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Piezoelectric properties of MnO_2 doped low temperature sintering $Pb(Mn_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–Pb $(Zr_{0.50}Ti_{0.50})O_3$ ceramics

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Abstract In this study, in order to develop the composition ceramics for low loss and low temperature sintering multilayer piezoelectric actuator, $Pb(Mn_{1/3}Nb_{2/3})O_3$–Pb $(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{0.50}Ti_{0.50})O_3$ (abbreviated as PMN-PNN-PZT) ceramics were fabricated using Li_2CO_3 and Na_2CO_3 as sintering aids, and their piezoelectric and dielectric characteristics were investigated according to the amount of MnO_2 addition. At the 0.2 wt% MnO_2 doped specimen sintered at 900 °C, density and mechanical quality factor (Q_m) showed the maximum values of 7.81 [g/cm^3]and 1186, respectively. And also, at 0.1 wt% MnO_2 doped specimen, electromechanical coupling factor (k_p), piezoelectric constant (d_{33}) of specimen showed the maximum values of 0.608 and 377[pC/N], respectively. Dielectric constant (ε_r) slightly decreased with increasing MnO_2. Taking into consideration the density of 7.81[g/cm^3], electromechanical coupling factor (k_p)of 0.597 the mechanical quality factor (Q_m) of 1,186, and piezoelectric constant (d_{33}) of 356[pC/N], it could be concluded that 0.2 wt% MnO_2 doped composition ceramics sintered at 900 °C was best for low loss and low temperature sintering multilayer piezoelectric actuator application.

Keywords Low loss multilayer piezoelectric actuator · Low temperature sintering · Mechanical quality factor · Electromechanical coupling factor

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1 Introduction

Piezoelectric actuators has been widely utilized for the applications as optical instrument, precision machine, miniature motor and mobile instrument because they have the merits such as high force per unit volume, rapid response velocity, precision position control and miniaturization [1, 2].

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. Therefore, multilayer structured piezoelectric actuators have been suggested to increase output displacements. 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.

In general, PZT system ceramics should be sintered at high temperatures between 1200 and 1300 °C in order to obtain complete densification. Accordingly, environmental pollution due to its PbO evaporation and the use of expansive Pd rich Ag/Pd internal electrode in case of manufacturing multilayer ceramic actuator are inevitable. Hence, to reduce its sintering temperature, various kinds of material processing methods such as hot pressing, high energy mill, liquid phase sintering, and using ultra fine powder have been performed. Among these methods, liquid phase sintering is basically an effective method for aiding densification at low temperature. The theoretical explanation for liquid phase sintering was already reported over 40 years ago [3].

Hence, in this study, in order to develop low loss and low temperature sintering composition ceramics for multilayer actuator application, PMN-PNN-PZT ceramics were fabricated using Li_2CO_3 and Na_2CO_3 as sintering aids [4, 5] and their piezoelectric and dielectric properties were investigated according to the amount of MnO_2 addition.

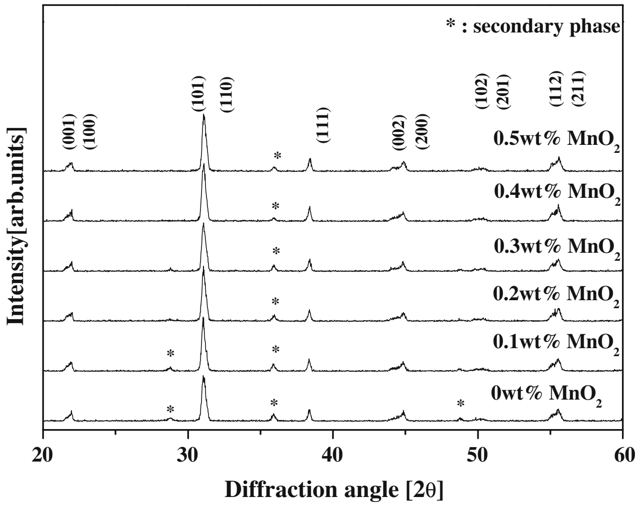

Fig. 1 X-ray diffraction pattern of specimens according to the amount of MnO_2 addition

2 Experimental

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

$$Pb\left(Mn_{1/3}Nb_{2/3}\right)_{0.02}\left(Ni_{1/3}Nb_{2/3}\right)_{0.12}\left(Zr_{0.50}Ti_{0.50}\right)_{0.86}O_3$$
$$+ X\text{wt\%}\,MnO_2$$
$$+ \text{sintering aids}\left(0.2\text{ wt\% }Na_2CO_3 + 0.2\text{ wt\% }Li_2CO_3\right).$$

$$(X = 0,\ 0.1,\ 0.2,\ 0.3,\ 0.4,\ 0.5).$$

The raw materials such as PbO, ZrO_2, TiO_2, MnO_2, Nb_2O_5 and NiO 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, Na_2CO_3 and Li_2CO_3 were added, ball-milled, and dried again. A polyvinyl alcohol (PVA: 5 wt% aqueous solution) 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 the samples were aged for 24 h prior to measuring the piezoelectric and dielectric properties. For investigating the dielectric properties, capacitance was measured at 1 kHz using an LCR meter (ANDO AG-4034) and dielectric constant (ε_r) 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 k_p and Q_m were calculated.

3 Results and discussion

Figure 1 shows X-ray diffraction pattern of specimens according to the amount of MnO_2 addition. All the specimens showed tetragonal structure and included secondary phase. With increasing the amount of MnO_2 addition, tetragonality (c/a) increased as shown in Table 1. This phenomenon can be illustrated as general hardener doping effect in the Pb(Zr,Ti)O_3 system ceramics. On the other hand, secondary phases were decreased, with increasing the amount of MnO_2 addition. It seemed that MnO_2 doping enhanced sinterability of $Pb(Mn_{1/3}Nb_{2/3})_{0.02}(Ni_{1/3}Nb_{2/3})_{0.12}(Zr_{0.50}Ti_{0.50})_{0.86}O_3$ system ceramics due to the increase of oxygen vacancies. That is, the oxygen vacancies promote lattice diffusion, thereby assisting the process of sintering and grain growth.

Figure 2 shows microstructure of fractured surface according to the amount of MnO_2 addition. The linear intercept method was used to measure the grain size. At 0.1 wt% MnO_2 doped specimen, grain size increased more or less up to 2.95 μm compared with 2.63 μm of non doped specimen. And the composition ceramics more than 0.1 wt % MnO_2 doping, it was nearly saturated. This result can be also explained by the improvement of sinterability.

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

Sintering temp. (°C)	MnO_2 addition (wt%)	Density (g/cm^3)	ε_r	k_p	Q_m	d_{33} (pC/N)	Tetragonality (c/a)	Curie temp. (°C)
900	0	7.807	1144	0.546	473	355	1.0089	355
	0.1	7.812	1010	0.608	980	377	1.0089	376
	0.2	7.816	920	0.597	1186	356	1.0098	371
	0.3	7.817	864	0.582	1032	320	1.0120	370
	0.4	7.815	810	0.570	980	300	1.0128	372
	0.5	7.815	788	0.564	776	293	1.0159	371

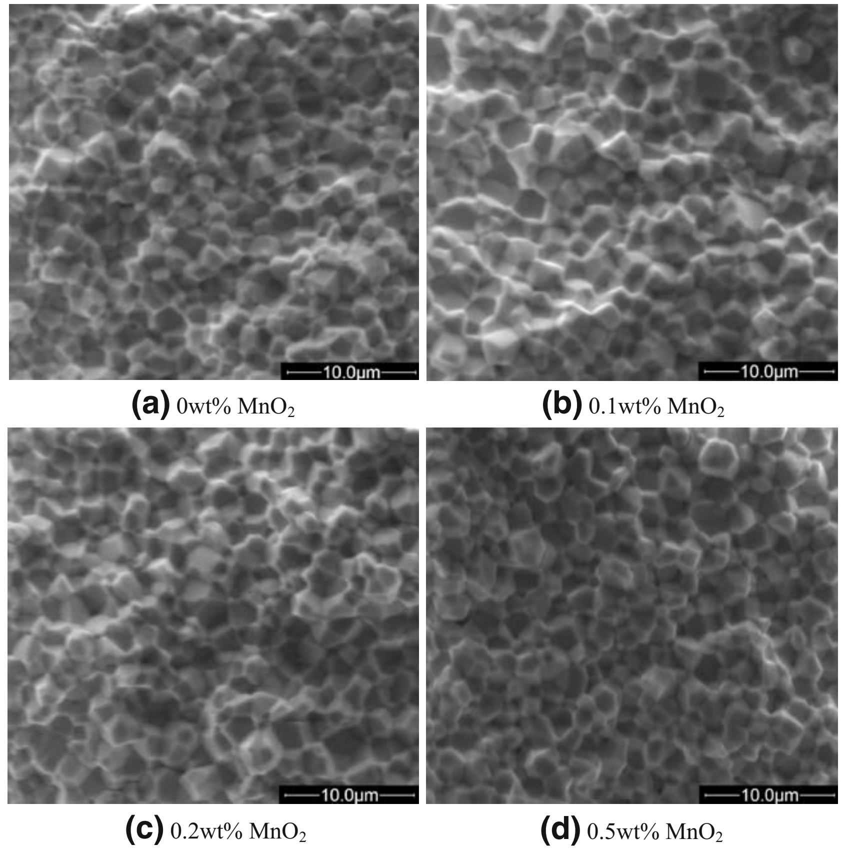

Fig. 2 (**a**)–(**d**) Microstructure of specimens according to the amount of MnO_2 addition

Figure 3 shows density of specimens according to the amount of MnO_2 addition. All the specimens were fully densified due to the liquid phase sintering. Eutectic temperature of Li_2CO_3 and Na_2CO_3 compound is about 514 °C. At the temperature, liquid phase is started and helps densification of specimens at low temperature. With increasing the amount of MnO_2 addition, density increased up to 0.3 wt% MnO_2 and then decreased. It is clear evidence that MnO_2 enhances sinterability of the composition.

Figure 4 shows dielectric constant (ε_r) of specimens according to the amount of MnO_2 addition. With increasing the amount of MnO_2 addition, ε_r linearly decreased because movement of domain is not feasible due to the hardener doping effect.

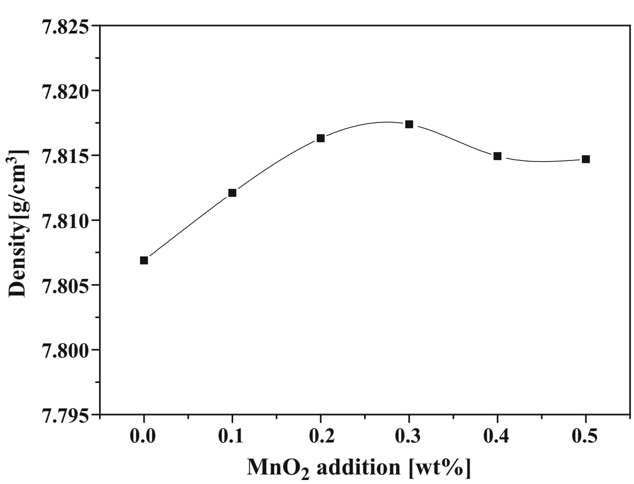

Fig. 3 Density of specimens according to the amount of MnO_2 addition

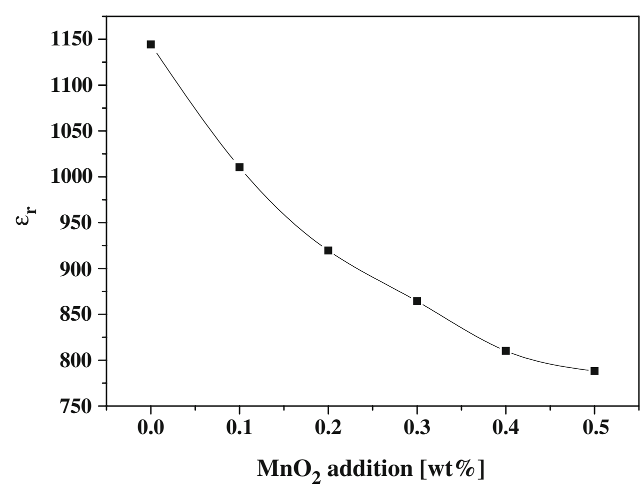

Fig. 4 Dielectric constant(ε_r)of specimens according to the amount of MnO_2 addition

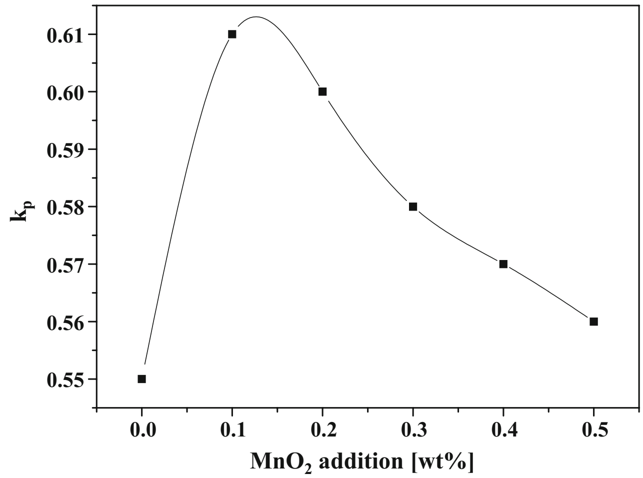

Fig. 5 Electromechanical coupling factor (k_p) of specimens according to the amount of MnO_2 addition

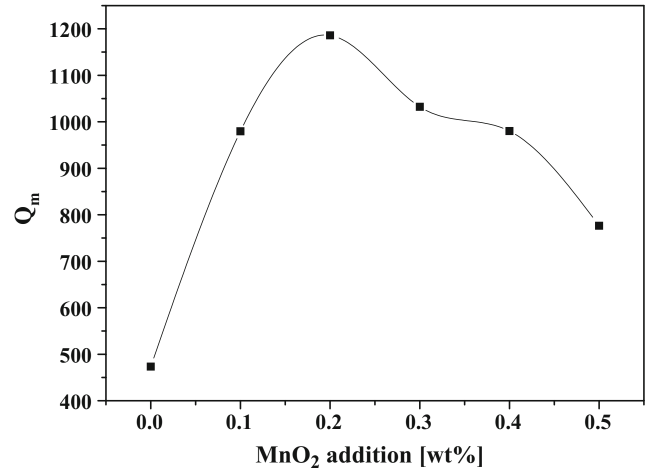

Fig. 7 Mechanical quality factor (Q_m) of specimens according to the amount of MnO_2 addition

Figure 5 shows k_p of specimens according to the amount of MnO_2 addition. The maximum value of k_p was 0.608 at 0.1 wt% MnO_2 doped specimen. Above 0.1 wt% MnO_2 doped specimen, k_p decreased. These results can be also explained by the increase of sinterability and hardener doping effect. First, the increase of k_p was due to the increasing of sinterability, thereafter, k_p deceased due to the hardener doping effect. And also, until now, it is well known that a little manganese ion can remarkably improve Q_m, k_p and tanδ of PZT system [6, 7]. In this study, the experimental results generally correspond with the above explanation.

Figure 6 shows piezoelectric d_{33} constant of specimens according to the amount of MnO_2 addition. The variation of d_{33} also coincided with the trend of k_p, and a maximum value of it shows 377[pC/N] at 0.1 wt% MnO_2 added specimen.

Figure 7 shows Q_m of specimens according to the amount of MnO_2 addition. With increasing the amount of MnO_2 addition, Q_m increased at 0.2 wt% MnO_2 added specimen and then decreased. This result can be explained by the fact that oxygen vacancies are created due to the accepter doping effect. That is, it is well-known that manganese mainly coexists in the Mn^{2+} and Mn^{3+} states in PZT systems, which enter into lattice structure in order to substitute Ti^{4+} and Zr^{4+} ion, thus the unbalance of valence led to the creation of oxygen vacancies. The oxygen vacancies cause the increase of Q_m. The maximum value of Q_m showed 1,186 at 0.2 wt% MnO_2 added specimen.

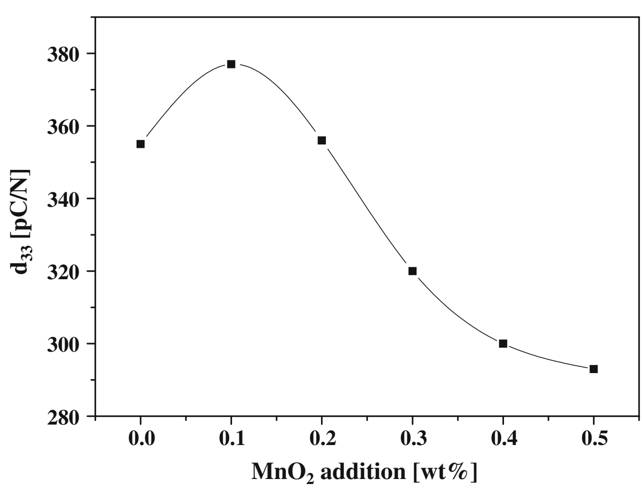

Fig. 6 Piezoelectric constant (d_{33}) of specimens according to the amount of MnO_2 addition

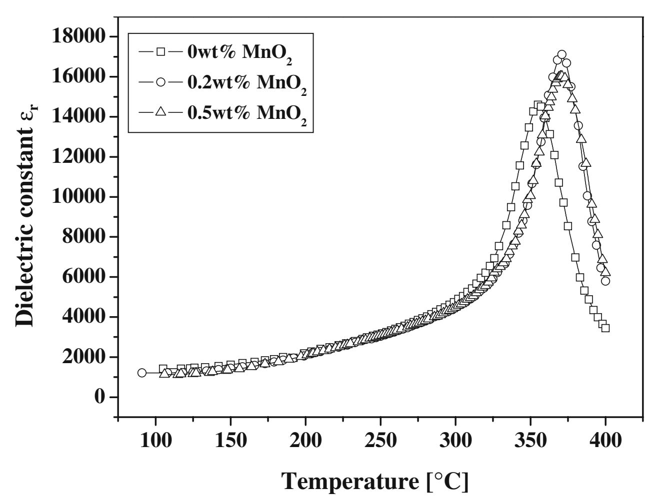

Fig. 8 Temperature dependence of dielectric constant of specimen according to the amount of MnO_2 addition

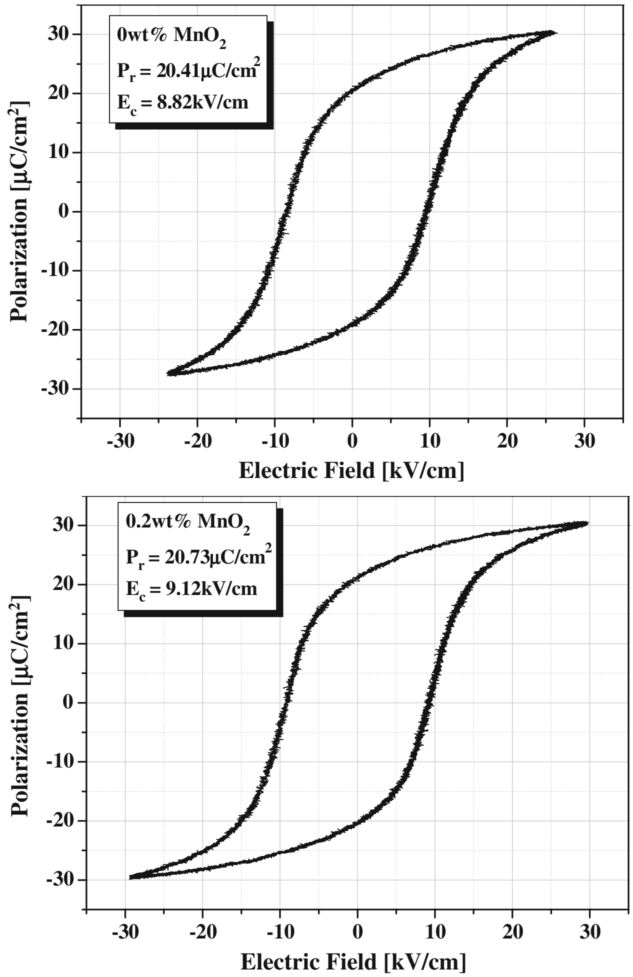

Fig. 9 Hysteresis curves of non doped and 0.2 wt% MnO_2 doped specimens

Figure 8 shows temperature dependence of dielectric constant of the MnO_2 doped specimen. Curie temperature increased up to 0.1 wt% MnO_2. And the composition ceramics more than 0.1 wt% MnO_2 addition, it was nearly saturated as about 370–372 °C.

Figure 9 shows hysteresis curve of non doped and 0.2 wt % MnO_2 doped specimen, respectively. Remanent polarization(Pr) and coercive field(Ec) of 0.2 wt% MnO_2 added specimen showed higher values than those of non doped one more or less. Above results could be also explained by the facts that Pr and Ec were simultaneously increased by virtue of the enhancement of sinterability and hardener doping effect due to MnO_2 doping.

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

4 Conclusions

In this study, in order to develop low loss and low temperature sintering composition ceramics for multilayer actuator application, PMN-PNN-PZT ceramics were fabricated using Li_2CO_3 and Na_2CO_3 as sintering aids and their piezoelectric and dielectric properties were investigated according to the amount of MnO_2 addition. The results obtained from the experiment are as follow:

1. All the specimens were densified at sintering temperature of 900 °C by sintering aids and MnO_2 addition enhanced sinterability of specimens. With increasing the amount of MnO_2 addition, dielectric constant (ε_r) rapidly decreased.
2. At 0.1 wt% MnO_2 added specimen, k_p and d_{33} showed the maximum value of 0.608 and 377[pC/N], respectively
3. At 0.2 wt% MnO_2 added specimen, Q_m showed the maximum value of 1186.

At 0.2 wt% MnO_2 added specimen, density, ε_r, k_p, Q_m and d_{33} showed optimum value of 7.816[g/cm^3], 920, 0.597, 1186 and 356[p/CN], respectively for low loss and low temperature sintering multilayer piezoelectric actuator application.

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