Fundamental Research on Ternary
\( \text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3-\text{Pb(Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3-\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 \) Solid Solutions for High-power Piezoelectric Applications

Mizuyo Yamaguchi*, Masafumi Kobune, and Takeyuki Kikuchi
Department of Chemical Engineering and Materials Science, Graduate School of Engineering, University of Hyogo, 2167, Shosha, Himeji Hyogo 671-2201
* Corresponding author: Fax: 81-079-267-4897, e-mail: et14m060@steng.u-hyogo.ac.jp

To develop high-performance materials for high-power piezoelectric applications, ternary high-density solid solutions with compositions of \( x \text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3-\text{yPb(Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3-\text{zPb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 \) (PZT,PMS,PZnN) with \( x = 0.82-0.96, y = 0.02-0.16, \) and \( z = 0.02-0.16 \), were fabricated by a conventional solid-state reaction method. A detailed investigation was carried out into the microstructure and crystal structure of the samples, together with their piezoe- and ferroelectric properties. It was found that a solid solution with \( x = 0.86, y = 0.085, \) and \( z = 0.055 \) and a rhombohedral structure exhibited excellent piezo- and ferroelectric properties. These included piezoelectric coefficients \( d_{33} \) (longitudinal length mode) = 170 pC/N and \( -d_{31} \) (transverse length mode) = 69 pC/N, a mechanical quality factor \( Q_m(p) \) (radial mode) = 2218, \( d_{33} Q_m(p) = 376 \times 10^3 \) pC/N, \( -d_{31} Q_m(p) = 133 \times 10^3 \) pC/N, electromechanical coupling factors \( k_p \) (radial mode) = 46% and \( k_{31} \) (transverse length mode) = 28%, a Curie temperature \( T_c = 259^\circ \)C, a remanent polarization \( P_r = 53 \) µC/cm², and a coercive field \( 2E_c = 34 \) kV/cm. Thus, this is a highly promising piezoelectric material for high-power ultrasonic vibrators and piezoelectric transformers.

Key words: PZTMSZnN, high-power piezoelectric material, morphotropic phase boundary, piezoelectricity

1. INTRODUCTION

In recent years, there is a strong demand for high-power piezoelectric materials because they offer performance advantages in ultrasonic vibrators and piezoelectric transformers. In order to further improve the performance of such materials, it is necessary to increase the piezoelectric coefficients \( d_{33} \) and \( d_{31} \), the electromechanical coupling factors \( k_p \) and \( k_{31} \), the mechanical quality factor \( Q_m(p) \), and the products \( d_{33} Q_m(p) \) and \( d_{31} Q_m(p) \), which are important for high-power piezoelectric materials [1-3]. One promising family of piezoelectric materials is \( x \text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3-\text{yPb(Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3-\text{zPb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 \), denoted by PZT,PMS,PZnN. Yang et al. fabricated PZT,PMS,PZnN solid solutions by adding PMS and PZnN to PZT, with 0.1 mol% CeO₂ as a sintering agent, using the molten salt synthesis method. They reported that PZTₙ₀₋ₚₙₐₓ₋ₙₜ₅ (PZnNₓ₋ₙₜ₅) solid solution exhibited good piezoelectric properties, with \( d_{33} = 369 \) pC/N, \( Q_m(p) = 1381, k_p = 64\% \), and \( T_c = 275^\circ \)C [4]. Moreover, Li et al. succeeded in further improving the piezoelectric properties by adding MnO, WO₃, and ZnO to PZT,PMS,PZnN. They reported that 0.2 mass% MnO₂- and 0.6 mass% WO₃-modified PZTₙ₀₋ₚₙₐₓ₋ₙₜ₅ solid solution with 0.1 mass% ZnO exhibited excellent piezoelectric properties, with \( d_{33} = 300 \) pC/N, \( Q_m(p) = 1899, k_p = 55\% \), and \( T_c = 270^\circ \)C [5,6]. From the viewpoint of green processing, Wan et al. investigated the use of CuO and La₂O₃ as sintering additives for PZT,PMS,PZnN solid solutions in order to reduce the sintering temperature. They found that PZT₀₉₋ₚₙₐₓ₋ₙₜ₅ (PZnNₓ₋ₙₜ₅) solid solutions with 0.5 mass% La₂O₃ and 1.0 mass% CuO could be sintered even at 900°C, which is 250-350°C lower than the conventional sintering temperature. The material exhibited excellent piezoelectric properties, with \( d_{33} = 355 \) pC/N, \( Q_m(p) = 936, \) and \( k_p = 58.4\% \) [7].

Thus, ternary PZT,PMS,PZnN solid solutions are attractive for high-power piezoelectric applications. However, there have been no systematic studies on the fundamental piezo- and ferroelectric properties of these materials for such applications. In the present study, PZT,PMS,PZnN solid solutions with \( x = 0.82-0.96, y = 0.02-0.16, \) and \( z = 0.02-0.16 \) were fabricated by a conventional solid-state reaction method. Their microstructure, crystal structure and piezoelectric properties were investigated in order to determine the composition that yields the optimal piezo- and ferroelectric properties.

2. EXPERIMENTAL

Reagent-grade PbO, ZrO₂, TiO₂, MnCO₃-0.46 H₂O, Sb₂O₃, ZnO, and Nb₂O₃ were used as starting...
materials. PZT-PMS-PZnN sintered bodies were fabricated by a two-step solid-state reaction using a columbite precursor, as follows [8]. MnCO3:0.46 H2O, Sb2O3, ZnO, and Nb2O5 were first mixed for 2 h at 200 rpm in ethanol using a planetary wet zirconia ball mill. The powder synthesized by calcining the mixture in air at 1000°C for 4 h was used as the (Mn,Zn)(Sb,Nb):O5 precursor for preparation of Pb(Mn1/3Sb2/3)O3–Pb(Zn1/3Nb2/3)O3, PbO, ZrO2, and TiO2 were then added, and the mixture was ground at 200 rpm for 2 h in ethanol using the same ball mill. The mixture was dried and calcined in air at 850°C for 3 h. The calcined powder was subsequently mixed and ground with a 1.5 mass% acrylic solution for 12 h at 200 rpm in the same ball mill. After drying and sieving, the resulting granules were pressed uniaxially under a pressure of 15 MPa to prepare disks with a diameter of 12.0 mm and a thickness of 1.2 mm, followed by cold isostatic pressing under a pressure of 200 MPa. These green compacts were then sintered at 1220–1260°C for 3 h in air by the powder-bed method [9] using calcined powders with the same composition as the compacts. The samples were subsequently polished to a thickness of 0.6 mm. The crystalline phases were identified using X-ray diffraction (XRD; Rigaku Ultima IV). The polished samples with silver electrodes were poled under a DC field of 30–40 kV/cm for 30 min at 80°C in silicone oil. d33 at room temperature was measured using a PIEZo d33 meter (Chinese Academy of Sciences ZJ-4B). Other piezoelectric parameters [-d31, Qm(p), k31, and k33] were measured at room temperature by the resonant-antiresonant frequency method [10] on the basis of the JEITA standard, using an impedance analyzer (Hewlett-Packard 4194A). The ferroelectric properties were evaluated based on polarization-electric field (P-E) hysteresis loop measurements at room temperature under an applied field of 50 kV/cm at 1 Hz, using a ferroelectric testing system (Radiant Tech. RT-66A). Observations of the cross-sectional microstructure and measurements of the average grain size were carried out using field-emission scanning electron microscopy (FE-SEM; JEOL JSM7001F). Tc was determined based on the temperature dependence of ϵ31/T60 in the range 25–500°C using an LCR meter (Agilent 4284A).

3. RESULTS AND DISCUSSION
Figure 1(A) shows XRD profiles for three typical PZT, PMS, PZnN, solid solutions with (a) PZT0.92PMS0.08PZnN0.04, (b) PZT0.88PMS0.08PZnN0.04, and (c) PZT0.88PMS0.11PZnN0.04 (A), XRD profiles in 2θ = 42–46° region for (a) and (b) (B), and a phase diagram for PZT, PMS, PZnN, and the resulting MPB region (C). The crystalline phases of compositions that are plotted by solid and open circles, and solid triangles in the figure display a mixture (tetragonal and rhombohedral phases), a single rhombohedral phase, and a mixture (perovskite and pyrochlore phases), respectively.

that the composition is in the morphotropic phase boundary (MPB) region. In contrast, for PZT0.88PMS0.08PZnN0.04, only the (200) diffraction peak for the rhombohedral phase is observed. In pattern (c) for PZT0.88PMS0.11PZnN0.04 in Fig. 1(A), weak peaks associated with a pyrochlore phase are present in addition to the main peaks due to the perovskite phase. It is known that pyrochlore-type compounds can be represented by the general formula A5B1O7, where the A sites can be occupied by alkaline earth ions such as Ca2+ and Sr2+, or rare earth ions such as La3+ and Nd3+. The B sites can be occupied by transition metal ions such as Ti4+, Nb5+, and Ta5+. The majority of these compounds are cubic (space group; Fd3m) and exhibit paraelectric behavior. Therefore, the piezo- and ferroelectric properties of the material are expected to deteriorate significantly with an increased ratio of the paraelectric phase in the solid solutions. Figure 1(C) shows a phase diagram for PZT, PMS, PZnN, with
the MPB region indicated. It can be seen that as the PMS content is increased, the material changes from a mixture of tetragonal and rhombohedral phases, to a single rhombohedral phase, and finally to a mixture of perovskite and pyrochlore phases.

Figure 2 shows the variations in (a) $d_{33}$, (b) $-d_{31}$, (c) $k_p$, and (d) $k_{31}$ at room temperature for the PZT,PMS,PZnN solid solutions. The maximum values for all the piezoelectric parameters ($d_{33} = 201 \text{ pC/N}$, $-d_{31} = 67 \text{ pC/N}$, $k_p = 50\%$, and $k_{31} = 30\%$) are obtained for the composition PZT.092PMS.004-PZnN.002, which is in the MPB region.

Figure 3 shows the variations in (a) $Q_m(p)$, (b) $d_{33} \cdot Q_p(p)$, and (c) $-d_{31} \cdot Q_m(p)$ at room temperature.

The contour map for $Q_m(p)$ is somewhat different to those for $d_{33}$, $-d_{31}$, $k_p$, and $k_{31}$ in Fig. 2. For high-power piezoelectric applications, a high vibration velocity $v_{0-p}$ and a large vibration amplitude are required. Since it is known that $v_{0-p}$ is proportional to the products $d_{33} \cdot Q_p(p)$ and $-d_{31} \cdot Q_m(p)$ for small vibration amplitudes, the material performance for high-power piezoelectric applications was evaluated by calculating $d_{33} \cdot Q_p(p)$ and $-d_{31} \cdot Q_m(p)$ for small-amplitude vibrations. In Figs. 3(b) and 3(c), it can be seen that for the composition PZT.096PMS.008PZnN.005, $d_{33} \cdot Q_p(p)$ has a maximum of $376 \times 10^3 \text{ pC/N}$, and $-d_{31} \cdot Q_m(p)$ has a maximum of $133 \times 10^3 \text{ pC/N}$. This can be attributed to the high $Q_m(p)$ of 2218 for this solid solution. Thus, sufficient PMS and PZnN codoping of PZT produces a hard piezoelectric material with large $d$, $k$, and $Q_m$ values. Here, the primary component of the present solid solutions is PZT, represented by the general formula $A\beta B\beta\delta O_3$. In the case of PMS and PZN as end members used in this study, the doping of Mn$^{2+}$ and Zn$^{2+}$ (acceptor doping effect) for Zr$^{4+}$/Ti$^{4+}$ produces the formation of domain pinning in the BO$_6$ octahedral structure, resulting in a marked increase of $Q_m(p)$. In contrast, the doping of Nb$^{5+}$ and Sb$^{5+}$ (donor doping effect) for Zr$^{4+}$/Ti$^{4+}$ provides the formation of A-site defects, resulting in a significant increase of $d$ and $k$, as has previously reported in another paper [11]. Thus, the codoping of acceptor and donor ions, such as Mn$^{2+}$, Zn$^{2+}$, Sb$^{5+}$, and Nb$^{5+}$ for Zr$^{4+}$/Ti$^{4+}$ was confirmed to provide significant increases in $Q_m(p)$, $d$, and $k$ simultaneously in the same sample. In particular, PZT.096PMS.008PZnN.005 is highly promising for high-power piezoelectric applications, since it exhibits excellent piezoelectric properties, with $d_{33} = 170 \text{ pC/N}$, $d_{31} = 60 \text{ pC/N}$, $Q_m = 2218$, $-d_{31} \cdot Q_m = 133 \times 10^3 \text{ pC/N}$, $k_p = 46\%$, and $k_{31} = 28\%$ (Figs. 2 and 3).

Figure 4 shows a $P$-$E$ hysteresis loop obtained under an applied electric field of 50 kV/cm for PZT.096PMS.008PZnN.005. As expected, the loop
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Fig. 5. Cross-sectional FE-SEM image of PZT0.86PMS0.085PZnN0.055 solid solution.

clearly exhibits an asymmetric shape. This suggests that oxygen vacancies formed by acceptor (Mn$^{2+}$) doping at B sites in the A$^4$B$^6$O$_{12}$-type perovskite structure causes domain pinning that restricts the movement of domain walls [12]. The mechanism by which this leads to high $Q_m$ has been previously reported [13]. The values of $2P_r$ and $2E_c$ estimated from the hysteresis loop in Fig. 4 are 53 $\mu$C/cm$^2$ and 34 kV/cm, respectively.

Figure 5 shows a cross-sectional FE-SEM image of a PZT0.86PMS0.085PZnN0.055 sample. The fracture is seen to be almost completely intergranular, suggesting that the intragranular strength is higher than the grain boundary strength. In addition, this sample has a dense microstructure containing almost no crystal defects such as voids. The average grain size was estimated to be approximately 2.2 $\mu$m using the linear intercept method. Kobune et al. investigated the grain size dependence on $d_{33}$ of Pb(Mn1/3Nb2/3)O3-PbZrO3-PbTiO3 solid solutions and reported that the solid solution with an average grain size of approximately 1.0 $\mu$m exhibited the highest $d_{33}$ value [14]. Consequently, the grain size in the present study is somewhat larger than optimal, if the effect of composition on $d_{33}$ can be ignored.

Figure 6 shows the variations in $T_c$ for the PZT-PMS-PZnN solid solutions. It can be seen that $T_c$ increases with increasing PZT content, and decreases with increasing PMS content. For the PZT0.86PMS0.085PZnN0.055 solid solution, which showed excellent piezo- and ferroelectric properties, the $T_c$ value is 259°C, which is suitable for a practical high-power piezoelectric material [4].

Thus, PZT0.86PMS0.085PZnN0.055 is a hard piezoelectric material exhibiting excellent piezo- and ferroelectric properties, with $d_{33} = 170$ $\mu$m/N, $d_{31} = 69$ $\mu$m/N, $Q_{m}(p) = 2218$, $d_{33} Q_{m}(p) = 376 \times 10^3$ $\mu$m/C/N, $-d_{33} Q_{m}(p) = 133 \times 10^3$ $\mu$m/C/N, $k_p = 46\%$, $k_{31} = 28\%$, $T_c = 259^\circ$C, $2P_r = 53$ $\mu$C/cm$^2$, and $2E_c = 34$ kV/cm, and has potential as a high-performance piezoelectric material for high-power piezoelectric applications.

4. CONCLUSIONS

High-density solid solutions with compositions

5. REFERENCES


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