Effects of MnO₂ Addition on Piezoelectric and Ferroelectric Properties of PbNi₁/₃Nb₂/₃O₃–PbTiO₃–PbZrO₃ Ceramics

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PbNi₁/₃Nb₂/₃O₃–PbTiO₃–PbZrO₃ 系セラミックスの圧電及び強誘電特性に及ぼす MnO₂ 添加の影響

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High-density 0.5PbNi₁/₃Nb₂/₃O₃–0.345PbTiO₃–0.155PbZrO₃ (0.5PNN–0.345PT–0.155PZ) ceramics were prepared by normal sintering with the addition of 0–3.66 mol% MnO₂ and their piezoelectric and ferroelectric properties were investigated. The effect of MnO₂ addition on significantly lowering the value of tan δ in the range of 0.37 to 0.93 mol% was proven. The lowest value (−0.37%) of tan δ was obtained in ceramics with 0.15 mol% MnO₂. Electromechanical coupling factors, k₈ and k₃₃, and the piezoelectric constant, d₃₃, decreased with increasing amount of MnO₂ addition. The highest values of k₈, k₉, and d₃₃ were 6.6, 0.38 and −362 pC/N, respectively, and were obtained in the ceramics without MnO₂. The effect of MnO₂ addition on improving the value of the mechanical quality factor, Qm, was proven in the range of 0.93 to 1.85 mol% and the improvement was around twenty times that of the sample without MnO₂. The distortion in the shape of P–E hysteresis loops for samples with MnO₂ addition suggested that oxygen vacancies formed by substituting Mn³⁺ ions for B-site ions (e.g., Ti⁴⁺ and Zr⁴⁺ ions) in the perovskite structure partially inhibited the polarization reversal in the ferroelectrics. 0.5PNN–0.345PT–0.155PZ ceramics with 0.75–0.93 mol% MnO₂ show great promise as practical materials for piezoelectric applications.

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1. Introduction

PbZrO₃–PbTiO₃ (PZT) with very small amounts of metal-oxide additives such as La₂O₃, Nb₂O₅, Sb₂O₃ and WO₃ has been widely utilized for piezoelectric materials. Recently, Luff et al.¹ reported that PbNi₁/₃Nb₂/₃O₆–PbTiO₃–PbZrO₃ (hereafter abbreviated to PNN–PT–PZ) ceramics with a composition of 0.5PbNi₁/₃Nb₂/₃O₆–0.5PbTiO₃–0.15PbZrO₃ (0.5PNN–0.35PT–0.15PZ) had excellent piezoelectric properties. On the basis of the phase diagram at room temperature for the PNN–PT–PZ ternary system previously studied by Banno et al.,² Kondo et al.³ further investigated ceramics of composition close to that reported by Luff et al.¹ in detail and consequently clarified that 0.5PNN–0.345PT–0.155PZ ceramics gave an extremely large longitudinal electromechanical coupling factor, k₃₃, of 80%. Thus, the applications of ceramics of this composition can be expected for multilayer ceramic actuators, and so on. However, a low dielectric loss (tan δ) and a high mechanical quality factor (Qm) are further required for the materials for piezoelectric applications. To solve this problem, on the other hand, Moon et al.⁴,⁵ reported that high-density specimens could be prepared via liquid-phase sintering at high temperatures by adding small amounts of SiO₂ and/or MnO₂ to PNN–PT–PZ with a composition of PbNi₁/₃Nb₂/₃O₆–3Pb(Zr₀.₄₈Ti₀.₅₂)O₃ (PNN–3PZT; 0.5PNN–0.35PT–0.36PZ) and that piezoelectric properties were strongly affected by oxygen vacancies (V₀) formed by substituting Mn³⁺ ions for B-site ions in the perovskite structure. Their investigation yielded important information for improving the properties of PNN–PT–PZ ceramics up to the level of practical materials for piezoelectric actuators. However, as the composition of PNN–PT–PZ examined by them was different from 0.5PNN–0.345PT–0.155PZ which showed excellent piezoelectric properties, we thought that investigating the effects of MnO₂ addition on the physical properties of 0.5PNN–0.345PT–0.155PZ ceramics was especially important from the viewpoint of the development of practical piezoelectric materials.

In this study, we attempted to prepare high-density 0.5PNN–0.345PT–0.155PZ ceramics with the addition of 0–3.66 mol% MnO₂ by normal sintering. The piezoelectric and ferroelectric properties of the obtained samples are investigated and the optimum amount of MnO₂ addition is examined from the viewpoint of piezoelectric applications.

2. Experimental procedures

Reagent-grade, PbO, Nb₂O₅, NiCO₃, TiO₂ and ZrO₂ were used as starting materials. The sintering aid was reagent-grade MnO₂. In this study, PNN–PT–PZ sintered bodies were fabricated by the two-step solid-state reaction using a columbite precursor.⁶ First, after grinding the mixture of 50 mol% Nb₂O₅ and 50 mol% NiCO₃ for 30 min in ethanol in a planetary zirconia ball mill, it was calcined at 1000°C for 4 h. The obtained powders were used as NiNb₂O₆ which was a precursor for PbNi₁/₃Nb₂/₃O₆. Next PbO, TiO₂ and ZrO₂ were added to the NiNb₂O₆ and ground for 30 min in ethanol in the ball mill described above. After drying the mixture, it was calcined in air at 850°C for 3 h. MnO₂ (0–3.66 mol%) as a sintering aid and 2 mass% polyvinyl alcohol (PVA) solution were added to the calcined powders which were then ground for around 12 h in the same zirconia wet ball mill. After drying the wet powders at 105°C for 1.5 h, they were sieved using a 120 mesh (opening: 125 μm) screen. The granules were pressed at around 196 MPa into discs of 12.0
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mm in diameter. The green compacts were placed in a high-purity MgO crucible and sintered at 1200°C for 3 h in air by the powder-bed method using calcined powders with the same composition as the compacts. The samples were then mirror-polished to a thickness of around 0.3 mm. After drying, silver electrodes were attached to their surfaces by firing silver paste coated on the surfaces of the discs at 800 °C for 10 min in air. The samples were poled under a DC field of 3 MV/m at room temperature in a silicone oil.

The crystalline phase was analyzed using an X-ray diffractometer (XRD; Rigaku, RINT-1500). The bulk density was measured using the Archimedean method. After etching the fractured surfaces of the samples with a mixed acid (HF : HCl : H₂O = 1 : 4 : 14), the microstructures were observed under a field-emission-type scanning electron microscope (FE-SEM; Hitachi, S-900). The average grain sizes were determined by the linear intercept method using FE-SEM photographs. Piezoelectric properties were measured by the resonant-antiresonant frequency method on the basis of EMAS-61007) using an impedance analyzer (Hewlett-Packard, HP4194A). Poisson’s ratio was measured by the ratio, f₂/f₁, of secondary resonant frequency, f₂, and fundamental resonant frequency, f₁, in the radial vibration mode.7) Ferroelectric properties were evaluated from the measurements of P–E hysteresis loops using a home-made computerized conventional Sawyer-Tower circuit.

3. Results and discussion

All the samples with and without MnO₂ addition were confirmed to be of the single-phase perovskite structure (JCPDS Card, No. 34-0103) by powder X-ray diffractometry. The bulk density of the PNN–PT–PZ ceramics decreased slightly in the range of 8.12 to 7.99 × 10³ kg/m³ with increasing the amount of MnO₂ addition. This result suggests that the bulk density is hardly affected by the addition of a small amount of MnO₂.

3.1 FE-SEM observation

The relationship between the average grain sizes calculated from the FE-SEM photographs and the amount of MnO₂ addition is shown in Fig. 1. The average grain size of PNN–PT–PZ ceramics increased with increasing amount of MnO₂ addition. The average grain size of ceramics with 3.66 mol% MnO₂ became around 3.2 times larger than that of ceramics without the MnO₂ additive. In addition, FE-SEM photographs of the fractured surfaces of PNN–PT–PZ ceramics with (a) 0 mol%, (b) 0.93 mol% and (c) 2.76 mol% MnO₂ are shown in Figs. 2 (a)-(c), respectively. It can be seen from Figs. 2 (a) that innumerable distinct pores existed in the grain boundary and no neck bonding developed. On the contrary, it is observed from Fig. 2 (b) that the grains grew simultaneously with the densification of the microstructure. Further addition of MnO₂ yielded undesirable large-sized grains, as indicated in Fig. 2 (c).

3.2 Piezoelectric properties

3.2.1 Relative dielectric constant, ε₃₃/ε₀ and dielectric loss, tan δ

The changes in ε₃₃/ε₀ and tan δ as a function of the amount of MnO₂ addition are shown in Fig. 3. After the value of ε₃₃/ε₀ decreased linearly with an increase in MnO₂, the changes in ε₃₃/ε₀ and tan δ as a function of the amount of MnO₂ addition.
content in the range of 0 to 0.75 mol%, it settled down to 2000-2800 in the range of 0.75 to 3.66 mol%. After tan δ exhibited the minimum value (≈ 0.37%) at 0.75 mol%, it linearly increased with an increase in MnO2 content in the range of 0.93 to 3.66 mol%. As a result, the value of tan δ for ceramics with 3.66 mol% MnO2 became larger than that for ceramics without MnO2 addition. This may be mainly attributable to enhancement of the grain growth and nonuniformity of the microstructure by MnO2 addition. To apply these piezoelectric materials to ultrasonic-wave motors or piezoelectric actuators, it is necessary to lower the value of tan δ as much as possible and suppress the change in material properties by decreasing the generation of heat due to tan δ during operation. From the above results, the significant effects of MnO2 addition in the range of 0.37 to 0.93 mol% were proven.

3.2.2 Electromechanical coupling factors, k31 and k33

Electromechanical coupling factors, k31 and k33, indicate the efficiency to transform electric energy into mechanical energy in the radial vibration mode for thin circular plates and in the length vibration mode for thin rectangular plates, respectively. Figure 4 shows the changes in k31 and k33 as a function of the amount of MnO2 addition. As can be seen from the figure, both coupling factors showed a tendency to decrease with increasing MnO2 content. Moreover, the maximum values of k31 and k33 were 0.66 and 0.38, respectively, and were obtained in the ceramic without MnO2 addition. Electromechanical coupling factors are generally known to increase with an increase in the grain size.2) However, the grain size increases with increasing amount of MnO2 addition from the vicinity of 0.93 mol% as the starting point, whereas k31 and k33 decrease. With respect to Mn addition to PT(PTiO3) and PZT sintered in air, it has been reported9,10) that Mn3+ ions are substituted for the B-sites in the perovskite structure and the charge deficit of Mn3+ ions is compensated by oxygen vacancies. Furthermore, it can also be expected from the report by Moon et al.4) that oxygen vacancies formed by substituting Mn3+ ions for B-site ions (e.g., Ti4+ and Zr4+ ions) increase with increasing amount of MnO2 addition. Accordingly, the above decrease may be caused by the fact that formed oxygen vacancies inhibit the movement of ferroelectric domain walls and the effects of the formation of oxygen vacancies consequently become more dominant than the effects of an increase in grain size in the range of 0.93 to 3.66 mol%.

3.2.3 Young's modulus, Ye

Young's modulus, Ye, is, in general, calculated as a reciprocal number of the compliance, s11. The hardness of PNN-PT-PZ elastic bodies gradually showed a tendency to increase with increasing amount of MnO2 addition in the range of 6.1 to 9.5 × 1010 N/m2. Based on this result, it was found that the MnO2 addition of 3.66 mol% enhanced the hardness of PNN-PT-PZ elastic bodies up to around 1.5 times that of the sample without MnO2 addition.

3.2.4 Piezoelectric constants, d31 and g31

The piezoelectric constant, d31, indicates the piezoelectric strain coefficient, whereas, g31 denotes the voltage output coefficient regarding the radial vibration mode. The changes in d31 and g31 as a function of the amount of MnO2 addition are shown in Fig. 5. The piezoelectric constant, d31, was derived from

\[ d_{31} = k_{31} \left( \varepsilon_{33}^{T} / Y_e \right)^{1/2} \] (C/N)

where \( \varepsilon_{33}^{T} \) is the dielectric constant and \( Y_e \) is Young's modulus (N/m²). The value of \( d_{31} \) is expected to be strongly affected by their behaviors as \( d_{31} \) has a proportional relation to \( k_{31} \) and \( (\varepsilon_{33}^{T})^{1/2} \), as seen in Eq. (1). Therefore, \( d_{31} \) showed a tendency to decrease with increasing MnO2 content, as well as the changes in \( \varepsilon_{33}^{T} / \varepsilon_0 \) (Fig. 3) and \( k_{31} \) (Fig. 4). Compared with \( d_{31} \) values (from ~131 to ~303 pC/N) of commercial piezoelectric ceramics4,8) for actuators and ultrasonic-wave motors, those (from ~185 to ~188 pC/N) of PNN-PT-PZ ceramics with 0.75 and 0.93 mol% MnO2 can be sufficiently applied to practical materials. On the other hand, \( g_{31} \) indicated almost the opposite change to \( d_{31} \), as can be seen from the figure. The high values (from ~7.0 to ~7.6 mV·m/N) of \( g_{31} \) were obtained in the range of 0.75 to 3.66 mol%.

3.2.5 Poisson's ratio, \( \sigma \) and mechanical quality factor, \( Q_m \)

The changes in \( \sigma \) and \( Q_m \) as a function of the amount of MnO2 addition are shown in Fig. 6. As shown, \( \sigma \) of the sample without MnO2 addition exhibited the highest value of 0.35, whereas those of samples with MnO2 less than 3.66 mol% were in the range of 0.28 to 0.32. To utilize piezoelectric ceramics as practical materials, it is, on the other hand, important to obtain the appropriately sharp mechanical vibration in the vicinity of the resonant frequency by improving \( Q_m \). The mechanical quality factor of the sample without MnO2 addition was an extremely low value of 50.7, while those of samples with 0.93-1.85 mol% MnO2 were 1050 to 1060, corresponding to around twenty times that of the sample without MnO2 addition. Moon et al.4 previously reported that they added a small amount of MnO2 to 0.25PNN-0.39PPT-0.36PZ, unlike our composition, and \( Q_m \) could be consequently improved appreciably. We disclosed that, similar to the case of Moon et al.,11 the effects of MnO2 addition were also obtained in 0.5PNN-0.345PPT-0.155PZ.
and the optimum amount of MnO₂ addition to obtain high Qₘ was in the range of 0.93 to 1.85 mol%.

3.3 Ferroelectric properties

Figure 7 shows P-E hysteresis loops for typical PNN–PT–PZ ceramics without and with MnO₂ additive. As can be seen in Figs. 7(A–1) and (A–2), there was no difference in the shape of P–E hysteresis loops measured at the positive and negative directions of applied voltage and a high spontaneous polarization, Pₛ (≈34.4 μC/cm²), remanent polarization, Pᵣ (≈24.3 μC/cm²), and a small coercive field, Eᵦ (≈6.2 kV/cm), were obtained in the case of the sample without MnO₂ addition. On the other hand, in the case of the sample with 0.75 mol% MnO₂, the shapes of both P–E loops observed in the positive polarization region of Fig. 7(B–1) and in the negative polarization region of Fig. 7(B–2) are very similar to those of normal ferroelectrics, whereas the P–E loops observed in the negative polarization region of Fig. 7(B–1) and in the positive polarization region of Fig. 7(B–2) have slightly distorted shapes. However, even this sample exhibited excellent ferroelectricity (Pₛ = 29.9 μC/cm², Pᵣ = 18.1 μC/cm² and Eᵦ = 5.7 kV/cm). Furthermore, in the case of the sample with 3.66 mol% MnO₂, the distortion in the shape of P–E loops observed in the negative polarization region of Fig. 7(C–1) and in the positive polarization region of Fig. 7(C–2) is further emphasized with increasing MnO₂ content. Although we cannot pinpoint a reason for the behavior, it is considered that the distortion in the shape of the above P–E loops

Fig. 6. Changes in σₑ and Qₑ as a function of the amount of MnO₂ addition.

Fig. 7. P–E hysteresis loops for typical PNN–PT–PZ ceramics without and with MnO₂ additive. (A–1) and (A–2): MnO₂ = 0 mol%, (B–1) and (B–2): MnO₂ = 0.75 mol%, (C–1) and (C–2): MnO₂ = 3.66 mol%.
is closely related to oxygen vacancies \((V_0)\) formed by substituting \(Mn^{3+}\) ions for B-site ions (e.g., Ti\(^{4+}\) and Zr\(^{4+}\) ions) in the perovskite structure. If we guess the origin of these occurrences from the viewpoint of the crystal structure, it can be considered that the strain caused by the lack of oxygen atoms occupying the site of each vertex in the oxygen octahedron of the perovskite structure acts as a pinning point in the ferroelectric domains. According to the above interpretation, it is determined from the figures that the polarization reversal can be partially inhibited by the pinning effect which the oxygen vacancies formed by adding a small amount of MnO\(_2\) pin the movement of the ferroelectric domain walls. Moreover, the result of piezoelectric properties previously described is in good agreement with that of ferroelectric properties studied here. It is thus concluded that 0.5PNN·0.345PT·0.155PZ ceramics with 0.75–0.93 mol\% MnO\(_2\), which have \(\tan \delta\) from 0.37 to 0.42\%, \(k_p\) from 0.57 to 0.58, \(d_{31}\) from −185 to −188 pC/N and \(Q_m\) from 602 to 1050, show great promise as practical materials for piezoelectric actuators and ultrasonic-wave motors.

4. Conclusions

We prepared high-density 0.5PNN·0.345PT·0.155PZ ceramics with the addition of 0–3.66 mol\% MnO\(_2\) by normal sintering and investigated the piezoelectric and ferroelectric properties of the samples. The optimum amount of MnO\(_2\) addition was examined from the viewpoint of piezoelectric applications. The results of this study can be summarized as follows:

1. Significant effects of MnO\(_2\) addition in the range of 0.37 to 0.93 mol\% on lowering the value of \(\tan \delta\) were proven. The lowest value (≈0.37\%) of \(\tan \delta\) was obtained in the ceramics with 0.75 mol\% MnO\(_2\).

2. Electromechanical coupling factors, \(k_p\) and \(k_{31}\), and the piezoelectric constant, \(d_{31}\), decreased with increasing amount of MnO\(_2\) addition. The highest values of \(k_p\), \(k_{31}\) and \(d_{31}\) were 0.66, 0.38 and −362 pC/N, respectively, and were obtained in the ceramics without MnO\(_2\) addition. The effect of MnO\(_2\) addition on improving the value of the mechanical quality factor, \(Q_m\), was proven in the range of 0.93 to 1.85 mol\% and the improvement was around twenty times that of the sample without MnO\(_2\) addition.

3. The distortion in the shape of \(P-E\) hysteresis loops for samples with MnO\(_2\) addition suggested that oxygen vacancies which formed by the substitution of Mn\(^{3+}\) ions for B-site ions (e.g., Ti\(^{4+}\) and Zr\(^{4+}\)) in the perovskite structure partially inhibited the polarization reversal in the ferroelectrics.

4. 0.5PNN·0.345PT·0.155PZ ceramics with 0.75–0.93 mol\% MnO\(_2\) which have \(\tan \delta\) from 0.37 to 0.42\%, \(k_p\) from 0.57 to 0.58, \(d_{31}\) from −185 to −188 pC/N and \(Q_m\) from 602 to 1050, show great promise as practical materials for piezoelectric applications.

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