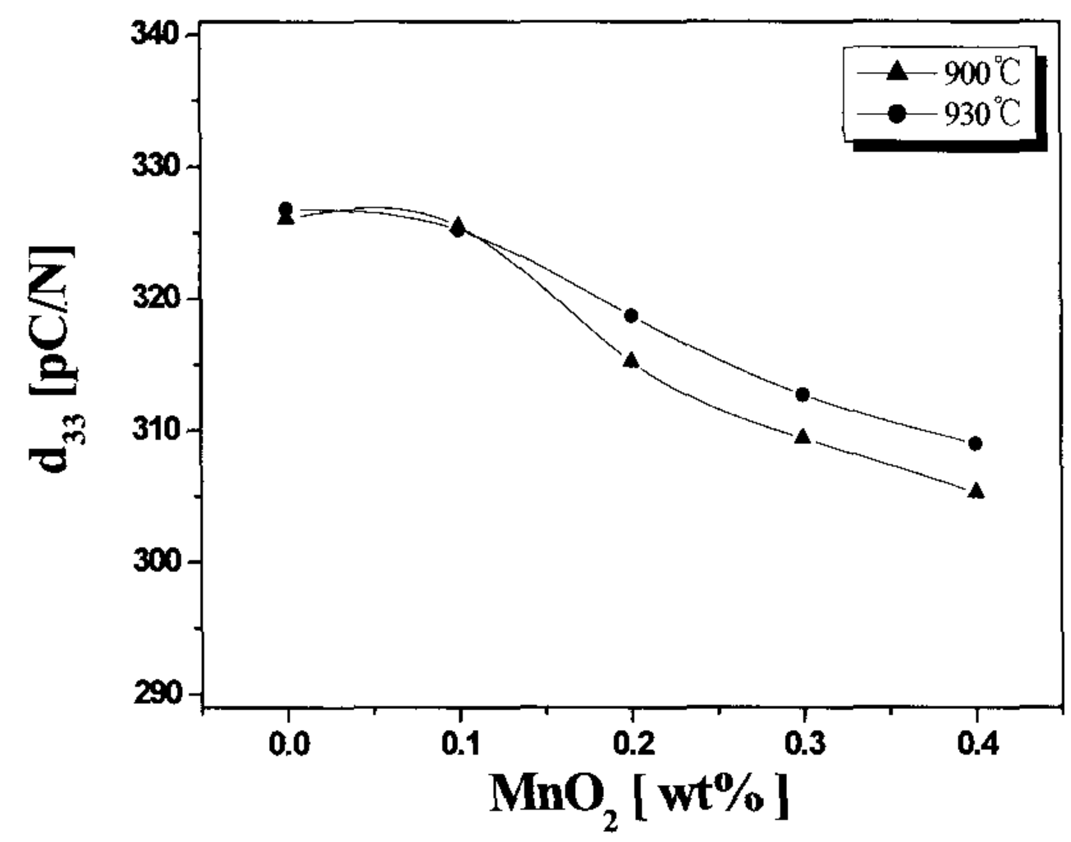


Fig. 5. Piezoelectric constant (d_{33}) according the amount of MnO_2 addition.

Figure 2 shows the X-ray diffraction pattern of specimens with the amount of MnO_2 addition at the sintering temperature of 930 °C. At the entire specimen, only peaks of tetragonal structure could be identified and no pyrochlore or other second phase was detected.

Figure 3 shows the density according to the sintering temperature and the amount of MnO_2 addition. All the specimens exhibited high density more than 7.80 g/cm^3, and the highest density of 7.90 g/cm^3 was shown in the no MnO_2 added specimen at sintering temperature of 930 °C. However, the density showed a tendency to be decreased with increasing amount of MnO_2 addition.

Figure 4 shows the electromechanical coupling factor (kp) according to the sintering temperature and the amount of MnO_2 addition. The kp of specimens sintered at 900 and 930 °C showed the maximum value of 0.540 and 0.552, respectively, at 0.1 wt% MnO_2 addition, and kp decreased in proportion to the amount of MnO_2 addition, and obtained the lowest value at 0.4 wt% MnO_2 doped ceramics. The decrease of kp ascribed to the dipole formation of the doping ions and lattice defect. That is, Mn^{4+} ion occupies the B-site of ABO_3 perovskite-structured piezoelectric ceramics and reduced to Mn^{2+} ion and Mn^{3+} ion during sintering, which leads to oxygen vacancies to keep electrical neutrality. The oxygen vacancies inhibited the domain wall mobility and subsequently decreased kp.

Figure 5 shows the piezoelectric constant (d_{33}) according to the sintering temperature and the amount of MnO_2 addition. The d_{33} of specimens sintered at 930 °C showed the maximum value of 327pC/N, in the no MnO_2 added specimen, and d_{33} decreased according to the increase of the amount of MnO_2 addition. It is known that the formed oxygen vacancies inhibited the movement of ferroelectric domain walls and resulted in the decrease of d_{33}.

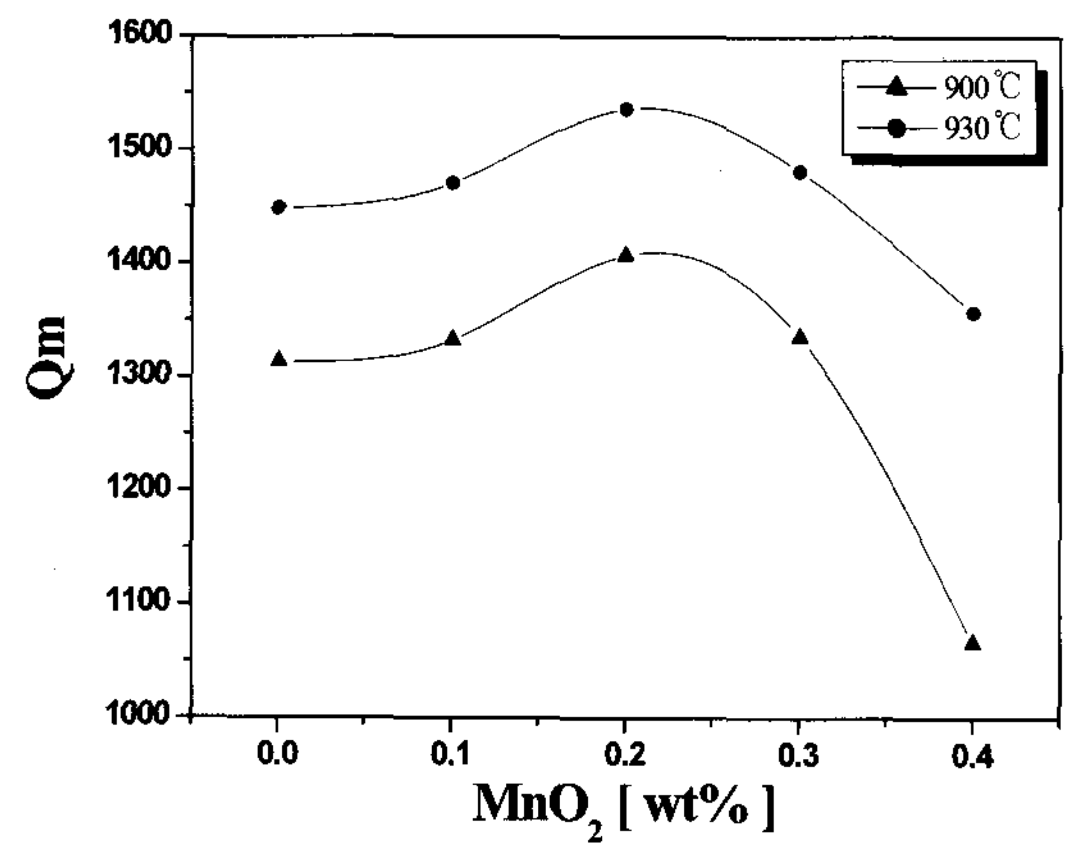


Fig. 6. Mechanical quality factor(Qm) according the amount of MnO_2 addition.

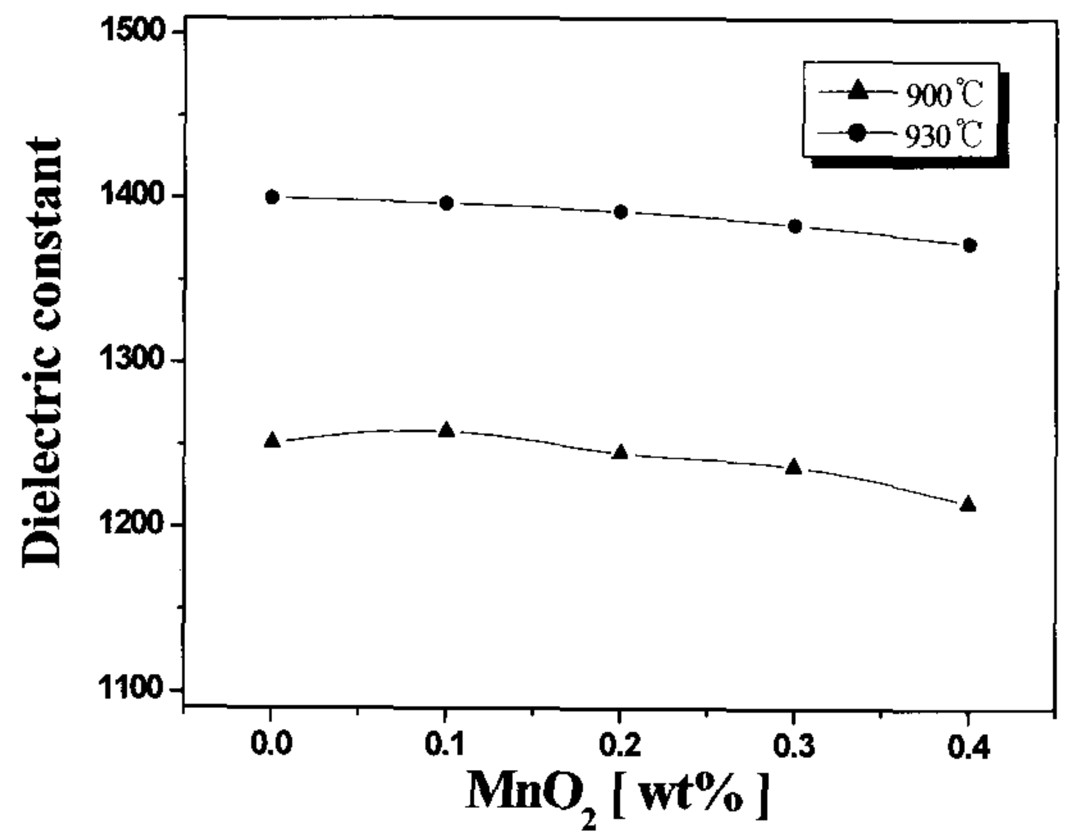


Fig. 7. Dielectric constant(ε_r) according to the amount of MnO_2 addition.

Figure 6 shows the mechanical quality factor (Qm) according to the sintering temperature and the amount of MnO_2 addition. Qm of specimens sintered at 930 °C showed the maximum values of 1,536, at 0.3 wt% MnO_2 addition. The increase of oxygen vacancy could be conjectured indirectly by the increase of Qm in 0.3 wt% MnO_2 doped ceramics. When the amount of MnO_2 is above 0.3 wt%, the excess MnO_2 will stay in the boundary and form a grain boundary layer, Qm decreased because of formed grain boundary layer.

Figure 7 shows the dielectric constant according to the sintering temperature and the amount of MnO_2 addition. The dielectric constant of specimens sintered at 930 °C showed the maximum value of 1,400, in the no MnO_2 added specimen, and dielectric constant decreased according to the increase of the amount of MnO_2 addition. The characteristics of dielectric constant showed the same trend as density. Table 1 shows physical characteristics of specimens summarized from experimental results according to the amount of MnO_2 addition.

Table 1. Physical characteristics of specimens according to the amount of MnO_2 addition.

Sintering temp. [℃]	MnO_2 [wt%]	Density [g/cm^3]	Dielectric constant	kp	Qm	d_{33} [pC/N]
900	0	7.69	1251	0.539	1313	326
	0.1	7.67	1258	0.540	1332	325
	0.2	7.63	1245	0.530	1406	315
	0.3	7.57	1237	0.522	1335	309
	0.4	7.57	1215	0.514	1066	305
930	0	7.90	1400	0.551	1448	327
	0.1	7.87	1397	0.552	1470	325
	0.2	7.84	1392	0.543	1536	318
	0.3	7.83	1384	0.540	1481	312
	0.4	7.81	1373	0.537	1357	308

4. CONCLUSION

In this study, in order to develop the low temperature sintering composition ceramics for low loss multilayer piezoelectric actuator application, PZW-PMN-PZT ceramics were manufactured according to the amount of MnO_2 addition and their piezoelectric characteristics were investigated.

The results obtained from the experiment are as follows:

1. All the specimens showed only peaks of tetragonal structure. And also, pyrochlore or other second phase did not detected.
2. The density of no MnO_2 added specimen and grain size of 0.3 wt% MnO_2 were 7.90 g/cm^3 and 3.08 μm, respectively.
3. At the 0.2 wt% MnO_2 added PZW-PMN-PZT ceramics sintered at 930 °C, density, electromechanical coupling factor k_p, dielectric constant ε_r, piezoelectric d_{33} constant and mechanical quality factor Q_m showed the optimum value of 7.84 g/cm^3, 0.543, 1,392, 318.7 pC/N, 1,536, respectively for multilayer ceramics actuator application.

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