Fundamental Research on Ternary Pb(Zr_{0.52}Ti_{0.48})O₃–Pb(Mn_{1/3}Sb_{2/3})O₃–Pb(Zn_{1/3}Nb_{2/3})O₃ Solid Solutions for High-power Piezoelectric Applications

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To develop high-performance materials for high-power piezoelectric applications, ternary high-density solid solutions with compositions of $x\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ – $y\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ – $z\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZT_{*x*}PMS_{*y*}PZN_{*z*}) 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 piezo- 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 $Q_m(\text{p})$ (radial mode) = 2218, $d_{33} \cdot Q_m(\text{p}) = 376 \times 10^3$ pC/N, $-d_{31} \cdot Q_m(\text{p}) = 133 \times 10^3$ pC/N, electromechanical coupling factors k_p (radial mode) = 46% and k_{31} (transverse length mode) = 28%, a Curie temperature $T_c = 259^\circ\text{C}$, a remanent polarization $2P_r = 53 \mu\text{C}/\text{cm}^2$, and a coercive field $2E_c = 34 \text{ kV}/\text{cm}$. 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 $Q_m(\text{p})$, and the products $d_{33} \cdot Q_m(\text{p})$ and $d_{31} \cdot Q_m(\text{p})$, which are important for high-power piezoelectric materials [1–3]. One promising family of piezoelectric materials is $x\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ – $y\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ – $z\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, denoted by PZT_{*x*}PMS_{*y*}PZN_{*z*}. Yang et al. fabricated PZT_{*x*}PMS_{*y*}PZN_{*z*} solid solutions by adding PMS and PZN to PZT, with 0.1 mol% CeO₂ as a sintering agent, using the molten salt synthesis method. They reported that PZT_{0.9}PMS_{0.05}PZN_{0.05} solid solution exhibited good piezoelectric properties, with $d_{33} = 369 \text{ pC}/\text{N}$, $Q_m(\text{p}) = 1381$, $k_p = 64\%$, and $T_c = 275^\circ\text{C}$ [4]. Moreover, Li et al. succeeded in further improving the piezoelectric properties by adding MnO₂, WO₃ and ZnO to PZT_{*x*}PMS_{*y*}PZN_{*z*}. They reported that 0.2 mass%-MnO₂- and 0.6 mass%-WO₃-modified PZT_{0.9}PMS_{0.05}PZN_{0.05} solid solution with 0.1 mass% ZnO exhibited excellent piezoelectric properties, with $d_{33} = 300 \text{ pC}/\text{N}$,

$Q_m(\text{p}) = 1899$, $k_p = 55\%$, and $T_c = 270^\circ\text{C}$ [5,6]. From the viewpoint of green processing, Wan et al. investigated the use of CuO and La₂O₃ as sintering additives for PZT_{*x*}PMS_{*y*}PZN_{*z*} solid solutions in order to reduce the sintering temperature. They found that PZT_{0.9}PMS_{0.05}PZN_{0.05} 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 $d_{33} = 355 \text{ pC}/\text{N}$, $Q_m(\text{p}) = 936$, and $k_p = 58.4\%$ [7].

Thus, ternary PZT_{*x*}PMS_{*y*}PZN_{*z*} solid solutions are attractive for high-power piezoelectric applications. However, there have as yet been no systematic studies on the fundamental piezo- and ferroelectric properties of these materials for such applications. In the present study, PZT_{*x*}PMS_{*y*}PZN_{*z*} 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 Nb₂O₅ were used as starting

materials. $\text{PZT}_x\text{PMS}_y\text{PZN}_z$ sintered bodies were fabricated by a two-step solid-state reaction using a columbite precursor, as follows [8]. $\text{MnCO}_3 \cdot 0.46 \text{H}_2\text{O}$, Sb_2O_3 , ZnO , and Nb_2O_5 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 $(\text{Mn,Zn})(\text{Sb,Nb})_2\text{O}_6$ precursor for preparation of $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$. PbO , ZrO_2 , and TiO_2 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. d_{33} at room temperature was measured using a PIEZO d_{33} meter (Chinese Academy of Sciences ZJ-4B). Other piezoelectric parameters [$-d_{31}$, $Q_m(p)$, k_p , and k_{31}] 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). T_c was determined based on the temperature dependence of $\varepsilon_{33}^T/\varepsilon_0$ 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 $\text{PZT}_x\text{PMS}_y\text{PZN}_z$ solid solutions with (a) $x = 0.94$, $y = 0.02$, and $z = 0.04$, (b) $x = 0.88$, $y = 0.08$, and $z = 0.04$, and (c) $x = 0.85$, $y = 0.11$, and $z = 0.04$. Both $\text{PZT}_{0.94}\text{PMS}_{0.02}\text{PZN}_{0.04}$ and $\text{PZT}_{0.88}\text{PMS}_{0.08}\text{PZN}_{0.04}$ are seen to have a single-phase perovskite structure with no pyrochlore or other secondary phases. Figure 1(B) shows XRD profiles in the $2\theta = 42$ – 46° region for (a) $\text{PZT}_{0.94}\text{PMS}_{0.02}\text{PZN}_{0.04}$ and (b) $\text{PZT}_{0.88}\text{PMS}_{0.08}\text{PZN}_{0.04}$. In the case of $\text{PZT}_{0.94}\text{PMS}_{0.02}\text{PZN}_{0.04}$, the pattern contains (002) and (200) peaks for the tetragonal phase, in addition to a (200) peak for the rhombohedral phase, indicating

Fig. 1. XRD profiles of three typical $\text{PZT}_x\text{PMS}_y\text{PZN}_z$ solid solutions with (a) $\text{PZT}_{0.94}\text{PMS}_{0.02}\text{PZN}_{0.04}$, (b) $\text{PZT}_{0.88}\text{PMS}_{0.08}\text{PZN}_{0.04}$, and (c) $\text{PZT}_{0.85}\text{PMS}_{0.11}\text{PZN}_{0.04}$ (A), XRD profiles in $2\theta = 42$ – 46° region for (a) and (b) (B), and a phase diagram for $\text{PZT}_x\text{PMS}_y\text{PZN}_z$ 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 $\text{PZT}_{0.88}\text{PMS}_{0.08}\text{PZN}_{0.04}$, only the (200) diffraction peak for the rhombohedral phase is observed. In pattern (c) for $\text{PZT}_{0.85}\text{PMS}_{0.11}\text{PZN}_{0.04}$ 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 $A_2B_2O_7$, where the A sites can be occupied by alkaline earth ions such as Ca^{2+} and Sr^{2+} , or rare earth ions such as La^{3+} and Nd^{3+} . The B sites can be occupied by transition metal ions such as Ti^{4+} , Nb^{5+} , and Ta^{5+} . The majority of these compounds are cubic (space group; $Fd\bar{3}m$) 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 $\text{PZT}_x\text{PMS}_y\text{PZN}_z$, with

Fig. 2. Variations in (a) d_{33} , (b) $-d_{31}$, (c) k_p and (d) k_{31} at room temperature for the ternary $\text{PZT}_{1-x}\text{PMS}_y\text{PZN}_z$ solid solutions.

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 $\text{PZT}_{1-x}\text{PMS}_y\text{PZN}_z$ solid solutions. The maximum values for all the piezoelectric parameters ($d_{33} = 201$ pC/N, $-d_{31} = 67$ pC/N, $k_p = 50\%$, and $k_{31} = 30\%$) are obtained for the composition $\text{PZT}_{0.92}\text{PMS}_{0.04}\text{PZN}_{0.04}$, which is in the MPB region.

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

Fig. 3. Variations in (a) $Q_m(p)$, (b) $d_{33} \cdot Q_m(p)$ and (c) $-d_{31} \cdot Q_m(p)$ at room temperature for the ternary $\text{PZT}_{1-x}\text{PMS}_y\text{PZN}_z$ solid solutions.

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 $d_{33} \cdot Q_m(p)$ and $-d_{31} \cdot Q_m(p)$ for small vibration amplitudes, the material performance for high-power piezoelectric applications was evaluated by calculating $d_{33} \cdot Q_m(p)$ 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 $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZN}_{0.055}$, $d_{33} \cdot Q_m(p)$ has a maximum of 376×10^3 pC/N, and $-d_{31} \cdot Q_m(p)$ has a maximum of 133×10^3 pC/N. This can be attributed to the high $Q_m(p)$ of 2218 for this solid solution. Thus, sufficient PMS and PZN 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 $A^{II}B^{IV}\text{O}_3$. 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 $\text{Zr}^{4+}/\text{Ti}^{4+}$ 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 Sb^{5+} and Nb^{5+} (donor doping effect) for $\text{Zr}^{4+}/\text{Ti}^{4+}$ 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 $\text{Zr}^{4+}/\text{Ti}^{4+}$ was confirmed to provide significant increases in $Q_m(p)$, d , and k simultaneously in the same sample. In particular, $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZN}_{0.055}$ is highly promising for high-power piezoelectric applications, since it exhibits excellent piezoelectric properties, with $d_{33} = 170$ pC/N, $d_{31} = -60$ pC/N, $Q_m = 2218$, $-d_{31} \cdot Q_m = 133 \times 10^3$ 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 $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZN}_{0.055}$. As expected, the loop

Fig. 4. P - E hysteresis loop at room temperature for $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZN}_{0.055}$ solid solution.

Fig. 5. Cross-sectional FE-SEM image of $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZnN}_{0.055}$ solid solution.

clearly exhibits an asymmetric shape. This suggests that oxygen vacancies formed by acceptor (Mn^{2+}) doping at B sites in the $A^{II}B^{IV}\text{O}_3$ -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 $53 \mu\text{C}/\text{cm}^2$ and $34 \text{ kV}/\text{cm}$, respectively.

Figure 5 shows a cross-sectional FE-SEM image of a $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZnN}_{0.055}$ 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 $2.2 \mu\text{m}$ using the linear intercept method. Kobune et al. investigated the grain size dependence on d_{33} of $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbZrO_3 - PbTiO_3 solid solutions and reported that the solid solution with an average grain size of approximately $1.0 \mu\text{m}$ 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 $\text{PZT}_x\text{PMS}_y\text{PZnN}_z$ solid solutions. It can be seen that T_c increases with increasing PZT content, and decreases with increasing PMS content. For the $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZnN}_{0.055}$ 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, $\text{PZT}_{0.86}\text{PMS}_{0.085}\text{PZnN}_{0.055}$ is a hard piezoelectric material exhibiting excellent piezo- and ferroelectric properties, with $d_{33} = 170 \text{ pC}/\text{N}$, $-d_{31} = 69 \text{ pC}/\text{N}$, $Q_m(\text{p}) = 2218$, $d_{33} \cdot Q_m(\text{p}) = 376 \times 10^3 \text{ pC}/\text{N}$, $-d_{31} \cdot Q_m(\text{p}) = 133 \times 10^3 \text{ pC}/\text{N}$, $k_p = 46\%$, $k_{31} = 28\%$, $T_c = 259^\circ\text{C}$, $2P_r = 53 \mu\text{C}/\text{cm}^2$, and $2E_c = 34 \text{ kV}/\text{cm}$, and has potential as a high-performance piezoelectric material for high-power piezoelectric applications.

4. CONCLUSIONS

High-density solid solutions with compositions

Fig. 6. Variation in T_c for the ternary $\text{PZT}_x\text{PMS}_y\text{PZnN}_z$ solid solutions.

of $\text{PZT}_x\text{PMS}_y\text{PZnN}_z$, 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 with no sintering additives. Their microstructure, crystal structure, and piezo- and ferroelectric properties were investigated in order to evaluate their suitability for high-power piezoelectric applications. The solid solution with $x = 0.86$, $y = 0.085$, and $z = 0.055$ was found to exhibit excellent piezo- and ferroelectric properties.

5. REFERENCES

- [1] H. Nagata, M. Seki, Y. Noumura, Y. Hiruma, and T. Takenaka, *Jpn. J. Appl. Phys.*, **50**, 09ND05 (2011).
- [2] Y. D. Hou, M. K. Zhu, C. S. Tian and H. Yan, *Sensors and Actuators A*, **16**, 455–460 (2004).
- [3] M. Yamaguchi, M. Kobune, H. Okuda and T. Kikuchi, *J. Korean Phys. Soc.*, **66**, 656–660 (2015).
- [4] Z. Yang, H. Li, X. Zong, and Y. Chang, *J. Eur. Ceram. Soc.*, **26**, 3197–3202 (2006).
- [5] H. Li, Z. Yang, L. Wei, and Y. Chang, *Mater. Res. Bull.*, **44**, 638–643 (2009).
- [6] H. Li, Z. Yang, X. Zong, and Y. Chang, *Mater. Sci. Eng. B*, **103**, 288–294 (2006).
- [7] D. Wan, Q. Li, J. Y. Choi, Y. Yang and S. J. Yoon, *Jpn. J. Appl. Phys.*, **49**, 071503 (2010).
- [8] S. L. Swartz and T. R. Shrout, *Mater. Res. Bull.*, **17**, 1245–1250 (1982).
- [9] M. Kobune, S. Fujii, K. Furuya, and R. Takayama, *J. Ceram. Soc. Jpn.*, **102**, 999–1004 (1994).
- [10] B. Jaffe, W.R. Cook, Jr. and H. Jahhe, “Piezoelectric Ceramics” (Academic Press, London and New York, 1971) pp. 30–35.
- [11] C. C. Tsai, S. Y. Chu, J. S. Jiang, C. S. Hong, and Y. F. Chiu, *Ceram. Int.*, **40**, 11713–11725 (2014).
- [12] B. Li, Z. Zhu, G. Li, Q. Yin, and A. Ding, *Jpn. J. Appl. Phys.*, **43**, 1458–1463 (2004).
- [13] J. S. Kim, S. J. Kim, H. G. Kim, D. C. Lee, and K. Uchino, *Jpn. J. Appl. Phys.*, **38**, 1433–1437 (1999).
- [14] M. Kobune, H. Okuda, H. Nishioka and T. Kikuchi, *Jpn. J. Appl. Phys.*, **52**, 09KD10 (2013).

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