Piezoelectric properties of BaTiO₃ ceramics prepared by hot isostatic pressing

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Barium titanate (BaTiO₃, BT) ceramics with various grain sizes were prepared by hot isostatic pressing (HIP) and post-annealing. The dielectric and piezoelectric properties were evaluated. Grain growth was suppressed in the ceramics prepared by HIP. The average grain sizes of the ceramics were controlled by changing the post-annealing temperature. Dense BT ceramics with submicron grain sizes were obtained by annealing below 1000°C. The highest piezoelectric d_{33} coefficient, 172 pC/N, measured by a d_{33} meter was obtained in the BT ceramics prepared by HIP at 900°C under the pressure of 200 MPa and annealed at 1100°C in air for 48 h. The dynamic electric field-induced strain increased with the annealing temperature, and 700 pm/V of Strain/Field was obtained in the BT ceramics prepared by HIP under the same conditions and annealed at 1300°C in air for 48 h.

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1. Introduction

With the increased demand for lead-free piezoelectrics in recent years, barium titanate (BaTiO₃, BT) has attracted attention. BT ceramics prepared by microwave sintering¹⁾ or two-step sintering^{2),3)} with fine grains (approx. 1 μm in size) show better piezoelectric properties compared to the conventionally sintered BT ceramics. These higher piezoelectric properties are thought to be derived from the small grain size. In the case of conventional sintering, the suppression of grain growth results in low-density samples, and thus in our previous study, spark plasma sintering (SPS) was used. SPS is a process that uses the electrical discharge between particles under pressure of several megapascals and enables a compact powder to be sintered to a high density at a relatively low temperature and with a shorter sintering period.⁴⁾ By using SPS, exaggerated grain growth can be suppressed.

BaTiO₃ ceramics obtained by SPS (SPS-BT) have an average grain size of approx. 1 μm and are characterized by high permittivity and linear field-induced strain corresponding to a dynamic strain/field of 540 pm/V under 15 kV/cm.⁵⁾ However, in our previous studies of SPS-BT there were problems with the low d_{33} coefficients, the mechanical quality factor (i.e., Q_m) and the low electromechanical coupling factor (i.e., k_p).⁶⁾ For example, the piezoelectric d_{33} coefficients (pC/N) measured by a d_{33} meter of BT ceramics with the average grain size 1.3 μm prepared by SPS at 950°C and post-annealed at 1000°C in air for 12 h and the same ceramics with additional annealing at 1000°C in oxygen for 100 h are 68 and 93 pC/N, respectively.⁷⁾ The reasons for the low d_{33} , Q_m and k_p values are not clear, but insufficient poling of the samples and the residual stress might play a role in the reduction of the d_{33} , Q_m and k_p values.⁷⁾

In the present study, hot isostatic pressing (HIP) was applied to obtain dense BT ceramics with smaller grains. HIP is a process in which externally applied pressure is used to provide a higher-

density sintered body.⁸⁾ Several authors succeeded in obtaining fine-grained barium titanate⁹⁾ and barium zirconate titanate¹⁰⁾ and reported their dielectric properties; however, the piezoelectric properties were not investigated. In the present study, the dielectric and piezoelectric properties of the BT ceramics including piezoelectric d_{33} meter measurement were investigated.

A piezoelectric d_{33} meter provides d_{33} coefficients by measuring the charge generated by the direct piezoelectric effect. The piezoelectric d_{33} coefficients obtained by a d_{33} meter would agree with the d_{33} coefficients measured by the resonant-antiresonant methods, theoretically; however, the operating mechanism, frequency and amplitude are different. The resonant-antiresonant methods use the vibration around the resonant frequency, and the measured d_{33} coefficients by using this method are suitable measure of the performance of the piezoelectrics applied to filter and sonar. Piezoelectric d_{33} meter subjects the clamped samples a low frequency force. Processing of the electrical signals from the sample, and comparison with a built-in reference, enables the system to give a direct reading of d_{33} coefficients. The d_{33} coefficients obtained with a d_{33} meter are considered to be suitable measure of the performance of the piezoelectrics applied to pressure and acceleration sensors.

2. Experimental procedure

The starting powder used was commercial BT ceramic powder prepared by an oxalic acid technique (HQBT, Fuji Titanium, Osaka, Japan). In the case of conventional sintering, the powder was supplemented with 1% polyvinyl alcohol (PVA) binder, pressed in a die at a pressure of 80 MPa, and sintered in air for 2 h from 1100 to 1400°C. For HIP, raw powder was placed in a resin capsule and HIPped at 200 MPa and 900°C for 1 h in an argon atmosphere. Since the pellet as-HIPped at 900°C was black and conductive, the pellet was annealed at 600–1300°C for 48 h in air.

The densities of the samples were measured by the Archimedes method. The crystal structure of the samples was analyzed by X-ray diffraction (XRD, X'Pert PRO, Philips Analytical, The Netherlands) using Cu K α radiation. The surface of the sintered

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ceramics was observed by scanning electron microscopy (SEM, S-2100A, Hitachi, Tokyo). The sintered samples were polished and then produced electrodes using a silver paste. Ceramics disk samples (10-mm dia., 0.5–0.6 mm thick) were used. The dielectric constant of each sample was calculated from the capacitance measured at 1 kHz. For the dynamic measurements of the ferroelectric properties, 3-mm² 0.5–0.6-mm-thick samples were used.

The measurements of the electric field-induced displacement and polarization in BT ceramics were performed using a displacement sensor (Millimar Nr. 1301, Mahr, Göttingen, Germany) and a charge-amplifier circuit (POEL-101, Kitamoto Electronics, Tokyo, Japan). An alternating electric field of 0.1 Hz was used in these measurements. Prior to the small-signal measurements, including the use of resonant-antiresonant methods and d_{33} measurements with the piezoelectric d_{33} meter, 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 (LF Impedance Analyzer HP 4192A, Hewlett Packard, U.S.A.) for an additional 24 h after the polarization. The piezoelectric d_{31} coefficients, the mechanical quality factor, Q_m and the electromechanical coupling factor, k_p were calculated on the basis of the IEEE standard. A piezoelectric d_{33} meter (Chinese Academy of Science ZJ-3B, China) was used for the d_{33} measurements. For the samples for the resonant-antiresonant measurements, different pellets whose capsule was cracked during hipping were used. The densities and the d_{33} coefficients measured by the piezoelectric d_{33} meter were almost identical to the samples without cracks after hipping.

3. Result and discussion

3.1 Structure

The density of the BT ceramic samples prepared by HIP (HIP-BT) at 900°C and post-annealed at 600–1200°C was 5.87–6.00 g/cm³. Considering that the theoretical density of BT is 6.00 g/cm³, these HIP-BT ceramics are close to theoretical densities. The SEM images of the HIP-BT are shown in **Fig. 1**. The average grain sizes obtained by a linear intercept method from SEM photographs are given in **Table 1**. Note that the grain growth was suppressed in the ceramics prepared by HIP. Dense, sub-micron grain-sized BT ceramics were obtained by annealing below 1000°C.

In the conventional sintering, the relative density was found to increase, and the grains grew with the increase in the sintering temperature. The relative densities were lower than those of the HIP-BT ceramics. However, it should be noted that the normally sintered ceramics show pores without application pressure during sintering, especially at low temperatures.

X-ray diffraction revealed that the HIP-BT ceramics annealed at over 600°C had a single perovskite phase. **Figure 2** shows the XRD patterns at around the (200) and (002) peaks of barium titanate. No peak split was recognized in the ceramics annealed at 600°C. The shoulder of the peak appeared in the sample annealed at 800°C. These results show that the structure of the samples was cubic or pseudo-cubic. This was frequently observed in the submicron grain-sized BT.

Clear peak splitting derived from a tetragonal structure can be seen in the sample annealed at over 1000°C. In the case of the SPS-BT, the abnormally split patterns differing from the 1:2 intensity ratio of tetragonal (002) and (200) appeared in the SPS-BT annealed at 900–1100°C. Such abnormal split patterns were not observed in the HIP-BT samples.

Fig. 1. SEM images of the surface of the hot isostatically pressed barium titanate (HIP-BT).

Table 1. The properties of the hot isostatically pressed barium titanate (HIP-BT) ceramics

Annealing temperature (°C)	Density (g/cm ³)	grain size (μm)	Dielectric constant	d_{33} (pC/N)
600	6.00	0.32	4050	45
800	5.98	0.39	4570	74
1000	5.95	1.05	7240	111
1100	5.94	2.86	6550	172
1200	5.87	18.42	4450	145
1300	5.80	47.37	2850	110

3.2 Dielectric properties

The dielectric constants of the samples at room temperature are given in Table 1 and shown in **Fig. 3**. It should be noted the highest dielectric constant was observed in the sample annealed at 1000°C. The average grain size of the sample was approx. 1 μm, and the high dielectric constant was observed in the BT ceramics with approx. 1-mm grain size by different preparation techniques, i.e., two-step sintering, normal sintering and SPS. Regarding these phenomena, Arlt et al. explained that the smaller the grains, the more the dielectric and the elastic constants are determined by the contribution of the 90° domain walls, and the

Fig. 2. X-ray Diffraction patterns of the HIP-BT ceramics.

Fig. 3. Dielectric constant of the HIP-BT ceramics.

permittivity below the Curie point shows a pronounced maximum $\epsilon_r \approx 5000$ at grain sizes $0.8\text{--}1\text{ }\mu\text{m}$.¹¹⁾

The present results are identical to those obtained in previous studies.^{3),5),11)–13)} Figure 4 shows the temperature dependence of the dielectric constant of the HIP-BT ceramics in the temperature range of $30\text{--}150^\circ\text{C}$. The behaviors are close to those of the SPS-BT and those described in other reports, suggesting that the dielectric properties are controlled by the grain size of the BT.^{1)–3),5),6)}

3.3 Dynamic field-induced strain

The bipolar and unipolar field-induced displacements of the HIP-BT are shown in Figs. 5 and 6, respectively. The strain-field loops changed from a parabolic shape to a butterfly shape with the increase in temperature. Even the sample annealed at 600°C exhibited unipolar electric field-induced strains over 300 pm/V of the Strain/Field. The dynamic electric field-induced strain increased with the increase in annealing temperature; 700 pm/V of the unipolar Strain/Field was obtained in the HIP-BT annealed at 1300°C .

3.4 Static piezoelectric properties

The d_{33} values measured with the d_{33} meter are shown in Fig. 7. The highest piezoelectric d_{33} coefficient measured by the d_{33}

Fig. 4. Temperature dependence of the dielectric constant of the HIP-BT ceramics.

Fig. 5. Bipolar field-induced strains of HIP-BT ceramics.

Fig. 6. Unipolar field-induced strains of HIP-BT ceramics.

meter, 172 pC/N , was obtained in the HIP-BT ceramics annealed at 1100°C for 48 h.

The resonance peaks were observed only for the HIP-BT ceramics annealed at $1000\text{--}1200^\circ\text{C}$. In the HIP-BT ceramics, the

Fig. 7. Piezoelectric d_{33} coefficients obtained with a piezoelectric d_{33} meter.

Table 2. The piezoelectric properties of the HIP-BT ceramics

Annealing temperature (°C)	d_{31} (pC/N)	Qm	kp
1000	119	44.6	19.2
1100	154	22.0	24.5
1200	171	9.8	39.8

resonance was more unclear compared to the normally sintered BT. The piezoelectric properties calculated by the resonance method are given in **Table 2**. In the case of the SPS-BT, the d_{31} , Qm and kp values were 46–86 pC/N, 44–62, and 16.2–22.5%, respectively.⁶⁾ The d_{31} and kp values of the HIP-BTs were larger than those of the SPS-BTs. The reason for this difference is not clear, but the residual stress might have contributed to the rise in the d_{31} and kp values. The d_{31} coefficients and kp increased with the increase in annealing temperature, whereas the Qm decreased with the increase in the annealing temperature.

3.5 Comparison of the electromechanical properties data

No clear relationship between the annealing temperature and electromechanical properties was recognized in the HIP-BT ceramics. The dynamic strain and piezoelectric coefficients obtained by the resonance methods increased with the increase in annealing temperature and resulting grain growth, but the highest piezoelectric d_{33} coefficient, 172 pC/N, measured by the d_{33} meter was obtained in the HIP-BT ceramics with the average grain size of 2.86 μm that were annealed at 1100°C for 48 h. The mechanisms underlying this behavior are not yet known, but in the case of inverse piezoelectric effects, the ceramics with larger grains exhibited larger piezoelectric motions, probably due to the dominant extrinsic piezoelectric domain motions.

In direct piezoelectric measurements, the contribution from the domain wall vibrations and internal pressures differed between

coarse- and fine-grained barium titanates, and the actual measurements differed from the inverse measurements.¹⁴⁾ The highest d_{33} coefficients measured by a d_{33} meter in the fine-grained BT are governed by high dielectric activities and piezoelectric domain motions activities in fine grains. In addition, the origins of the complexity are thought to be partly due to the internal stress in the HIP-BT.

4. Conclusions

The piezoelectric properties of the BT ceramics prepared by HIP were evaluated. Dense BT ceramics with various grain sizes were obtained by changing the annealing temperature. The BT ceramics obtained by HIP generally had superior electromechanical properties compared to the BT ceramics prepared by SPS. The highest piezoelectric d_{33} coefficient, 172 pC/N, measured by a d_{33} meter was obtained in the BT ceramics prepared by HIP at 900°C under the pressure of 200 MPa and annealed at 1100°C in air for 48 h. The dynamic electric field-induced strain increased with the increase in annealing temperature, and 700 pm/V of the unipolar Strain/Field was obtained in the BT ceramics prepared by HIP under the same conditions and annealed at 1300°C in air for 48 h.

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