Grain-size dependence of piezoelectric properties in thermally annealed BaTiO$_3$ ceramics

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BaTiO$_3$ ceramics with grain sizes of 4.7–26.1 µm were fabricated using 100 and 300 nm BaTiO$_3$ powders by employing a two-step sintering (TSS) or conventional one-step sintering (CS) method. Polished and cut BaTiO$_3$ samples were annealed for the recovery and relaxation of mechanical-processing-induced surface damage and lattice strain, and the piezoelectric properties were investigated. TSS-BaTiO$_3$ ceramics annealed at 1000°C for 1 h with a grain size of 4.9 µm exhibited an excellent piezoelectric property of $d_{33}=529$ pC/N, while the $d_{33}$ value of CS-BaTiO$_3$ ceramics annealed at 1200°C for 8 h with a grain size of 26.1 µm was 272 pC/N. Besides the excellent piezoelectric properties of the fine-grained BaTiO$_3$ ceramics, the performance of the coarse-grained ceramics was higher than previously reported. The observed superior piezoelectric and electromechanical properties in annealed samples despite the increase in grain size suggested that the effect of annealing was more crucial than that of grain size.

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Key-words : Surface mechanical damage, Thermal annealing, Resonance-antiresonance, Two-step sintering, Piezoelectric properties

1. Introduction

Lead zirconate titanate has been used for sensor and actuators due to the superior piezoelectric properties. However, after the regulations such as directives Waste Electrical and Electronic Equipment and Restriction of the use of certain Hazardous Substances in electrical and electronic equipment were implemented, lead-free piezoelectric materials had been intensively studied. Barium titanate (BaTiO$_3$, BT) is the prototype perovskite-structured piezoelectric material and it is also lead-free. The grain size of BT ceramics has long been known to strongly affect their dielectric,1–4 ferroelectric,5,6 and piezoelectric4) performances. For example, the moderate piezoelectric coefficient $d_{33}$ value of 191 pC/N of BT ceramics with coarse grains was increased to 338, 500, and 519 pC/N by decreasing grain size to 0.94, 1, and 0.99 µm, respectively.8–11) The maxima of the $d_{33}$ values in the BT ceramics at grain sizes of ~1 µm has been attributed to the increased 90° domain wall density.12) However, a change in the $d_{33}$ values from 419 to 185 pC/N by increasing grain size from 7 to 19 µm despite the almost maintained domain width of 480 nm was reported,13) which suggested another mechanism involved.

J. C. Wang14) suggested that the grain-size effect in BT ceramics was not absolute and there was a trend different from the traditional one. Moreover, the electrical properties could be affected by the nature of raw materials, their stoichiometry, and processing techniques used.9) Strain and/or surface mechanical damage induced by mechanical processing (polishing and cutting) have been pointed out to affect their ferroelectric and piezoelectric properties.15,16) The stress imposed on the ceramics’ surface was reported to be removed by annealing treatment.17) Surface status of a sample holds a crucial importance in the performance of the material.18) Although numerous reports have been published regarding the grain-size effect on the piezoelectric properties in fine- and coarse-grained BT ceramics, there is no systematic study conducted on the correlation of grain size and piezoelectric properties after heat treatment on the mechanically processed BT ceramics.

Understanding of the effect of grain size and mechanical-processing-associated lattice strain induced in the samples on piezoelectric properties of BT ceramics before and after the heat treatment is of great importance from the scientific and technological point of view. In this study, the polished and cut BT ceramics were annealed at various temperatures and durations, and their piezoelectric properties were investigated as a function of grain size.
2. Experimental procedure

The BT ceramics were fabricated using 100 and 300 nm BT powders (Sakai Chemical Industry), which hereafter are referred to as BT01 and BT03, respectively. The BT01 and BT03 powders were mixed with a binder (2 wt% polyvinyl butyral; PVB) and hand-milled to a fine powder, and sieved through a 250 μm mesh screen. Green pellets with a diameter of 10 mm and thickness of ~1.5 mm were then prepared by uniaxial pressing at 250 MPa. After the binder was removed at 700°C for 10 h, the pellets of BT01 were sintered by the modified two-step sintering (TSS) program as reported by Karaki et al., at which the temperature was first raised up to 1000°C at a rate of 5 °C/min and then rapidly increased to 1260°C at a heating rate of 10 °C/min. After keeping for 1 min at 1260°C, the temperature was rapidly decreased to 1150°C at a cooling rate of 30 °C/min and was maintained for 15 h. The BT03 pellets were sintered by conventional one-step sintering (CS) at 1350°C for 5 h in air. The density of the sintered sample was evaluated by an Archimedes method. The sintered-disc-BT ceramics were polished down to 0.4 or 0.8 mm in thickness on an automatic polishing machine (MA-200E, Musashino Denshi) using a diamond slurry of particle size of 9 and 3 μm with polishing discs rotating at 150 rpm. The pressure imposed by a sample holder on the disc BT ceramics was 26 kPa. The polished samples were cut using a cutting machine (IsoMet 1000 precision saw, Buehler) with a diamond blade. The 0.4-mm-thick disc ceramics were cut to a size of 4 × 1.5 × 0.4 mm³ (plate-type samples). These samples were used for evaluation of dielectric and ferroelectric properties. On the other hand, the 0.8-mm-thick disc samples were initially cut to a size of 1.4 × 0.8 × 3.0 mm³, and then they were polished down to a size of 0.8 × 0.8 × 2.4 mm³ (bar-type samples for evaluation of piezoelectric properties). Here, the surfaces of 2.4 × 0.8 and 0.8 × 0.8 mm² were polished with pressures of 50 and 187 kPa, respectively. Then, the as-prepared (polished and cut) TSS-BT01 plate- and bar-type samples were annealed in air at 1000°C for 1 or 4 h, while CS-BT03 plate- and bar-type samples were annealed in air at 1200°C for 4 or 8 h. The crystal structures of the annealed powders and the surfaces of BT plate samples that were prepared in a dimension of 5 × 5 × 0.5 mm³ were identified by X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu Kα radiation. For the measurement of electrical properties, Au-electrodes were sputtered on the upper and lower surfaces (4.0 × 1.5 mm² and 0.8 × 0.8 mm²) of both the annealed and samples without annealing (WA) treatment via sputter deposition and fired at 300°C for 10 min. The microstructures were evaluated by scanning electron microscopy (SEM) (JEOL JSM-6510, Japan). Thermal etching was done at 1160°C (TSS-BT01) and 1250°C (CS-BT03) for 10 min and the average grain size was estimated using a line intercept method.

The ferroelectric properties were investigated by polarization–electric field responses, which was measured at 0.1 Hz and room temperature using a ferroelectric and strain measuring system (JP005-SE, Kitamoto Denshi). The frequency dependence of the dielectric constant was measured using an impedance analyzer (HP4294A, Agilent). The dielectric and ferroelectric properties were measured for the plate-type samples. For piezoelectric measurements, the bar-type samples were poled under the DC electric field of 40 kV cm⁻¹ for 30 min in the silicone oil bath at 100°C and the electric field was maintained during cooling to 50°C. The piezoelectric charge constant d₃₃, electromechanical coupling factor k₄₃, and elastic compliance constant s₃₂ were calculated for the poled sample by the resonance-antiresonance method. The d₃₃ value was also measured by an d₃₃ meter (PiezoMeter PM300, Piezotest).

3. Results and discussion

The densities of the two-step sintered BT01 (TSS-BT01) and conventionally sintered BT03 (CS-BT03) ceramics with and without annealing were higher than 96% with no significant differences, before and after the annealing. XRD patterns investigated for the powdered BT-samples with and without annealing are shown in Figs. 1(a) and 1(b). Similar patterns were observed among the samples, with single phase perovskite structures and tetragonal symmetry. However, remarkable differences of peak inten-

![Fig. 1. Cu Kα X-ray diffraction patterns of powdered BT ceramics (a, b) and ceramics’ surfaces (c, d) measured at RT for TSS-BT01 and CS-BT03 ceramics. Measurement range is (a, c) 20° < 2θ < 60°, (b, d) 44° < 2θ < 46° for (002) and (200) peaks.](image-url)
sities for [(002), (200)], [(102), (201)], and [(112), (211)] peaks were observed in the XRD patterns exhibited by the samples’ surfaces before and after the annealing as shown in Figs. 1(c) and 1(d). Broad diffraction peaks of the polished surfaces in both of the BT ceramics became sharper after the annealing. Moreover, the increase in the intensity of the (200) peak was observed. The broadening of diffraction peaks with lowered peak intensities has been ascribed to the surface damage.\(^ {19}\) In unpoled polycrystalline tetragonal piezoelectric ceramics with randomly oriented domains, the ratio of the intensities of the two peaks \(I_{(002)}/I_{(200)}\) is expected to be \(\sim 0.5\), although the ratio is usually 0.58 in the unstressed state.\(^ {20}\) The value of the intensity ratio higher than 0.5 indicates that the c-domains are preferentially existed by polishing.\(^ {21}\) The \(I_{(002)}/I_{(200)}\) in the TSS-as-polished BT01 ceramics was 1.36, while the value was 1.18 for the CS-as-polished BT03 ceramics. The higher values of the intensity ratio for the TSS-as-polished BT01 ceramics suggested the presence of greater extent of mechanical damage in comparison to the CS-as-polished BT03 ceramics. The lateral force exerted during the mechanical processing may be responsible for the expansion of the surface damage.\(^ {19}\) In unpoled polycrystalline tetragonal piezoelectric ceramics with randomly oriented domains, the ratio of the intensities of the two peaks \(I_{(002)}/I_{(200)}\) is expected to be \(\sim 0.5\), although the ratio is usually 0.58 in the unstressed state.\(^ {20}\) The value of the intensity ratio higher than 0.5 indicates that the c-domains are preferentially existed by polishing.\(^ {21}\) The \(I_{(002)}/I_{(200)}\) in the TSS-as-polished BT01 ceramics was 1.36, while the value was 1.18 for the CS-as-polished BT03 ceramics. The higher values of the intensity ratio for the TSS-as-polished BT01 ceramics suggested the presence of greater extent of mechanical damage in comparison to the CS-as-polished BT03 ceramics. The lateral force exerted during the mechanical processing may be responsible for the expansion of lattice along c-axis thus imparting c-domain preference. Annealing has been reported to be effective in removing the polishing-induced c-domain preference.\(^ {21–23}\) After the annealing at 1000°C for 1 and 4 h, the value of \(I_{(002)}/I_{(200)}\) in the TSS-BT01 ceramics was 0.69 for both annealing durations, which suggested the annealing condition was still not sufficient to remove the surface mechanical damage completely. On the other hand, the ratio was 0.48 in the CS-BT03 ceramics after the annealing at 1200°C for 4 and 8 h. The heat treatment of the CS-BT03 ceramics at 1200°C revealed the complete removal of the c-domain preference. In addition, the Williamson-Hall analysis of in situ synchrotron radiation X-ray diffraction patterns of the CS-BT03 ceramics in our previous study has suggested the reduction of lattice strain of surface mechanical damaged layer after the heat treatment at 1200°C.

The microstructures of the TSS-BT01 and CS-BT03 ceramics before and after the annealing are shown in Fig. 2. The average grain size of the as-sintered TSS-BT01 ceramics was 4.7 \(\mu m\). After the annealing at 1000°C for 1 and 4 h, the average grain size was increased to 4.9 and 5.5 \(\mu m\), respectively. The conventionally prepared BT03 ceramics sintered at 1350°C for 5 h exhibited a grain size of 15.9 \(\mu m\), while after annealing at 1200°C for 4 and 8 h, the grain size was increased to 20.7 and 26.1 \(\mu m\), respectively. No significant differences were observed other than the increase of the grain size by the annealing.

The dielectric constant as a function of grain size is shown in Fig. 3. Data from previous reports were also included.\(^ {3,6,9,10,12,13,24}\) The fine-grained thermally annealed TSS-BT01 ceramics with grain sizes of 4.9 and 5.5 \(\mu m\) exhibited the dielectric constant of 6000 and 5700, respectively, which are higher than those reported previously.\(^ {43–46}\) The coarse-grained BT03 ceramics exhibiting a grain size of 20.7 and 26.1 \(\mu m\) revealed the dielectric constant comparable to the previous reports.\(^ {5,13}\)
4.9–26.1 μm was 12.7–17.5 μC/cm², the value significantly higher than that of preceding reports. On the other hand, coercive field (E_c) with the values comparable to previous studies were observed. At grain size of 4.9 μm, the increase in P_r value was attributed to the fine-grain-size associated effect, while the increase in E_c value was due to the difficult domain switching in the mechanically distorted lattice that pinned the domains.

Figure 5 shows the frequency dependence of the impedance and phase angle of poled BT ceramics with different grain sizes. The phase angle for the TSS-BT01 ceramics without annealing (WA-TSS-BT01) was 46° [Fig. 5(a)], which was rather low and indicated that poling was difficult. The phase angle of 46° was similar to the previous report for BT-based piezoelectric ceramics (44°). The difficult poling due to the restricted domain wall motion has been reported in fine-grained BT-based piezoelectric ceramics (44°).25) However, in this study, insufficient poling in TSS-BT01 ceramics could be related to the inhibited domain wall motion that was originated from the mechanical-processing-induced surface mechanical damage and stress. The phase angles of 46° was similar to the previous report for BT-based piezoelectric ceramics (44°).25) However, in this study, insufficient poling in TSS-BT01 ceramics could be related to the inhibited domain wall motion that was originated from the mechanical-processing-induced surface mechanical damage and stress. The phase angles of 46° was similar to the previous report for BT-based piezoelectric ceramics (44°).

Table 1 summarizes the grain sizes, d_{33} measured by the d_{33}-meter and the resonance method, k_{33}, and s_{33}E of the BT ceramics without and with annealing treatment. The d_{33} value for the WA-TSS-BT01 ceramics was 330 pC/N, which was increased to 529 and 459 pC/N after the thermal annealing at 1000°C for 1 and 4 h, respectively. Meanwhile, the grain size was increased from 4.7 μm to 4.9 and 5.5 μm after the annealing at 1000°C for 1 and 4 h, respectively. The d_{33} value of 529 pC/N with an electromechanical coupling factor of 53% is the highest value reported so far for conventionally prepared randomly oriented BT ceramics besides the exceptionally high d_{33} value of grain-oriented BT ceramics.26)

The d_{33} values after the annealing were remarkably large in comparison to the value of the sample without the heat treatment. This enhancement was due to the annealing out of the surface mechanical damaged layers and relaxation of the induced lattice strain. However, the d_{33} value of

Fig. 4. Ferroelectric properties in thermally annealed BT ceramics. (a) Bipolar P–E hysteresis loops measured at 0.1 Hz and RT, (b) Variation of remanent polarization (P_r) and coercive field (E_c) with grain size.

Fig. 5. Frequency dependence of impedance and phase in poled BT01 (a–c) and BT03 (d–f) ceramics. a) without annealing, b) annealed at 1000°C-1 h, c) annealed at 1000°C-4 h, d) without annealing, e) annealed at 1200°C-4 h, and f) annealed at 1200°C-8 h.
the TSS-BT01 ceramics annealed for 4h was lower than that for 1h. The difference was attributed to the increased grain size. The $d_{33}$ value calculated from the resonance method also exhibited the similar trend as the results from the $d_{33}$-meter. Following the similar trend, the BT03 ceramics conventionally sintered at 1350°C exhibited the piezoelectric constant increase from 195 pC/N to 329 and 272 pC/N after thermal annealing at 1200°C for 4 and 8h, respectively. The average grain size of the CS-BT03 without the heat treatment was $\sim 16\mu m$, which was increased to 20.7 and 26.1 $\mu m$ by annealing at 1200°C for 4 and 8h, respectively. In comparison to the piezoelectric and electromechanical properties of the 1200°C-4h annealed CS-BT03 ceramics, the properties of the 1200°C-8h annealed ceramics was lower in a similar way as the 1000°C-4h annealed TSS-BT01 ceramics did.

With increasing grain size above 1–2 $\mu m$, there are several reports showing the decrease of the piezoelectric and electromechanical properties.9),12),14) Despite the smaller grain size of the WA-TSS-BT01 and WA-CS-BT03, the properties were lower than those of the annealed ceramics. Thus, the variations of $d_{33}$, $k_{33}$, and $s_{33}$ E observed in this study could not be explained solely in terms of varying grain size. The variation was explained in terms of the simultaneous effect of annealing and grain size. Annealing effect was more pronounced in the 1000°C-1 h annealed TSS-BT01 ceramics and the 1200°C-4 h annealed CS-BT03 ceramics, which were attributed to the relaxation of the mechanical stress and the removal of surface mechanical damage with the limited increases in the grain size. On the other hand, the longer annealing of the TSS-BT01 ceramics at 1000°C for 4h and the CS-BT03 ceramics at 1200°C for 8h increased the grain size, which reduced the properties. However, the properties were still higher than those of the samples without the annealing, which was attributed to the recovery of the mechanical damage by the annealing.

The grain-size dependence of the $d_{33}$ value measured by the $d_{33}$-meter in this study was compared with the previous reports5),6),9),10),12),13),14) and plotted as shown in Fig. 6. The plot clearly distinguishes the $d_{33}$ values for both fine- and coarse-grained BT ceramics obtained in this study and previous reports. The piezoelectric constant of 529 pC/N obtained for the TSS-BT01 ceramics with the grain size of 4.9 $\mu m$ is the highest value reported so far for randomly oriented BT ceramics. Moreover, the $d_{33}$ values obtained for the coarse-grained BT ceramics were also higher than previously reported. The enhancement of the piezoelectric constant was attributed to the annealing effect that recovered the surface mechanical damage of the polished and cut BT ceramics and relaxed the induced lattice strain.

4. Conclusion

Highly dense BT ceramics with varying grain size in the range of 4.7–26.1 $\mu m$ were prepared by CS and TSS method using 100 and 300 nm BT powders. The trend of the average grain-size dependence of the $d_{33}$ values observed in this study is in agreement with previous reports, however, the obtained values were higher. The $d_{33}$ of 529 pC/N and $k_{33}$ of 53%, exhibited for the TSS-BT01 ceramics with the grain size of 4.9 $\mu m$, are the highest values ever reported for the polycrystalline randomly oriented BT ceramics. Besides the observed higher piezoelectric and electromechanical properties in fine-grained BT ceramics, superior properties were obtained in coarse-grained ceramics with a grain size larger than 20 $\mu m$. The variation of $d_{33}$, $k_{33}$, and $s_{33}$ E with varying grain size was explained by the combined effect of annealing and grain size.Annealing was found to decrease mechanical-processing associated stress thereby increasing the $d_{33}$ value measured using the resonance method by 84% in the TSS-BT01 ceramics and 56% in the CS-BT03 ceramics. The extent of piezoelectric-enhancement-difference in TSS-BT01 and CS-BT03 revealed the effectiveness of annealing

Table 1. Various properties parameters in BT ceramics (Note: TSS = two-step sintering, CS = conventional sintering, WA = without annealing, A10 = annealing at 1000°C, and A12 = annealing at 1200°C)

| Status            | Grain Size ($\mu m$) | $d_{33}$ (pC/N) | $d_{33}$ (pC/N) | $k_{33}$ (%) | $s_{33}$ (-) |
|-------------------|----------------------|-----------------|-----------------|--------------|--------------|
| TSS-BT01, WA      | 4.7                  | 330             | 244             | 33           | 14.4         |
| TSS-BT01, A10-1 h | 4.9                  | 529             | 455             | 53           | 15.9         |
| TSS-BT01, A10-4 h | 5.5                  | 459             | 371             | 48           | 14.9         |
| CS-BT03, WA       | 15.9                 | 195             | 184             | 36           | 10.9         |
| CS-BT03, A12-4 h  | 20.7                 | 329             | 287             | 54           | 12.1         |
| CS-BT03, A12-8 h  | 26.1                 | 272             | 222             | 42           | 11.4         |

Fig. 6. Grain-size dependence of piezoelectric constant in poled BT ceramics prepared by various methods.
treatment for the samples having mechanical-processing-induced surface mechanical damage. This study suggested that the factor that primarily affected the performance of BT ceramics was the extent of surface mechanical damage induced in the sample, which was followed by grain size. Based on the finding of this study, fine-grained (grain size of $\sim 1-2\mu m$) BT ceramics, free of mechanical processing induced stress, is expected to exhibit further high piezoelectric properties.

Acknowledgment The authors would like to thank Sakai Chemical Industry Co., Ltd. for providing BT powders.

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