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Piezoelectric Properties of 0.2[Pb($Mg_{1/3}Nb_{2/3}$)]-0.8[$PbTiO_3$-$PbZrO_3$] Ceramics Sintered at a Low Temperature with the Aid of Li_2O

BYUNG MOON JIN[1,*], ILL WON KIM,[2] JIN SOO KIM,[2] DAE SU LEE,[2] CHANG WON AHN,[2] JEONG HO KWON,[3] JAE SHIN LEE,[3] JAE SUNG SONG,[4] & SOON JONG JEONG[4]

[1]*Department of Physics, Dong Eui University, Busan, Korea*
[2]*Department of Physics, University of Ulsan, Ulsan, Korea*
[3]*School of Materials Science and Engineering, University of Ulsan, Ulsan, Korea*
[4]*Electric & Magnetic Devices Group, KERI, Korea*

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Abstract. The dielectric and piezoelectric properties of 0.2Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.8Pb($Zr_{0.475}Ti_{0.525}$)O_3 (abbr. as PMNZT) ceramics were measured. Extremely low sintering temperatures of 950°C using liquid-phase sintering aid of Li_2O is achieved which was very useful for multi-layered applications. X-ray study shows the splitting of rhombohedral (200) in pure PMNZT to (002) and (200) peaks in Li_2O doped samples. 10 times higher dielectric constant was achieved in Li_2O doped samples to compare to pure ones although the Curie temperature ($T_c = 322$°C) of Li_2O doped PMNZT ceramics was not changed. The value of k_p and k_{33} increased up to 0.1 wt% of Li_2O and saturating thereafter.

Keywords: PMN-PZT, dielectric & piezoelectric, low sintering temperature

1. Introduction

Lead-containing perovskite is known to have excellent piezoelectric properties. $PbMg_{1/3}Nb_{2/3}$-$PbTiO_3$-$PbZrO_3$ (PMN-PZT) ceramic is an attractive material for many applications, such as multi-layered ceramic actuator, ultrasonic motors and piezoelectric transformers. To make a multi-layered actuator for controlling a generating frequency, it is very important to reduce the sintering temperature given the relatively low melting point of the electrodes inter-electrodes. A number of studies have reported efforts to reduce the sintering temperature to fit this requirement although the matrix materials are not the same [1–5]. Among them, a few reports are very interesting.

He et al. [6] reported that PZT ceramics modified with multiple substitutions, that is, Cr_2O_3 doped $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ ceramics have been fabricated at 1200–1320°C and exhibited excellent piezoelectricity with an electromechanical coupling factor, k_p, of 68%. The sintering temperature about 1200°C is too high for multi-layered ceramic actuator application although this material can improve the piezoelectric properties a lot. At such a high temperature, Ag-rich inner electrodes cannot be used, because Ag diffusion from Ag/Pd inner electrodes deteriorated the reliability of piezoelectric properties. To solve this problem, low temperature sintering is necessary.

Low sintering temperature has been attempted using various methods: (a) sol-gel method [7], (b) hot-pressing in oxygen [8, 9], (c) fine powders prepared by chemical routes [10, 11], (d) by adding low-melting substances [12, 13].

In this paper, the results of dielectric and piezoelectric properties of 0.2Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.8Pb($Zr_{0.475}Ti_{0.525}$)O_3 (abbr. as PMNZT) ceramics that were fabricated at low sintering temperatures of 950°C using sintering aid of Li_2O are presented.

*To whom all correspondence should be addressed. E-mail: bmjin@dongeui.ac.kr

2. Experimental Procedure

The 0.2 PMN-0.8PZT: x wt% of Li_2O ceramics were prepared by a two-step method. In first step, MgO, Nb_2O_5, ZrO_2 and TiO_2 powders were properly weighed and ball milled with zirconia balls for 24 h. The mixed powders were dried and calcined at 1000°C for 4 h to form a columbite phase $MgNb_2O_6$. In the second step, the appropriate amounts of PbO were weighed and mixed with calcined powders by ball milling for 24 h. After drying, it was calcined at 850°C for 2 h. Li_2O was added as liquid-phase sintering aid. They were pressed into disk shape of 18 mm in diameter at 100 MPa. The specimens were sintered at 800–1200°C for 2 h in a covered alumina crucible. To prevent PbO evaporation from the pellets, a powder of $PbZrO_3$ was used as the bedding powder. The sintered pellets were polished into 1 mm in thickness. Silver paint was pasted on both sides of the samples and fired at 700°C for 30 min. Before measuring the piezoelectric properties, the samples were poled in silicon oil bath at 120°C by applying a DC electric field of 3 kV/mm.

The bulk densities of sintered ceramics were determined by the Archimedes method. The dielectric constant for as-sintered samples was measured in a broad region of temperatures at 1 kHz (HP 4192 Impedance Analyzer USA). A longitudinal vibration mode was measured using rectangular sample of $1.3 \times 1.3 \times 4$ mm. And a radial vibration mode was measured using radial sample of $13d \times 0.8t$ mm. The electromechanical coupling (k_p, k_{33}) and mechanical quality factor (Q_m) were calculated by using the resonance-antiresonance method. The piezoelectric coefficient (d_{33}) was measured by Berlincourt Piezo d_{33}-meter (CPDT 3300, Channel Products, OH 44022). The microstructure was analyzed using a scanning electron microscope (SEM).

3. Results and Discussions

Figure 1 shows the shrinkage of PMNZT ceramic with Li_2O (0, 0.05, 0.1, 0.2 and 0.3 wt%) additive as a function of sintering temperatures. The PMNZT ceramics without sintering aid is well characterized above 1150°C. With the help of Li_2O, on the other hand, shrinkage was saturated up to 850°C and the sintering temperature also reduced more than 200°C.

The reason that we had focused on the sample that was sintered at 950°C is as follows: among the PMNZT ceramics with Li_2O additive sintered at several temperatures, the density of that sample is highest and electromechanical coupling factor is saturated at that temperature.

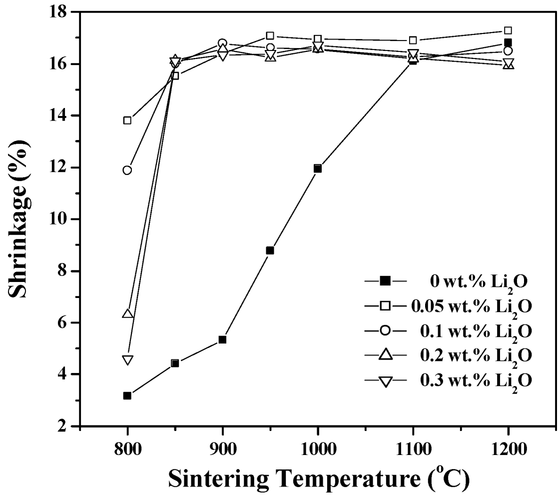

Fig. 1. Shrinkage of PMNZT ceramics with Li_2O (0, 0.05, 0.1, 0.2 and 0.3 wt%) additives as a function of sintering temperatures.

Figure 2 shows the SEM micrographs of PMNZT ceramics with Li_2O (0, 0.05, 0.1, 0.2 and 0.3 wt%) additives sintered at 950°C. Grains are well developed with the help of Li_2O additions. Grains were increased up to 3 microns in 0.1 wt% Li_2O added PMNZT.

Figure 3 shows the XRD patterns of PMNZT with the Li_2O additives sintered at 950°C. All peaks belong to the perovskite structure. The secondary phase was not observed. Pure PMNZT has rhombohedral (200) peak. The splitting of (002) and (200) peaks indicates ferroelectric tetragonal phase.

Figure 4 shows the dielectric constants of PMNZT ceramics sintered at 950°C as a function of temperature. The dielectric constant of Li_2O added PMNZT ceramics were much higher than that of pure ones. This abrupt increase can be explained by the increase of grain sizes as shown in Fig. 2. If the grain size increases then the cavities that can dissipate the energy will be reduced and therefore the capacitance would be increased. The room temperature dielectric constant was increased with increasing Li_2O up to 0.1 wt% and thereafter decreased. The Curie temperature ($T_c = 322$°C) of Li_2O added PMNZT ceramics were not changed.

Figure 5 shows planar electromechanical coupling, k_p and longitudinal electromechanical coupling factor, k_{33} of PMNZT ceramic sintered at 950°C with different

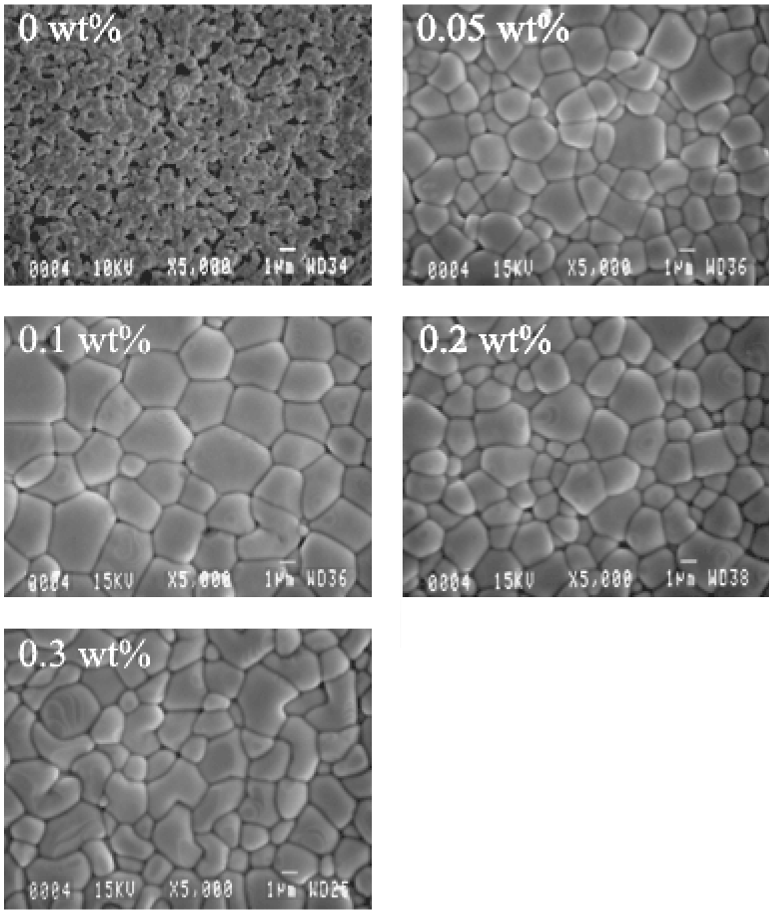

Fig. 2. SEM micrographs of PMNZT ceramics with Li_2O (0, 0.05, 0.1, 0.2 and 0.3 wt%) additives sintered at 950°C.

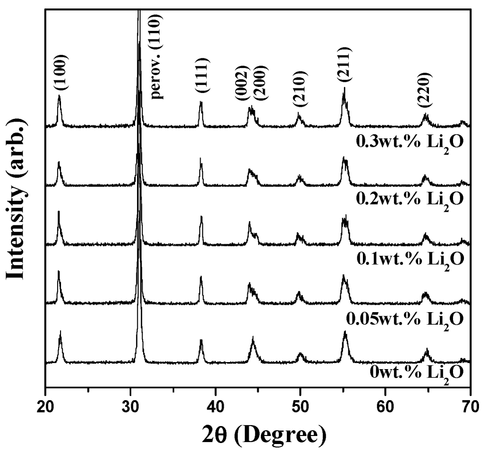

Fig. 3. XRD patterns of PMNZT with Li_2O additives sintered at 950°C.

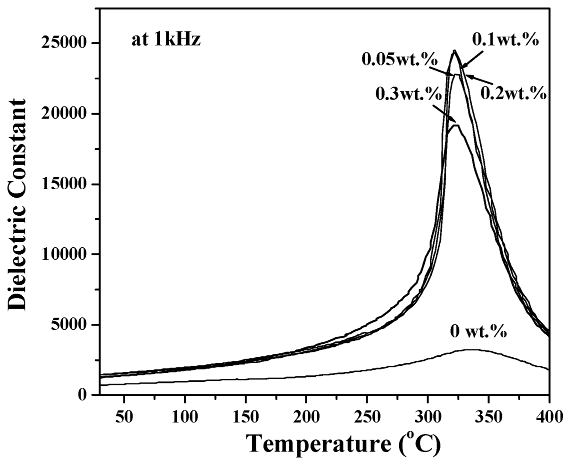

Fig. 4. Dielectric constant of PMNZT with Li_2O additives sintered at 950°C.

Table 1. Dielectric and piezoelectric properties of PMNZT with Li_2O additives sintered at 950°C.

Li_2O (wt.%)	ρ (g/cm^3)	T_c (°C)	ε_r	$\tan\delta$	P_r (μC/cm^2)	k_p (%)	k_{33} (%)	d_{33} (pC/N)	Q_m
0	7.52	336	716	0.038	0.8	19.94	27.75	170	66.15
0.05	7.83	322	1431	0.021	26.26	41.34	70.29	477	67.70
0.1	7.84	322	1448	0.022	27.16	63.70	77.92	565	77.02
0.2	7.80	322	1307	0.024	27.16	53.70	76.64	486	86.29
0.3	7.78	322	1264	0.029	26.26	51.83	68.71	374	87.69

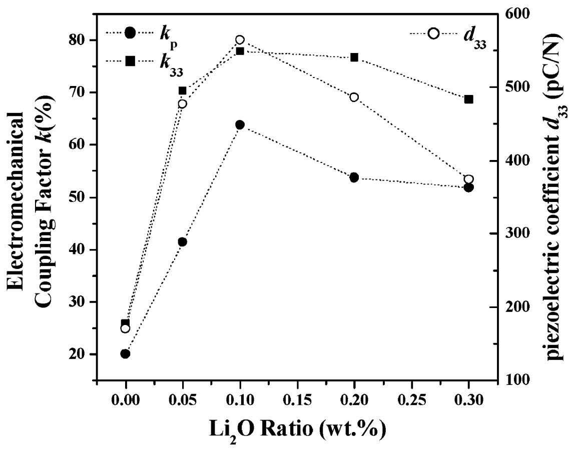

Fig. 5. Electromechanical coupling factor (k_p, k_{33}) and piezoelectric coefficient (d_{33}) of PMNZT with Li_2O additives sintered at 950°C.

Li_2O ratio. The values of k_p and k_{33} increased with an increase of Li_2O below 0.1 wt%. However, the values of k_p and k_{33} tended to decrease slightly over 0.1 wt%. It was found that k_p depends on the material parameters such as grain size, porosity, and chemical composition [14]. According to the concepts of grain size in domain wall motion, the k_p increase with increasing grain size.

4. Conclusions

Low sintering temperature, piezoelectric and dielectric properties of 0.2PMN-0.8PZT ceramics with Li_2O added were investigated. The sintering temperature for sufficient densification was reduced from 1200 to 950°C. For the sample with 0.1 wt% Li_2O addition sintered at 950°C, the dielectric constant, electromechanical coupling factor (k_p, k_{33}) and piezoelectric coefficient (d_{33}) were 1448, 63.7%, 77.9% and 565pC/N, respectively. It was confirmed that 0.1 wt% Li_2O added ceramic sintered at 950°C is the most suitable material for multi-layer ceramic actuator applications.

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