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Domain Wall Engineering in Lead-free Piezoelectric Materials

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Lead-free ferroelectrics have become highly attractive materials from the viewpoint of a solution to environmental problems. However, as compared with $Pb(Zr,Ti)O_3$ (PZT) ceramics, their ferroelectric related properties were poor, and it is difficult to replace the PZT ceramics. To achieve much higher piezoelectric properties than those of PZT ceramics, the domain average engineering i.e., engineered domain configuration, is an important technique, and should be applied to lead-free ferroelectric materials. Barium titanate ($BaTiO_3$) crystal is typical lead-free ferroelectrics and there have been a number of reports on its domain average engineering. Recently, for the tetragonal $BaTiO_3$ crystals with the engineered domain configurations, it was found that the piezoelectric properties were significantly improved with increasing domain wall densities. This result suggests a possibility that the domain walls in the engineered domain configuration could contribute to the piezoelectric properties. Thus, to explain the domain wall contribution to the piezoelectric properties, the piezoelectric properties of the $BaTiO_3$ crystals were investigated as a function of domain size. Moreover, this concept was applied to grain oriented $BaTiO_3$ ceramics, and finally the lead-free piezoelectrics with d_{33} of 800 pC/N were prepared by domain wall engineering.

Key words: lead-free piezoelectrics, domain wall engineering, barium titanate, grain oriented ceramics

1. INTRODUCTION

Recently, lead-free ferroelectrics have become highly attractive materials from the viewpoint of providing a solution to environmental problems.[1] However, as compared with $Pb(Zr,Ti)O_3$ (PZT) ceramics,[2] their ferroelectric related properties are very poor, and therefore, it is difficult to replace PZT ceramics. Many researchers have attempted to improve the piezoelectric properties of lead-free ferroelectrics such as bismuth layer-structure ferroelectrics, $BaTiO_3$, and potassium niobate ($KNbO_3$) by chemical modification; however, no significant improvement has been achieved.[1-4] Recently, however, chemically modified $KNbO_3$ and sodium niobate ($NaNbO_3$) solid solution ceramics have been reported as new lead-free piezoelectrics with a new morphotropic phase boundary (MPB) and to have similar piezoelectric properties to those of PZT ceramics.[5,6] Thus, there are still some possibilities to obtain high performance lead-free piezoelectrics by chemical modification.

To achieve much higher piezoelectric properties, domain engineering is an important technique for obtaining enhanced piezoelectric properties. In [001]-oriented rhombohedral $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) – lead titanate ($PbTiO_3$, PT) single crystals, ultrahigh piezoelectric activities were found by Park and Shrout[7,8] and Kuwata et al.[9,10] and these ultrahigh piezoelectric properties originated from the application of domain engineering techniques.[11-12]

$BaTiO_3$ crystal is a typical lead-free ferroelectric and there have been a number of reports on its domain engineering.[13-16] Park et al.[14] reported that [001]-poled orthorhombic $BaTiO_3$ crystals with the engineered domain configurations exhibited a d_{33} of over 500 pC/N and a k_{33} of over 85%. Moreover, for tetragonal $BaTiO_3$ crystals with the engineered domain configurations, it has recently been found that their piezoelectric properties significantly improved with decreasing domain sizes.[15-17]

However, for the $BaTiO_3$ crystals, it was very difficult to induce domain sizes much finer than 5 μm. On the other hand, for the $BaTiO_3$ ceramics, Takahashi et al. reported that the introduction of fine domains with a size of 50 nm into these ceramics resulted in a high d_{33} of 350 pC/N[18], while Karaki et al. reported that the introduction of fine domains into these ceramics resulted in a high d_{33} of 460 pC/N[19]. These results suggest that for these ceramics, it is very easy to induce domain sizes much finer than 5 μm. Therefore, if grain-oriented $BaTiO_3$ ceramics along the engineered domain direction, i.e., the [111] and [110] directions, are prepared, much finer domain sizes can be induced very easily. Moreover, we can expect very high d_{33} values from the 90° domain wall region.

In this study, [110]-oriented $BaTiO_3$ ceramics were prepared by templated grain growth (TGG) method using [110]-oriented $BaTiO_3$ platelike particles as a template and hydrothermal $BaTiO_3$ sphere particles with different particle sizes as a matrix, and their piezoelectric properties were measured. Moreover, their piezoelectric properties were discussed as a function of the degree of orientation along the [110] direction, F_{110}, and domain size.

2. EXPERIMENTAL PROCEDURE

[110]-oriented $BaTiO_3$ ceramics were prepared by the TGG method reported by Sugawara et al.[20] To prepare [110]-oriented $BaTiO_3$ ceramics, [110]-oriented $BaTiO_3$ platelike particles (Konoshima Chemical) were used as the template particles, while hydrothermal $BaTiO_3$ sphere nanoparticles with different sizes [BT-01 (100 nm), BT-03 (300 nm), and BT-05 (500 nm), Sakai Chemical Industry] were used as the matrix particles. The mixture of the template and matrix particles was ball-milled using mixed organic solvents of ethanol and toluene for 24 h. Then, after the addition of polyvinyl butyral as binder and di-n-butyl phthalate as plasticizer into the above mixture, these materials were ball-milled for 3 h, and the slurry was used for tape casting. The slurry was tapecast on the plastic film and a green sheet was prepared with a thickness of around 0.5 mm. After drying in atmosphere, the green sheet was cut, stacked and pressed at 80 °C and 24.5 MPa for 3 min. The thickness of the green compact was always more than 2 mm.

The binder and plasticizer were burned out at 650 °C for 2 h with a very slow heating rate below 5 °C/min, then heated up to 800 °C with a heating rate of 10 °C/min, and further heated up to sintering temperatures from 900 to 1,500 °C with a heating rate of 2.5 °C/min. The green compact was sintered at various temperatures from 900 to 1,500 °C for 12 h, and then cooled down to room temperature. The crystal structure and the degree of orientation along [110], F_{110}, were measured by X-ray diffraction (XRD) measurement (RINT2000, Rigaku, Cu Kα, 50 kV, 30 mA), and F_{110} value determined using the XRD pattern from 20 to 80° by the Lotgering method[21]. The density of the ceramics was measured by the Archimedes method. The grain size was measured using a scanning electron microscopy (SEM).

The ceramics were cut, polished and sized into the shape of 31 resonators with a size of 4.0x1.2x0.3 mm^3, and Au electrodes were sputtered on the top and bottom surfaces with a size of 4.0x1.2 mm^2. Prior to the piezoelectric measurement, poling treatment was performed for these 31 resonators. DC electric fields from 10 to 20 kV/cm were applied to the resonators in silicone oil at 100 °C using a high-voltage amplifier. After the poling treatment, their domain configurations were observed using a polarizing microscope (Nikon LABOPHOTO2-POL). Finally, their piezoelectric properties were measured using an impedance analyzer (Agilent HP-4294A) and the special designed attachment[22] by the resonance-antiresonance method.[23] Moreover, d_{33} was also measured using a piezo d_{33} meter (ZJ-4B, Chinese Academy of Science).

3. RESULTS AND DISCUSSION

3.1 Preparation of [110]-grain-oriented $BaTiO_3$ ceramics

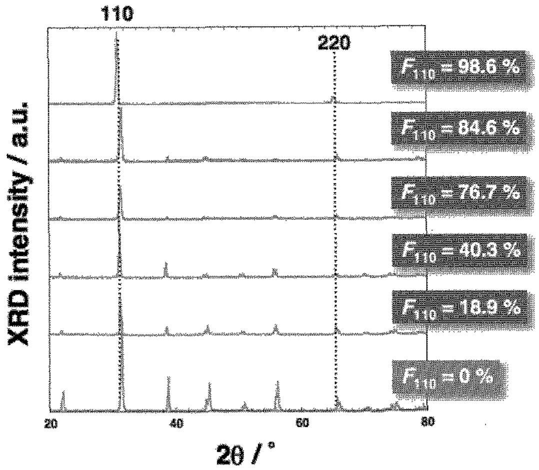

Fig. 1 XRD patterns and F_{110} values measured using Lotgering method for grain-oriented $BaTiO_3$ ceramics.

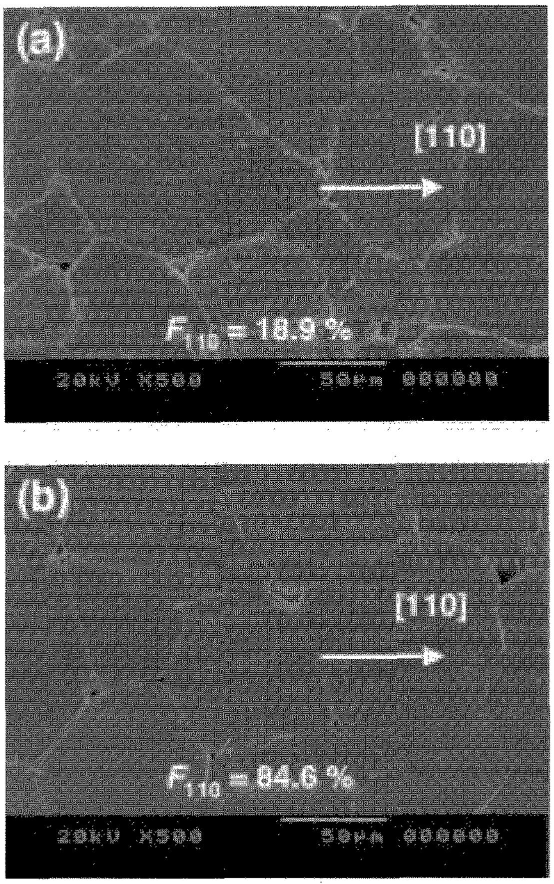

Fig. 2 Microstructure parallel to stacking [110] directions for $BaTiO_3$ ceramics with F_{110} values of (a) 18.9 and (b) 84.6 %

The grain-oriented $BaTiO_3$ ceramics were prepared by the TGG method with the template and matrix particles. First, the effect of the size of the matrix particles was investigated. The BT-01, BT-03, and BT-05 particles were mixed with the template particles at various weight ratios from 0 to 100 %, and the green compacts were sintered at 1400 °C. After that, density and F_{110} were measured. In this study, as for the parameters for the preparation of grain-oriented $BaTiO_3$ ceramics, (1) template particle content to matrix particle content, (2) BT-01 particle content to BT-03 particle content, and (3) sintering temperature were optimized. Figure 1 shows the XRD patterns and F_{110} values measured using the Lotgering method. From Fig. 1, it was revealed that the F_{110} values were continuously controlled from 0 to 98.6 %. Moreover, the density dependence on F_{110}

values for the $BaTiO_3$ ceramics was also investigated. Despite various F_{110} values, the relative densities were always more than 96 %, and the high density suggested that poling treatment can be performed using these ceramics.

Finally, the microstructure of these ceramics were observed using SEM. Figure 2 shows the microstructure parallel to the stacking [110] directions for the $BaTiO_3$ ceramics with F_{110} values of 18.9 and 84.6 %. From Fig. 2, the average grain sizes were around 75 μm for both ceramics, and these average grain sizes were almost the same for all of the ceramics prepared in this study despite various F_{110} values. In this study, the main objective is to induce and obtain fine domain sizes, and to decrease grain size down to 1 μm.

3.2 Piezoelectric properties of [110]-grain-oriented $BaTiO_3$ ceramics

In a previous study using $BaTiO_3$ crystals, the poling treatment above the Curie temperature of 133 °C was required to induce fine domain configuration.[15-17] However, the $BaTiO_3$ ceramics in this study had a high leakage current above the Curie temperature, and thus, the poling treatment was performed at 100 °C. To induce a finer domain configuration, the preparation of $BaTiO_3$ ceramics with a low leakage current is required in the future. After the poling treatment, the piezoelectric constant d_{31}, the elastic compliance s_{11}^E, the electromechanical coupling coefficient k_{31}, and the dielectric constant ε_{33}^T were measured using the resonance-antiresonance measurement[23], while d_{33} was measured using a piezo d_{33} meter. From the resonance-antiresonance measurement for the 31 mode, the maximum phase was around −30°, which suggested that the poling treatment was not complete for these ceramics.

Table I shows a summary of the F_{110} dependence of the piezoelectric properties. As for the reference, the data of the [110]-poled $BaTiO_3$ single–domain crystal was also listed. For this measurement, the maximum phase was around +90° for the 31 mode resonance peak. From Table I, the k_{31} and ε_{33}^T were around 15 % and 1,500, respectively, and were almost constant despite various F_{110}. On the other hand, the s_{11}^E was almost constant at around 11 pN/m^2 below an F_{110} of 70 %, but above an F_{110} of 70 %; the s_{11}^E increased significantly and at an F_{110} of 84.6 %, there was a maximum value of 20.1 pN/m^2. Over an F_{110} of 85 %, the s_{11}^E decreased significantly down to 9.1 pN/m^2.

Figure 3 shows the F_{110} dependences of d_{31} and d_{33}. From Fig. 3, the d_{31} was almost constant at −50 pC/N despite various F_{110} values, while the d_{33} increased with increasing F_{110} and at an F_{110} of 84.6 %, the d_{33} reached a maximum of 788 pC/N. However, over an F_{110} of 84.6 %, the d_{33} decreased significantly down to 240 pC/N. For the $BaTiO_3$ ceramics, a large d_{33} of 788 pC/N was first reported, and it should be noted that the d_{33} of 788 pC/N was an average value for the values from 680 to 1,050 pC/N. As a double-check, the strain vs. electric field behavior was also measured at 1 Hz below 2 kV/cm and the apparent d_{33} estimated from this slope almost consisted of the d_{33} measured using the piezo d_{33} meter.

Table I. F_{110} dependence of piezoelectric properties for grain-oriented $BaTiO_3$ ceramics and $BaTiO_3$ single-domain crystal.

F (%)	ε_{33}^T	s_{11}^E (pN/m²)	d_{33} (pC/N)	$-d_{31}$ (pC/N)	k_{31} (%)
18.9	1,704	11.9	84	47.5	11.2
40.3	1,184	9.7	209	40.2	12.6
76.7	1,233	14.6	355	57.3	14.4
82.2	1,339	9.2	507	56.6	17.1
84.6	1,661	20.1	788	93.2	17.1
98.6	1,667	9.1	240	42.8	11.7
100*	2,093	7.7	220	180	47

*measured using [110] poled $BaTiO_3$ single-domain crystal

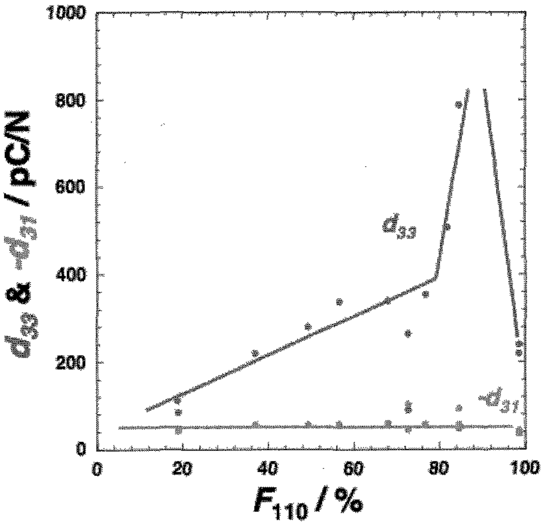

Fig. 3 F_{110} dependence of d_{31} and d_{33} for grain-oriented $BaTiO_3$ ceramics.

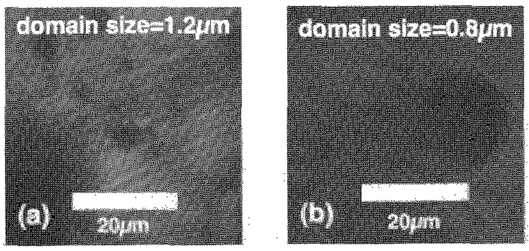

Fig. 4 Domain configurations of $BaTiO_3$ ceramics with F_{110} values of (a) 82.2 (d_{33} ~ 507 pC/N) and (b) 84.6 % (d_{33} ~ 788 pC/N).

To investigate the origin of this high d_{33} values, the domain configuration was observed using a polarizing microscope. Figure 4 shows the domain configurations of the $BaTiO_3$ ceramics with F_{110} values of 82.2 (d_{33} ~ 507 pC/N) and 84.6 % (d_{33} ~ 788 pC/N). From Fig. 5, the average domain size of the $BaTiO_3$ ceramics with an F_{110} of 82.2 % was around 1,200 nm, while that of the $BaTiO_3$ ceramics with an F_{110} of 84.6 % was around 800 nm. Previously, for the [111]-poled $BaTiO_3$ crystals, it was reported that when the 90° domain size became

1,000 nm, d_{33} could become to almost 1,000 pC/N.[17] Thus, the results of this study confirmed that the previous estimation is valid. As mentioned previously, to obtain much finer domain sizes, much smaller grain sizes will be required.[24] Therefore, grain-oriented $BaTiO_3$ ceramics with smaller grain sizes below 1 μm should be prepared in the future.

4. CONCLUSION

In this study, [110]-oriented $BaTiO_3$ ceramics were successfully prepared by the TGG method. It was revealed that the $BaTiO_3$ ceramics had a high density of over 96 % despite various F_{110} values. However, the average grain sizes were around 75 μm, and this size was too large compared with those (1.6~2.1 μm) reported by Takahashi *et al.*[18] and Karaki *et al.*[19] In the future, the grain size should be below 1 μm for grain-oriented $BaTiO_3$ ceramics. To achieve this, a new preparation method without using a template is required. In this study, $BaTiO_3$ ceramics with a d_{33} of 788 pC/N were first obtained. These ceramics had the engineered domain configuration with an average domain size of 800 nm. This high domain wall density was the origin of the d_{33} higher than 500 pC/N. The most important point in this study is the confirmation that the structure gradient region such as the 90° domain wall region had an ultrahigh piezoelectric property intrinsically. This concept is universal, and can be applied to any ferroelectric materials. Using this concept, we can prepare ultrahigh-piezoelectric materials with a d_{33} of 10,000 pC/N in the future.

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