Reactive sintering and piezoelectric properties of 0.94Bi0.5Na0.5TiO3–0.06BaTiO3 ceramics with ZnO additive

Tasuku KAWASHIMA* and Yoshikazu SUZUKI**,***

*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1–1–1 Tennodai, Ibaraki 305–8573, Japan
**Faculty of Pure and Applied Sciences, University of Tsukuba, 1–1–1 Tennodai, Ibaraki 305–8573, Japan

Bismuth sodium titanate (Bi0.5Na0.5TiO3, BNT) and its solid-solution with BaTiO3 (BNT–BT) are promising lead-free piezoelectric ceramics. Around the morphotropic phase boundary (MPB), the 0.94BNT–0.06BT composition shows high piezoelectric performance. In this paper, we have investigated the effect of ZnO-doping on the reactive sintering and piezoelectric properties of 0.94BNT–0.06BT ceramics. Bi2O3, anhydrous Na2CO3, TiO2 (anatase), BaCO3 and ZnO powders were wet ball-milled in ethanol, cold isostatically pressed at 200 MPa for 10 min, and reactively sintered at 1150°C for 2 h in air. The relative density drastically increased from 83.3% (without ZnO) to 93.7% (with 0.5 mol% ZnO). The sample with 0.5 mol% ZnO showed the highest piezoelectric constant d33 of 124 pC/N. Even by the one-step reactive sintering, the d33 value was comparable with that of the two-step conventional sintering.

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1. Introduction

Currently, lead-based piezoelectric ceramics [e.g. Pb(Zr,Ti)O3 or PZT families] are widely used, however, many problems are suggested during the manufacturing and after the use because of the toxicity of lead. Among the many studies about lead-free piezoelectric ceramics, bismuth sodium titanate (Bi0.5Na0.5TiO3, BNT) is promising due to its high Curie temperature of 320°C,1,2) relatively high piezoelectric constant of d33 = 72.9 pC/N,3,4) facile processing, and so on. Takenaka et al.4) reported that much higher piezoelectricity was obtained for Bi0.5Na0.5TiO3–BaTiO3 (BNT–BT) solid solutions; there is a morphotropic phase boundary (MPB) around the 0.94BNT–0.06BT composition, which showed the maximum piezoelectricity (d33 = 125 pC/N).

Recently, we have reported an environmental friendly processing of BaTiO3 piezoelectric ceramics, viz., one-step reactive sintering.5) Besides the low energy consumption, the merits of reactive sintering are to reduce the contamination during the milling after calcination and to suppress the compositional change by volatilization. However, the reactive sintering method is hardly applied for the industrial process for piezoelectric ceramics because of its less densification compared with the conventional sintering (i.e., two-step heating including preliminary calcination and main sintering). The relative density of the reactively sintered BaTiO3 (without additive) was at most ~85%.5)

To improve the densification of BNT–BT ceramics, oxide sintering additives were used not only for the conventional sintering (e.g. with Nb2O5, La2O3, Co3O4 and CeO2,6,7) but also for the reactive sintering (with In2O3).8) Zhou et al.9) reported that In2O3-doping was effective to improve the densification, and the 0.93BNT–0.07BT ceramics with 0.16 wt.% In2O3 doping, reactively sintered at 1150°C for 3 h, exhibited a high piezoelectric constant of d33 = 205 pC/N. However, the relative density, the elemental distribution and the temperature dependence of dielectric constants were not reported in their report.

In this paper, we have tried to use another oxide additive, ZnO, for the reactive sintering of 0.94BNT–0.06BT ceramics. ZnO was used as an additive for the conventional sintering of BT9) and BNT ceramics,10,11) however as far as we know, it is not used for the reactive sintering of BNT–BT. The effect of ZnO doping on the density, piezoelectric properties and the temperature dependence of dielectric constants were investigated in detail.

2. Experimental procedure

Targeting the final compositions of 0.94BNT–0.06BT + 0.01xZnO (x = 0–5), Bi2O3 (99.9% purity, Wako Pure Chemical Industries Ltd., Osaka, Japan), anhydrous Na2CO3 (99.8% purity, Wako), TiO2 (anatase) (99% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), BaCO3 (99.9% purity, Wako) and ZnO (99.9% purity, Wako) powders were used. These powders were wet ball-milled in ethanol with ZrO2 balls for 8 h in a polyethylene bottle. The slurry was dried in a rotary evaporator to obtain the mixed powders, and then, they were sieved through a 150 mesh (~<100 μm) screen. Green disk-shape pellets (15 mm in diameter and ~2 mm in thickness) was prepared by uniaxial metallic die pressing (22.2 MPa) for 1 min. The green compacts were cold isostatically pressed at 200 MPa for 10 min. The green samples were degassed at 500°C for 2 h, and then sintered at 1150°C for 2 h in an air atmosphere, with heating rate of 100°C/h in each step. In an alumina crucible, platinum wires were used to prevent the direct contact between the samples and the crucible.

Constituent phases of sintered samples were analyzed by X-ray diffraction (XRD, Multiflex, Cu-Kα, 40 kV and 40 mA, Rigaku, Japan). Prior to the XRD measurement, sintered samples were crushed and pestled with an agate mortar using ethanol, and the XRD patterns were collected in the range of 2θ = 10–70°. ICDD-JCPDS database was used to identify the constitution phases.

Surface microstructure of the sintered samples was observed by scanning electron microscopy (SEM, JSM-5600/SV, JEOL, USA).
can be attributed to an impurity phase, most probably \( \text{Zn}_2\text{TiO}_4 \) quality factor (planar electromechanical coupling factor \( k_p \)) and mechanical quality factor \( Q_m \) were measured by the resonance-antiresonance method by using the impedance analyzer. For the calculation of \( k_p \) and \( Q_m \), the following equations were used:

\[
k_p = \frac{1}{\sqrt{0.395 + \frac{f_a}{f_r} - 0.574}}
\]

\[
Q_m = \frac{1}{2\pi f_r R_1 C_1 \left(1 - \left(\frac{f_c}{f_r}\right)^2\right)}
\]

where \( f_r \) (Hz): Resonance frequency, \( f_c \) (Hz): Antiresonance frequency, \( R_1 (\Omega) \): Impedance at \( f_c \), and \( C_1 (\text{F}) \): Capacity at 1 kHz.

3. Results and discussion

Figure 1 shows XRD patterns of sintered samples. Almost single phase of the rhombohedral perovskite structure was obtained for each sample. The peaks were slightly shifted to lower angles with increasing \( x \) [Fig. 1(b)], which can be attributed to the lattice expansion by the substitution of \( \text{Zn}^{2+} \) into \( \text{Ti}^{4+} \) (6-coordination) for Ti\(^{4+}\) \( \cdot \text{Ba}^{2+} \text{TiO}_3 \) (6-coordination). Only in \( x = 5 \), a very small peak was detected around \( 2\theta = 35.1^\circ \). The strongest peak of \( \text{Zn}_2\text{TiO}_4 \) locates at \( 2\theta = 35.1^\circ \).

Figure 2 demonstrates the surface microstructure of sintered samples. Comparing Figs. 2(a) and 2(b) \( (x = 0 \) and 0.5), the grain shape at the surface was changed from roundish to cubic-like, and the grain size increased with increasing \( \text{ZnO} \) doping. The samples with \( \text{ZnO} \) doping had dense microstructure, and that of \( x = 0.5 \) showed the finest microstructure among them. With increasing \( \text{ZnO} \) content [Figs. 2(c)–2(e)], cubic-like grain shape gradually changed into irregular shapes. In Figs. 2(d)–2(e) \( (x = 3 \) and 5), grain boundary glassy phase was observed, which contained somewhat more \( \text{Na}^+ \) ions (confirmed by EDS analysis, see Fig. S1). In Fig. 2(e) \( (x = 5) \), some second-phase particles with triangle shape were observed; the second phase will be \( \text{Zn}_2\text{TiO}_4 \), which is in good agreement with the XRD analysis. Figure 3 shows the EDS analysis for the mirror polished sample of \( x = 5 \). Within the sample (i.e., not on the surface) [Fig. 3(a)], the darker contrast corresponds to the glassy phase (Na, Ti, and \( \text{Zn} \), and \( \text{Ba} \)). The brighter contrast corresponds to the matrix. \( \text{Bi} \) was mainly dispersed in the matrix, whereas \( \text{Ba} \) and Ti were dispersed in both areas.

Figure 4 shows the density changes with \( \text{ZnO} \) doping. The relative density in the figure was calculated from theoretical X-ray density (determined by Rietveld analysis, see Table S1). Note that the theoretical densities of \( \text{BNT} \) and \( \text{BT} \) are 5.992 (13) and 6.012 \( \text{g/cm}^3 \) (14), respectively (the glassy phase was ignored in this calculation). The relative density drastically increased from 83.5\% \( (x = 0) \) to 93.6\% \( (x = 0.5) \), and was saturated (ca. 92–95\%) which was in good agreement with the SEM observation in Fig. 2. The real relative density (considering the glassy phase and \( \text{Zn}_2\text{TiO}_4 \)) will be somewhat higher. According to these results, a small amount of \( \text{ZnO} \) is effective for the densification. With \( \text{ZnO} \) doping, the densification was accelerated by the liquid phase formation and the oxygen defect formation (accompanied by the \( \text{Zn}^{2+} \) substitution into the B-site of the perovskite structure).

Figure 5 shows the temperature dependence of dielectric constant and dielectric loss (tan \( \delta \)) at 1 kHz: (a, c) before poling, and (b, d) after poling. In Fig. 5(a), before poling, the peak-top values of dielectric constant were clearly observed for \( x = 0 \) and 0.5 at \( \sim 220^\circ \text{C} \). However, for \( x \geq 1 \), the peaks became gentle and the
peak-top shifted to somewhat higher temperatures (~230°C). In Fig. 5(b), after poling, clear inflection points were observed at ~100–150°C, which can be attributed to the depoling temperature. The depoling temperature increased with increasing ZnO doping. In Fig. 5(c), before poling, tan δ steeply increased for \( x \geq 1 \), however, tan δ kept small for \( x = 0 \) and 0.5. In Fig. 5(d), after poling, clear inflection points were also observed for tan δ \( (x = 0.5) \), similarly to the dielectric constant.

In Figs. 5(a)–5(d), different trends were seen in each graph shape before and after the \( x = 0.5 \). The different trends can be explained as follows. Thinking about the effective ionic radius, doped Zn\(^{2+}\) ions tend to substitute the Ti\(^{4+}\) ions in the B-site, and hence, oxygen defects will be introduced to compensate the charge balance. Such oxygen defects can act as conductive paths, which resulted in the increase of the electric conductivity. Moreover, at >200°C, the charge distributes not only at the surface but also the sample inside, which increases the dielectric constants and tan δ.

After the poling, the planar electromechanical coupling factor \( (k_p) \) and mechanical quality factor \( (Q_m) \) were calculated from the

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**Fig. 3.** EDS analysis of 0.94BNT–0.06BT + 0.05ZnO sintered at 1150°C for 2 h: (a) SEM image, (b) Bi, (c) Na, (d) Ti, (e) Ba and (f) Zn. The brightness of Zn was amplified. Before the analysis, the sample was heated at 400–500°C for 30 min to remove the possible contamination from the diamond slurry.

**Fig. 4.** Density of 0.94BNT–0.06BT + 0.01xZnO \( (x = 0–5) \) sintered at 1150°C for 2 h.

**Fig. 5.** Temperature dependence of dielectric constant and dielectric loss at 1 kHz; (a, c) before poling, and (b, d) after poling. In (b, d), the result of \( x = 0 \) after poling was not shown because the \( x = 0 \) sample was so porous that the high electric field could not be applied.
frequency dependence of impedance for each sample [Fig. 6(a)]. The highest $k_p$ was observed on $x = 0.5$, which suggests the highest piezoelectric constant is expected on this composition. $Q_m$ increased with increasing ZnO doping. High $Q_m$ materials tend to have higher Curie temperature and lower piezoelectric constant than low $Q_m$ materials, which are in good accordance with Fig. 5(b).

Figure 6(b) represents the piezoelectric property. The sample of $x = 0.5$ showed the highest $d_{33}$ value of 124 pC/N. The highest piezoelectric property is attributable to the faceted cubic-like grains and fine microstructure, as can be seen in Fig. 2(b), enabling the easy poling. Somewhat lower $d_{33}$ values for $x \geq 1$ can be explained by the grain growth (>10 µm), as shown in Figs. 2(c)–2(e), and hence, by the lower dielectric constant at room temperature [Fig. 5(a)]. For the $x \geq 1$, $d_{33}$ was almost constant of ~110 pC/N. As discussed in Fig. 3, excess Zn$^{2+}$ ions tend to form the glassy phase, and hence, the BNT–BT matrix composition will be almost constant around the solid solubility limit. Resonance–antiresonance measurements suggest that the further optimization of poling state is still needed in this system (Fig. S2).

From this study, ZnO doping is really effective to obtain dense reactively-sintered BNT–BT; the sample of $x = 0.5$ is favorable for the near-room temperature applications with high piezoelectric properties, and the samples of $x \geq 1$ are suitable for applications at somewhat higher temperatures with moderate piezoelectric properties.

4. Conclusions

In this study, the effect of ZnO doping on the density, piezoelectric properties and the temperature dependence of dielectric constants were investigated.

(1) We succeeded in the densification of reactively sintered 0.94BNT–0.06BT solid solution by doping 0.5 mol% ZnO. The nominal relative density drastically increased from 83.3% (without ZnO) to 93.7% (with 0.5 mol% ZnO).

(2) For all compositions, the depoling temperature was at ~100–150°C.

(3) The sample with 0.5 mol% ZnO showed the highest $k_p$, the lowest $Q_m$ and the highest $d_{33}$ of 124 pC/N. The sample with 0.5 mol% ZnO is favorable for the near-room temperature applications with high piezoelectric properties, and the samples with ≥1 mol% ZnO are suitable for applications at somewhat higher temperatures with moderate piezoelectric properties.

(4) Even by the one-step reactive sintering, the $d_{33}$ value was comparable with that of the two-step conventional sintering. This result will contribute environmental-friendly processing of lead-free piezoelectric ceramics.

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