TECHNICAL REPORT

Preparing 0.15BaTiO₃–0.85(Bi_{0.5}Na_{0.5})TiO₃ ceramics using spark plasma sintering

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Sodium bismuth titanate [(0.15BaTiO₃–0.85(Bi_{0.5}Na_{0.5})TiO₃], hereafter 0.15BT–0.85BNT, powder was prepared using hydrothermal synthesis. The particle size was approximately 0.1 μm. In addition, 0.15BT–0.85BNT ceramics were fabricated using the spark plasma sintering technique. Sintering was performed at 1273 K for 10 min. The relative density, grain size, and piezoelectric constant of the obtained ceramics were approximately 97%, 0.25 μm, and 12 pC/N, respectively. To our knowledge, this would be the first attempt to synthesize 0.15BT–0.85BNT piezoceramics featuring submicron-sized grains.

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1. Introduction

Owing to their superior characteristics, Pb(Zr,Ti)O₃ ceramics have been widely used as piezoelectric materials for a long time. Nowadays, lead-free piezoelectric ceramics are in high demand, since they are more environmentally friendly compared to the lead-containing ones. Moreover, barium titanate (BaTiO₃), hereafter BT, ceramics have been known to be piezoelectric or dielectric materials for a long time, and therefore they have been investigated as candidates for lead-free piezoelectric materials. Therefore, many scientists developed BT ceramics featuring high piezoelectric constants (d_{33}).^{1)–3)} Wada et al.¹⁾ obtained BT ceramics with the high d_{33} value of 788 pC/N using plate-like BT powder (Konoshima Chemical) and the templated grain growth method. Takahashi et al.³⁾ fabricated BT ceramics with grain size (GS) of 2.1 μm using microwave sintering, and the d_{33} value of the ceramics was 350 pC/N. Moreover, they demonstrated that as GS decreased, d_{33} increased. Karaki et al.²⁾ obtained BT ceramics with the d_{33} value of 460 pC/N using a two-step sintering technique. The GS of these ceramics was approximately 1.6 μm, which was smaller than the GS of the BT ceramics obtained by Takahashi et al.³⁾ Consequently, the d_{33} values of small-grained piezoelectric ceramics are higher than those of large-grained piezoelectric ceramics. Spark plasma sintering (SPS)⁴⁾ is a promising method for fabricating full-density and small-grained ceramics, owing to lack of grain growth. Moreover, while fabricating BT ceramics using SPS has already been reported in the

literature,⁵⁾ the d_{33} values of these ceramics were not analyzed. Since the Curie temperature (T_c) of BT ceramics is low, sodium bismuth titanate [(Bi_{0.5}Na_{0.5})TiO₃],⁶⁾ hereafter BNT, is an excellent candidate for lead-free piezoelectric materials owing to its high d_{33} value⁷⁾ and high T_c (~593 K). In addition, the composition of 0.15BNT–0.85BT contributed to its higher T_c .⁸⁾ Grain oriented 0.15BT–0.85BNT ceramics with the d_{33} value of 103 pC/N, which were obtained utilizing the reactive templated growth method using plate-like H_{1.08}Ti_{1.73}O₄·nH₂O (HTO, Konoshima Chemical) were reported by Ueno et al.⁹⁾ In this study, the properties of 0.15BT–0.85BNT ceramics obtained using SPS, have been analyzed.

2. Experimental procedure

Two methods were used to prepare 0.15BT–0.85BNT powder as follows. The hydrothermal synthesis generated 0.15BT–0.85BNT powder (P_{HT} 0.15BT–0.85BNT) featuring particles approximately 0.1 μm in size. First, HTO was prepared using a solvothermal soft chemical process.¹⁰⁾ Subsequently, HTO and Ba(OH)₂·8H₂O (Wako Pure Chemical) were mixed, and the Ba/Ti molar ratio of the mixture was 0.15. The mixture along with 30 mL pure water was poured into a 50 mL polytetrafluoroethylene (PTFE) vessel. Then, the vessel was placed in an autoclave for hydrothermal treatment. The autoclave was maintained at 423 K while the mixture was stirred, and BT–HTO was obtained after 12 h. Then, Bi₂O₃ (EM Japan Inc.) was added to the obtained BT–HTO, and the Bi/Ti molar ratio of the mixture was 0.425. The mixture along with 30 mL 15M NaOH was poured into a 50 mL PTFE vessel. Afterward, the vessel was placed into an autoclave for hydrothermal treatment. The autoclave was maintained at

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473 K while the mixture was stirred, and P_{HT} 0.15BT–0.85BNT was obtained after 12 h. The second method consisted of solid-state synthesis using BT (BT01, Sakai Chemical Industry Co., Ltd.) and (Bi_{0.5}Na_{0.5})TiO₃ (BNT-501, Shang Hai Dian Yang Industry Co., Ltd., China) powders. The powders were mixed using a ball mill for 12 h, and after drying, 0.15BT–0.85BNT powder (P_{SL} 0.15BT–0.85BNT) was obtained. The P_{HT} 0.15BT–0.85BNT was sintered using an SPS apparatus (Dr Sinter 625KT, Fuji Electric Industrial Co., Ltd.) at sintering temperatures of 1173, 1273, and 1373 K, at the heating rate and holding pressure of 0.5 Ks^{−1} and 40 MPa, respectively. The sintering temperature was maintained for 10 min. The P_{SL} 0.15BT–0.85BNT was formed using a cold isostatic press at the pressure of 196 MPa. The obtained compacts were sintered using conventional (CV) sintering at 1273 K for 6 h in air. The relative densities of the specimens were measured using the Archimedes method, and the volumetric densities were calculated using the masses and volumes of the specimens. The microstructure of the obtained ceramics was analyzed using scanning electron microscopy (SEM, S4700, Hitachi Co., Ltd.) The specimen surfaces were mirror-polished and thermally etched, and the GS of each specimen was determined using SEM by freely drawing lines on the high-resolution images of the specimens. The average GS was calculated using the following equation:¹¹⁾

$$GS = (1.56 \times L)/(N \times MAG), \quad (1)$$

where L is the length of the line, N is the number of grains on the line, and MAG is the magnification of the SEM image.

Each specimen obtained using SPS was annealed at 1073 K for 24 h in air. To measure the piezoelectric properties of the specimens after annealing, each specimen was cut into 10 × 10 × 3 mm³ parts. The parts were silver-plated on both surfaces at 973 K for 1 h in air, and then polarized in a silicone oil bath under the DC field of 4 kV/mm at 448 K for 10 min in air. A d_{33} meter (YE2730A, APC Products Inc.) was used to measure the d_{33} values of all specimens, and the crystal phases of the specimens were identified utilizing X-ray diffraction (XRD; RINT2500V, Rigaku, Japan) using Cu K α radiation.

3. Results and discussion

The obtained results are summarized in **Table 1**. **Figure 1** depicts the SEM image of the P_{HT} 0.15BT–0.85BNT. The SEM images of the microstructure of the

Table 1. Dependence of physical properties of 0.15BT–0.85BNT ceramics on sintering conditions

Sintering conditions		Density		GS (μ m)	d_{33} (pC/N)
Method	Temperature (K)	Relative (%)	Volume (g/cm ³)		
SPS	1173	96.3	5.80	0.12	3
	1273	96.8	5.67	0.25	12
	1373	92.9	5.49	1.29	14
CV	1273	72.8	4.24	0.65	—

0.15BT–0.85BNT ceramics obtained using SPS at 1373, 1273, and 1173 K are illustrated in **Figs. 2(a)–2(c)**, respectively, while the XRD patterns of these ceramics are presented in **Figs. 3(a)–3(c)**, respectively. Furthermore, the XRD pattern of the 0.15BT–0.85BNT ceramics obtained using CV sintering at 1273 K is depicted in Fig. 3(d). The XRD patterns of the ceramics obtained using SPS presented the single BT–BNT phase. Because the XRD patterns of BT–BNT⁹⁾ were almost same as our obtained results. However, the peaks in the XRD pattern of the ceramics obtained using CV sintering separated at approximately 40°, which suggested the presence of mixed phase BT and BNT in the structure of these ceramics. Therefore, CV sintering was insufficient, the density and crystallinity of the ceramics obtained using CV sintering were low, and consequently single-phase ceramics were not obtained. As the sintering temperature increased, GS and d_{33} also increased, while the density of the ceramics decreased. The d_{33} and GS values of the 0.15BT–0.85BNT ceramics obtained using SPS at 1373 K were 14 pC/N and 1.29 μ m, respectively. However, the GS and d_{33} values of the ceramics obtained using SPS at 1173 K were 0.12 μ m and 3 pC/N, respectively, which were very small compared to those of the sample obtained using SPS at 1373 K. Figures 3(a)–3(c) illustrate that the separation of peaks occurs at approximately 45°. Therefore, the ceramics were crystallized, and their crystal structure was tetragonal. The higher d_{33} value of the ceramics sintered at higher temperature was attributed to their crystal structure. Moreover, the ceramics that presented large GS also featured large d_{33} values. Nevertheless, the d_{33} values of the ceramics in this study were very low compared with those reported by Ueno et al.⁹⁾ Their ceramics exhibited high degree of orientation, which could have been the most probable reason for their high d_{33} values. However, the relative density decreased. The ceramics obtained using SPS at 1373 K presented the largest GS and d_{33} values. The relative density of the ceramics obtained using SPS at 1273 K was approximately 97%, while their GS was small (0.25 μ m).

Fig. 1. SEM image of hydrothermally synthesized 0.15BT–0.85BNT powder.

Fig. 2. SEM images of microstructure of 0.15BT-0.85BNT ceramics obtained using SPS at (a) 1373, (b) 1273, and (c) 1173 K.

On the other hand, the relative density of the ceramics obtained using CV sintering was 72.8%, which was lower than those of the ceramics obtained using SPS.

4. Conclusions

We successfully fabricated high-density fine-grained 0.15BT-0.85BNT ceramics using the SPS method. Unfortunately, the d_{33} values of the obtained ceramics were very low. Since the GS values of the dense ceramics obtained

Fig. 3. XRD patterns of 0.15BT-0.85BNT ceramics obtained using SPS at (a) 1373, (b) 1273, and (c) 1173 K, and (d) CV sintering at 1273 K.

using SPS were smaller than those of the ceramics obtained using CV sintering, it was concluded that the properties of the ceramics obtained using the SPS method were superior compared with those of the ceramics obtained using CV sintering.

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