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Structure and properties of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared by spark plasma sintering

Hiroshi Maiwa

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Abstract $Ba(Zr_{0.2}Ti_{0.8})O_3$ (BZT) ceramics are prepared from spray-dried powder by spark plasma sintering (SPS) and by normal sintering. By the application of SPS, ceramics with >96% relative densities could be obtained by sintering at 1,100 °C for 5 min in air atmosphere. The pellet as sintered by SPS at 1,100 °C was black and conductive. Although SPS was carried out in air atmosphere, the samples were deoxidized by heating the carbon die. By post-annealing at 1,000 °C for 12 h in air, the pellet was oxidized and became white and insulating. Grain growth was suppressed in the ceramics prepared by SPS, and the average grain size was 0.52 μm. The starting powder contained 1.90% carbon, mainly as binder, and the SPS-prepared ceramics and ordinary prepared ceramics contained 0.15 and 0.024% carbon, respectively. The BZT ceramics obtained by SPS and the subsequent annealing at 1,000 °C for 12 h exhibited a mild temperature dependence of their dielectric constant. The field-induced displacement of the BZT ceramics was less hysteretic and smaller than that of the ceramics sintered by the conventional method.

Introduction

$Ba(Zr_{1-x}Ti_x)O_3$ (BZT) ceramics have ferroelectric relaxor characteristics [1, 2], and they have been studied for application in capacitor devices. Recently, we have observed a mild temperature-dependent dielectric constant of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ thin films prepared by chemical solution deposition. The grain size of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ films was <100 nm [3]. Also recently, barium titanate has attracted attention because of the demand for lead-free piezoelectrics. Barium titanate with fine grains of ~1-μm diameter shows excellent piezoelectric properties because of the small grain size [4, 5]. The characterization of fine-grained $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics is important for clarification of the temperature dependence of dielectric behavior and electromechanical properties of this system. However, it is well known that the preparation of fine-grained and dense ceramic samples is difficult by conventional sintering. Therefore, microwave sintering [4] or two-step sintering [5] has been applied to the fabrication of high-density ceramics with suppressed grain growth. Although these processes are effective in some cases, both processes are pressureless sintering methods, and dense ceramics are not always obtained.

In order to prepare fine-grained and dense BZT ceramic samples, I chose spark plasma sintering (SPS) in this study. Since SPS enables compact powder to be sintered to a high density at a relatively lower temperature in a shorter sintering period, SPS has an advantage of suppressing exaggerated grain growth over conventional sintering [6, 7]. $BaTiO_3$ ceramics obtained by SPS have an average grain size of <1 μm and show a high dielectric constant of 10,000 at room temperature, as reported by Takeuchi et al. [8]. However, to the best of my knowledge, the electromechanical properties of SPS $BaTiO_3$ ceramics have not yet been reported. Recently, I described the preparation of preliminary SPS BZT ceramics starting from the powder prepared by hydrothermal methods. The dielectric and electromechanical properties of the dense BZT are unique compared with the BZT ceramics prepared by conventional sintering [9].

In this paper, I report the structure and dielectric and electromechanical properties of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics

H. Maiwa (✉)
Department of Materials Science and Engineering, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa 251-8511, Japan
e-mail: maiwa@mate.shonan-it.ac.jp

prepared by SPS from spray-dried $Ba(Zr_{0.2}Ti_{0.8})O_3$ powders. Those properties of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared by conventional sintering are also reported for comparison with the SPS-prepared ceramics. Since spray-dried powders are widely used in manufacturing, the investigation of the properties of ceramics starting from spray-dried powders is meaningful work. In addition, this paper contains the crystallographic information and details about the carbon content of the SPS and ordinal sintered ceramics that were not included in previous reports [9]. The obtained information may be helpful for application to the fabrication of multilayer capacitors and lead-free piezoelectrics.

Experimental procedures

The starting powder used was the commercial BZT ceramic powder prepared by the spray-drying method, with $Ba(Zr_{0.2}Ti_{0.8})O_3$ composition (Hayashi Chemicals). The ceramic powder contains organic binder to help in ceramic formation. In the case of conventional sintering, the powders were pressed in a die at a pressure of 80 MPa and sintered in air for 2 h from 1,200 to 1,450 °C. In the case of SPS, SPS-511S (SPS Syntex Inc.) raw powder was placed in a graphite die (10-mm diameter) without experiencing binder-burnout process, and sintering was carried out in air atmosphere at a pressure of 60 MPa. The temperature was increased to 1,100 °C within 11 min and maintained for 5 min. Applied electric current was controlled to follow the sintering temperature. After the temperature was maintained for 5 min, the applied current was switched off, pressure was released, and the sample was cooled to room temperature. The as-sintered pellet was annealed at 1,000 °C for 12 h in air. We determined the carbon content of the powder and ceramics using infrared light absorption during combustion of the powder in oxygen flow in an inductively coupled furnace (Horiba carbon/sulfur analyzer EMIA-710). The sintered samples were polished and then electroded using silver paste. The dielectric constant was estimated from the capacitance measured at 1 kHz using an impedance analyzer (HP 4192A). The measurements of the electric-field-induced displacement and polarization in BZT ceramics were performed using a strain gauge and a charge-amplifier circuit. An alternating electric field of 0.1 Hz was used in these measurements.

Results and discussion

Density and microstructure

The photographs of the pellet as sintered by SPS at 1,100 °C and the pellet post-annealed at 1,000 °C for 12 h in air are shown in Fig. 1. The pellet as sintered by SPS at 1,100 °C was black and conductive. Although SPS was carried out in air atmosphere, the samples were deoxidized by heating the carbon die. By post-annealing at 1,000 °C for 12 h in air, the pellet was oxidized and became white and insulating. The relative density of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared by SPS at 1,100 °C was 5.91 g/cm^3. These ceramics were almost fully sintered. In conventional sintering, the relative densities of the samples increase with sintering temperature and saturate over 1,350 °C, as shown in Fig. 2. The saturation of the density is considered to be due to the exaggerated grain growth of the ceramics. The sintered ceramics' surface was observed by scanning electron microscopy (SEM). SEM images of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics are shown in Fig. 3. The average grain sizes of samples of these ceramics are shown in Fig. 4. Grain growth is promoted by high-temperature annealing in conventional sintering. Note that grain growth was suppressed by SPS. The average grain size of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared by SPS at 1,100 °C was

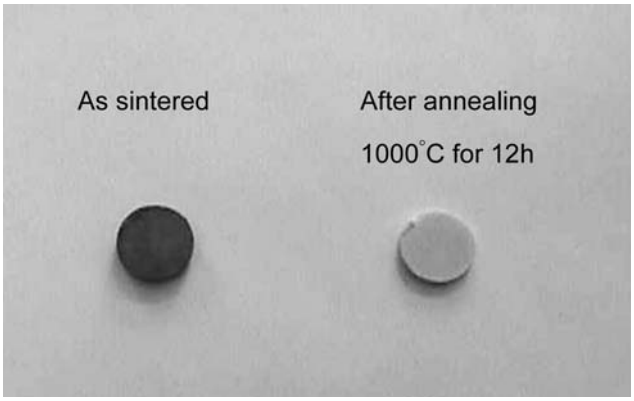

Fig. 1 Photograph of as-SPS $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics and the ceramics after post-annealing at 1,000 °C for 12 h

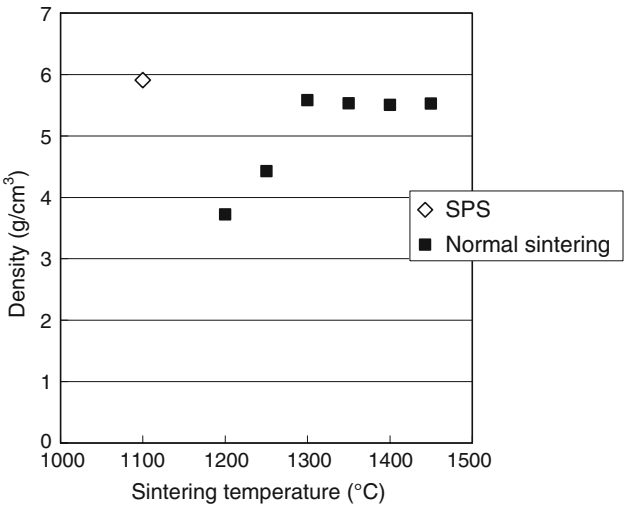

Fig. 2 Relative densities of $Ba(Zr_{0.2}Ti_{0.8})O_3$ samples

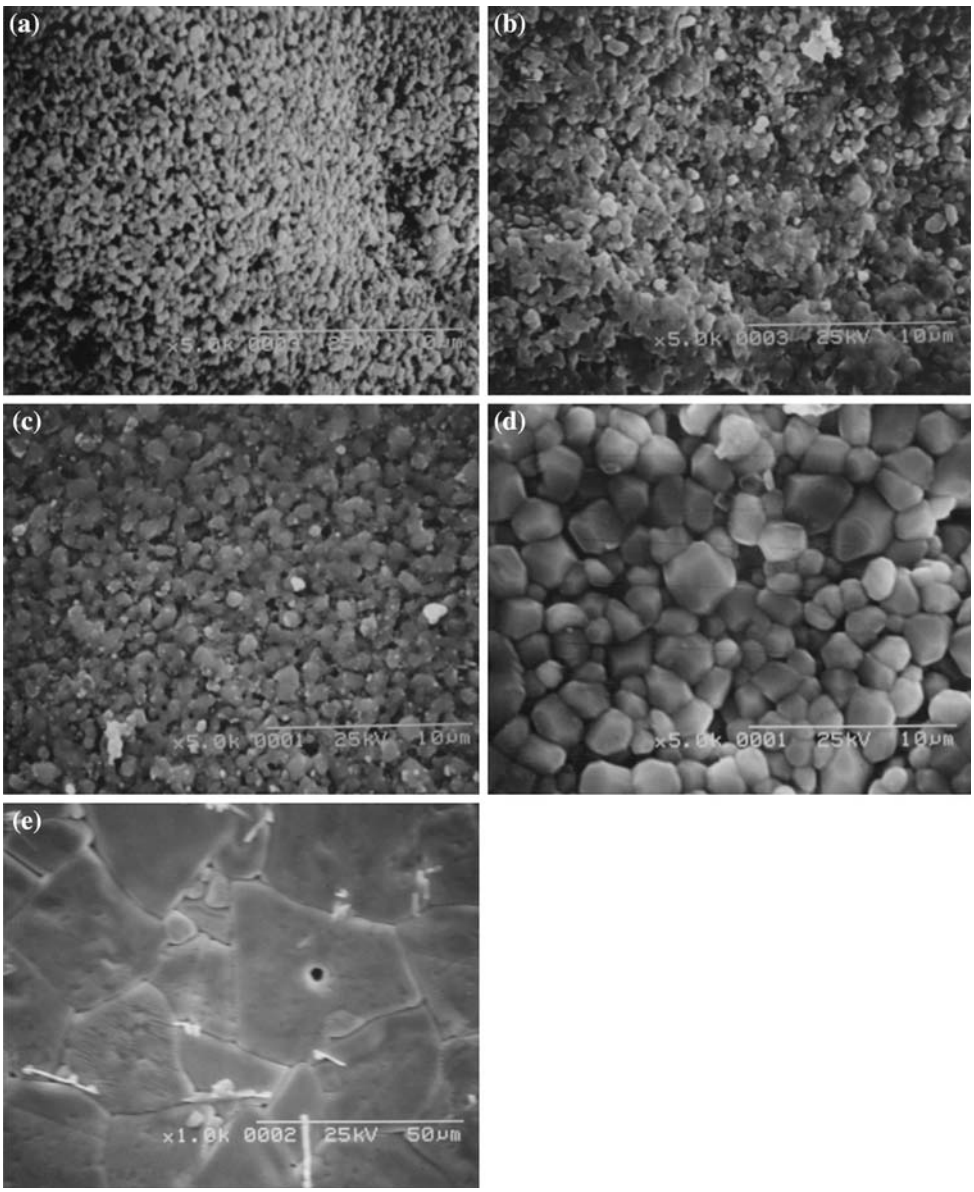

Fig. 3 SEM images of (**a**) starting powders and $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics SPS-prepared at (**b**) 1,100 °C and sintered at (**c**) 1,200 (**d**) 1,300, and (**e**) 1,400 °C

0.52 μm, which is smaller than those of ceramics conventionally sintered at 1,200 °C. It is also smaller than the 0.86 μm of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared from hydrothermal powder by SPS at 1,100 °C [9].

Carbon content

Carbon contents of the starting powder, the pellet as sintered by SPS at 1,100 °C and then annealed at 1,000 °C for 12 h in air, and the pellet conventionally sintered at 1,350 °C are shown in Table 1. Carbon contents of the starting powder were derived from the organic binder. SPS-prepared samples did not experience the binder-burnout process; the organic binders remained after the short-term heat process of SPS. SPS-prepared samples contained approximately six times as much carbon as the conventionally sintered samples. The proportion of carbon was 0.15%, but the samples were good insulators that withstood more than 15 kV/cm electric-field application after post-annealing. Therefore, the carbon content of the SPS-prepared ceramics is not considered to be a serious problem.

Crystallographic analysis

Figures 5 and 6 show X-ray diffraction patterns of SPS-prepared samples and ordinal sintered samples. The as-SPS samples show a sharp peak compared with the post-annealed samples. The reason is not clear at present; it indicates the as-SPS samples have higher crystallinity compared with the post-annealed samples. The peak position of the as-SPS samples is 0.06° lower than that of the post-annealed samples. This difference occurred because the as-SPS sample has

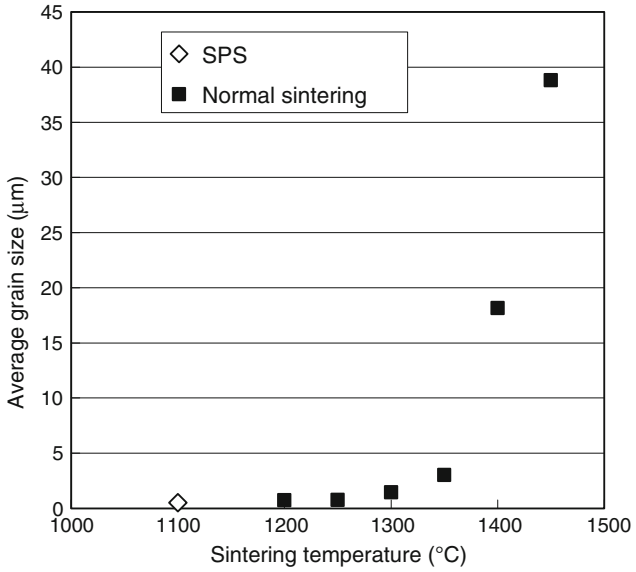

Fig. 4 Average grain sizes of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramic samples

Table 1 Carbon content of the starting powder and ceramics

Samples	Carbon content (%)
Starting powder	1.90
SPS-prepared ceramics post-annealed at 1,000 °C for 12 h	0.15
Ceramics conventionally sintered at 1,350 °C for 12 h	0.024

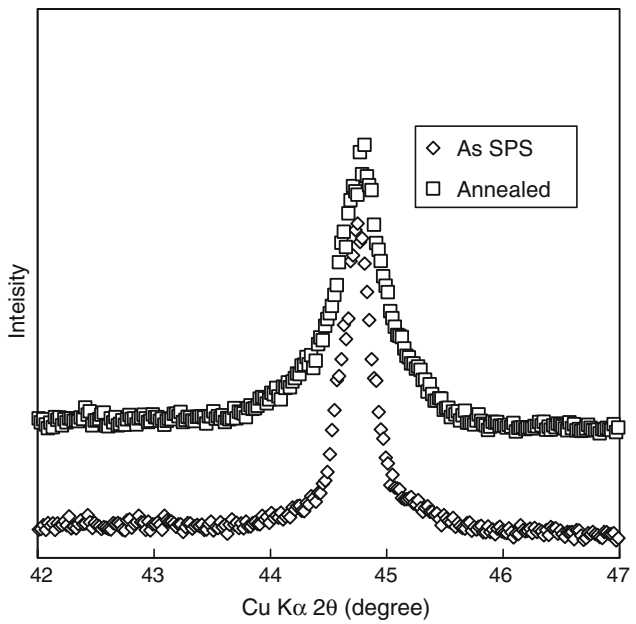

Fig. 5 X-ray diffraction patterns of as-SPS $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics and the ceramics after post-annealing at 1,000 °C for 12 h

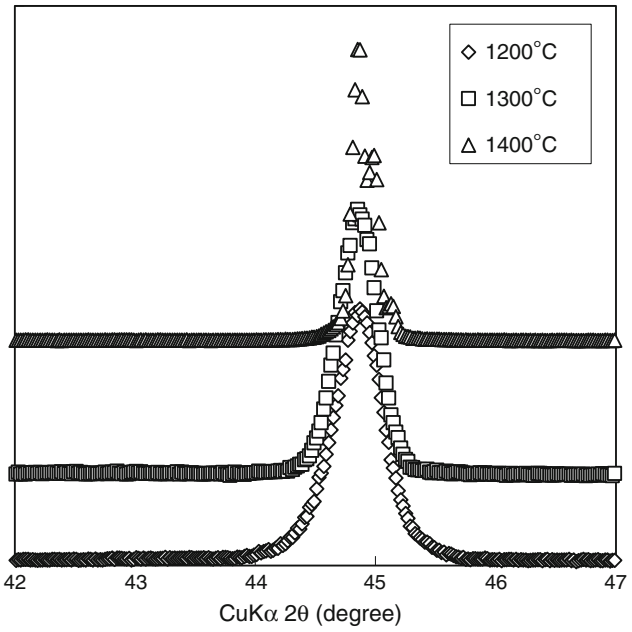

Fig. 6 X-ray diffraction patterns of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics sintered at 1,200, 1,300, and 1,400 °C

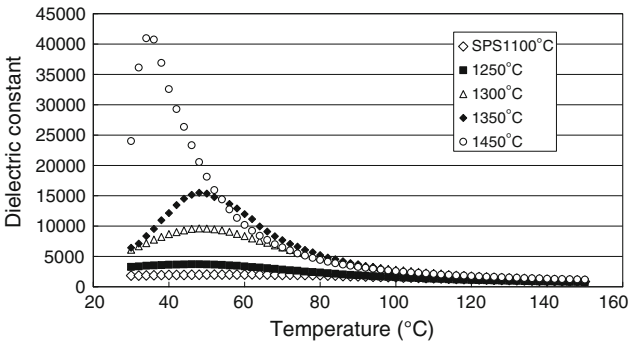

Fig. 7 Temperature dependence of the dielectric constant of Ba $(Zr_{0.2}Ti_{0.8})O_3$ ceramics

a larger lattice constant by deoxidizing. The annealed SPS samples and ordinal samples sintered at 1,200 and 1,300 °C have similar peaks, while the peak from the ceramics sintered at 1,400 °C is sharper than that of the other samples due to improved crystallinity by grain growth.

Dielectric properties

Figure 7 shows the temperature dependence of the dielectric constant of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics. The dielectric anomalies of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics occur at 40–50 °C according to the literature. Our findings coincide well with reported values [1]. As the sintering temperature is increased in normal sintering, the jumps accompanying the dielectric anomaly become clear. The temperature dependence of the SPS-prepared BZT ceramics is relatively mild, and the

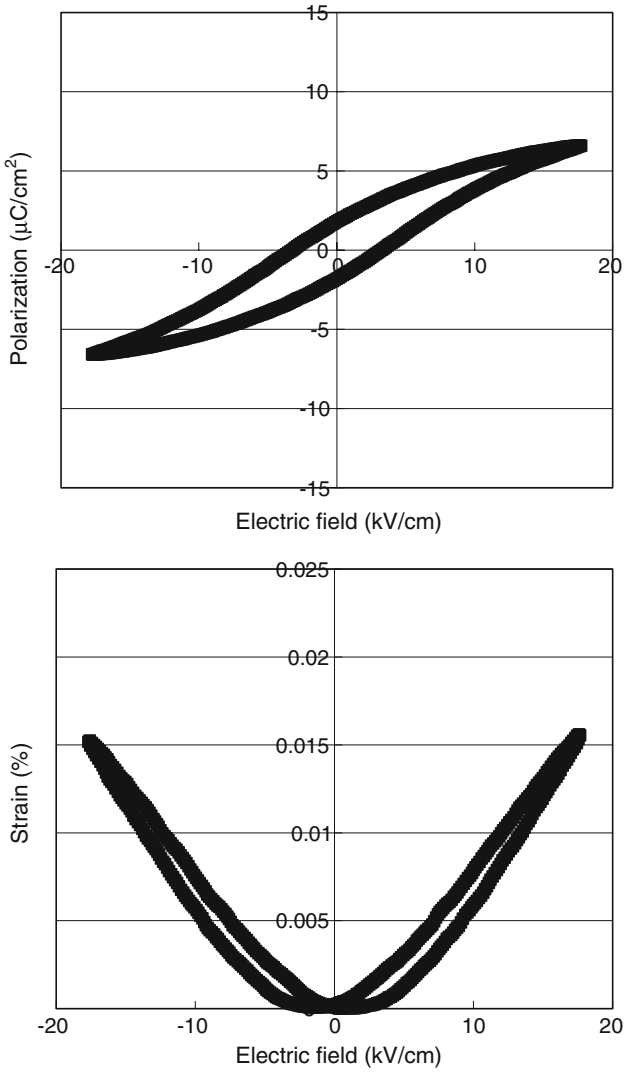

Fig. 8 Polarization hysteresis loops and field-induced displacement of SPS-prepared $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics

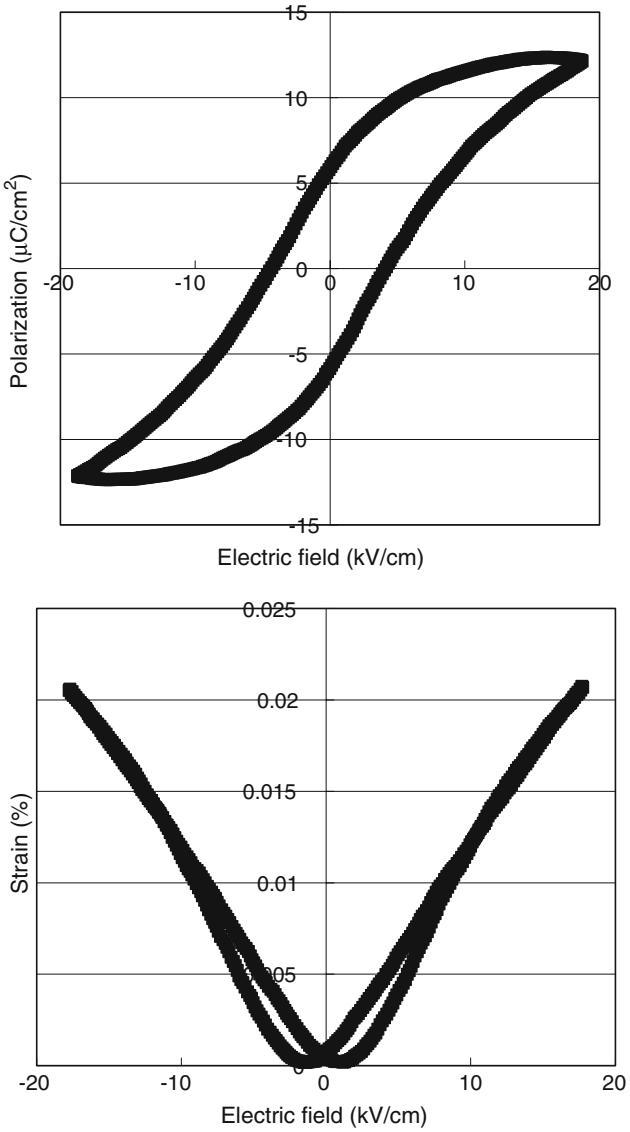

Fig. 9 Polarization hysteresis loops and field-induced displacement of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics conventionally sintered at 1,350 °C

nominal value is comparable with that of the sample sintered at 1,250 °C. The mild temperature dependence of the SPS BZT ceramics is considered to be due to the grain size. The tendency is similar to the case of ceramics sintered with hydrothermal method; however, the obtained samples in this study were less temperature dependent, probably due to the smaller grain size [9].

Electromechanical properties

The polarization hysteresis and field-induced strain loops of the SPS-$Ba(Zr_{0.2}Ti_{0.8})O_3$ and the $Ba(Zr_{0.2}Ti_{0.8})O_3$ conventionally sintered at 1,350 °C are shown in Figs. 8 and 9, respectively. SPS-prepared samples show slim and hyperbolic loops, compared with the conventionally sintered ceramics. It should be noted that the shrinkages accompanying polarization switching are negligible in the SPS-prepared samples. The displacement of the SPS BZT ceramics is smaller than those of the conventionally sintered ceramics. This tendency is similar to the case of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared with the hydrothermal method. Compared with the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared with the hydrothermal method, the strain of the ceramics obtained in this study is smaller [9]. This is mainly due to smaller grain size.

Conclusions

$Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics were prepared by SPS. Ceramics with >96% relative densities could be obtained by sintering at 1,100 °C for 5 min. The grain growth was suppressed, and the average grain size of the SPS ceramics was

0.52 μm. The BZT ceramics obtained by SPS and the subsequent annealing at 1,000 °C for 12 h exhibited mild temperature dependences of their dielectric constant and less hysteretic field-induced strain loops. In conclusion, SPS enabled us to obtain $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics with high densities and small grains. The properties of the SPS-prepared ceramics are unique and are favored for the application to multilayer capacitors with a rigid temperature stability requirement and to actuator applications that require analogue operations.

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