Engineered hard piezoelectric materials of MnO$_2$ doped PZT-PSN ceramics for sensors applications

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ABSTRACT

In this study, MnO$_2$-doped 0.96Pb(Zr$_{0.515}$Ti$_{0.485}$)O$_3$-0.04Pb(Sb$_{0.5}$Nb$_{0.5}$)O$_3$ (0.96PZT-0.04PSN) hard piezoelectric ceramics were fabricated by employing a conventional mixed-oxide process. Hard piezoelectric materials are suitable for mechanical device applications such as transducers or piezoelectric ultrasonic motors owing to their high mechanical quality factor. To improve the hard piezoelectric properties, MnO$_2$ was selected and doped into 0.96PZT-0.04PSN ceramics in this study. When MnO$_2$ was introduced into piezoelectric lead zirconate titanate (PZT) ceramics, the resistivity and dielectric permittivity decreased, leading to an increase in the mechanical quality factor. MnO$_2$-doped 0.96PZT-0.04PSN ceramics have a lower piezoelectric charge coefficient and dielectric permittivity compared to those of 0.96PZT-0.04PSN ceramics. However, an enhanced mechanical quality factor of 1600 was obtained for the 0.96PZT-0.04PSN ceramics doped with 0.5 wt% of MnO$_2$. In contrast to other hard piezoelectric materials, MnO$_2$ doped 0.96Pb(Zr$_{0.515}$Ti$_{0.485}$)O$_3$-0.04Pb(Sb$_{0.5}$Nb$_{0.5}$)O$_3$ ceramics have a high $Q_m$ value while having an appropriate piezoelectric charge coefficient $d_{33}$ and electromechanical coupling coefficient $k_{pm}$.

1. Introduction

Piezoelectric materials have been intensively investigated for sensors, actuators, and self-powered device applications [1]. Specifically, materials such as (Pb,Zr)TiO$_3$, Pb(Zn,Nb)O$_3$, and PbTiO$_3$ have been intensively investigated for device applications [2]. To improve their piezoelectric properties, dopants are typically added to the ceramics. In general, dopants can be categorized as donor-type (La$^{3+}$, Nd$^{3+}$ for Pb$^{2+}$ or W$^{6+}$ for Ti$^{4+}$, Zn$^{2+}$, Sb$^{3+}$, and Nb$^{5+}$ site), acceptor type (Na$^{+}$, K$^{+}$ for Pb$^{2+}$ site or Mg$^{2+}$, Cu$^{2+}$ for Ti$^{4+}$, Zn$^{2+}$, Sb$^{3+}$, and Nb$^{5+}$), and low-temperature sintering aids [3–5]. Dopants can be added to piezoelectric materials to create vacancies in the crystal structure, and based on the dopant used, either hard or soft piezoelectric materials can be prepared. Hard piezoelectric materials can be used in mechanical devices such as sensors and motors [6], whereas soft piezoelectric materials can be used in energy conversion devices such as piezoelectric transformers [7].

Hard piezoelectric materials can be used in power generators and sensor applications. In general, an acceptor dopant in a ceramic creates oxygen (anion) vacancies in the crystal structure [8] and results in the formation of hard piezoelectric ceramics. These materials usually have a high Curie temperature exceeding 300°C, low piezoelectric charge constants ($d_{33}$), low dielectric permittivity ($\varepsilon_r$), low electromechanical coupling coefficients ($k_{pm}$), low electrical resistance, and high mechanical quality factors ($Q_m$) [9]. They are also more difficult to polarize or depolarize. Among these characteristics, a high mechanical quality factor is the most crucial aspect to be considered when these materials are used for industrial applications. These materials are good for sensors and energy harvesting applications [6]. Soft piezoelectric materials can be prepared by using the donor doping process, which can create cations in the metal oxide structure. Adding the donor dopant such as Nb into piezoelectric materials can be made soft-piezoelectric materials [10].

These materials usually exhibit high dielectric permittivity, high electromechanical coupling coefficient, large piezoelectric constant, high displacement, relatively low Curie temperature, very high resistivity, and low mechanical quality factor [8]. Moreover, these types of materials are easier to polarize or depolarize and can be applied in various functional device applications.

In this research, we focused on the preparation and analysis of hard piezoelectric materials for application in sensors and generators. The mechanical quality factors of hard piezoelectric materials should be high enough for them to be used in these devices. To enhance $Q_m$, acceptor dopants have been considered and tested [11]. In this study, MnO$_2$ was selected as the acceptor dopant and its effect on the enhancement of
was investigated. A high mechanical quality factor and low dielectric loss tangent (tan δ) can be obtained by using metal dopants to increase the conductive component. In a previous study, by employing MnO2 as the dopant for hard piezoelectric-material applications, the mechanical quality factor Qm was improved from 100 to 1600 [12]. As Mn ions are replaced by B-sites, oxygen vacancies increase to balance valence. As a result of increased oxygen vacancies, impede the motion of the domain walls. Thus, domain switching is difficult in the PZT-PSN system, resulting in improved hard piezoelectric properties [13]. However, the piezoelectric charge coefficient (d33) and phase transition temperature (Tc) are inversely related to each other. In general, hard piezoelectric materials have a high Qm and Tc values with lower d33 values. Therefore, it is difficult to obtain hard piezoelectric materials with high piezoelectric properties. Previous research results for hard piezoelectric materials are summarized in Table 1 for PZT and PZT with other dopants. As shown in the Table 1, it is difficult to simultaneously improve both the Qm and d33 values.

In this research, we focused on achieving hard piezoelectric properties. We revealed the impedance properties, Qm, kp, d33, and εr of MnO2-doped Pb(Zr,Ti)O3-Pb(Sb,Nb)O3 (PZT-PSN) ceramics [15].

### 2. Experimental methods

Starting powders of Pb(Zr,Ti)O3-Pb(Sb,Nb)O3 piezoelectric materials were prepared by employing PbO (99.0%), ZrO2 (99.9%), TiO2 (99.9%), Sb2O3 (99.9%), MnO2 (99.9%), and Nb2O5 (99.9%). MnO2-doped 0.96Pb(Zr0.515Ti0.485)O3-0.04Pb(Sb0.5,Nb0.5)O3 (0.96PZT-0.04PSN) ceramics with the desired stoichiometric composition were prepared by employing a conventional mixed-oxide sintering process. The powders were weighed according to the chemical formula and ball milled for 24 h in ethyl alcohol with zirconia balls, dried at 100°C in an oven, and calcined at 850°C for 4 h. The calcined powders were ball milled again and sintered at 1250°C with different MnO2 dopant compositions. The calcined powders were then mixed with 5 wt% of polyvinyl alcohol (PVA) and uniaxially pressed into disks of 12 mm diameter under 300 MPa pressure. The rate at which the temperature was increased and decreased was set to 5°C/min. MnO2 was doped into the PZT-PSN ceramics from 0 to 1 wt% composition with a variation of 0.25 wt%. Sintering was performed at 1250°C with different MnO2 dopant compositions. The synthesized samples were polished and silver paste was applied on both sides of the sample at 700°C for 10 min, to form electrodes. The sintered MnO2-doped PZT-PSN ceramic specimens were pole under a direct current (DC) electric field of 4.0 kV/mm in a silicon oil bath at 100°C for 30 min. The crystalline structures of the MnO2-doped PZT-PSN ceramics were investigated using X-ray diffraction (XRD) analysis (Bruker-AXS/New D8-Advance). The piezoelectric charge coefficient, d33, was determined using a Berlincourt quasi-static d33 meter (YE 2730A). An impedance analyzer (Agilent 4294A) was employed to determine the dielectric permittivity (εr) according to the frequency of the ceramics.

### 3. Results and discussion

#### 3.1. Crystalline properties

Figure 1(a) shows the XRD patterns of the MnO2-doped PZT-PSN ceramics sintered at 1250°C. The doped ceramics exhibited a perovskite structure, but a pyrochlore phase, which is an undesired secondary phase that causes the piezoelectric properties to decrease, was slightly observed at 29°. We inferred that the MnO2-doped PZT-PSN ceramics have tetragonal structures because they have sets of (001)(100) and (002)(200) reflective indices. Figure 1(b) shows that the (002)/(200) ratio decreases with increasing MnO2 content. The (002) peak intensities doubled the (200) peak intensities as MnO2 dopants increased, indicating that orientation in the (002) direction became the dominant crystalline property with increase in MnO2 dopant content. Figure 1(c) displays the Rietveld refinement results of 0.5 wt% MnO2-doped PZT-PSN ceramics. As shown in the figure, good agreement between the observed and calculated intensity values was observed. The simulated parameters of profile factor, Rp, weighted profile factor, Rwp, and reduced Chi-squared, χ2, were 8.1, 10.5, and 1.9, respectively. As a result, it was confirmed that MnO2-doped PZT-PSN ceramics with a tetragonal symmetry was well matched with the P4mm space group.

#### 3.2. Equivalent circuit and electrical properties

Figure 2 displays the equivalent circuit of the piezoelectric properties or resonator properties. The equivalent circuit is composed of series-connected resistors, inductors, capacitors, and shunt-connected inner-electrode capacitors. Since this equivalent circuit is composed of two capacitive components and one inductive component, the system exhibits two different resonance behaviors in...
the frequency domain [13,16]. This behavior can be observed in the impedance plot in Figure 4. The first and the second resonances correspond to the resonance and anti-resonance behaviors, respectively. The impedance behavior of MnO$_2$-doped PZT-PSN changed from capacitive to inductive near the resonance frequency range, and then changed from inductive to capacitive near the anti-resonance frequency range. This change in the impedance behavior with frequency is well explained by the frequency-dependent impedance response plot in Figure 4.

Figure 3 shows SEM image of MnO$_2$-doped PZT-PSN ceramics. When MnO$_2$ dopants were increased from 0 to 0.5 wt %, the grain size slightly increased and the grain boundaries decreased vice versa. However, as the MnO$_2$ contents increased from 0.5 to 1.0 wt %, grain size was decreased. Therefore, the grain boundaries also increased. It is worth to know that the grain
boundary is consist of defects and pores in ceramic specimen. Therefore, there is a tendency that if the grain boundaries are increased, resistivity is also increased as well. We conclude that the decrement of grain boundary region in ceramic specimen has an advantageous affect in low impedance application.

Figure 4 displays the frequency-dependent impedance plot with the amplitude and phase angle of the 0.5 wt% MnO₂-doped PZT-PSN ceramic, which was obtained after the analysis. The resonance and anti-resonance frequencies were 223.6 and 265.8 kHz, respectively. Moreover, the phase degree varied from −89.2° to +89.6° near the resonance frequency and varied again from +89.2° to −89.0° in the anti-resonance frequency range. Between these ranges, the piezoelectric materials showed inductive behavior in accordance with the equivalent circuit. Therefore, the phase degree of the MnO₂-doped PZT-PSN ceramics remained near +90°. According to the impedance resonance plot, the obtained MnO₂-doped PZT-PSN ceramics showed good piezoelectric properties.

Figure 4 shows the frequency-dependent impedance plots for the piezoelectric ceramics with the same resistance and different capacitance values, as shown in Figure 5. The differences between the resonance and anti-resonance frequencies increased as the capacitance increased, although the resistance values did not change. In addition, the amplitude of the impedance decreased with an increase in capacitance at the same resistance values. Hence, capacitance is a more dominant parameter for this piezoelectric material. At the same resistance values, by decreasing the capacitance or relative dielectric permittivity, the impedance values can be increased. In addition, by employing lower resistance values in the equivalent circuit, the amplitude of the impedance value was lowered. In general, by introducing anion dopants (MnO₂), the resistance can be decreased because of
the presence of mobile ions. Therefore, the doping process can be considered to influence the quality factor.

3.3. Piezoelectric and dielectric properties

Figure 6 shows the variation in the electromechanical coupling coefficient of the MnO$_2$-doped PZT-PSN ceramics according to MnO$_2$ content. Undoped 0.96PZT-0.04PSN ceramics exhibited an electromechanical coupling coefficient, $k_p$, of 0.656, and $k_p$ decreased as the amount of MnO$_2$ dopant increases [14]. However, the decreased value of $k_p$ remained sufficiently high for industrial applications (>0.58) [17]. Many piezoelectric materials have a $k_p$ of approximately 0.6, except for single-crystal materials.

Figure 7 presents the variation in the piezoelectric charge coefficient of PZT-PSN ceramics according to doped MnO$_2$ content. Undoped 0.96PZT-0.04PSN ceramics have a high $d_{33}$ of 440. However, with the introduction of MnO$_2$ dopants, $d_{33}$ decreased to 320 pC/N. This decreased $d_{33}$ value remained sufficiently high for industrial applications (>265) [17]. Moreover, the value of $d_{33}$ did not change by a large margin after increasing the MnO$_2$ dopant content. This high value of $d_{33}$ is suitable for device and sensor applications.

Figure 8 shows the variation in the frequency-dependent relative dielectric permittivity $\varepsilon_r$ of the MnO$_2$ content.

Figure 5. Frequency-dependent impedance plots of MnO$_2$-doped Pb(Zr,Ti)O$_3$-Pb(Sb,Nb)O$_3$ ceramics with a resistance of 1 $\Omega$ and capacitance values of 0.1, 1, and 1 nF.

Figure 6. Variation in electromechanical coupling coefficient $k_p$ of MnO$_2$-doped Pb(Zr,Ti)O$_3$-Pb(Sb,Nb)O$_3$ ceramics according to the MnO$_2$ content.
MnO₂-doped PZT-PSN ceramics according to variation of the MnO₂ content. Undoped 0.96PZT-0.04PSN ceramics have a high relative dielectric permittivity of 1190 at approximately 1 kHz, while other specimens have a decreased relative dielectric permittivity of 950 or less as the MnO₂ dopant content increases. By introducing MnO₂, the relative dielectric permittivity decreased by a large margin, from 1180 (undoped) to 944 (0.25 wt% MnO₂ doped), which was approximately a 20% decrease, and then decreased slightly as the MnO₂ content increased. The reason for this phenomenon is that, in general, hard piezoelectric materials have small piezoelectric constant and dielectric permittivity, while a high mechanical quality factor. As mentioned in the introduction, MnO₂ is acceptor dopant. As a result of doping, shows hard piezoelectric properties. Therefore, the dielectric permittivity was reduced by a large margin in MnO₂ doped PZT-PSN compared to the undoped PZT-PSN piezoelectric ceramics. A lower relative dielectric permittivity is required for hard piezoelectric materials because it can increase the mechanical quality factor Qm. Therefore, the mechanical quality factors can be increased by doping.

Figure 7. Variation in piezoelectric charge coefficient d₃₃ of MnO₂-doped Pb(Zr,Ti)O₃-Pb(Sb,Nb)O₃ ceramics according to the MnO₂ content.

Figure 8. Variation in frequency-dependent relative dielectric permittivity of MnO₂-doped Pb(Zr, Ti)O₃-Pb(Sb, Nb)O₃ ceramics according to the MnO₂ content in the frequency range of 1 kHz to 1 MHz.
Figure 9 shows the dependence of $Q_m$ on the MnO$_2$ content in MnO$_2$-doped PZT-PSN ceramics. The mechanical quality factor of the 0.96PZT-0.04PSN ceramics was very low when MnO$_2$ was not added to the piezoelectric ceramics. However, following MnO$_2$ doping, the mechanical quality factor was increased by a large margin [18,19]. It approached 1600 when 0.5 wt% MnO$_2$ was doped into the PZT-PSN ceramics.

The mechanical quality factor can be expressed using the following expression by considering the resonance- and anti-resonance-frequency impedances and capacitances.

$$Q_m = \frac{f_r^2}{2\pi f_c (f_r^2 - f_a^2) ZC} \quad (1)$$

where $f_r$ is the resonance frequency, $f_a$ is the anti-resonance frequency, $Z$ is the impedance, and $C$ is the capacitance. As discussed in the introduction, hard piezoelectric materials should exhibit relatively low resistivity. The impedance can be decreased by the MnO$_2$ doping process; therefore, PZT-PSN ceramics doped with MnO$_2$ have a lower resistance and dielectric permittivity than PZT-PSN ceramics without doping. Considering Equation (1), it can be inferred that the impedance and capacitance values should be decreased while the piezoelectric properties are maintained, in order to improve the mechanical quality factor. Therefore, some dopant materials are suitable for increasing the mechanical quality factor by decreasing the resistivity while maintaining the piezoelectric properties constant. MnO$_2$ was selected as such a dopant owing to the enhanced mechanical quality factor achieved. In this study, we used analysis and simulation to determine how to increase hard piezoelectric properties by modulating the material properties such as resistivity and dielectric permittivity which can influence hard piezoelectric properties. This analysis is based on Equation (1). The composition of Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$ was different in a reference paper [11], wherein the composition was 0.95Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$-0.05Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$. However, we used a composition of 0.96Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$-0.04Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$. Therefore, due to this composition difference, the reference paper showed higher dielectric permittivity and mechanical quality factors compared to ours. However, our composition had a higher piezoelectric charge coefficient and electromechanical coupling coefficient values. Therefore, we argue that some material properties have a trade-off relationship when the composition values are varied.

4. Conclusions

In this study, hard piezoelectric ceramic materials were engineered and investigated by introducing an anion MnO$_2$ dopant into 0.96Pb(Zr$_{0.515}$Ti$_{0.485}$)O$_3$-0.04Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$. To obtain hard piezoelectric properties, MnO$_2$ was doped into 0.96Pb(Zr$_{0.515}$Ti$_{0.485}$)O$_3$-0.04Pb(Sb$_{0.5}$Nb$_{0.3}$)O$_3$ ceramics. After doping, the resistivity and relative dielectric permittivity decreased, indicating that this method can be used to produce hard piezoelectric materials with high mechanical quality factors. In contrast to other hard piezoelectric materials, MnO$_2$-doped 0.96PZT-0.04PSN ceramics exhibited good piezoelectric properties with a suitable $d_{33}$. This increases the applicability of piezoelectric...
ceramics in sensor devices. By measuring and simulating the impedance properties of MnO₂-doped 0.96PZT-0.04PSN ceramics by considering an equivalent circuit, hard piezoelectric materials can be designed and optimized.

Acknowledgments
This research was supported by the MSIT (Ministry of Science and ICT), Korea, under the ITRC (Information Technology Research Center) support program (IITP-2020-2020-0-01655) supervised by the IITP (Institute of Information & Communications Technology Planning & Evaluation) and Competency Development Program of the Korean Ministry of Trade, Industry and Energy (MOTIE), operated by Korea Institute for Advancement of Technology (KIAT). (No.P0002397, Human Resources Development program for Industrial Convergence of Wearable Smart Devices).

Disclosure of potential conflicts of interest
No potential conflict of interest was reported by the author(s).

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