Effect of oxygen partial pressure during sintering on electric properties of BiFeO$_3$-based piezoelectric ceramics

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The effects of oxygen partial pressure (pO$_2$) during sintering and post-annealing treatment on the microstructure and electrical properties of Mn-added 0.3BaTiO$_3$–0.1Bi(Mg$_{1/3}$Ti$_{2/3}$)$_2$O$_3$–0.6BiFeO$_3$ ceramics were investigated. The ceramics sintered at pO$_2$ of 0.1–1 atm showed pinched polarization–electric field (P–E) loops, while the ceramics sintered in nitrogen gas could not be measured due to dielectric breakdown. By annealed at 800°C for 5 h and cooled slowly, the ceramics showed increased remanent polarizations although their P–E loops were still pinched. When the as-sintered ceramics were annealed at 800°C for 5 h and then quenched into water, well-developed ferroelectric hysteresis loops were observed. These results were discussed with grain size and defect dipoles consisted of oxygen vacancies and bismuth vacancies or iron ions with a different valence.

Key-words : Piezoelectric, Ferroelectric, Oxygen partial pressure, Perovskite

1. Introduction

Demand for piezoelectric materials has been increased because more and more actuators and sensors are required for coming Internet of Things society. However, the most of piezoelectric materials used are lead-based materials, which adversely affect the environment. Therefore, it is necessary to develop high performance lead-free materials. BaTiO$_3$–Bi(Mg$_{1/3}$Ti$_{2/3}$)$_2$O$_3$–BiFeO$_3$ (BT–BMT–BF) is the solid solutions of relaxor-like BT–BMT$^1$ and ferroelectric BiFeO$_3$ $^{2-10}$ and it has been reported that BT–BMT–BF ceramics have a phase boundary between a rhombohedral phase and a pseudocubic phase at 0.3BT–0.1BMT–0.6BF, with a high Curie temperature (T$_C$~450°C). However, their piezoelectric properties did not reach to those of Pb-based piezoelectric ceramics. This can be attributed to the formation of various defects during sintering in the 0.3BT–0.1BMT–0.6BF ceramics. For example, the decrease of the A site to B site ratio of the ABO$_3$ perovskite oxide (if the A/B ratio is 1, the composition is stoichiometric, and if it is smaller than 1, it is off-stoichiometric and Bi volatilization is occurred) was reported for the 0.3BT–0.1BMT–0.6BF ceramics after sintering. $^{11}$ Accompanied by Bi volatilization, oxygen vacancies are expected to be formed due to charge compensation, as shown below.

$$2Bi^{2+}_\text{bi} + 3O^{2-}_0 \rightarrow 2V^{m-}_\text{bi} + 3V^{o-}_0 + 2Bi(g) + 3/2O_2(g)$$

It is also suggested that Fe$^{3+}$ ions are generated owing to the formation of oxygen vacancies.

$$2Fe^{3+}_\text{Fe} + O^{2-}_0 \rightarrow 2Fe^{2+}_\text{Fe} + V^{o+}_0 + 1/2O_2(g)$$

These defects could form defect dipoles, which pinned domain-walls and decreased ferroelectric and piezoelectric properties. $^{12}$

Since these reactions involving the defects occur during sintering, sintering atmosphere is expected to have strong influence on the reactions. Therefore, many studies regarding the sintering atmosphere have been conducted. For example, by sintering BT–BF ceramics in an oxygen atmosphere, the dielectric loss was decreased and the piezoelectric properties were increased. $^{13}$ It was suggested that the reason was associated with the decreased amount of oxygen vacancies by the sintering in the oxygen atmosphere. On the other hand, when BT–BF ceramics were sintered in a nitrogen atmosphere, large amounts of oxygen vacancies and Fe$^{2+}$ ions were generated. $^{14}$ Unexpectedly, the decrease of dielectric loss and the increase of remanent polarization were observed. It was suggested that the ceramics sintered in the nitrogen atmosphere had a secondary phase, which resulted in the increase of electric resistivity. Therefore, it is interesting to study which sintering atmosphere is suitable for improving the ferroelectric and piezoelectric properties of 0.3BT–0.1BMT–0.6BF ceramics. In this study, we sintered 0.3BT–0.1BMT–0.6BF ceramics at various oxygen partial pressures (pO$_2$), and...
investigated the effect of the \( \text{pO}_2 \) on microstructure and electrical properties. The improvements of ferroelectric properties by quenching from high temperatures has been reported for 0.3BT–0.1BMT–0.6BF ceramics.\(^4\),\(^15\),\(^16\) This quenching treatment was explained to de-pin domain-walls which were pinned by defect associates and the domain-walls contributed to the ferroelectric and piezoelectric responses.\(^12\) In addition, the measurements of the temperature dependence of polarization–electric field (\( P–E \)) hysteresis loops is an effective way to investigate the influence of defects on electric properties.\(^11\) Thus, we investigated the influence of cooling rate after post-annealing in air and the temperature dependence of the \( P–E \) loops for the ceramics.

2. Experimental procedure

A 0.3BT–0.1BMT–0.6BF powder (the powder size of 0.5 \( \mu \text{m} \), Nippon Chemical Industrial) was added with 0.05 wt \% \( \text{MnO}_2 \) to reduce leakage current, and mixed with a mortar and pestle. A polyvinyl butyral binder was added to the \( \text{MnO}_2 \)-added powder, and the powder was uniaxially pressed at 250 MPa to disc compact with a diameter of 10 mm. Then, the binder was removed by heating at 700°C. The compacts were sintered at 1030°C for 2 h at the different \( \text{pO}_2 \) values of 0 (nitrogen gas only), 0.1, 0.2, 0.4, 0.6, 0.8, and 1 (oxygen gas only) atm, which were controlled by changing the ratios of nitrogen and oxygen gases. The total pressure was fixed at 1.0 atm. The density of the ceramics was measured by an Archimedes method. Crystal structure was examined by X-ray diffraction (XRD; Rigaku, RINT 2000). The microstructure of the ceramics was observed by scanning electron microscopy (SEM, JSM-6510, JEOL). Average grain size and the error bar were determined as an average and standard deviation of diameters of 50–70 grains observed on an SEM image.

For electric characterizations, the samples were polished down to 0.4 mm in thickness. They were cut to a size of 4.0 \( \times \) 1.5 \( \times \) 0.4 mm\(^3\). After this, some samples were put into a furnace preheated at 800°C for 5 h, and then they were either slowly cooled (furnace-cooled) or quenched in water. The heat treatment for the furnace-cooled and quenched samples was performed in air. The grain sizes of the slowly cooled and quenched samples were also measured. Gold electrodes were formed on both surfaces by sputtering, and the samples were heated at 300°C for 10 min to improve the adhesion. The room temperature dielectric constant and loss were measured at 1 kHz using an impedance analyzer (HP4294A, Agilent). \( P–E \) 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). The temperature dependence of \( P–E \) hysteresis loops was measured by a ferroelectric characteristic evaluation system (FCE-3, TOYO Corporation). For this measurement, lead zirconate titanate (PZT) ceramics were also studied for reference.

3. Results and discussion

3.1 Crystal structure and microstructure

Figure 1 shows the XRD patterns of the as-sintered samples. All the diffraction peaks could be assigned to a perovskite phase with pseudo-cubic symmetry, and no impurity phases were observed. For the samples cooled slowly or quenched from 800°C after sintering in the nitrogen gas and at \( \text{pO}_2 = 0.2, \) and 1.0 atm, XRD patterns were also measured. The patterns were almost the same as those of the as-sintered, which indicated that the crystal structure of the as-sintered samples was not changed by the heat treatment. Relative densities as high as about 95% were obtained for all the samples. Figure 2 shows the SEM images of the as-sintered ceramics. The grain sizes of the samples sintered in nitrogen gas and at \( \text{pO}_2 = 0.1, 0.2, 0.4, 0.6, 0.8, \) and 1.0 atm were 1.54 \( \pm \) 0.65, 1.11 \( \pm \) 0.38, 1.09 \( \pm \) 0.36, 1.04 \( \pm \) 0.35, 1.00 \( \pm \) 0.28, 1.07 \( \pm \) 0.34, and 1.01 \( \pm \) 0.44 \( \mu \text{m} \), respectively. The grain size of the sample sintered in the nitrogen gas was larger than those of the samples sintered at \( \text{pO}_2 \geq 0.1 \) atm. For BT–BF ceramics, the ceramics sintered in a nitrogen atmosphere had a larger grain size than the ceramics sintered at an oxygen atmosphere.\(^14\) This was attributed to an increased oxygen diffusion rate by the existence of oxygen vacancies. For the samples sintered in the nitrogen gas and at \( \text{pO}_2 = 0.2, \) and 1.0 atm, grain sizes were measured at the slowly cooled and quenched states. The grain sizes were 1.61 \( \pm \) 0.55, 1.09 \( \pm \) 0.29 and 0.97 \( \pm \) 0.29 \( \mu \text{m} \) for the slowly cooled state of the ceramics sintered in the nitrogen gas and at \( \text{pO}_2 = 0.2, \) and 1.0 atm, respectively. On the other hand, the grain sizes were 1.64 \( \pm \) 0.50, 1.00 \( \pm \) 0.31 and 1.05 \( \pm \) 0.33 \( \mu \text{m} \) for the quenched state of the ceramics sintered in the nitrogen gas and at \( \text{pO}_2 = 0.2, \) and 1.0 atm, respectively. These results suggested that the grain sizes did not strongly depend on the heat treatment.

3.2 Ferroelectric and piezoelectric properties

Figure 3 shows room temperature dielectric constant and loss (\( \tan \delta \)) measured at 1 kHz. The samples sintered at \( \text{pO}_2 \geq 0.1 \) atm showed no significant changes of the dielectric constant and \( \tan \delta \) for the as-sintered, slowly cooled, and quenched states. That is, the dielectric constant

![Fig. 1. XRD patterns of the as-sintered 0.3BT–0.1BMT–0.6BF ceramics.](image)
was about 600 and tan δ was ~0.01. For the sample sintered in the nitrogen gas, a large dielectric constant and tan δ were observed for the as-sintered state. This could be attributed to the increased electronic conductivity caused by formation of oxygen vacancies. For slowly cooled and quenched states, the dielectric constant and tan δ became similar to those of the ceramics sintered at other pO₂. This suggested that the oxygen vacancies of the samples sintered in the nitrogen gas were annihilated by annealing in air.

Figure 4 shows the P–E hysteresis loops and S–E curves of the samples. For the as-sintered state, the samples sintered at pO₂ $\geq$ 0.1 atm showed pinched loops and smaller strain. Such pinching has been reported to be caused by defect dipoles.\textsuperscript{12-17} It was suggested that Bi was volatilized from 0.3BT–0.1BMT–0.6BF ceramics when they were sintered at high temperature, making many defect dipoles of $V_{\text{Bi}}' - V_{\text{O}}'^\ast$ and $V_{\text{Bi}}' - Fe'_{\text{Fe}}$ in the ceramics.\textsuperscript{11} Furthermore, processing strain caused by polishing and cutting may deteriorate ferroelectric and piezoelectric properties.\textsuperscript{18} Lattice distortion induced by the processing was reported for BT–BF ceramics.\textsuperscript{19} On the other hand, the P–E loop and S–E curve of the ceramics sintered in the nitrogen gas for the as-sintered state could not be measured due to dielectric breakdown. This may be attributed to electron hopping through leakage paths created by the alignment of a large number of oxygen vacancies.

Samples cooled slowly from 800°C showed increased remanent polarizations and strain, although the P–E loops were still pinched. Reduced amounts of defect dipoles and reduced mechanical distortion by the annealing might contribute to the increased responses. The slowly cooled sample which was sintered in the nitrogen gas showed a smaller remanent polarization and smaller strain. This suggested the existence of more defect dipoles such as $V_{\text{O}}'^\ast - Fe'_{\text{Fe}}$ derived from oxygen vacancies in the sample.
For the quenched state, well-developed ferroelectric $P$–$E$ loops and butterfly-like $S$–$E$ curves were observed. We considered that the annealing treatment at high temperature dissociated the defect dipoles and thus de-pinned domain walls. The dissociated point defects were frozen at room temperature by the quenched treatment. Thus, the density of the defect dipoles was reduced and the ferroelectric properties were improved. These responses were similar for all the quenched samples. Among these, the sample originally sintered in the nitrogen gas had the largest remanent polarization value and strain. This could be, in part, due to the larger grain size of the sample. For BiFeO$_3$-based ceramics, it was reported that the remanent polarization and piezoelectric $d_{33}$ coefficient decreased when the grain size was below 2 μm.\textsuperscript{11,20} In addition, the larger remanent polarization was partly attributed the leakage current of the sample, since the shape of the $P$–$E$ loop was slightly round.

The $P$–$E$ hysteresis loops of the quenched ceramics were measured at temperatures of 25–150°C, and those

![Fig. 4. $P$–$E$ loops and $S$–$E$ curves of the 0.3BT–0.1BMT–0.6BF ceramics.](image)

![Fig. 5. Temperature dependence of $P$–$E$ hysteresis loops of the quenched 0.3BT–0.1BMT–0.6BF ceramics sintered in (a) nitrogen gas and at pO$_2$ = (b) 0.2, and (c) 1 atm and that of (d) Pb(Zr,Ti)O$_3$ ceramics. The temperature dependence of (e) the remanent polarization and (f) the coercive field for the quenched 0.3BT–0.1BMT–0.6BF ceramics.](image)
of the quenched ceramics sintered in the nitrogen gas and at pO₂ = 0.2, and 1 atm are shown in Figs. 5(a)–5(c), as examples. The remanent polarization values of the samples were gradually increased with increasing temperature [Fig. 5(e)]. This was different from the results of reference PZT ceramics as shown in Fig. 5(d). The reason for this may be de-pinning of domain pinning due to the temperature rise in the 0.3BT–0.1BMT–0.6BF ceramics. The coercive electric field of the sample showed a decreasing tendency with increasing temperature [Fig. 5(f)]. The coercive field of the sample sintered in the nitrogen gas was the lowest until 75°C. It increased at 100°C, followed by decrease. At temperatures higher than 100°C, larger coercive fields were observed for the sample sintered in the nitrogen gas. This could be associated with the larger defect (space charge) content of the sample, which made $P$–$E$ responses round and the coercive field (and the remanent polarization) increased. From this result, it is considered that more defects are present in the sample sintered in the nitrogen gas.

In this study, it was found that the dielectric, ferroelectric, and piezoelectric properties were not strongly dependent on the pO₂ during sintering for the samples sintered at pO₂ ≥ 0.1 atm. The ferroelectric and piezoelectric properties were increased by annealing in air and subsequent quenching. These increases could be attributed to relaxed strain caused by the processing and the dissociation of the defect dipoles and domain-walls. For the sample sintered in the nitrogen gas, the larger piezoelectric response was observed for the quenched state, which was attributed to the larger grain size.

4. Conclusions

Dense Mn-added 0.3BaTiO₃–0.1Bi(Mg₁/₂Ti₁/₂)O₃–0.6BiFeO₃ (BT–BMT–BF) ceramics were sintered in the nitrogen gas and changing oxygen partial pressure (pO₂ = 0.1, 0.2, 0.4, 0.6, 0.8 and 1 atm). The sintering atmosphere had no strong effect on the XRD patterns and the relative densities for the ceramics. The grain size and dielectric, ferroelectric, and piezoelectric properties of the samples sintered at pO₂ ≥ 0.1 atm had no strong dependence on the pO₂, although ferroelectric and piezoelectric properties were improved by heat treatment. For the sample sintered in the nitrogen gas, the larger grain size was observed for the as-sintered state, probably due to the increased diffusion rate of oxygen. The sample cooled slowly from the 800°C annealing after sintering in the nitrogen gas showed a more pinched hysteresis loop. This suggested larger amounts of oxygen vacancies and Fe²⁺ ions. However, the sample quenched from 800°C after sintering in the nitrogen gas showed the larger piezoelectric response, which was attributed to the larger grain size.

The $P$–$E$ hysteresis loops of the quenched ceramics were measured at temperatures of 25–150°C, which showed the coercive field of the sample sintered in the nitrogen gas was the lowest until 75°C, but it increased at 100°C and then decreased. This suggested that the sample sintered in the nitrogen gas was leakier than other samples.

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