Piezoelectric and Dielectric Properties of Low Temperature Sintered $Pb(Mn_{1/3}Nb_{2/3})_{0.02}(Ni_{1/3}Nb_{2/3})_{0.12}(Zr_xTi_{1-x})_{0.86}O_3$ System Ceramics

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In this study, in order to develop compositions of ceramics suitable for piezoelectric actuator and ultrasonic vibrator applications using low temperature sintering, multilayer, PMN-PNN-PZT ceramics were fabricated using Li_2CO_3 and Na_2CO_3 as sintering aids. Their structural, piezoelectric and dielectric characteristics were investigated according to the Zr/Ti ratio. As the Zr/Ti ratio increased, the electromechanical coupling factor k_p and piezoelectric constant d_{33} and the mechanical quality factor Q_m all increased with Zr/Ti ratio and then decreased after the ratio exceeded 50/50. At the ratio of Zr/Ti =49/51 and sintering temperature of 900℃; the density, electromechanical coupling factor k_p, dielectric constant ε_r, piezoelectric d_{33} constant and mechanical quality factor Q_m all showed the optimum values of 7.900 g/cm^3, 0.576, 856, 312 pC/N, 1,326, respectively. These property values are very suitable for multilayer ceramics actuator applications.

Keywords: Multilayer piezoelectric actuator, Sintering aids, Electromechanical coupling factor(k_p), Mechanical quality factor(Q_m)

1. INTRODUCTION

In general, $Pb(ZrTi)O_3$ system ceramics should be sintered at high temperatures i.e. more than 1200℃ in order to obtain complete densification[1]. Accordingly, because of their high sintering temperature, environmental pollution due to the evaporation of PbO and the use of expansive Pd rich Ag/Pd internal electrodes in the case of the manufacture of multilayer ceramic actuators are indispensable[2]. Also, the loss of PbO and the resultant variation in composition greatly affect the piezoelectric characteristics of the specimens. Therefore, it is necessary to adjust the vapor phase equilibrium of PbO between the ceramic to be sintered and the powder atmosphere in which the ceramics is embedded. On the other hand, in order to reduce the sintering temperature at which satisfactory densification could be obtained, various kinds of material processing methods such as the 2-stage calcination method, hot pressing, high energy mill, liquid phase sintering, and the use of ultra fine powder have been performed. Among these methods, liquid phase sintering is basically an effective method for aiding densification of specimens at low sintering temperatures. The calcination process is also important for aiding densification. The MPB (Morphotrophic Phase Boundary) region of PZT ceramics systems showed excellent piezoelectric and dielectric characteristics due to the ease of domain motion and polarizability[3]. It has been reported that compositions near MPB of the PMN–PZT, PNN–PZT and PMN-PNN-PZT systems demonstrated excellent piezoelectric properties for actuator and sensor applications[1,2,4,5]. Nevertheless, these piezoelectric properties significantly weaken when the composition component of them moves away from the MPB. Also, the MPB region in the PZT system can be significantly changed by alteration of the component ratios and by added impurities.

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Hence, in this study, from these viewpoints, ceramic samples of compositions in the MPB region showed high electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) values suitable for multilayer actuator applications $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ (abbreviated as PMN-PNN-PZT) ceramics were fabricated using 2-stage calcination method and Li_2CO_3, Na_2CO_3 and ZnO as sintering aids and their piezoelectric and dielectric properties were investigated according to the ratio of Zr/Ti and sintering temperature.

2. EXPERIMENTS

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

$Pb(Mn_{1/3}Nb_{2/3})_{0.02}(Ni_{1/3}Nb_{2/3})_{0.12}(Zr_xTi_{1-x})_{0.86}O_3 + MnO_2 + Fe_2O_3 + CuO +$ Sintering aids (Li_2CO_3, Na_2CO_3 and ZnO) (x = 0.48, 0.49, 0.50, 0.51, 0.52)

The raw materials, ZrO_2, TiO_2, MnO_2, NiO, Fe_2O_3, 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 1,100℃ for 4 h. Thereafter, PbO was added and ball-milled again. After drying, they were calcined at 750℃ for 2 h. Thereafter, and sintering aids such as Li_2CO_3, Na_2CO_3 and ZnO were added and ball-milled again. A polyvinyl alcohol (PVA: 5 wt% aqueous solution) was added to the dried powders. The powders were molded at a pressure of 1,000 kg/cm^2 in a mold which had a diameter of 21mm, burned out at 600℃ for 3 h, and then sintered at 870, 900 and 930℃ for 2 h. For the measurement of piezoelectric characteristics, the specimens were polished to 1 mm thickness and then electrodeposited with Ag paste. Poling was carried out at 120℃ 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 measurement of the piezoelectric and dielectric properties.For the investigation of dielectric properties, the capacitance was measured at 1 kHz

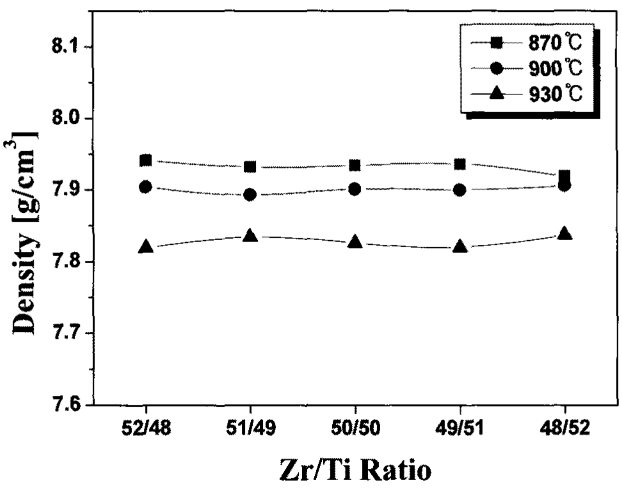

Fig. 1. Density of specimens as a function of the Zr/Ti ratio and sintering temperature.

using an LCR meter (ANDO AG-4034) and εr was calculated. For investigation of piezoelectric properties, the resonant and anti-resonant frequencies were measured by an Impedance Analyzer (Agilent 4294A) according to the IEEE standard and then the kp and Qm were calculated.

3. RESULTS AND DISCUSSION

Figure 1 shows density of specimens as a function of the Zr/Ti ratio and sintering temperature. The variation of density did not show significant change as a function of Zr/Ti ratio. Furthermore, all the composition ceramics could be sintered even the sintering temperature of 870℃ by a 2-stage calcination method and the addition of sintering aids. However, entire specimens sintered at 930℃ showed low density values due to the over-firing effect.

Figure 2 shows the microstructure of specimens as a function of the Zr/Ti ratio at the sintering temperature of 900℃. The grain size also did not show a large change.

Figure 3 shows X-ray diffraction patterns of specimens as a function of the Zr/Ti ratio at a sintering temperature of 900℃. The entire specimen showed a perovskite structure including a secondary phase. With increasing Zr/Ti ratio, the lattice structure was changed from a tetragonal to rhombohedral form. As can be seen from the (002) and (200) peaks of the X-ray diffraction patterns, it is evident that the crystal structure of the specimens changes from a tetragonal phase to rhombohedral phase, and the MPB appeared at the vicinity of the ratio of Zr/Ti =50/50.

Figure 4 shows the k_p of specimens as a function of the Zr/Ti ratio and sintering temperature. k_p rapidly increased rapidly up to the ratio of Zr/Ti =50/50, and thereafter decreased. This behavior can be confirmed by the fact that k_p and Q_m generally show a maximum value and a minimum value at MPB due to the various poling directions and easy domain wall motion, respectively[3]. At a sintering temperature of 900℃, k_p showed a maximum value of 0.598.

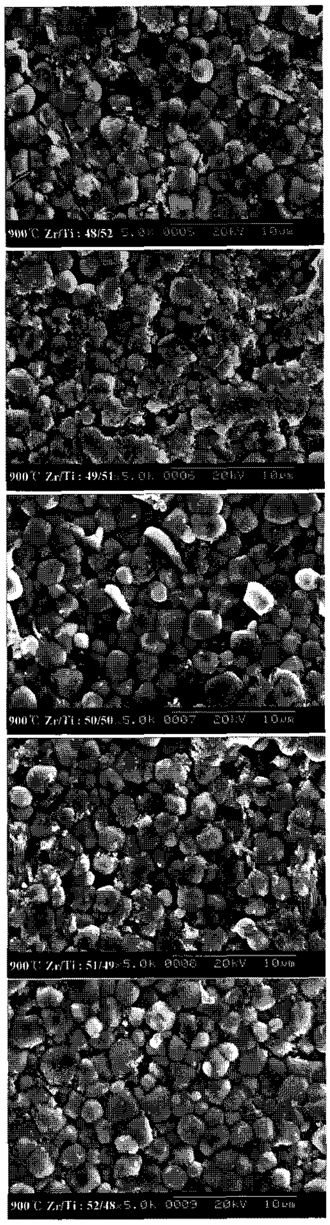

Fig. 2. Microstructure of specimens as a function of the Zr/Ti ratio.

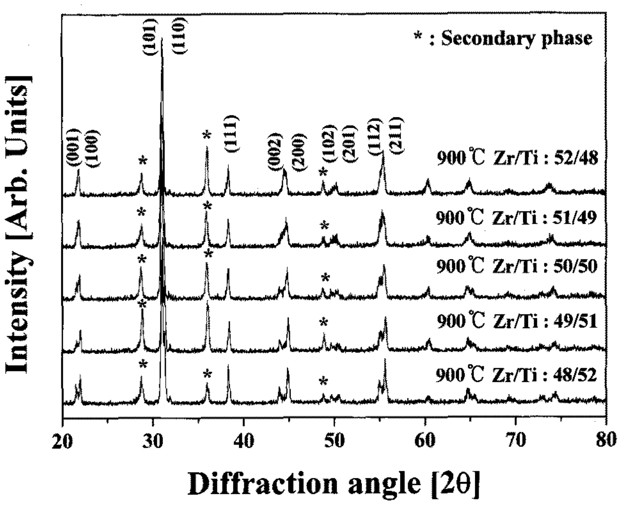

Fig. 3. X-ray diffraction pattern of specimens as a function of the Zr/Ti ratio.

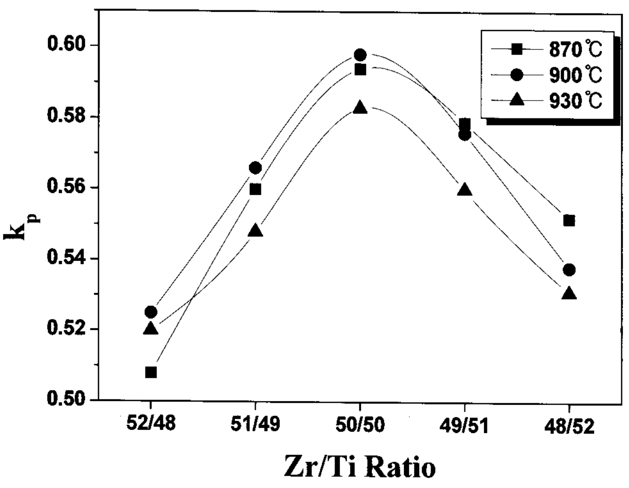

Fig. 4. k_p of specimens as a function of the Zr/Ti ratio and sintering temperature.

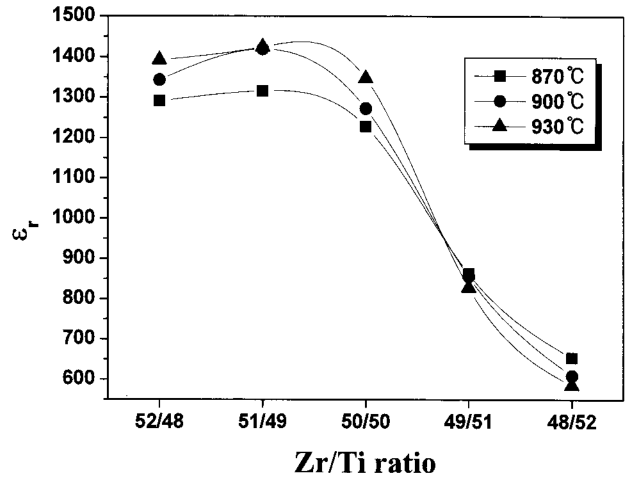

Fig. 6. ε_r of specimens as a function of the Zr/Ti ratio and sintering temperature.

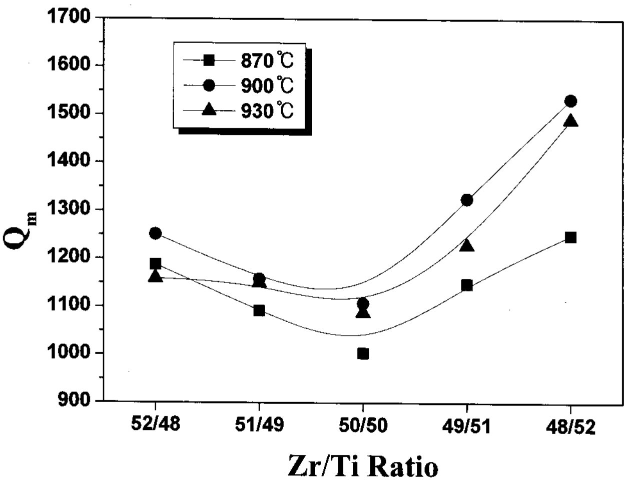

Fig. 5. Q_m of specimens as a function of the Zr/Ti ratio and sintering temperature.

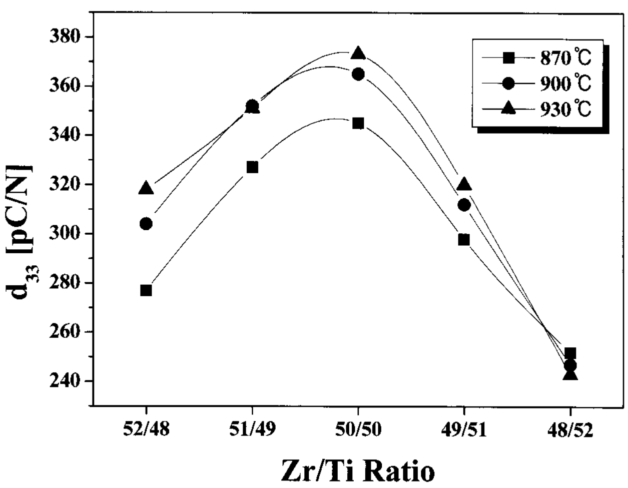

Fig. 7. d_{33} of specimens as a function of the Zr/Ti ratio and sintering temperature.

Figure 5 shows the Q_m of specimens as a function of the Zr/Ti ratio and sintering temperature. The variation of Q_m showed the opposite properties to k_p, and a minimum value of Q_m appeared at the ratio of Zr/Ti =50/50. This result can also can be explained by the piezoelectric characteristics in the MPB region as explained in the above k_p analysis.

Figure 6 and 7 show ε_r and d_{33} for the specimens as a function of the Zr/Ti ratio and sintering temperature, respectively. The variations of ε_r and also d_{33} coincided with the trend of k_p. These results can be illustrated by the fact that the coexistence of the tetragonal and rhombohedral phases in the MPB region readily aids the polarizability and domain rotation of the specimens.

Table 1. Physical characteristics of the specimens.

Sintering Temp. [℃]	Zr/Ti Ratio	Density [g/cm^3]	ε_r	k_p	Q_m	d_{33} [pC/N]	Grain Size [μm]	Tetragonality [c/a]
	52/48	7.941	1291	0.508	1188	277		
	51/49	7.932	1316	0.560	1092	327		
870	50/50	7.934	1229	0.594	1004	345		
	49/51	7.936	863	0.579	1149	298		
	48/52	7.919	654	0.552	1250	252		
	52/48	7.904	1343	0.525	1251	304	2.253	1.0234
	51/49	7.893	1419	0.566	1158	352	2.289	1.0224
900	50/50	7.901	1273	0.598	1108	365	2.230	1.0186
	49/51	7.900	856	0.576	1326	312	2.551	1.0017
	48/52	7.906	609	0.538	1534	247	2.348	1.0000
	52/48	7.819	1392	0.520	1159	318		
	51/49	7.834	1424	0.548	1150	351		
930	50/50	7.826	1347	0.583	1088	373		
	49/51	7.820	828	0.560	1228	320		
	48/52	7.837	585	0.531	1491	243		

4. CONCLUSIONS

In this study, in order to develop low loss and low temperature sintered ceramics for multilayer actuator application, $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ ceramics were fabricated using a 2-stage calcination method. In addition Li_2CO_3, Na_2CO_3 and ZnO were used as sintering aids and their piezoelectric and dielectric properties were investigated according to the ratio of Zr/Ti and sintering temperature.

1. All the specimens showed a satisfactorily high density at all temperatures due to the use of the 2-stage calcination method and other sintering aids.
2. All the specimens displayed a perovskite structure including a secondary phase.
3. As the Zr/Ti ratio decreased, the crystalline structure was changed from a rhombohedral to tetragonal phase.
4. At the ratio of Zr/Ti =49/51 and sintering temperature of 900°C, the density, electromechanical coupling factor k_p, dielectric constant ε_r, piezoelectric d_{33} constant and mechanical quality factor Q_m all showed the optimum value of 7.900 g/cm^3, 0.576, 856, 312 pC/N, 1326, respectively, very suitable for the intended multilayer ceramics actuator applications.

In comparison with previous work, the density and mechanical quality factor of the specimens are enhanced. However the electromechanical coupling factor and dielectric properties of the specimens were adversely influenced by the MPB region effect[6].

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