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

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Abstract

$Ba(Zr_{0.2}Ti_{0.8})O_3$ (BZT20) ceramics were prepared by spark plasma sintering (SPS) and conventional sintering. The dynamic field-induced displacement and small-signal remnant piezoelectric constant measured by a resonant–antiresonant frequency method were evaluated. By normal sintering, the density, grain size, and dielectric constant of the ceramics increased with sintering temperature. The BZT20 ceramics prepared by SPS were characterized by linear field-induced strain. In response to the application of post-annealing at 1300 °C, BZT20 ceramics exhibited linear strain loop and high field-induced strain corresponding to dynamic strain/field d_{33} at 20 kV/cm of 290 pm/V. The remnant piezoelectric properties of the BZT20 ceramics were found to largely depend on the preparation conditions, including the sintering temperature and annealing temperature. The BZT20 ceramics prepared by SPS and post-annealed at 1300 °C showed Q_m and k_p values of 325 and 25.1 (%), respectively.

Keywords: A. Sintering; C. Piezoelectric properties; D. $BaTiO_3$ and titanates; E. Actuators

1. Introduction

Barium titanate has recently attracted attention due to the demand for lead-free piezoelectrics. Barium titanate ceramics prepared by microwave sintering [1] or two-step sintering [2] with fine grains approximately 1 μm in size show excellent piezoelectric properties. These high piezoelectric properties are considered to be due to the small grain size. It is well known that the suppression of grain growth results in low-density samples by conventional sintering. Therefore, spark plasma sintering (SPS) was applied in the present study. SPS is a process that uses electrical discharge between particles under pressure of several megapascals. SPS enables a compact powder to be sintered to a high density at a relatively low temperature and with a shorter sintering period. In addition, SPS has an advantage over conventional sintering in that it suppresses exaggerated grain growth. $BaTiO_3$ ceramics obtained by SPS (SPS-BT) have an average grain size at around 1 μm and are characterized by high permittivity, linear field-induced strain corresponding to a dynamic strain/field of 540 pm/V under 15 kV/cm [3]. However, there is a problem with the low Q_m and low k_p for SPS-BT [4].

Zr-doped $BaTiO_3$ (BZT) ceramics are interesting materials that exhibit linear field-induced strain for actuator applications. We have previously reported the microstructure and the dielectric and preliminary electromechanical properties of these materials [5,6]; however, a detailed characterization of the electromechanical properties of BZT has not yet been carried out. In this paper, the electromechanical properties of $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics prepared by SPS (SPS-BZT20) are reported. Those of BZT20 ceramics prepared by conventional sintering are also reported for comparison with the SPS-prepared ceramics. The obtained information is helpful for possible application to the fabrication of lead-free piezoelectrics.

2. Experimental procedures

The starting powder used was commercial $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramic powder (Sakai Chemicals, Japan) prepared by the hydrothermal method. The purity of the sample powder was more than 99%. In the case of conventional sintering, the powder was supplemented with 1% polyvinyl alcohol (PVA) binder, pressed in a die at a pressure of

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80 MPa and sintered in air for 2 h from 1300 to 1450 °C. In the case of SPS, no binder was added to avoid residual organics. Since the pellet is pressed during SPS, a binder is not required. For SPS, SPS-511S (SPS Syntex Inc., Japan) was used; raw powder was placed in a graphite die (10 mm diameter), and sintering was carried out in air atmosphere at a pressure of 60 MPa. The temperature was increased to 1100 °C within 11 min and maintained at that temperature for 5 min, after which the pressure was released and the sample was cooled to room temperature. Since the pellet as-sintered by SPS at 1100 °C is black and conductive, the pellet was annealed at 1100–1400 °C for 12 h in air.

The sintered samples were polished and then produced electrodes using a silver paste. Measurements of the electric field-induced displacement and polarization in BZT ceramics were performed using displacement sensor (Mahr GmbH, Millimar Nr. 1301, Germany) and a charge-amplifier circuit (Kitamoto Electronics, POEL-101, Japan). An alternating electric field of 0.1 Hz was used in these measurements. Prior to the small-signal measurements, including resonant–antiresonant methods and d_{33} measurements with the d_{33} meter (Chinese Academy of Science ZJ-3B, China), the ceramic specimens were polarized for 20 min in a silicone bath under a DC field of 20 kV/cm at room temperature. The resonant–antiresonant methods were carried out using an impedance analyzer (HP 4192A) for an additional 24 h after the polarization.

3. Results and discussion

3.1. Density and microstructure

The relative density of the BZT20 ceramics prepared by SPS at 1100 °C without annealing was 5.89 g/cm^3. The SPS-BZT20 ceramics prepared by SPS at 1100 °C and then annealed at 1100, 1200, and 1300 °C were 5.89, 5.87, and 5.83 g/cm^3, respectively. These ceramics were almost fully sintered. The surface of the sintered ceramics was observed by scanning electron microscopy (SEM, Hitachi S-2100A). SEM images of the BZT20 ceramics prepared by SPS and normal sintered are shown in Figs. 1 and 2, respectively. The SPS-BZT20 ceramics annealed at 1200 °C were found to have very small grains less than 1 μm in diameter. In the SPS-BZT20 ceramics annealed at 1300 °C, small grains less than 1 μm in diameter and relatively large grains several tens of microns in diameter coexisted. Since SPS provided rapid sintering at 1100 °C within 5 min, grain growth was suppressed. As described later, grain growth is limited by normal sintering at 1300 °C and lower, and the fine grains of as-SPS ceramics are taken over after a lower post-annealing temperature of 1200 and 1300 °C. The grains of the SPS-BZT20 ceramics annealed at 1400 °C were all relatively large, more than several tens of microns in diameter.

In conventional sintering, the relative density was found to increase and the grains grew with increases in the sintering temperature. The relative densities of the ceramics sintered at 1300, 1350, 1400, and 1450 °C were 4.67, 5.03, 5.68, and 5.77 g/cm^3, respectively. These values were lower than those of the SPS-BZT20 ceramics. It should be noted that the normally sintered ceramics contained pores, as show in Fig. 2. The average grain sizes were approximately 1 μm for the samples annealed at 1300–1400 °C, with the size increasing slightly with temperature. Grain growth occurred over the range from 1400 to 1450 °C. These characteristics of microstructure development in the normally sintered ceramics are similar to those reported previously [7].

3.2. Field-induced displacement

Figs. 3 and 4 show the field-induced strain of SPS-BZT20 ceramics annealed at 1200 and 1300 °C and the BZT20 ceramics normally sintered at 1300–1450 °C, respectively. The SPS-BZT20 ceramics annealed at 1200 °C exhibited a strain loop with less shrinkage and lower displacement. Since the strain hysteresis behavior accompanying shrinkage is derived from ferroelectric domain switching, ferroelectric domain activities are suppressed, probably due to the residual stress or small grains, or both. The SPS-BZT20 annealed at 1300 °C exhibited a strain loop with large shrinkage and larger displacement. The SPS-BZT annealed at 1400 °C was too leaky to measure the dynamic strain loop under application of a DC field of 10 kV/cm and higher.

In the case of normal sintering, the BZT20 ceramics sintered at 1350 °C exhibited the highest strain among the samples measured. The sample sintered at 1300 °C exhibited

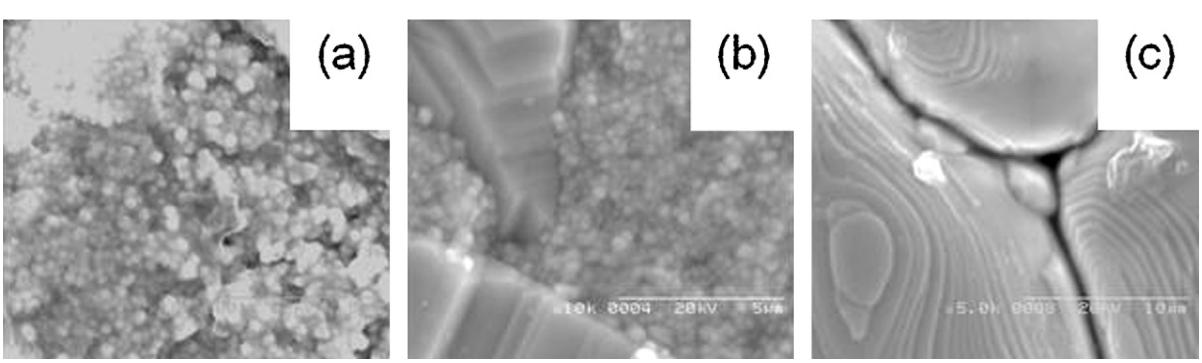

Fig. 1. SEM images of the Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ ceramics SPS-prepared at 1000 °C and annealed at (a) 1200, (b) 1300, and (c) 1400 °C.

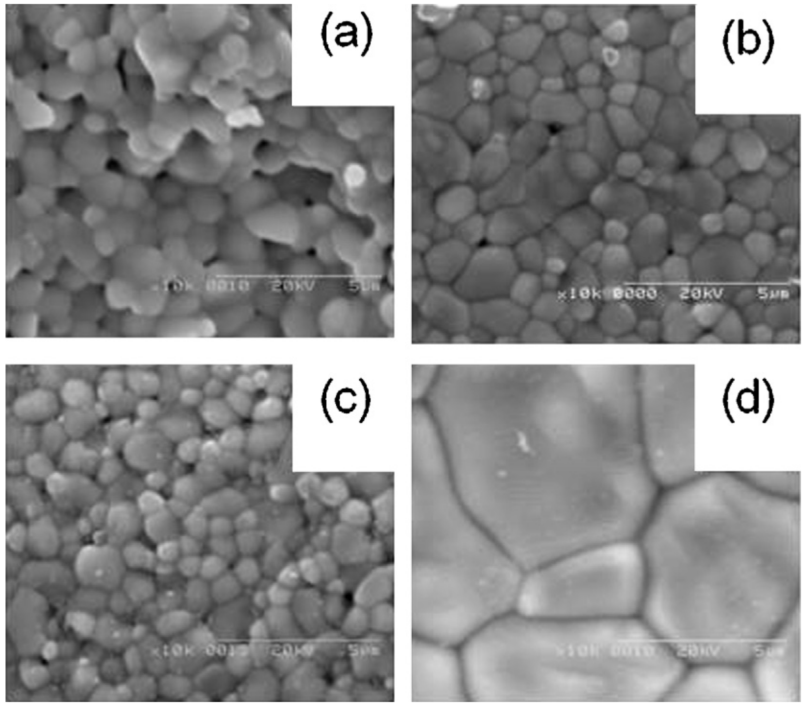

Fig. 2. SEM images of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics normally sintered at (a) 1300, (b) 1350, (c) 1400, and (d) 1450 °C.

smaller strain due to the small grains, low density, or both. The samples sintered at 1400 and 1450 °C exhibited smaller displacement than that sintered at 1350 °C. The grain sizes of these samples were considered to be larger than appropriate for this material. The strain loops became more hysteretic with increasing sintering temperature. In the case of pure $BaTiO_3$ [3], the ceramics with a grain size of 0.61–0.74 μm exhibited the largest field-induced strain, and the ceramics with smaller and larger grains exhibited lower strain. The results obtained here for BZT followed the grain size dependencies seen in pure $BaTiO_3$.

The unipolar field-induced strains of these samples were also measured. The general tendencies were the same as those observed with the bipolar strain loops. The dynamic strain/field at 20 kV/cm of SPS-BZT annealed at 1300 °C and the BZT20 ceramics normally sintered at 1350 °C were 290 and 280 pm/V, respectively. These two values are comparable; however, the SPS-BZT20 yielded a more linear strain curve compared with the sample normally sintered at 1350 °C. This difference can be shown clearly in the dependence of electric field on dynamic d_{33}, which is calculated from the strain/field. The results are shown in

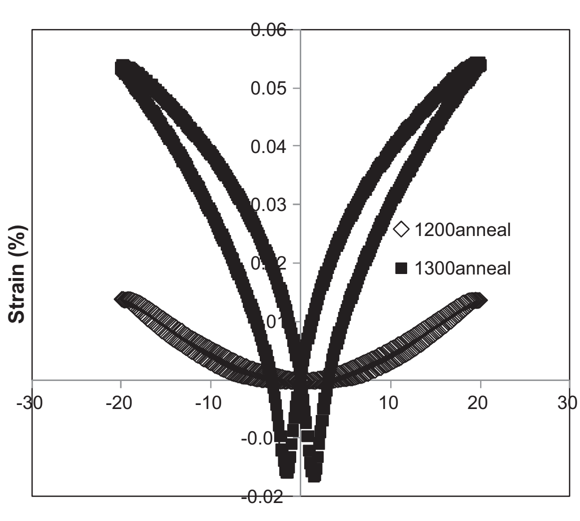

Fig. 3. Field-induced strain of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics SPS-prepared at 1100 °C and then annealed at 1200 and 1300 °C.

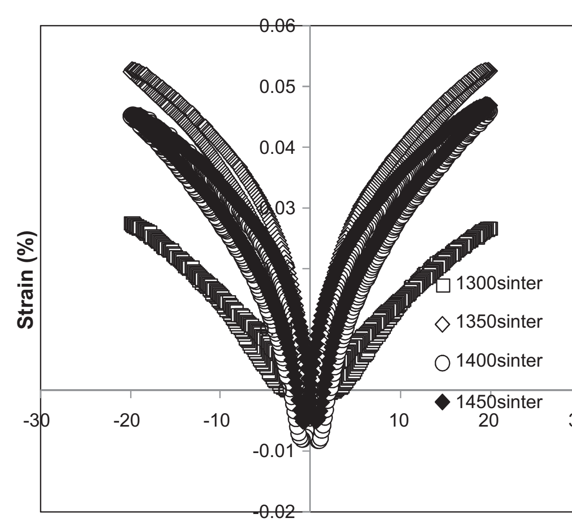

Fig. 4. Field-induced strain of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics normally sintered at 1300, 1350, 1400, and 1450 °C.

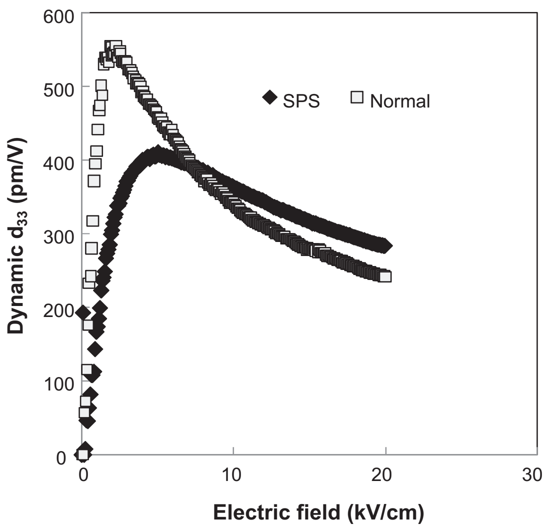

Fig. 5. Field dependence of the dynamic d_{33} calculated from the unipolar field-induced strain.

Fig. 5. Considering the relatively low dielectric constant of 1204, the reason for the linear strain of SPS-BZT20 is considered to be due to the suppressed polarization rotation [3]. The lower hysteretic strain with good linearity for the SPS-BZT20 ceramics is unique and might be desirable for actuator applications that require analogue operations.

3.3. Static measurement

The clear resonance was observed only for the SPS-BZT annealed at 1300 °C and the BZT20 ceramics normally sintered at 1400 °C, as shown in Fig. 6. The piezoelectric properties calculated by the resonance method are included in Table 1. In the case of the SPS-BT, the Q_m and k_p values are 44–62 and 16.2–17.5, respectively [4], which are smaller than the Q_m and k_p values of 325 and 25.1 (%) for the SPS-BZT20 annealed at 1300 °C. The reason for this difference is not clear, but the unique microstructure composed of submicron and coarse grains might play a role in producing the reasonably high Q_m and k_p values. These ceramics exhibit a small loss tangent, generally less than 2%.

Table 1
Piezoelectric properties of samples.

Sample	Q_m	k_p (%)	Dielectric constant	d_{33} (pC/N)
SPS1300	312	25	1204	43
Normal 1400	119	21	7869	91

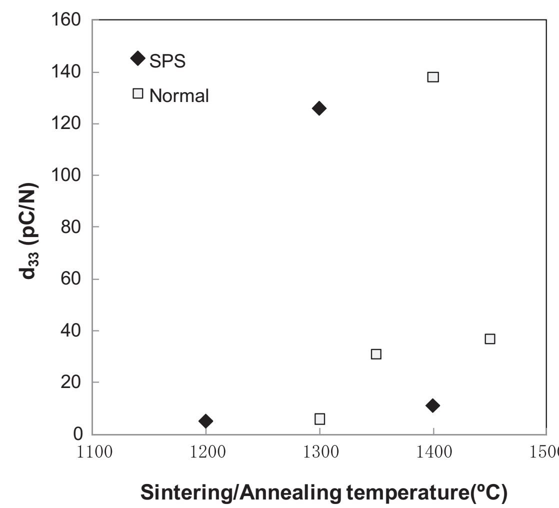

Fig. 7. The d_{33} values measured by d_{33} meter.

The d_{33} values measured with the d_{33} meter are shown in Fig. 7. This measurement method is more sensitive than dynamic measurement. The low values are due to the insufficient polarization due to the grains being too small or high conductivity of the samples. The d_{33} values for the SPS-BZT20 annealed 1300 °C and the BZT20 ceramics normally sintered at 1400 °C are of 126 and 138 pC/N, respectively. Yu et al. have reported d_{33} values of 130 pC/N measured in $Ba(Zr_{0.08}Ti_{0.92})O_3$ ceramics by resonance–antiresonance measurements [8], and the values obtained in this study are reasonable in comparison with these values.

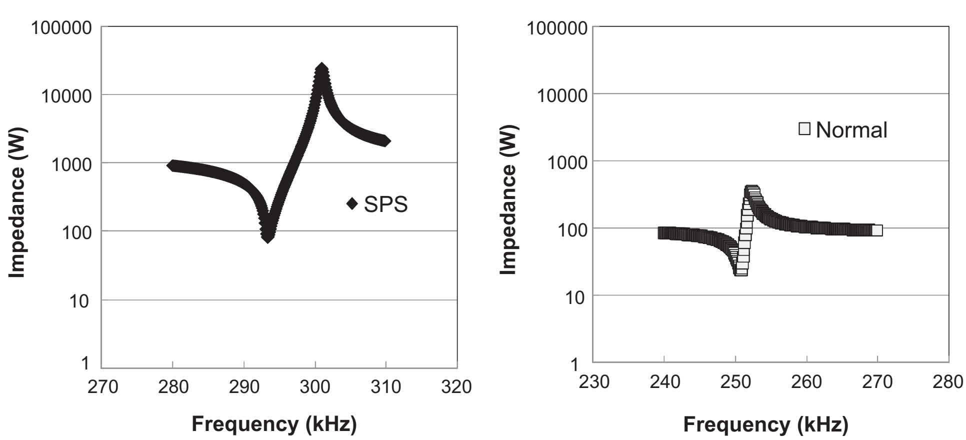

Fig. 6. Resonance–antiresonance measurement of the $Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics SPS prepared at 1100 °C and then annealed at 1300 °C and normally sintered at 1400 °C.

4. Conclusions

BZT20 ceramics with various grain sizes were prepared by SPS, conventional sintering. The dense ceramics with fine grains could be obtained by the application of SPS and post-annealing at 1200–1300 °C. SPS-BZT20 ceramics annealed at 1300 °C exhibited a linear strain loop and large strain corresponding to dynamic strain/field d_{33} at 20 kV/cm of 290 pm/V. The remnant piezoelectric properties of the BZT20 ceramics were found to be largely dependent on the preparation conditions such as sintering temperature or annealing temperature. The SPS-BZT20 ceramics annealed at 1300 °C showed Q_m and k_p values of 325 and 25.1 (%), respectively. The d_{33} value measured by d_{33} meter for the samples was 126 pC/N. In conclusion, SPS enables the preparation of BZT20 ceramics with high densities, fine grains, and unique electromechanical properties with reduced hysteresis and reasonable static piezoelectric properties.

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