FULL PAPER

Effect of powder size in BiFeO₃-based piezoelectric ceramics fabricated by spark plasma sinteringTomoya AIZAWA¹, Ichiro FUJII¹, Shintaro UENO¹ and Satoshi WADA^{1,†}¹Graduate Faculty of Interdisciplinary Research, University of Yamanashi, Kofu 400–8510, Japan

Dense Mn-added 0.3BaTiO₃–0.1Bi(Mg_{1/2}Ti_{1/2})O₃–0.6BiFeO₃ (0.3BT–0.1BMT–0.6BF) ceramics were fabricated by spark plasma sintering of 0.3BT–0.1BMT–0.6BF powders with different powder sizes of 0.3, 1.0, and 1.4 μm. It was found that use of larger powders suppressed Bi volatilization during the sintering, which was judged by maintained perovskite A site/B site component (A/B) ratios of 1.000 and 0.997 for the 1.0 and 1.4 μm samples and a decreased A/B ratio from 1.000 to 0.998 for the 0.3 μm sample. Grain sizes of the ceramics prepared from the 0.3, 1.0, and 1.4 μm powders were 0.7, 1.2, and 1.9 μm, respectively. These results contributed to increased remanent polarizations of 6.7, 28.3, and 36.6 μC/cm² and maximum electric-field-induced strains/applied electric fields ($S_{\max}/E_{\max}$) of 251, 332, and 362 pm/V for the 0.3, 1.0, and 1.4 μm samples, respectively. Comparison with conventionally sintered ceramics was also made.

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1. Introduction

Lead zirconate titanate (PZT) has been used for sensors and actuators due to the superior piezoelectric properties at the morphotropic phase boundary (MPB) composition with a high Curie temperature.¹⁾ It was suggested that the origin of the large responses was associated with nano-sized domains,²⁾ which could easily respond to an applied electric field and thus contributed the electric properties.³⁾ However, PZT contains toxic lead and it has harmful effect on the environment and human beings. Therefore, high-performance lead-free piezoelectric materials are required to replace PZT.^{4),5)}

BaTiO₃–Bi(Mg_{1/2}Ti_{1/2})O₃–BiFeO₃ (BT–BMT–BF) is one of the lead-free piezoelectric materials, and it is solid solutions of relaxor-like BT–BMT⁶⁾ and ferroelectric BiFeO₃ (BF).⁷⁾ Coexistence of macro-sized domains and nano-sized domains was observed at the composition of 0.3BT–0.1BMT–0.6BF.^{8)–13)} Because macro-sized domains with nano-sized domains were also observed in PZT ceramics at the MPB composition,²⁾ large piezoelectric responses could be expected for the 0.3BT–0.1BMT–0.6BF ceramics. However, the piezoelectric properties are not comparable to those of PZT. This could be attributed to domain pinning by various defects such as Bi and O vacancies and Fe⁴⁺ ions, which were generated by Bi

volatilization and subsequent charge compensation, as reported for BF ceramics.^{14)–16)}

Low temperature sintering is considered to suppress the Bi volatilization. A spark plasma sintering (SPS) method can sinter powders at a lower temperature in a short time. It has been reported that various materials such as BaTiO₃ and (Na_{1/2}K_{1/2})NbO₃ could be sintered by the SPS method.^{17)–19)} Successful fabrication of single phase BF ceramics by the SPS method was also reported.²⁰⁾

In this study, 0.3BT–0.1BMT–0.6BF ceramics were prepared by the SPS method. Effect of 0.3BT–0.1BMT–0.6BF powder sizes on Bi volatilization and piezoelectric responses was investigated. To evaluate the Bi volatilization, the A site/B site component ratio (A/B) was measured by a fluorescent X-ray analysis; if the A/B ratio was 1, the Bi volatilization did not occur, and if it was smaller than 1, the Bi volatilization did occur. In addition, 0.3BT–0.1BMT–0.6BF ceramics were prepared by conventional sintering (CS) for comparison.

2. Experimental procedure

Three 0.3BT–0.1BMT–0.6BF powders with different powder sizes and A/B ratios were used in this study: powder 1 with an average powder size of 0.3 μm and the A/B ratio of 1.000, powder 2 with an average powder size of 1.0 μm and the A/B ratio of 1.000, and powder 3 with an average powder size of 1.4 μm and the A/B ratio of 0.997. These powders were prepared by Nippon Chemical Industrial. They were added with 0.05 wt% MnO₂ for reducing leakage current, and mixed with a mortar and pestle. The mixed powders were put into a graphite die

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with a diameter of 15 mm, and then they were sintered with a spark plasma sintering technique (DR. SINTER LAB™, SPS-515YN) by heating at 800°C for 5 min at a heating rate of 100 °C/min with uniaxial pressing at 3.3 kN under reduced pressure of 7 Pa or less. For a sample prepared by conventional sintering, a polyvinyl butyral binder was added to the MnO₂-added powder 1, and the powder was uniaxially pressed at 250 MPa to disc compacts with the diameter of 10 mm. The binder was removed by heating at 700°C. The compacts were sintered at 1000°C for 2 h at a heating rate of 300 °C/h. Density of the ceramics was measured by an Archimedes method. Crystal structure was examined by X-ray diffraction (XRD; Rigaku, RINT 2000). Microstructure of the ceramics was observed by scanning electron microscopy (SEM, JSM-6510, JEOL). Average grain size was measured by a linear intercept method. The A/B ratio was measured by a fluorescent X-ray analysis with an error of ± 0.002 .

For electric characterizations, the samples were polished down to 0.4 mm in thickness. They were cut to the size of $4 \times 1.5 \times 0.4 \text{ mm}^3$, and re-oxidized in furnace in air at 800°C for 5 h. After this, the samples were put into a furnace preheated at 800°C for 1 h, and then they were quenched in water. This quenching treatment was performed to increase ferroelectric and piezoelectric properties, reportedly due to de-pinning of domain walls pinned by defect associates.¹⁶⁾ Gold electrodes were formed on both surfaces by sputtering, and the samples were heated at 300°C for 10 min to improve the adhesion. Polarization–electric field (P – E) hysteresis and strain–electric field (S – E) curves were measured at room temperature at 0.1 Hz by a polarization and strain measuring system (Model JP005-SE, Kitamoto Denshi) with a displacement meter (Millitron 1202 IC, Mahr). Temperature dependence of P – E hysteresis loops and dc resistivity were measured by a ferroelectric characteristic evaluation system (FCE-3, TOYO Corporation).

3. Results and discussion

3.1 Crystal structure, microstructure, and chemical composition analysis

Figure 1 shows XRD patterns of the sintered samples. All the diffraction peaks could be assigned to a BT–BMT–BF perovskite phase with a pseudo-cubic symmetry, and no impurity phases were observed. **Figure 2** shows SEM images of the ceramics. The average grain size of the ceramics fabricated by conventional sintering of the powder 1 (CS 1) was 1.2 μm and those of the ceramics fabricated by spark plasma sintering of the powders 1, 2 and 3 (SPS 1, 2 and 3) were 0.7, 1.2, and 1.9 μm , respectively. Grain growth of the SPS 1 ceramics was smaller than that of the CS 1 ceramics, although the starting powder was the same. This was attributed to the lower sintering temperature and the shorter sintering time of the SPS process. Relative densities of the CS 1, SPS 1, SPS 2, and SPS 3 ceramics were 93, 98, 99, and 95%, respectively. The higher densities were obtained by the SPS method. The relative density of the SPS 3 ceramics was smaller than those of the SPS 1 and 2 ceramics. This was ascribed to the decrease in sinterability due to the use of the larger

Fig. 1. XRD patterns of the 0.3BT–0.1BMT–0.6BF ceramics (CS 1, SPS 1, SPS 2, and SPS 3).

Fig. 2. SEM images for the 0.3BT–0.1BMT–0.6BF ceramics (CS 1, SPS 1, SPS 2, and SPS 3).

Table 1. A/B ratios of the 0.3BT–0.1BMT–0.6BF raw powders (Powders 1, 2 and 3) and ceramics (CS 1, SPS 1, SPS 2 and SPS 3)

Sintering method and condition	Powder 1	Powder 2	Powder 3
	Average particle size: 0.3 μm A/B = 1.000	Average particle size: 1.0 μm A/B = 1.000	Average particle size: 1.4 μm A/B = 0.997
CS 1000°C -2h	A/B = 0.997	N/A	N/A
SPS 800°C -5 min	A/B = 0.998	A/B = 1.000	A/B = 0.997

Fig. 3. *P*–*E* hysteresis and *S*–*E* curves of the 0.3BT–0.1BMT–0.6BF ceramics ((a) CS 1, (b) SPS 1, (c) SPS 2 and (d) SPS 3).

powder. **Table 1** lists the A/B ratios of the ceramics. The A/B ratios of the CS 1 and SPS 1 ceramics were 0.997 and 0.998, respectively. This suggested that Bi was volatilized in both ceramics. This was different from the anticipation that the Bi volatilization was suppressed by the use of the SPS method. It was reported that the vapor pressures of Bi from Bi_2O_3 were 10 Pa at 800°C and 3×10^2 Pa at 1000°C,²¹⁾ and the extrapolated vapor pressures of Bi from a Bi-based piezoelectric material $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ were 3×10^{-2} Pa at 800°C and 10 Pa at 1000°C.^{22),23)} Thus, Bi would be more difficult to evaporate from BT–BMT–BF at 800°C. However, the reduced atmosphere of 7 Pa during the SPS process could facilitate the Bi evaporation, and therefore the A/B ratio of the SPS 1 ceramics was reduced. Meanwhile, no change in the A/B ratios were observed for the SPS 2 and 3 ceramics. This indicated that the Bi volatilization was suppressed by increasing average powder size of the starting material, probably due to smaller powder surface areas where Bi was volatilized. To support this idea, the following simple calculations were conducted. It was considered that a Bi evaporation rate was proportional to the surface area per volume for BT–BMT–BF particles. Suppose that the BT–BMT–BF particles were spheres with a radius *r*. Then, the surface area

was $A = 4\pi r^2 \times n$ and the volume was $V = (4/3)\pi r^3 \times n$, where *n* was the number of the particles. Thus, the surface area per volume was $A/V = 3/r$. Since the particle sizes (diameters) for the SPS 1, 2, and 3 ceramics were 0.3, 1.0, and 1.4 μm , the *A/V* values were 20, 6, and 4.3 μm^{-1} , respectively. Therefore, the Bi evaporation of the SPS 2 and 3 ceramics were reduced compared to the SPS 1 ceramics, and the A/B ratios were not changed after the sintering.

3.2 Ferroelectric and piezoelectric properties

The dc electric resistivity of all the ceramics was higher than $10^{11} \Omega\cdot\text{cm}$ at the electric field of 50 kV/cm, which suggested that the samples had high electric resistivity. **Figures 3(a)** and **3(b)** show the *P*–*E* hysteresis loops and the *S*–*E* curves of the CS 1 and SPS 1 ceramics. Although the A/B ratio of the SPS 1 ceramics was similar to that of the CS 1 ceramics, the SPS 1 ceramics showed the pinched *P*–*E* loop and the smaller strain. Pinched *P*–*E* loops were reported for ferroelectrics with defect dipoles.^{24),25)} In this study, the following defects were considered to exist. In the conventional sintering, the Bi volatilization occurred due to the high vapor pressure, and formation of oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$) was accompanied for charge compen-

Fig. 4. Temperature dependence P - E hysteresis of 0.3BT-0.1BMT-0.6BF ceramics (CS 1, SPS 2 and SPS 3).

sation. Recently, the existence of Fe^{4+} ions has been suggested for charge compensation of the Bi volatilization.^{14),15)} With these point defects, defect dipoles of $\text{V}_{\text{Bi}}'''-\text{V}_{\text{O}}''$ and $\text{V}_{\text{Bi}}'''-\text{Fe}_{\text{Fe}^{3+}}^{4+}$ could be formed, which might pin domain walls and decrease ferroelectric and piezoelectric properties. On the other hand, in the SPS sintering, oxygen vacancies were generated by sintering in the reducing atmosphere. As a result, Fe^{3+} ions were reduced to Fe^{2+} ions for the charge compensation, and defect dipoles of $\text{V}_{\text{O}}''-\text{Fe}_{\text{Fe}^{3+}}^{2+}$ could be formed. These $\text{V}_{\text{O}}''-\text{Fe}_{\text{Fe}^{3+}}^{2+}$ defect dipoles might be remained after the re-oxidation. The pinched P - E loop of the SPS 1 ceramics suggested that the $\text{V}_{\text{O}}''-\text{Fe}_{\text{Fe}^{3+}}^{2+}$ defect dipoles had stronger effect on domain wall pinning, compared to the defect dipoles of $\text{V}_{\text{Bi}}'''-\text{V}_{\text{O}}''$ and $\text{V}_{\text{Bi}}'''-\text{Fe}_{\text{Fe}^{3+}}^{4+}$ due to the Bi volatilization. In addition, the reduction in the ferroelectric and piezoelectric properties of the SPS 1 ceramics would be facilitated by the smaller grain size. In 0.33BT-0.67BF ceramics, a decrease in ferroelectric and piezoelectric properties with decreasing grain size below $2\mu\text{m}$ was reported.²⁶⁾ It was assumed that a similar grain size effect was also present in the 0.3BT-0.1BMT-0.6BF ceramics. With these defect dipoles and the grain size effect, the ferroelectric and piezoelectric properties of the SPS 1 ceramics might be smaller than those of the CS 1 ceramics.

Figure 3(c) shows the P - E hysteresis loop and the S - E curve of the SPS 2 ceramics. The ferroelectric and piezo-

electric responses of the SPS 2 ceramics were improved compared to those of the SPS 1 ceramics. For the SPS 2 ceramics, the Bi volatilization was suppressed as the A/B ratio was maintained to 1.000 and the grain size was larger than that of the SPS 1 ceramics. These could contribute to the improved ferroelectric and piezoelectric properties in the SPS 2 ceramics. Note that similar P - E hysteresis loops and S - E curves were observed for the CS 1 and SPS 2 ceramics with similar grain sizes, which suggested that the grain size was a strong factor for the electric properties in the ceramics.

Figure 3(d) shows the P - E hysteresis loop and the S - E curve of the SPS 3 ceramics. Although the A/B ratios were the same (0.997) for the SPS 3 and CS 1 ceramics, the remanent polarization was larger and the coercive field was smaller for the SPS 3 ceramics. Since the A/B ratio of the starting material of SPS 3 was 0.997, Fe^{4+} ions were considered to be originally present. With the SPS sintering process, the Fe^{4+} ions could preferentially be reduced to Fe^{3+} ions, and thus the remaining defect dipoles were only $\text{V}_{\text{Bi}}'''-\text{V}_{\text{O}}''$. As a result, the ferroelectric and piezoelectric properties could be improved due to decreased domain wall pinning. In addition, the grain size of the SPS 3 ceramics was larger than the CS 1 and SPS 2 ceramics. This was also considered to affect the ferroelectric and piezoelectric properties.

Figure 4 shows the temperature dependence of P - E hysteresis loops of the CS 1, SPS 2, and SPS 3 ceramics.

The remanent polarization increased and the coercive field decreased with increasing temperature. This suggested that the defect dipoles which pinned domains were depinned. The temperature dependence of the remanent polarization was affected by the sample preparation. The coercive fields of the CS 1 and SPS 2 ceramics were gradually decreased with increasing temperature. On the other hand, for the SPS 3 sample, it was rapidly decreased up to 80°C and then the coercive field was saturated above 100°C. The remanent polarization behavior of the SPS 3 ceramics could be attributed to smaller defect content compared to other samples.

In this study, it was found that the ferroelectric and piezoelectric properties of the 0.3BT–0.1BMT–0.6BF ceramics could be improved by using the SPS method and the raw powder with the large powder size. However, the defect dipoles of $V_{Bi}'''-V_O''$ could still exist in the SPS 3 sample. We believe that the addition of bismuth oxide in excess can suppress the formation of this defect dipoles and increases the piezoelectric properties.

4. Conclusions

Mn-added 0.3BT–0.1BMT–0.6BF ceramics were fabricated by the CS and SPS methods using the raw powders with the different powder sizes. When the small 0.3 μm powder was used, the A/B ratios of both CS- and SPS-derived ceramics were reduced. As a result, the pinched P – E loop and the small electric-field-induced strain were observed for the SPS-derived ceramics, which was attributed to the possible defect dipoles of $V_{Bi}'''-V_O''$, $V_{Bi}'''-Fe^{4+}_{Fe^{3+}}$, and $Vo''-Fe^{2+}_{Fe^{3+}}$, along with the small grain size of 0.7 μm . On the other hand, the use of the larger 1.0 and 1.4 μm powders suppressed Bi volatilization, and the ferroelectric and piezoelectric properties of the SPS-derived ceramics with the 1.4 μm powder were superior to those of the CS ceramics with the 0.3 μm powder. The improved properties were ascribed to the larger grain size of 1.9 μm and the reduced defect dipole concentration, the latter of which was suggested by the rapid decrease and the saturation in the remanent polarization as a function of temperature and possibly achieved by the preferential reduction of Fe^{4+} to Fe^{3+} ions. These results are important to fabricate high performance BF-based lead-free piezoelectric ceramics.

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