TRANSACTIONS ON ELECTRICAL AND ELECTRONIC MATERIALS
Vol. 18, No. 6, pp. 334-337, December, 2017

Regular Paper

pISSN: 1229-7607 eISSN: 2092-7592
DOI: https://doi.org/10.4313/TEEM.2017.18.6.334
OAK Central: http://central.oak.go.kr

Physical Properties of PNN-PMN-PZT Doped with Zinc Oxide and CLBO for Ultrasonic Transducer

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Received July 13, 2017; Revised September 1, 2017; Accepted September 6, 2017

In this paper, to develop the ceramics with high d_{33} and high Q_m for ultrasonic transducer applications, 0.10 $Pb(Ni_{1/3}Nb_{2/3})O_3$-0.07 $Pb(Mn_{1/3}Nb_{2/3})O_3$ -0.83 $Pb(Zr_{0.5}Ti_{0.5})_{0.83}O_3$ (PNN-PMN-PZT) ceramics were sintered at 940℃ using CuO-Li_2CO_3-Bi_2O_3 (CLBO) as a sintering aid by a traditional solid-state technique. The influence of zinc oxide additive on the physical properties of the prepared ceramics were systematically investigated. The R-T (rhombohedral-tetragonal) phase coexistence was found in the ceramics without zinc oxide additive and with increasing amounts of ZnO additive, the specimens showed a tetragonal phase. The formation of a liquid phase between ZnO and Bi_2O_3 contributed significantly to the grain growth of specimens. For the 0.1 wt% ZnO ceramics, the optimal physical properties of d_{33}= 370 pC/N, ε_r= 1,344, k_p= 0.621, and Q_m= 1,523 were obtained.

Keywords : Ultrasonic transducer, Sintering aids, Piezoelectric constant (d_{33}), Mmechanical quality factor (Q_m)

1. INTRODUCTION

Ultrasonic waves are widely used in washing machines, surgery, welding machines, sensors, and medical instruments. Low-frequency (20~50 kHz) ultrasonic waves are used in ultrasonic washing and welding machines that require high output power, and high-frequency (1 MHz or more) ultrasonic waves are generally used for medical devices and sensors that require extreme precision. The effect of ultrasound on body tissues can largely be classified as either a thermal or mechanical effect. It is possible to accelerate metabolism through ultrasound mainly by minute temperature rise of cells and to perform mechanical micro-massage through high frequency vibration. Medical ultrasonic surgery is also possible due to the cavitation effect of ultrasonic waves, and devices for this purpose have been developed by a few advanced companies with commercial success. The US market for medical ultrasound cutting machines for laparoscopic surgery is worth $1.2 billion. Based on capital strength and brand power, multinational corporations such as Johnson & Johnson and Covidien have dominated the market for medical ultrasonic surgery devices mounted with piezoelectric transducers. Therefore, the development of similar

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devices by more regional entities is urgent. $Pb(Zr,Ti)O_3$ ceramics have been extensively utilized in transducers, actuators, filters, and medical devices for ultrasonic surgery, as well as piezoelectric transformers owing to their advantageous piezoelectric properties [1-3]. However, although(PZT)eramics are widely used in the field of electronic ceramics, environmental pollution from PbO, which rapidly volatilizes around 1,000℃, and deterioration of piezoelectric properties due to changes in ceramic composition are problematic [4-7].

One of the methods for decreasing the sintering temperature and improving the electrical characteristics of ceramic materials is to include various additives in the preparation process [6]. In this study, to develop ceramics with high d_{33} and Q_m for increasing field induced displacement and decreasing temperature increase when operated at high power, 0.10 $Pb(Ni_{1/3}Nb_{2/3})O_3$-0.07 $Pb(Mn_{1/3}Nb_{2/3})O_3$-0.83 $Pb(Zr_{0.5}Ti_{0.5})_{0.83}O_3$ ceramics were used and CuO-Li_2CO_3-Bi_2O_3 (CLBO) selected as a sintering aid. Zinc oxide was used as an additive to induce the formation of a liquid phase with Bi_2O_3. The physical characteristics of the resulting ceramics were then investigated as a function of ZnO addition.

2. EXPERIMENTAL

In this study, the compositions of the ceramics were generally as follows:

0.10 $Pb(Ni_{1/3}Nb_{2/3})O_3$-0.07 $Pb(Mn_{1/3}Nb_{2/3})O_3$-0.83 $Pb(Zr_{0.5}Ti_{0.5})_{0.83}O_3$ + x wt% ZnO+sintering aids (CuO-Li_2CO_3-Bi_2O_3) (x = 0, 0.1, 0.2, 0.3, 0.4)

The raw materials of MnO_2(High Purity, 0.99%), ZrO_2(Junsei, 0.99%), PbO(Junsei, 0.995%), TiO_2(Hayashi, 0.99%), NiO(Sigma, 0.99%), ZnO(Kanto, 0.99%), and Nb_2O_5(Junsei, 0.999%) were weighed with a small amount of Nb_2O_5 additive and then were ball-milled for 24 h. After drying, the mixture was calcined at 850℃ for 2 h. Thereafter, CuO-Li_2CO_3-Bi_2O_3 (CLBO) as a sintering aid was added and ball-milled again. A 5 wt% polyvinyl alcohol solution was added to the calcined powders. The calcined powders were molded with a pressure of 1 ton/cm^2 using a mold with a diameter of 17 mm and then sintered at 940℃ for 2 h. To measure the physical characteristics of the samples, they were polished to a thickness of 1 mm and poling was performed at 120℃ under a 30 kV/cm electric field. The capacitance (C) was measured by a LCR(Inductance Capacitance Resistance) meter (Ando, AG-4304) for the investigation of the dielectric properties of the materials and the dielectric constants (ε_r) were precisely calculated. The fr(resonant frequency) and fa(anti-resonant frequency) were measured by an impedance analyzer (Agilent 4294A) to measure the piezoelectric properties of the materials and then the Q_m and k_p were calculated. The piezoelectric d_{33} coefficient was also measured by the APC-90-2030 d_{33} meter.

3. RESULTS AND DISCUSSION

The XRD patterns of the samples as a function of ZnO addition is shown in Fig. 1(a). Typical perovskite structures were observed in all samples. Fig. 1(b) shows the enlarged XRD pattern of the specimens. The manufactured specimens show strong peaks corresponding to the (002) and (200) phases. With increasing ZnO addition, crystal structure was changed from a rhombohedral–tetragonal coexistence phase (MPB) to a tetragonal phase. That is, the tetragonality (c/a) increased with values of 1.0129, 1.0154, 1.0163, and 1.01544 for the 0, 0.1, 0.2, and 0.3 wt% ZnO preparations, respectively. Tetragonality (c/a) decreased to 1.0128 for 0.4 wt% ZnO sample. This decrease is likely due to the fact that ZnO can partially act as an acceptor dopant and can form a liquid phase with other additives in lead zirconate titanate ceramics. With the occasional substitution of Zn^{2+} ions in Nb^{5+}, Zr^{4+}, and Ti^{4+} ion sites, the sinterability of the samples is enhance d due to the generation of oxygen vacancies and formation of a liquid phase between ZnO, Bi_2O_3 (eutectic melting point of 750℃), and CLBO.

Figure 2 shows microstructures of the samples with various additions of ZnO. With increasing ZnO content, the grain size increased to values of ~4.21, ~4.76, ~4.78, ~4.60 and ~5.52 μm for the 0, 0.1, 0.2, 0.3, and 0.4 wt% ZnO samples, respectively. The generation of oxygen vacancies and the formation of a liquid phase between ZnO and Bi_2O_3 causes the increase in grain size.

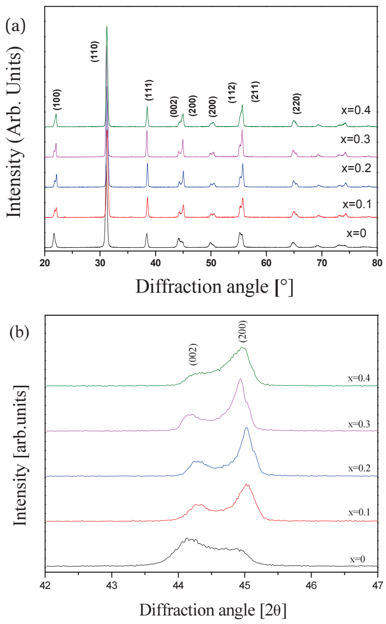

Fig. 1. (a) X-ray diffraction patterns of the PNN-PMN-PZT ceramics with ZnO addition in the 2θ range 20~80° and (b) enlarged X-ray diffraction patterns of the PNN-PMN-PZT ceramics with ZnO addition in the 2θ range 42~47°.

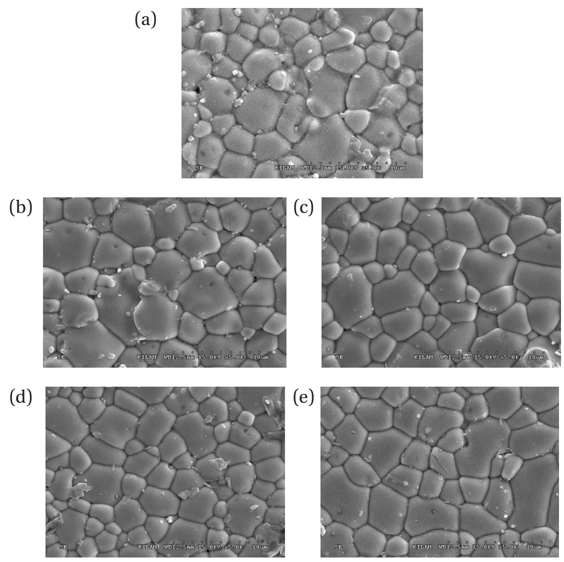

Fig. 2. SEM micrographs of the PNN-PMN-PZT ceramics with various additions of ZnO: (a) 0 wt%, (b) 0.1 wt%, (c) 0.2 wt%, (d) 0.3 wt%, and (e) 0.4 wt%.

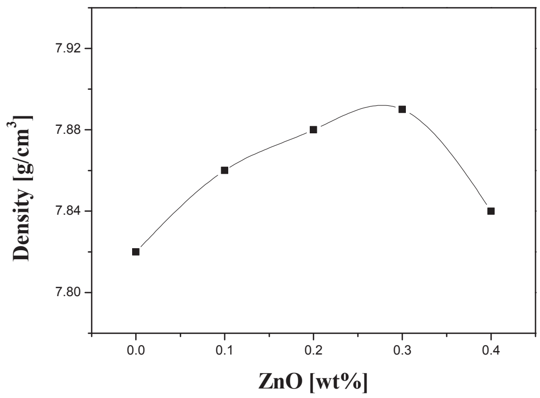

Fig. 3. Density of the ceramic specimens as a function of ZnO addition.

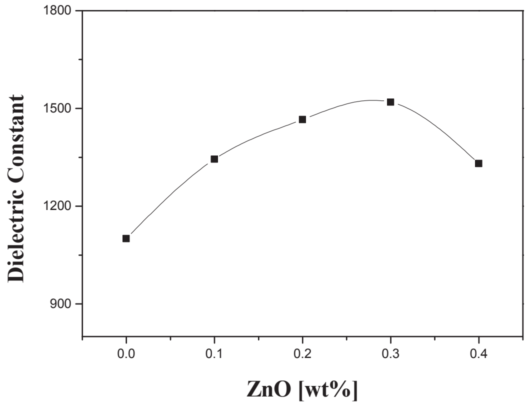

Fig. 4. Dielectric constant (ε_r) of the specimens as a function of ZnO addition.

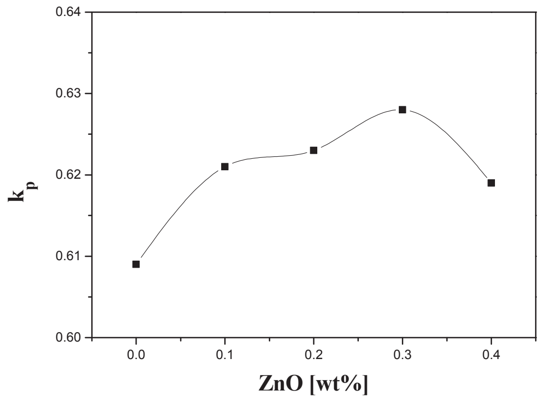

Fig. 5. Electromechanical coupling factor (k_p) of the specimens as a function of ZnO addition.

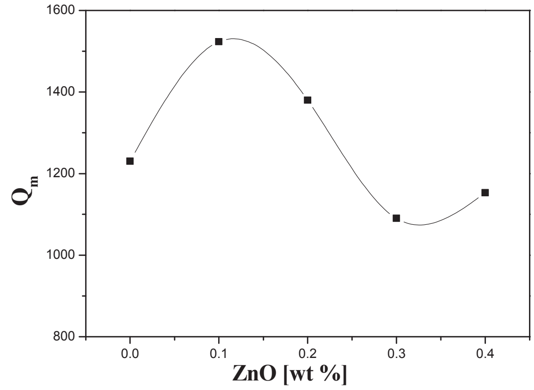

Fig. 6. Electromechanial quality factor (Q_m) of the specimens as a function of ZnO addition.

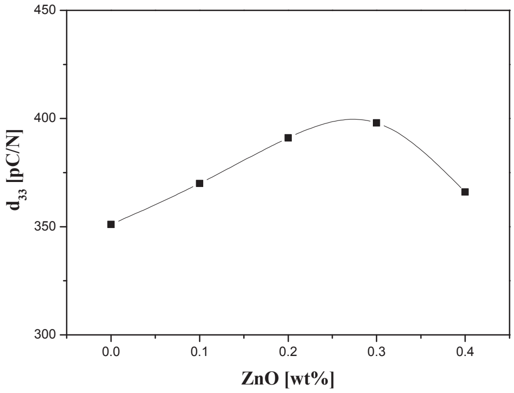

Fig. 7. Piezoelectric coefficient (d_{33}) of the specimens as a function of ZnO addition.

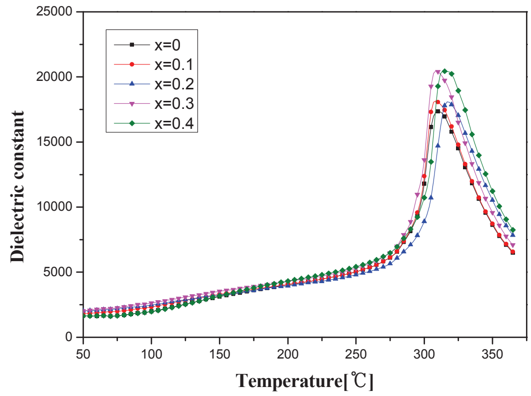

Fig. 8. The temperature dependence of the dielectric constant and Curie temperature (T_c) as a function of ZnO addition.

The density of the samples as a function of ZnO addition is shown in Fig. 3. All samples were fully densified owing to the formation of a liquid phase. With increases in the ZnO content, the density of the materials increased until reaching a ZnO content of 0.3 wt% and then the density decreased with further ZnO addition. This is likely because ZnO can significantly improve the sinterability of the sample.

The dielectric constant (ε_r) as a function of ZnO addition is shown in Fig. 4. With increasing amounts of ZnO, ε_r increased up to 0.3 wt% and then decreased for the 0.4 wt% ZnO preparation. With rapid

Table 1. Physical properties of samples with various ZnO content.

ZnO [wt%]	Density [g/cm^3]	k_p	Dielectric constant	d_{33} [pC/N]	Q_m
0	7.82	0.609	1,101	351	1,230
0.1	7.86	0.621	1,344	370	1,523
0.2	7.88	0.623	1,466	391	1,380
0.3	7.89	0.628	1,519	398	1,090
0.4	7.84	0.619	1,331	366	1,153

liquid phase formation due to ZnO addition, ε_r increased due to the enhancement of sinterability and the densified grain of the ceramics. The ε_r decreased at more than 0.4 wt% ZnO.

Figure 5 shows the changes in k_p as a function of ZnO addition. The maximum value of k_p was 0.628 when the ZnO content was 0.3 wt%. The trend in k_p was similar to that of density because ZnO simultaneously plays an important role in the enhancement of sinterability with the CLBO sintering aid. Figure 6 shows the changes in Q_m as a function of ZnO addition. With increasing ZnO content, Q_m increased up to 0.1 wt% ZnO and thereafter decreased with further ZnO addition. In addition to the formation of a liquid phase, ZnO can partially coexist in the Zn^{2+} state in lead zirconate titanate systems, which substitute for Zr^{4+}, Ti^{4+}, and Nb^{5+}. Thus, the oxygen vacancies generated by differences in charge valence can cause an increase in the mechanical quality factor (Q_m). Q_m showed the largest value of 1,523 in the 0.1 wt% ZnO material.

Figure 7 shows d_{33} as a function of ZnO addition. The d_{33} also followed the trends of k_p and ε_r and its greatest value was 398 pC/N in the sample containing 0.3 wt% ZnO. Taking into consideration both the high d_{33} (370 pC/N) and Q_m (1,523), it can be concluded that the 0.1 wt% ZnO sample is the most suitable for use in high power ultrasonic transducers. The temperature dependence of the dielectric constant of the samples as a function of ZnO content is shown in Fig. 8. All samples showed a high Curie temperature (T_c) of more than 300℃. Table 1 lists the physical properties of the samples with various ZnO contents.

4. CONCLUSIONS

In this study, to develop ceramics with high Q_m and high d_{33} for use in ultrasonic transducers, 0.10 $Pb(Ni_{1/3}Nb_{2/3})O_3$-0.07 $Pb(Mn_{1/3}Nb_{2/3})O_3$-0.83 $Pb(Zr_{0.5}Ti_{0.5})_{0.8}O_3$ ceramics were fabricated using CLBO as a sintering aid. The physical properties of the prepared materials were systematically investigated as a function of ZnO addition. All samples were densified at a 940℃ sintering temperature because ZnO plays an important role in the enhancement of sinterability along with CLBO. ZnO addition improved the sinterability and enhanced the physical properties of the prepared ceramics. At a ZnO content of 0.1 wt%, the ceramic material sintered at 940℃ showed a k_p of 0.621, a Q_m of 1,523 and a d_{33} of 370 pC/N. These physical properties are suitable for applications in low temperature sintering ultrasonic transducers owing to the large values Q_m and d_{33}.

ACKNOWLEDGMENT

This paper was supported by the 2015 economic cooperation industry promotion project(MOTIE) ‘Development of ultrasonic cutting machine and hand piece for surgical operation equipped with cooling device’.

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