FULL PAPER

Influence of post-annealing treatment on dielectric and ferroelectric properties of dense BaTiO₃ ceramics prepared by solvothermal solidification method

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We investigated an influence of post-annealing treatment on dielectric and ferroelectric properties of BaTiO₃ (BT) ceramics with a high relative density of around 90% prepared by a solvothermal solidification method at 200°C. In the solvothermal solidification method, green compacts consisting of TiO₂ nanoparticles were converted into the BT ceramics in Ba(OH)₂ ethanol/water reaction solutions, and the BT formation reaction accompanied by a volume increase was utilized for densification of the BT ceramics. By reducing mixing ratios of organic binder in formation of TiO₂ green compacts, the relative density of the BT ceramics reached to around 90% after the solvothermal treatment at 200°C for 36 h. The as-prepared BT ceramics with pseudo-cubic symmetry show the lower dielectric constant of around 500 in spite of the high relative density due possibly to the size effect and/or incorporation of hydroxyl groups in crystal lattices. Therefore, we tried to enhance the dielectric constant by the post-annealing treatment at 500–1200°C for 2 h in air. Although the BT ceramics showed the pseudo-cubic symmetry even after the post-annealing at 500–1100°C, the dielectric constant increases with the post-annealing temperature and the polarization–electric field (*P*–*E*) loops and strain–electric field (*S*–*E*) curves show the improved ferroelectric behavior. The post-annealing treatment was effective to enhance the electrical properties of the BT ceramics prepared by the solvothermal solidification method owing mainly to facilitating grain growth. The dielectric constant of over 1000 could be obtained by annealing at 800°C.

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1. Introduction

Barium titanate (BaTiO₃, BT) is one of the typical ferroelectric materials^{1)–4)} and has been commonly used for dielectric layers in various types of ceramic capacitors because of its relatively high dielectric constant. Conventionally, high-temperature sintering processes are employed for manufacturing these ceramics capacitors, which require sufficiently high relative density for high dielectric property and reliability.⁵⁾ In the conventional sintering process, a densification of ceramic powders is accomplished by the mass transportation derived from the reduction of total surface energy at higher temperature.⁶⁾ However, the thermal sintering process is not suitable for some materials, which contain volatile elements or poor heat-resistance substances, as well as multi-phase composites without solid-solution formation. In contrast, lower-

temperature processes are capable of microstructure- and/or interface-structure design for the ceramics and multi-phase composites. Thus, the low-temperature densification technique is required for development of advanced ceramics. We believe the low-temperature-densification processes can be also adopted for one of the important components, multi-layer ceramic capacitors, consisting of alternating thin layers of thin dense dielectric layers and metallic electrode using such as Ni and Cu. The melting points of Ni and Cu are respectively 1455 and 1084°C, and these metals are easily oxidized by heating at 950°C for Ni and 400°C for Cu in air.^{7)–9)} The low-temperature processes may be suitable for these metals and may solve the delamination problem arising from the difference in thermal expansion between metals and dielectrics.

Hydrothermal and solvothermal methods are promising low-temperature methods to synthesize nanocrystals and micrometer-sized crystals with high crystallinity, and there are many reports on synthesis of the BT or BT-based nanoparticles.^{10)–13)} Moreover, these methods can be applied to prepare ferroelectric and piezoelectric thin

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films^{14)–16)} and also ceramics. We have demonstrated that the dense BT ceramics with a relative density of around 90% could be prepared by a solvothermal solidification method, which is the low-temperature process utilizing solvothermal reaction.¹⁷⁾ In this method, TiO₂ nanoparticles, which are precursor of BT, are pressed into green compacts, and then the green compacts are converted into BT ceramics typically in Ba(OH)₂ reaction solution under the solvothermal condition. During the solvothermal treatment, as the formation reaction of BT accompanied by a volume increase proceeds in the whole compacts, pores inside the green compacts are eliminated by the synthesized crystalline BT layers. As a result, densification of the BT ceramics can be achieved without shrinkage of the compacts. The BT ceramics with a relative density of 91% prepared by the solvothermal solidification method exhibited the dielectric constant of 682.¹⁷⁾ In addition, this solvothermal approach could be adopted for the preparation of base metal/oxide composite ceramics by avoiding oxidation of Ti metal particles.¹⁸⁾

Meanwhile, Randall's group also reported on the low-temperature preparation method utilizing hydrothermal state, which is known as a cold sintering method. They prepared the BT ceramics with a relative density of 93% by applying uniaxial stress on the BT nanoparticles and additives at 180°C. While the as-prepared BT ceramics exhibited the lower dielectric constant of around 70, the annealed ceramics exhibited high dielectric constant of over 1000 because of the crystallization of the glass BT phase.¹⁹⁾

In this study, we tried to prepare the dense BT ceramics with a relative density of around 90% by the solvothermal solidification method, and their dielectric properties and microstructures were investigated. To increase the relative density of the BT ceramics, mixing ratios of the organic binder were reduced for formation of dense TiO₂ green compacts. Then, for an enhancement in dielectric properties, the post-annealing treatment was performed in the temperature range from 500 to 1200°C on the dense BT ceramics prepared by the solvothermal solidification method at 200°C, and the effect of the post-annealing was investigated.

2. Experimental

2.1 Preparation of TiO₂ green compacts

To obtain the dense BT ceramics by the solvothermal solidification method, dense green compacts consisting of rutile-type TiO₂ nanoparticles were prepared. The rutile-type TiO₂ nanoparticles, which were provided by Ishihara Sangyo Kaisha, LTD. (MPT-881; a particle size is around 10 nm), were mixed with ethanol and an organic binder, poly(vinyl butyral) (PVB; an average degree of polymerization is 630, Wako Pure Chemical Industries), in various PVB mixing ratios (0.50, 0.75, and 1.00 wt %). After drying at room temperature, these powders were pressed into disk compacts by a uniaxial press at 375 MPa. Finally, the TiO₂ green compacts were obtained after debinding at 600°C for 10 h.

2.2 Preparation of BT ceramics by solvothermal solidification method and post-annealing

The TiO₂ green compact was immersed into 0.2 M Ba(OH)₂·8H₂O (Wako Pure Chemical Industries, 99.9%) ethanol/water solution (ethanol/water = 1 v/v) in a Teflon container sealed by a stainless steel autoclave. The Ba/Ti atomic ratio was fixed to 3. Then, the solvothermal treatment was performed at 200°C for 36 h. The resultant ceramics were washed with water and 10 vol % acetic acid aqueous solution and were dried at 80°C. In post-annealing process, the obtained BT ceramics were annealed in the temperature range from 500 to 1200°C for 2 h in air (a heating rate was 300 °C/h).

2.3 Characterization

The relative density of the samples was calculated from the experimental density measured by an Archimedes method. Crystal structures of the samples were investigated by synchrotron-radiation X-ray diffraction (SR-XRD) at a wavelength of 0.07798 nm at beamline BL02B2 of SPring-8. Microstructures of the samples were observed by field-emission scanning electron microscopy (FESEM; JSM-6500F, JEOL). A detection of residual solvents inside the samples was tried by thermal gravimetric-differential thermal analysis (TG-DTA; DTG-60, Shimadzu) in an atmosphere of air flow and fourier transform infrared spectroscopy (FT-IR; IRAffinity-1S, Shimadzu) using the KBr method in air.

For electrical measurements, gold electrodes were formed on top and bottom surfaces of the polished samples, and then the samples were cut down to 2 × 2 × 0.4 mm³. The dielectric constant and loss tangent of the samples were measured using an impedance analyzer (HP4294A, Agilent) at the frequency range from 1 kHz to 1 MHz at room temperature. The temperature dependence of dielectric properties was recorded using an LCR meter (6440B, Wayne Kerr) in the temperature range from room temperature to 300°C. Polarization–electric field (*P*–*E*) hysteresis loops and strain–electric field (*S*–*E*) curves were measured using a ferroelectric character evaluation system (JP005-SE, Kitamoto Denshi) at room temperature at 0.1 Hz. Before the electrical measurements, these samples were dried at 200°C in vacuum to remove adsorbed water.

3. Results and discussion

3.1 Characterization of BT ceramics prepared by the solvothermal solidification method

In the solvothermal solidification method, the density of precursor substances is one of the key factors for densification. We selected rutile-type TiO₂ (*d* = 4.25 g/cm³²⁰⁾ nanoparticles because the volume increases approximately by 2.1 times by the reaction with barium source into BT. On the other hand, the volume of anatase-type TiO₂ (*d* = 3.89 g/cm³²⁰⁾ increases by 1.9 times by the BT formation reaction. Additionally, the TiO₂ green compacts with a higher relative density are possible to give

more dense BT ceramics. **Table 1** summarizes the relative density of the samples before and after the solvothermal treatment in the Ba(OH)₂ solution at 200°C for 36 h. As the resultant BT ceramics included open-pores of around 10 vol %, these values calculated based on Archimedes method can include uncertainty. In the TiO₂ green compacts, the pores were additionally formed by the removal of PVB, and thus the mixing ratio of PVB is associated with the relative density of the green compacts. The maximum relative density of 54% were obtained for the sample with the PVB mixing ratio of 0.50 wt %, and the relative density of this sample reaches up to about 94% after the solvothermal treatment at 200°C. Thereafter, we discuss the samples prepared from the TiO₂ green compacts with the PVB mixing ratio of 0.50 wt %.

Figure 1(a) shows SR-XRD patterns for the ground powders of the samples before and after the solvothermal treatment. The diffraction peaks of the sample prepared by the solvothermal treatment are identified mainly as BT, but a trace amount of residual TiO₂ is also detected. It suggests that most of TiO₂ green compact was converted into BT possibly by the following chemical reactions in the basic condition.^{21),22)}

Figure 1(b) shows the enlarged XRD peak located in the 2θ range from 22 to 23° for the BT ceramics shown in Fig. 1(a). It is found that the diffraction peak is slightly split into 002 and 200 reflections. The diffraction peaks of the BT ceramics obtained by the solvothermal solidification method could be indexed as pseudo-cubic symmetry.

FESEM images of the chemically-etched polished surface of the TiO₂ green compact and BT ceramics obtained by the solvothermal treatment are shown in **Figs. 2(a)** and **2(b)**, respectively. The green compact consists of the

Table 1. The relative density of the TiO₂ green compacts (before the solvothermal treatment) and BT ceramics (after the solvothermal treatment)

PVB mixing ratio (wt %)	Relative density of compacts (%)	
	Before treatment	After treatment
0.50	54	94
0.75	53	92
1.00	51	87

homogeneous TiO₂ nanoparticles smaller than 100 nm, and a large amount of pores is observed. After the solvothermal process, although the pores remain in the BT ceramics, the BT grain network developed owing to the densification of BT. Then, we tried to confirm the removal of the solvents or Ba compounds in these pores using TG-DTA and FT-IR. According to the results of TG-DTA, a weight loss of the samples reached up to 0.2% by heating from room

Fig. 1. (a) The SR-XRD patterns measured at a wavelength of 0.07798 nm at beamline BL02B2 of SPring-8 for the samples before and after the solvothermal treatment at 200°C for 36 h and (b) the enlarged diffraction peak located in the 2θ range of 22–23° for the BT ceramics prepared by the solvothermal treatment.

Fig. 2. FESEM images of the chemically-etched polished surface of (a) the TiO₂ green compact and (b) the BT ceramics prepared by the solvothermal treatment at 200°C for 36 h.

Fig. 3. The frequency dependence of the dielectric constant (ϵ_r) and loss tangent ($\tan \delta$) measured at room temperature for the BT ceramics prepared by the solvothermal treatment at 200°C for 36 h.

temperature to 900°C. In addition, there is no absorption band associated with the solvents or Ba compounds in the FT-IR spectrum of the as-prepared BT ceramics. These facts suggest that the reaction solution could be removed through the open-pores inside the BT ceramics in the washing process.

Figure 3 shows the frequency dependence of the dielectric constant and loss tangent measured at room temperature for the BT ceramics prepared by the solvothermal solidification method. For this BT ceramics, the dielectric constant of 506 was recorded at 1 MHz, which is much lower than that of the sintered BT ceramics ($\epsilon_r > 1500$ ¹⁸⁾) in spite of the high relative density of around 90%. In general, sintered BT ceramics, which exhibit the typical ferroelectricity and high dielectric constant, consist of micrometer-sized grains, and their crystal symmetries are tetragonal. In contrast, the BT ceramics prepared by the solvothermal solidification method consisted of submicron-sized BT grains and was identified as the pseudo-cubic perovskite structure, suggesting a low tetragonality (c/a ratio). There are two possibilities to lower the tetragonality of BT synthesized by the hydrothermal or solvothermal method: (1) a size effect of BT nanoparticles or (2) an incorporation of hydroxyl groups in the crystal lattices.^{1)-4),11),23)-27)} For the BT ceramics prepared by solvothermal solidification, it may be attributed to the size effect because the particle size of the BT ceramics was less than a few hundreds of nanometers. For enhancement in the tetragonality and dielectric properties of the BT ceramics, the post-annealing is considered to be effective because the grain growth and reduction of defects can be expected.^{23),25)-27)} We performed post-annealing on the BT ceramics prepared by the solvothermal solidification method, and its effect on the crystal structure and electrical properties was investigated.

3.2 Influence of post-annealing effect on electrical properties of BT ceramics

Table 2 summarizes the relative density of the as-prepared BT ceramics by the solvothermal solidification method and the BT ceramics annealed at 500–1200°C for

Table 2. The relative density of the BT ceramics prepared by the solvothermal solidification method before and after annealing at 500–1200°C

Post-annealing temperature	Relative density of samples (%)	
	Before annealing	After annealing
500°C	90	90
600°C	91	90
700°C	91	91
800°C	91	94
900°C	90	89
1000°C	90	90
1100°C	89	86
1200°C	89	88

Fig. 4. The enlarged SR-XRD peaks measured at the Spring-8 (BL02B2) in the 2θ range of 21.5–23.5° for the BT ceramics prepared by the solvothermal solidification method at 200°C for 36 h and the BT ceramics annealed at 500–1200°C for 2 h in air.

2 h in air. The relative density of the BT ceramics is not drastically changed after the post-annealing treatment, that is, the further densification did not occur in this process. Then, we investigated the crystal structure of the annealed BT ceramics by the SR-XRD measurements. All the diffraction peaks of the BT ceramics annealed at 500–1000°C could be identified as BT and TiO_2 as well as the BT ceramics before annealing [Fig. 1(a)]. However, the unknown phases were observed for the BT ceramics annealed at 1100 and 1200°C. It may be attributed to the chemical reaction between BT and residual TiO_2 at higher annealing temperature. **Figure 4** compares the SR-XRD peaks indexed as 002 and 200 reflections of BT. The splitting of 200 and 002 peaks becomes smaller when the post-annealing temperature increased from 500 to 1000°C contrary to the expectation; the tetragonality of the BT ceramics may be enhanced by the post-annealing treatment owing to the grain growth and/or defect reduction.^{26),27)}

For the BT ceramics annealed at 500–1000°C, in which the unknown phase was not detected, the variations of the dielectric constant and loss tangent with the post-annealing temperature are shown in **Fig. 5**. The dielectric constant tends to increase with an increase in the post-annealing temperature, and reaches to approximately 1400 at the

post-annealing temperature of 1000°C. These results suggest that the post-annealing is effective to enhance the dielectric constant of the BT ceramics prepared by the solvothermal solidification method. **Figure 6** shows the temperature dependence of the dielectric properties for the as-prepared BT ceramics and the BT ceramics annealed at 600–1000°C for 2 h in air. The tetragonal to cubic phase transition, commonly seen in sintered BT ceramics at the Curie temperature (T_C), cannot be clearly observed for the as-prepared BT ceramics and the BT ceramics annealed at 600°C. On the other hand, for the BT ceramics annealed at 700–1000°C, the peaks of dielectric constant can be found at around T_C , suggesting the development of ferroelectric tetragonal BT phase by the post-annealing above 700°C. These unclear or broad phase transition peaks are often

found in the BT ceramics with smaller grains due possibly to the size effect.^{1),28)} The temperature of the peak maximum is almost constant among the as-prepared BT ceramics and the BT ceramics annealed at 700–1000°C ($116^\circ\text{C} \pm 3^\circ\text{C}$), which is similar to the T_C of the BT reference sample sintered at 1350°C (119°C). **Figure 7** shows the P - E hysteresis loops and S - E curves measured at 0.1 Hz for the as-prepared BT ceramics and the BT ceramics annealed at 600, 800, and 1000°C for 2 h in air. The maximum polarization (P_{max}) at the electric field of $50 \text{ kV}\cdot\text{cm}^{-1}$ is clearly increased by the post-annealing above 800°C. The coercive electric field (E_C) is around $14 \text{ kV}\cdot\text{cm}^{-1}$ for the as-prepared BT ceramics and the ceramics annealed at 600°C, while the BT ceramics annealed at 800 and 1000°C show the lower E_C of around $6 \text{ kV}\cdot\text{cm}^{-1}$. The post-annealing treatment above 800°C could improve the ferroelectricity of the BT ceramics, and in Fig. 7(b) the strain is also increased by the post-annealing. For the P - E hysteresis loops, the relatively small remnant polarization of these BT ceramics is due possibly to the clamping effect from the grain boundary which can be typically observed in the BT ceramics consisting of smaller grains.^{29),30)} Hence, these dielectric and ferroelectric enhancement caused by the post-annealing is considered to be associated with the microstructures of the BT ceramics. However, it is difficult to discuss the microstructures of these BT ceramics based on the particle size from the SEM or TEM images due to the wide size-distributions. Here, we tried to calculate the crystalline size from the (111) reflections of the SR-XRD by using the Scherrer equation:³¹⁾

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (2)$$

Fig. 5. The variations of the dielectric constant and loss tangent measured at 1 MHz at room temperature with the post-annealing temperature for the BT ceramics prepared by the solvothermal treatment at 200°C for 36 h.

Fig. 6. The temperature dependence of the dielectric constant and loss tangent for (a) the BT ceramics prepared by the solvothermal treatment at 200°C for 36 h and the BT ceramics annealed at (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C, and (f) 1000°C for 2 h in air.

Fig. 7. (a) P - E hysteresis loops and (b) S - E curves of the BT ceramics prepared by the solvothermal treatment at 200°C for 36 h and the BT ceramics annealed at 600, 800, and 1000°C for 2 h in air.

Table 3. The Scherrer diameter of the BT ceramics prepared by the solvothermal solidification method before and after annealing at 600–1000°C

Post-annealing temperature	Scherrer diameter (nm)
as-prepared	74
600°C	82
800°C	89
1000°C	92

where λ is the wavelength of the X-ray radiation, β is the full width of half maximum (FWHM) of the peak, and θ is the diffraction angle. The calculated crystalline size of the BT ceramics is summarized in Table 3. For these BT ceramics, the crystalline size increases with an increase in the post-annealing temperature, and the polar phase developed at higher annealing temperature. These results are consistent with the variation of the dielectric properties with the post-annealing temperature (Fig. 5) and measurement temperature (Fig. 6). These experimental facts suggest that the smaller splitting of 002 and 200 SR-XRD peaks of the annealed BT ceramics in Fig. 4 might be attributed to strains in the annealed BT ceramics. The defects are also possible to affect the dielectric and ferroelectric properties. It has been reported that the hydroxyl groups are possible to be incorporated in crystal lattices of the BT nanoparticles synthesized by the hydrothermal and solvothermal methods.²³⁾ The oxygen vacancies arising from a removal of these hydroxyl groups are formed by annealing below 500°C, and at 600°C these point defects significantly decrease. Therefore, the main role of the post-annealing above 600°C is facilitating the grain growth of the BT ceramics.

As the BT ceramics prepared by the solvothermal solidification method consisted of the grains less than a few hundreds of nanometers, the size effect deteriorated dielectric and ferroelectric properties of the BT ceramics in spite of their high relative density. The post-annealing treatment at 500–1000°C in air was effective to enhance the dielectric constant and ferroelectricity of these BT ceramics owing mainly to the grain growth. In this study, we propose one of the low-temperature processes, consist-

ing of the solvothermal and post-annealing treatments, for the preparation of dense BT ceramics below 1000°C.

4. Conclusions

We successfully prepared the BT ceramics with a relative density of around 90% by the solvothermal solidification method at 200°C for 36 h in the Ba(OH)₂ ethanol/water solution by optimizing the mixing ratio of the PVB binder in preparation of the TiO₂ precursor compacts. The resultant BT ceramics consisted of the submicron-sized grains, and their crystal symmetries were pseudo-cubic. The relatively lower dielectric constant of 506 was recorded at 1 MHz in spite of the high relative density for this BT ceramics because of the size effect. The post-annealing treatment at 500–1000°C in air could facilitate the grain growth of the BT ceramics without the formation of secondary phase, and the dielectric constant tends to increase with an increase in the post-annealing temperature. The dielectric constant of over 1000 could be obtained by annealing at 800°C. Additionally, the post-annealing also gave rise to enhancement in the ferroelectric and piezoelectric properties of the BT ceramics.

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