

# Piezoelectric and dielectric properties of low temperature sintering $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$ ceramics with variation of sintering time

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**Abstract**  $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$  (abbreviated as PMN–PZN–PZT) ceramics containing  $\text{Li}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{CuO}$  as sintering aids were fabricated using two-stage calcinations method in order to develop low temperature sintering ceramics for multilayer piezoelectric actuators. Their dielectric and piezoelectric properties were investigated according to the variation of sintering time. All the specimens sintered at  $930^\circ\text{C}$  for 60–150 min showed tetragonal phases without secondary phases. Electromechanical coupling factor ( $k_p$ ), dielectric constant ( $\epsilon_r$ ) and piezoelectric constant ( $d_{33}$ ) increased with the increase of the sintering time. The mechanical quality factor ( $Q_m$ ) exhibited maximum of 1,815 with the increase of sintering time for 120 min and then slightly decreased. At the sintering temperature of  $930^\circ\text{C}$  and the sintering time of 120 min, the optimal values such as the density of  $7.69\text{ g/cm}^3$ ,  $k_p$  of 0.516,  $\epsilon_r$  of 1158,  $Q_m$  of 1815, and  $d_{33}$  of 287 pC/N were found for multilayer piezoelectric actuators.

**Keywords** Two-stage calcination · Sintering aids · Sintering time · Multilayer piezoelectric actuators

## 1 Introduction

Lead zirconate titanate (PZT) ceramics are widely used for high power devices such as piezoelectric transformers and ultrasonic motors because of their superior piezoelectric properties [1]. In general, PZT ceramics are created at high sintering temperature over  $1200^\circ\text{C}$ , which leads evaporation of  $\text{PbO}$  during sintering process, resulting in environmental pollution and variation of ceramic composition. Furthermore, multilayer or stacking structures for piezoelectric actuators and piezoelectric transformers are used to obtain increased displacement, increased output power, and lower driving voltage. Multilayer piezoelectric ceramics include expensive internal electrodes with high melting points such as Palladium alloy or Platinum. Silver electrode is an economical material capable of being effectively used as internal electrodes of multilayer ceramic devices [2]. However, the cofiring technique is not allowed due to its low melting point of below  $960^\circ\text{C}$ . Low temperature sintering has been, therefore, suggested as less than  $950^\circ\text{C}$  to achieve both benefits including use of the inexpensive internal electrode and fabrication of multilayer device. In other words, various manufacturing techniques such as hot pressing, high energy milling, liquid phase sintering, and use of ultra fine powders can be applied to lower the sintering temperature. Among these methods, liquid phase sintering is one of promising technique to assist densification of ceramics at low temperature of below  $950^\circ\text{C}$  [3]. In addition to liquid phase sintering, a modified calcining process including two-stage calcination can help the

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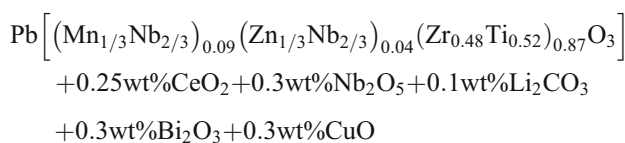
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densification of ceramics to reduce the shrinkage ratio of ceramic bodies during sintering. It was found that the two stage calcination improves homogeneity of ceramic composition and gets rid of secondary phases by applying sufficient thermal energy to the reactions between PbO, ZrO<sub>2</sub>, and TiO<sub>2</sub>. [4, 5]

In this study, in order to develop low temperature sintering ceramics for multilayered actuator applications, PMN–PZN–PZT ceramics were fabricated using two-stage calcination method according to the variation of sintering time. And also, sintering aids such as Li<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and CuO were doped to lower the sintering temperature and their piezoelectric and dielectric properties were investigated [6–8].

## 2 Experimental

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



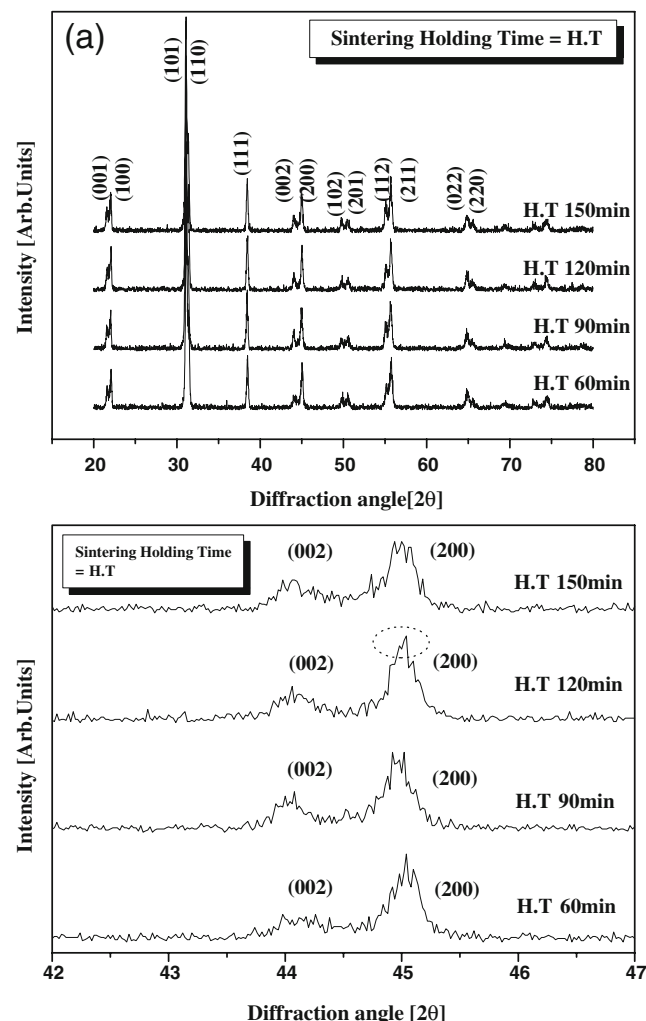
The PMN–PZT ceramics generally exhibit good piezoelectric properties but the sintering temperature approaches to 1100°C. To lower the sintering temperature, PZN solid solution was added to PMN–PZT ceramics. This composition was successfully applied for the piezoelectric transformer in the previous report [9]. The raw materials such as ZrO<sub>2</sub>, TiO<sub>2</sub>, MnO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> for the given composition were weighted by mole ratio and the powders were ball-milled for 24 h. After drying, they were first calcined at 1100°C for 4 h. Thereafter, PbO was added and ball-milled again. After drying, they were second calcined at 750°C for 2 h. Thereafter, the sintering aids of Li<sub>2</sub>CO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and CuO were added and ball-milled again. A polyvinyl alcohol (PVA: 5 wt% aqueous solution) was added to the dried powders. The powders were molded under the pressure of 1,000 kg/cm<sup>2</sup> in a mold which has a diameter of 21 mm, burned out at 600°C for 3 h, and then sintered at 930°C for 60–150 min. For measuring the piezoelectric characteristics, the specimens were polished to 1 mm thickness and then electroded 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  $\epsilon_r$  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 the  $Q_m$  were calculated.

## 3 Results and discussion

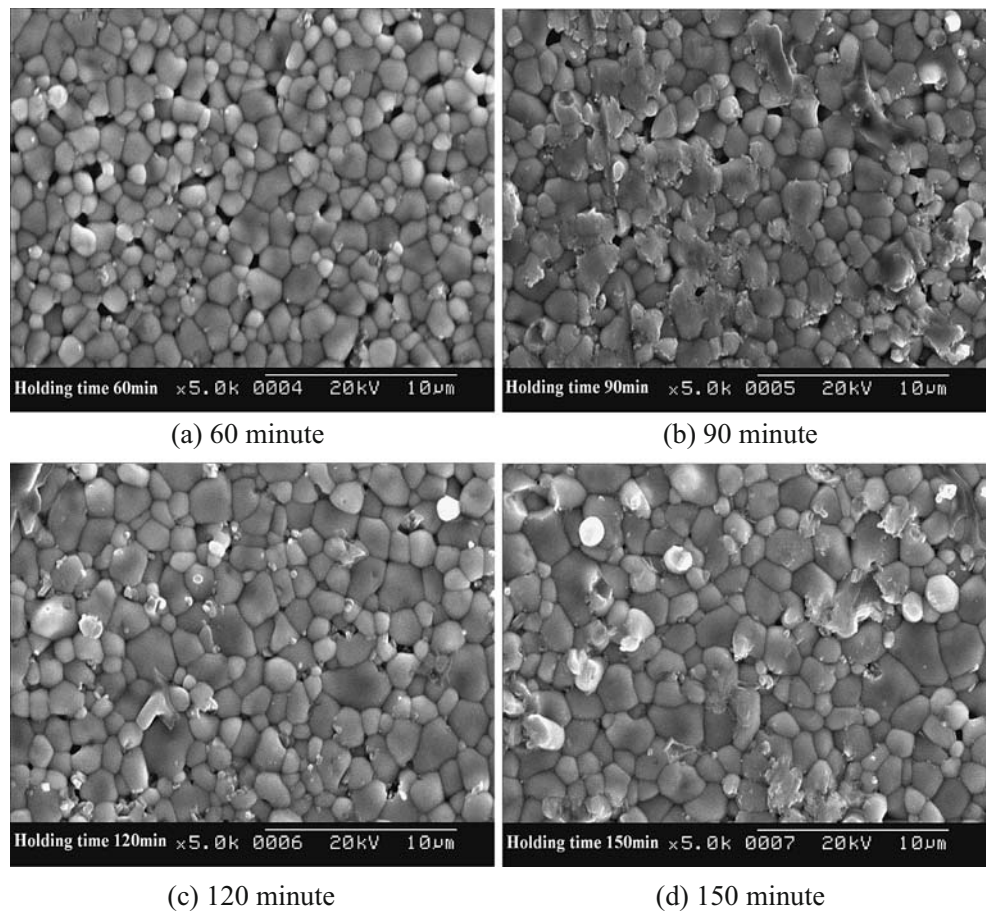
Figure 1(a) shows X-ray diffraction patterns (XRD) of the PMN–PZN–PZT powders with the variation of sintering time. All the specimens showed tetragonal structures without secondary phase. The tetragonality was calculated using the peak split between (002) and (200) planes as shown in Fig. 1(b). With increasing the sintering time, tetragonality was slightly increased. It seemed that the densification was still promoted with the increased sintering time, corresponded to the result appeared in Fig. 4.

Figure 2 shows microstructures of the specimens as a function of sintering time. The grain size of specimens

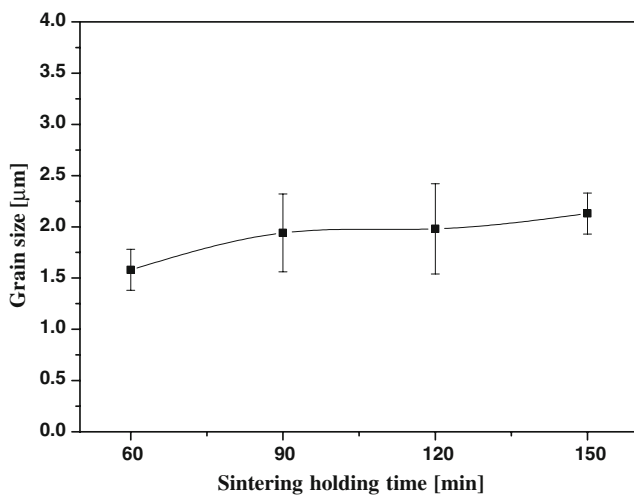


**Fig. 1** X-ray diffraction patterns of PMN–PZN–PZT powders as a function of sintering time; (a) full scale and (b) extended angle

**Fig. 2** Microstructures of the fractured surface of the specimens as a function of sintering time

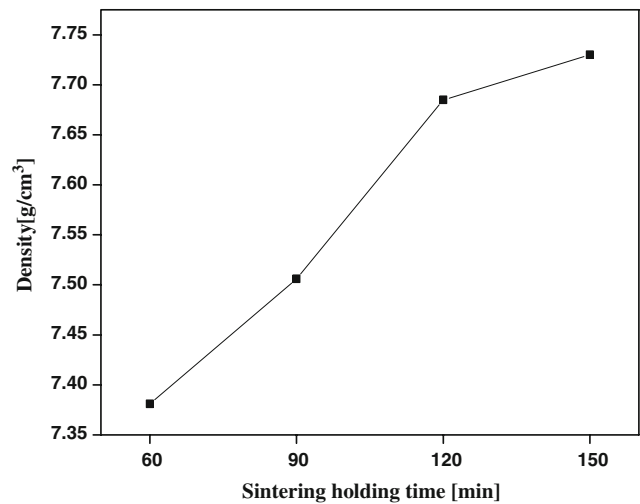


increased with increase of sintering time and showed maximum value of 2.13  $\mu\text{m}$  at the sintering time of 150 min. The grain size was rapidly grown with the increased sintering time as a result of liquid phase sintering effect. And also, two-stage calcination might affect the grain growth. The variation of grain size measured from the microstructure as a function of sintering time is presented in Fig. 3.

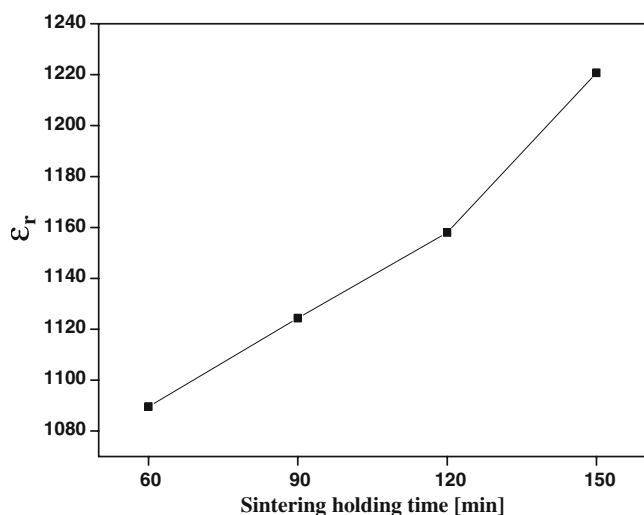


**Fig. 3** Variation of grain size as a function of sintering time

Figure 4 shows density of the specimens as a function of sintering time. The density of specimens rapidly increased with the increase of sintering time. The density of specimens showed the maximum value of 7.73  $\text{g}/\text{cm}^3$  at the sintering time of 150 min. It can be illustrated by the fact that the increase of sintering time helps the densification of ceramics.



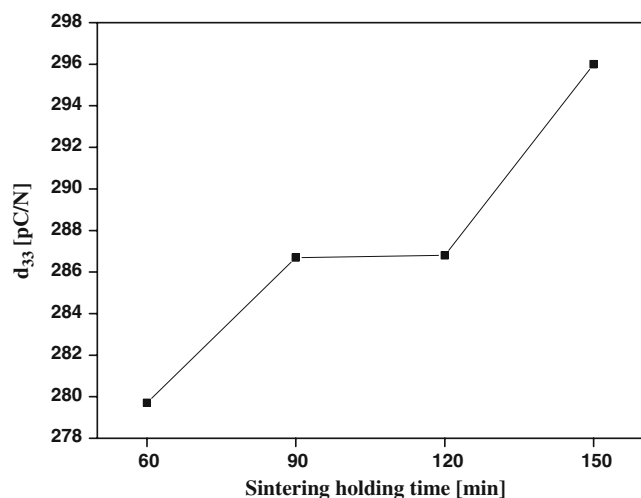
**Fig. 4** Variation of density as a function of sintering time



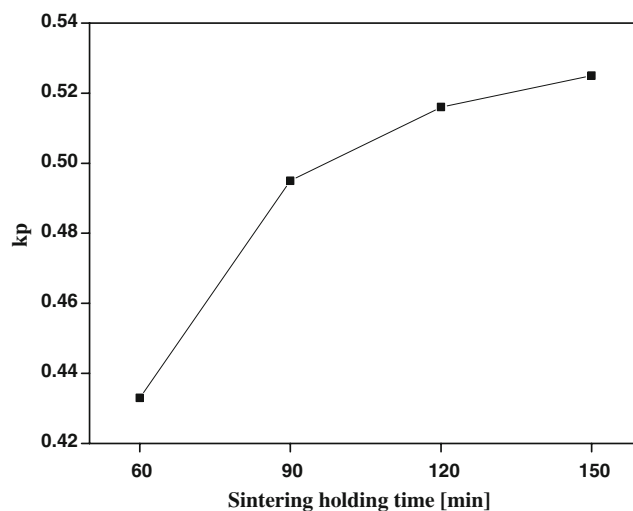
**Fig. 5** Dielectric constant of the specimens as a function of sintering time

Figures 5 and 6 show  $\epsilon_r$  and  $d_{33}$  of the specimens as a function of sintering time. The increases of  $\epsilon_r$  and  $d_{33}$  are the results of the increase in the grain size with the increase of sintering time. At the sintering time of 150 min, the  $\epsilon_r$  and  $d_{33}$  show the maximum values of 1,221 and 296 pC/N, respectively. It can be explained by the facts that the increase of the grain size contributed the enhanced movement of domain wall.

Figures 7 and 8 shows  $k_p$  and  $Q_m$  of the specimens as a function of sintering time. With the increase of sintering time, the  $k_p$  exhibited substantially increased values up to 0.525 at the sintering time of 150 min, corresponding to the results in the variation of grain size and density. Although the  $Q_m$  gradually increased to 1,815 until the sintering time reached 120 min, it tended to decrease in over the sintering



**Fig. 6** Piezoelectric constant of the specimens as a function of sintering time

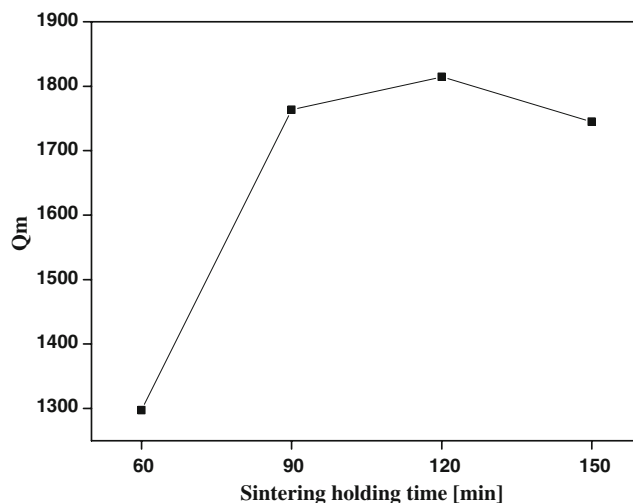


**Fig. 7** Electromechanical coupling factor of the specimens as a function of sintering time.

time of 120 min. Despite of the improvement of sinterability at the initial stage of sintering resulted in the increase of  $Q_m$ , the continuous grain growth brought the decrease of  $Q_m$  due to the feasibility of domain switching in the grain of ceramics. The summarized values including morphological and electrical properties of PMN–PZN–PZT ceramic were presented in Table 1.

#### 4 Conclusions

PMN–PZN–PZT ceramics doped with sintering aids such as  $\text{Li}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{CuO}$  were manufactured using two-stage calcinations in order to develop low temperature sintering for multilayer actuator applications, and subsequently structural,



**Fig. 8** Mechanical quality factor of the specimens as a function of sintering time

**Table 1** Physical characteristics of the specimens with variation of sintering time.

Sintering temp. [°C]	Sintering holding time [min]	Density [g/cm <sup>3</sup> ]	$\epsilon_r$	kp	Qm	$d_{33}$ [pC/N]	Grain size [ $\mu\text{m}$ ]	Tetragonality (c/a)
930	60	7.39	1,090	0.433	1,297	280	1.58	1.0167
	90	7.51	1,124	0.495	1,763	287	1.94	1.0180
	120	7.69	1,158	0.516	1,815	287	1.98	1.0210
	150	7.73	1,221	0.525	1,745	296	2.13	1.0198

dielectric and piezoelectric properties were investigated as a function of sintering time. The results obtained from the experiment are as follow:

1. All the specimens sintered at 930°C over 60 min showed tetragonal structure without secondary phase.
2. All the parameters such as density, grain size, relative permittivity, piezoelectric constant, and electromechanical coupling factor increased with the increase of sintering time since the increase of sintering time at lower sintering temperature compared to that of conventional piezoelectric ceramics resulted in the improvement of sinterability.
3. At the sintering holding time of 120 min, density, kp, Qm,  $\epsilon_r$  and  $d_{33}$  of the specimens showed the optimum values of 7.69 g/cm<sup>3</sup>, 0.516, 1,815, 1,158 and 287 pC/N, respectively, applicable to low temperature sintering multilayer piezoelectric actuator applications.

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