FULL PAPER

Quenching effects on depolarization temperature and ^{18}O tracer diffusion in $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics with acceptor and donor additives

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Lead-free ferroelectric and piezoelectric ceramics, $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT), with Mg and Nb additives were prepared and the concentration of oxygen vacancies as the ^{18}O tracer diffusion of these ceramics were clarified by secondary ion mass spectroscopy (SIMS). Moreover, the samples were quenched after sintering to examine the depolarization temperature T_d , and then their electrical properties were investigated. As a result, the obtained values of volume diffusion coefficient D of BNT doped with 0.4 wt % Mg and 0.4 wt % Nb were determined to be 9.2×10^{-11} and $1.1 \times 10^{-13} \text{ cm}^2/\text{s}$, respectively. The oxygen vacancy concentration increased with the amount of Mg added and decreased with that of Nb added. Moreover, quenching increased T_d by $\sim 50^\circ\text{C}$ in BNT with the Mg additive (Mg x) and ΔT_d also increased. Thus, the effect of quenching was promoted by Mg x . On the other hand, the T_d of BNT with the Nb additive (Nb y) also increased despite the low concentration of oxygen vacancies. This is because the D of pure BNT (no additives) was revealed found to be $2.5 \times 10^{-11} \text{ cm}^2/\text{s}$, that is, pure BNT originally contained a high concentration of oxygen vacancies. The concentration was maintained even after quenching, then D showed $1.8 \times 10^{-11} \text{ cm}^2/\text{s}$. In addition, the electromechanical coupling factor k_{33} of the quenched ceramics remained similar to that of the ordinarily fired samples of BNT with the Mg and Nb additives.

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1. Introduction

From the viewpoint of environmental protection, it is necessary worldwide to reduce the discharge of toxic materials from the electric industry. Some regulations such as Restriction of Hazardous Substances have already been applied to prevent the discharge of hazardous waste. Piezoelectric ceramics are widely used in many devices such as ceramic filters, actuators, and sensors. However, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)-based ceramics with a large amount of Pb have been mainly used in piezoelectric applications because of their outstanding properties.^{1),2)} Therefore, the development of lead-free piezoelectric materials is strongly demanded. Candidates for lead-free piezoelectric materials with several perovskite-structure ferroelectrics are reported as follows: BaTiO_3 ,³⁾⁻⁵⁾ $(\text{Bi,K})\text{TiO}_3$,⁶⁾⁻¹⁰⁾ $(\text{Bi,Na})\text{TiO}_3$,¹¹⁾⁻¹⁷⁾ $(\text{K,Na})\text{NbO}_3$,¹⁸⁾⁻²⁵⁾ and their solid-solution systems.

Bismuth sodium titanate, a $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT)-based solid-solution system, exhibits relatively high piezo-

electric properties. The manufacturing method for BNT ceramics is simple, and it is easy to produce a high-density sample. BNT exhibits an effective ferroelectric characteristic with a rhombohedral symmetric ($R3c$) perovskite structure at room temperature (RT).^{17),26)} The remanent polarization P_r of BNT ceramics is relatively large, $38 \mu\text{C}/\text{cm}^2$. In the polarized state of BNT, the orbitals of bismuth (Bi^{3+}) and oxygen (O^{2-}) at the A site hybridize in a perovskite structure.¹⁶⁾ On the other hand, BNT shows a low depolarization temperature T_d of $\sim 180^\circ\text{C}$. This is a problem to overcome and hinders the commercialization of this valuable lead-free piezoelectric material. On the basis of the BNT crystal structure, T_d is considered to be a structural phase transition from rhombohedral ($R3c$) to tetragonal ($P4bm$)^{17),27)} or orthorhombic ($Pnma$).^{16),28)} As the temperature increases, the hybrid orbitals of Bi^{3+} and O^{2-} disappear, and hence, the BNT ceramics depolarize.¹⁶⁾ Such a contribution of the bonding enhances disorder in the lattice, and then the structural phase of the unit cell changes from $R3c$ to $P4bm$ or $Pnma$.^{16),17),27)-29)}

The quenching process after sintering is effective to increase the T_d of BNT ceramics with the rhombohedral phase and the quenching does not deteriorate their piezoelectric and ferroelectric properties.^{30),31)} The T_d of BNT ceramics reaches 223°C after quenching from 1100°C ,

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that is, the T_d is about 50°C higher than that by the conventional cooling process. Moreover, $(0.96 - x)\text{BNT} - 0.04(\text{Bi}_{0.5}\text{La}_{0.5})\text{TiO}_3 - x(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ ceramics have T_d higher than 300°C in the tetragonal phase ($x = 0.4$) and the T_d elevates 223°C at the morphotropic phase boundary composition of $x = 0.18$ owing to the quenching effect.³²⁾ The increase in T_d strongly correlates with increase in the lattice distortion $90^\circ\alpha$ on a rhombohedral phase caused by the quenching procedure. Such an increase in the $90^\circ\alpha$ was also found by Yoneda et al., in Li-substituted BNT (BNLT) ceramics.³³⁾ The T_d of BNLT increased by $\sim 20^\circ\text{C}$, which is higher than that of pure BNT.³⁴⁾ From the observed enhancement of $90^\circ\alpha$, Bi ions play an important role.³⁵⁾ Bi ions are considered to slightly move to the off-center position around the A site at high temperatures, as shown by average structural analysis such as Rietveld refinement and Monte Carlo simulations.^{36)–38)} Quenching freezes the off-centered structure and stabilizes the $R3c$ structure.²⁹⁾ On the other hand, recently, the Ti off-center has been demonstrated by local structural analysis.³⁹⁾ Both of these reports showed that the order of the crystal structure is commonly enhanced by the quenching process. In addition, it is necessary to elucidate the origin of the off-center structures formed by quenching. After quenching, the concentration of oxygen vacancies was found to increase by X-ray photoelectron spectroscopy⁴⁰⁾ and electrical conductivity⁴¹⁾ analysis of BNT-based ceramics. It is very important to examine the contribution of oxygen vacancies to the quenching effects on BNT to clarify the mechanism underlying these effects. We focus on controlling the concentration of oxygen vacancies with additives.

Mg^{2+} or Mn^{3+} ions as additives substitute for the Ti^{4+} sites in the BNT ceramics with the perovskite structure; and subsequently, oxygen vacancies are produced to compensate for the electrical neutrality. That is, Mg^{2+} and Mn^{3+} ions behave as acceptors. Mg^{2+} is expected to generate more oxygen vacancies; because its valency is smaller than that of Mn^{3+} . In contrast, Nb^{5+} ions as additives of reduce the amount of oxygen vacancies; hence, Nb^{5+} ions behave as donors. The acceptor-added BNT ceramics such as Mn-doped BNT ceramics, have improves high-power characteristics,^{18),42)–45)} which surpass those of hard PZTs.^{46),47)} Also, Mn-doped BNT ceramics have enhance electrical properties such as resistivity and electromechanical coupling, owing to the presence of oxygen vacancies.^{48)–52)} However, the T_d of Mn-doped BNT ceramics gradually decreases with increasing amount of Mn substitution.⁴⁷⁾ In our previous study, the T_d of these ceramics was increased by $\sim 50^\circ\text{C}$ owing to quenching effects. The capability of quenching effects to increase the T_d (ΔT_d) was enhanced by increasing the amount of Mn substitution. At that time, the increase or decrease in the amount of oxygen vacancies was indirectly estimated from the coercive electric field E_c .⁵³⁾ In this study, we added Mg^{2+} ions to BNT as acceptors and then specifically determined the concentration of oxygen vacancies as the ^{18}O tracer diffusion by secondary ion mass spectroscopy (SIMS) and electrical measurement. Nb^{5+} ions were also added to BNT as donors

and the concentration of oxygen vacancies in these samples was compared with that in samples with acceptors. On the basis of the concentration of oxygen vacancies, we examined the electrical characteristics and the effect of quenching on the T_d of these ceramics and then considered the contribution of the oxygen vacancies to quenching effects.

2. Experimental procedure

$(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 + \text{MgO } x$ ($\text{Mg } x$, $x = 0, 0.05, 0.1, 0.2, 0.4, 0.8$ wt % of BNT) and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 + \text{Nb}_2\text{O}_5 y$ ($\text{Nb } y$, $y = 0, 0.4, 0.8, 1.2$ wt % of BNT) were prepared by a conventional solid-phase reaction process. Reagent-grade powders of Bi_2O_3 (Kojundo Chemical Laboratory Co., Ltd.), TiO_2 (Kojundo Chemical Laboratory Co., Ltd.), Na_2CO_3 (Sigma-Aldrich Co., LLC.), MgO (Soekawa Chemical Co., Ltd.), and Nb_2O_5 (Mitsui Mining & Smelting Co., Ltd.) were mixed for 20 h in ethanol by ball milling. The mixture was calcined at 850°C for 2 h after drying and then mixed again for 20 h. Next, these samples were compressed at 150 MPa using a cold isostatic press. The samples were sintered at 1140°C for 2 h and cooled to RT at a rate of -200°C/h in the ordinary firing (OF) process, which is referred to as OF-Mg x or OF-Nb y as shown in Fig. 1. Some samples were sintered and then removed from an electric furnace at 1100°C . These ceramics were exposed to the atmosphere and were immediately cooled to RT with a blower. These quenched samples are referred to here as q-Mg x and q-Nb y . The crystal structure and lattice constant were measured by X-ray diffraction using $\text{Cu K}\alpha$ radiation (XRD: Rigaku RINT-2000, 40 kV, 40 mA). Each sample was polarized under optimum conditions close to saturation, and the piezoelectric characteristics were measured by the resonance–antiresonance method based on the IEEE standards using an impedance analyzer (HP4294A). The depolarization temperature T_d was estimated from the temperature dependence of the electromechanical coupling factor k_{33} . P – E hysteresis loops were evaluated using a virtual ground system (Toyo Corporation; Model 6252 Rev. C) at RT and 10 Hz. The ^{18}O concentration profile was measured using the SIMS system (Cameca IMS-4F) of the National Institute for Materials Science, Japan. $^{133}\text{Cs}^+$ accelerated at

Fig. 1. Sintering process for OF and quenched ceramics.

10 kV was used as a primary ion beam to irradiate the sample surface. The primary beam was scanned in a raster over an area of $100 \times 100 \mu\text{m}^2$ on the sample surface. To be stabilized the potential at the surface during $^{133}\text{Cs}^+$ irradiation, a Cameca normal-induced electron gun was used during the analyses. The measurement area of secondary ions is defined by the dynamic transfer system, and the window of its raster area is 40–50 %. Secondary ions, $^{16}\text{O}^-$ (reference mass) and $^{18}\text{O}^-$, from this area were measured using an electron multiplier. The concentration profile was calculated from oxygen intensities as

$$C = \frac{I(^{18}\text{O})}{I(^{18}\text{O}) + I(^{16}\text{O})}, \quad (1)$$

where $I(^{16}\text{O})$ and $I(^{18}\text{O})$ are the intensities of ^{16}O and ^{18}O , respectively. The volume diffusion contribution in the profile was fitted of a solution to the diffusion equation for a constant concentration at the surface as

$$\frac{C_x - C_{\text{bg}}}{C_s - C_{\text{bg}}} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \quad (2)$$

where C_x is the ^{18}O concentration at depth x , C_s the surface concentration of ^{18}O , and C_{bg} the background natural abundance of ^{18}O . Equation (2) presumes an equilibrium between the crystal surface and the gas phase, and thus a constant C_s value. D and t are the volume diffusion coefficient and annealing time, respectively.

3. Results and discussion

In both OF and quenched samples, the relative densities of Mg x and Nb y were higher than 90 % of the theoretical densities. **Figure 2** shows the XRD patterns of BNT, Mg 0.4, and Nb 0.4 for OF and quenched samples, respectively. The XRD patterns indicated a single-phase perovskite structure with rhombohedral phases. Thus, no secondary phases were observed in these samples with additives and quenching. The lattice constants of OF-Mg x and OF-Nb y were estimated from these patterns. The average lattice constant of the a -axis was 3.90 Å in the rhombohedral

Fig. 2. XRD patterns of BNT, Mg 0.4, and Nb 0.4 ceramics indicated by black, blue, and red lines, respectively. The solid and dotted lines with rhombohedral plane indices represent OF and quenching, respectively.

perovskite structures and was maintained even after quenching.

Figure 3 shows the ^{18}O tracer diffusion profiles of OF-Mg 0.4 and OF-Nb 0.4 samples annealed in ^{18}O atmosphere at 450 °C for 30 min. The volume diffusion coefficients D of ^{18}O in Mg 0.4 and Nb 0.4 were 9.2×10^{-11} and $1.1 \times 10^{-13} \text{ cm}^2/\text{s}$, respectively. The D of the Mg 0.4 was larger than that of the Nb 0.4. In a previous study, the D of BNT doped at approximately the same concentration as that of Mg 0.4 with ^{18}O -annealing at 632 °C was $1.2 \times 10^{-8} \text{ cm}^2/\text{s}$.⁵⁴⁾ The D of pure-BNT with ^{18}O -annealing at 632 °C was reported to be $2.6 \times 10^{-10} \text{ cm}^2/\text{s}$ and that with ^{18}O -annealing at 650 °C was $8.0 \times 10^{-12} \text{ cm}^2/\text{s}$.⁵⁵⁾ That is, the D of Mg-doped BNT is significantly higher than that of pure-BNT. Thus, many oxygen vacancies were contained in Mg 0.4. That is, the concentration of oxygen vacancies increased with the amount of Mg-substitution. Mg^{2+} ions substitute for Ti^{4+} at the B-site of the perovskite structure similarly to Mn^{3+} ions;^{48)–50)} subsequently, oxygen vacancies are produced to compensate for the electrical neutrality. On the other hand, in the case of Nb y , the concentration of oxygen vacancies was decreased by Nb-substitution. To examine the effects of Mg and Nb additives on ferroelectric properties, the P – E hysteresis loops were compared among OF-BNT, -Mg 0.4, and -Nb 0.4 samples at RT and 10 Hz as shown in **Fig. 4(a)**. These loops were fully saturated and showed good rectangularity. The E_c values of BNT, Mg 0.4, and Nb 0.4 were 68.4, 99.7, and 63.5 kV/cm, respectively. The E_c of Mg 0.4 was larger and that Nb 0.4 was slightly smaller than that of BNT. The concentration of oxygen vacancies in Mg x is higher than that in Nb y , because the valency of Mg^{2+} is higher than that of Nb^{5+} . Therefore, E_c of OF-Mg 0.4 was significantly larger than those of OF-Nb 0.4 and OF-BNT. **Figure 4(b)** shows the E_c values of OF-Mg x and OF-Nb y as a function of the substitution amounts x and y , respectively. The units of wt % was converted to mol % for comparison with the amount of Mg x and Nb y additives. The E_c of OF-Mg x increased from 68.4 to 108.9 kV/cm with Mg-substituted amount x , and the E_c of Nb y did not change significantly depending on the Nb substituted

Fig. 3. ^{18}O tracer diffusion profiles of Mg 0.4 and Nb 0.4 after exchange at 450 °C for 30 min, shown by blue and red lines, respectively.

Fig. 4. (a) P - E hysteresis loops of BNT, Mg 0.4, and Nb 0.4 shown by black, blue and red lines, respectively. (b) E_c of the substituted amount of OF-Mg x and OF-Nb y .

Fig. 5. Resistivity as a function of substituted amounts of OF-Mg x and OF-Nb y .

amount of y . The oxygen vacancies are reported to pin the domain switching^{56)–58)} and make poling difficult owing to the pinning effects on domain walls. The concentration of oxygen vacancies contributes to E_c in the P - E hysteresis loop.^{59),60)} Thus, the E_c of Mg x increases, owing to the suppression of domain wall vibration. In contrast, the concentration of oxygen vacancies is low in Nb y ; hence, the contribution of the domain-pinning effect to E_c is small. Furthermore, the resistivities ρ of OF-Mg x and OF-Nb y were compared to estimate the concentration of oxygen vacancies, as shown in Fig. 5. The amount of Mg x decreased with the amount of Mg-substitution. In contrast, the ρ of OF-Nb y increased with the amount of Nb-substitution. That is, since BNT is originally of the P-type, the charge approached neutrality upon adding donors, Nb_2O_5 ; subsequently, ρ increased. From the above results, we considered that the concentration of oxygen vacancies can be controlled using additives, Mg as acceptors and Nb as donors. Next, we examined the effects of quenching on the piezoelectric properties and the depolarization temperature T_d in these samples.

Figure 6 shows the piezoelectric properties (a) k_{33} , (b) d_{33} , and (c) $\varepsilon_{33}^T/\varepsilon_0$ of OF- and q-Mg x as functions of the Mg-substituted amount x , and (d) k_{33} , (e) d_{33} , and (f) $\varepsilon_{33}^T/\varepsilon_0$ of OF- and q-Nb y as functions of the Nb-substituted

amount y . The k_{33} and d_{33} values of OF-Mg x were almost the same from $x = 0.002$ to $x = 0.01$ mol, as shown in Figs. 6(a) and 6(b). This tendency was similar to that observed in the quenched sample. The d_{33} slightly decreased after quenching. At $x = 0.02$ mol, the k_{33} and d_{33} of OF-Mg x sharply decreased; this is because of the high concentration of oxygen vacancies injected into BNT, as shown in Fig. 3. These oxygen vacancies pinned the domain walls⁶⁰⁾ and thus increase the coercive electric field E_c . As a result, OF-Mg x with $x = 0.02$ mol was not fully poled. In the quenched sample, the domain-wall pinning effect is small because the oxygen vacancies were dispersed without gathering around the domain walls; subsequently, these samples were easily poled. In addition, at $x = 0.045$ mol, the density of ceramics decreased because the concentration of oxygen vacancies was too high; hence, they were difficult to pole sufficiently. On the other hand, the k_{33} and d_{33} values of Nb y remained almost the same, as shown in Figs. 6(d) and 6(e). In the case of Nb y , the E_c tended to decrease, as shown in Fig. 4(b); subsequently, poling easily occurred because the concentration of oxygen vacancies was small as shown in Fig. 3. The k_{33} of Nb y remained the same and d_{33} slightly decreased after the quenching. Also, the relative free permittivity $\varepsilon_{33}^T/\varepsilon_0$ of quenched samples was lower than that of OF-samples as shown in Figs. 6(c) and 6(f). In the quenched samples, previous reports reveal that the enhancement of lattice distortion enhances the order of the lattice structure and then stabilizes the structural phase.²⁹⁾ Our results (Fig. 7) also showed that the lattice distortion was enhanced by quenching, and we considered that the lattice of the quenched samples has a more ordered structure than that of OF-samples. The stabilization of the order of the ferroelectric phase reduces $\varepsilon_{33}^T/\varepsilon_0$.⁵³⁾ $\varepsilon_{33}^T/\varepsilon_0$ showed a similar trend to d_{33} ; hence, the reduction in d_{33} caused by the quenching depended on $\varepsilon_{33}^T/\varepsilon_0$.

Figure 7(a) shows the T_d values of OF- and q-samples for Mg x and Nb y as a function of the substituted amounts x and y , respectively. The T_d values of OF-samples decreased from 180 °C for $x = 0$ to 158 °C for $x = 0.01$ mol for Mg x , and from 180 °C for $x = 0$ to 118 °C for $y =$

Fig. 6. Piezoelectric properties (a) k_{33} , (b) d_{33} , and (c) $\epsilon_{33}^T/\epsilon_0$ as functions of Mg-substituted amount x in OF- and q-Mg x . Similarly, (d), (e), and (f) are those of the Nb substituted amount of y in OF- and q-Nb y .

Fig. 7. (a) T_d of Mg x and Nb y in OF- and q-samples. (b) Rhombohedral distortions, $90-\alpha$, of Mg x and Nb y in OF- and q-samples.

0.02 mol for Nb y . Thus, the T_d values of OF-Mg x and OF-Nb y decreased with increasing in the substituted amount of x and y . Also, the T_d values of quenched Mg x and Nb y increased by $\sim 50^\circ\text{C}$ compared with those of OF-samples. The lattice distortion values $90-\alpha$, of Mg x and Nb y are shown in Fig. 7(b). The $90-\alpha$ of OF-Mg x and OF-Nb y decreased with increasing in the substituted amount of x and y . Moreover, the $90-\alpha$ values of each quenched Mg x and Nb y were larger than those of OF-samples. Therefore, T_d strongly correlated with $90-\alpha$. These results are consistent with previously reported trends.^{30)–32)} Furthermore, we examined the capability of quenching effects on T_d . **Figure 8** shows a significant difference in T_d between OF- and quenched samples (ΔT_d). ΔT_d increased with the substituted amount of Mg, and this trend was similar to that of BNT added with Mn³⁺.⁵³⁾ That is, quenching was effective on the T_d of Mg x with a high

Fig. 8. Dependences of ΔT_d for Mg x and Nb y .

concentration of oxygen vacancies. Mg²⁺ add at a smaller amount than Mn³⁺⁵³⁾ increased the T_d . This result supports our assumption that the oxygen vacancy concentration

Fig. 9. ^{18}O tracer diffusion profiles of (a) OF- and (b) q-BNT after exchange at 450°C for 30 min.

contributes to the quenching effect. On the other hand, the ΔT_d for Nb y also tended to increase despite the low concentration of oxygen vacancies. As a result, the quenching effect was promoted by not only Mg^{2+} but also Nb^{5+} regardless of the concentration of oxygen vacancies. Here, to determine the reason for this result, the concentration of oxygen vacancies as the ^{18}O -tracer of pure-BNT (no additives) was measured by SIMS, as shown in Fig. 9. The D of OF-pure BNT was $2.5 \times 10^{-11} \text{ cm}^2/\text{s}$, which was similar to that of an ion conductor.⁵⁴⁾ The OF-pure BNT originally contained a high concentration of oxygen vacancies. Moreover, the D of q-pure BNT was $1.8 \times 10^{-11} \text{ cm}^2/\text{s}$. In the pure-BNT, D did not change significantly even after quenching. Thus, additive-controlled oxygen vacancies did not contribute significantly to the quenching effects on T_d because pure BNT already contained a high concentration of oxygen vacancies.

4. Conclusion

The concentration of oxygen vacancies was controlled by the Mg and Nb additives in BNT and the concentration was clarified by ^{18}O tracers. For each sample, the effects of quenching on the T_d and electrical properties were revealed. The concentration of oxygen vacancies increased with the amount of Mg added and decreased with that of Nb added. Moreover, quenching increased T_d by $\sim 50^\circ\text{C}$ in Mg x and ΔT_d also increased. Thus, the effect of quenching was promoted for Mg x with a high concentration of oxygen vacancies. Mg^{2+} added at an amount smaller than that of Mn^{3+} previously reported⁵³⁾ increased T_d . On the other hand, the T_d of Nb y also increased despite the low concentration of oxygen vacancies. This means that pure BNT originally contained a high concentration of oxygen vacancies and the concentration was maintained even after quenching. Additionally, the values of k_{33} of the quenched ceramics remained similar to those of the OF samples in BNT with Mg and Nb additives. Thus, the quenching process did not degrade the electrical properties.

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