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High-temperature X-ray diffraction analysis and reactive sintering of $BaTiO_3$ piezoelectric ceramics

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Barium titanate is a potential lead-free piezoelectric ceramic with high dielectric and piezoelectric constants. In this study, the reaction behavior of a mixed powder of $BaCO_3$ and anatase TiO_2 was investigated by using high-temperature X-ray diffraction analysis. Frequency and temperature dependences of the dielectric constant were studied for the reactively-sintered $BaTiO_3$ ceramics. Relatively high piezoelectric constant (d_{33} ~120 pC/N) was obtained for $BaTiO_3$ reactively-sintered at 1300°C for 2 h, even with a density only of ~85%, which implies the future improvement for reactively-sintered $BaTiO_3$.

Key-words : $BaTiO_3$, High-temperature X-ray diffraction, Reactive sintering, Piezoelectric material, Curie temperature, Dielectric constant

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1. Introduction

Barium titanate ($BaTiO_3$) is a lead-free piezoelectric ceramic with the perovskite-type structure.[1] Although its relatively low Curie temperature (~130°C) limits its temperature range for piezoelectric applications, its high dielectric constant of 1700 and its high piezoelectric constant d_{33} of 190 pC/N are promising.[2] Currently, the size and alignment effects for polycrystalline $BaTiO_3$ are intensively studied to improve the dielectric properties.[3)–5)] Various methods, such as sol–gel,[6] hydrothermal precipitation,[7] co-precipitation,[8] mechanochemical synthesis[9] and plasma spray coating,[10] have been investigated for the processing of $BaTiO_3$ powders and bulk ceramics. To utilize $BaTiO_3$ as a piezoelectric material, cation doping[11] and two-step sintering[12] are attractive techniques to improve the piezoelectric properties. Karaki et al.[13] reported the $BaTiO_3$ ceramics produced by a two-step sintering with high piezoelectric constant d_{33} of 460 pC/N, which is much higher than that of conventional $BaTiO_3$.

From an engineering point of view, environmental friendliness and cost effectiveness become more and more inevitable for the ceramic processing. Reactive sintering, where chemical reactions and sintering take place within single heat treatment, is a candidate process to meet these requirements. As for piezoelectric ceramics, reactively-sintered perovskite-type $Pb(Zr,Ti)O_3$ (PZT),[14] $Ba_{0.7}Sr_{0.3}TiO_3$,[15] and $(Ba_xSr_{1-x})(Zn_{1/3}Nb_{2/3})O_3$[16] have been already reported. Liou et al.[17] have synthesized relatively dense $BaTiO_3$ ceramics (>95%) by reactive sintering at 1400°C for 6 h. However, the reaction behavior of Ba and Ti sources during the reactive sintering has not yet been analyzed in detail.

Here we focus the reactive sintering of $BaTiO_3$ for piezoelectric applications. Firstly, the reaction behavior of $BaCO_3$ and anatase TiO_2 was investigated by high-temperature X-ray diffraction (HT-XRD). Secondly, frequency dependence and temperature dependence of dielectric constant were studied for reactively-sintered $BaTiO_3$ ceramics without a poling treatment. Finally, d_{33} was evaluated for the $BaTiO_3$ ceramics with a poling treatment.

2. Experimental procedure

As starting materials, $BaCO_3$ powder (99.9%, Wako Pure Chemical Industries Ltd., Osaka, Japan) and anatase TiO_2 powder (99%, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) were used. The $BaCO_3$ and TiO_2 powders (1:1 in molar fraction, total 20 g) were wet ball-milled in 50 ml ethanol with nylon balls (10 mm in diameter, with iron cores) for 2 h. The slurry was dried in a rotary evaporator to obtain the mixed powder. For the $BaCO_3$–TiO_2 mixed powder, the high-temperature reaction behavior was analyzed by HT-XRD (Multiflex, Cu-Kα, 40 kV, 40 mA, Rigaku, Tokyo, Japan) up to 1200°C in air on a Pt stage.

Green pellets with dimensions of 15 mm in diameter and ~2.5 mm in thickness were prepared by uniaxial metallic die pressing (16.6 MPa) of the $BaCO_3$–TiO_2 mixed powder. Then, the pellets were cold isostatically pressed at 200 MPa for 10 min. The pellets were put in an alumina crucible and sintered in air at 1200, 1250, 1300, 1350 or 1400°C for 2 h. For the bulk $BaTiO_3$ pellets, the samples were pulverized, and then, their constituent phases were analyzed by room-temperature XRD (Multiflex, 40 kV, 40 mA). The interior microstructure of the bulk samples was observed by scanning electron microscopy (TM3000, Hitachi, Tokyo, Japan) after Au coating. The bulk density was measured by mass and dimensions. At each sintering temperature, bulk densities of two samples were measured and averaged.

To measure ferroelectric properties, the sintered $BaTiO_3$ pellets were machined into cylindrical plates with the thickness of 1.5 mm. Silver paste was coated on the both sides of surface-polished $BaTiO_3$ pellets and sintered at 700°C for 100 min in air to form Ag electrodes. Frequency dependence (0.1–10 kHz) and temperature dependence (100–150°C, at 10 kHz) of the dielectric constant (ε_r) were measured by an impedance analyzer (HP4194A, Hewlett-Packard, U.S.A.).

To measure piezoelectric properties, the sintered $BaTiO_3$ pellets with silver electrodes (i.e., after ferroelectric measurement) were polarized under 3 kV/mm in silicone oil at room

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temperature. 24 h after the polarization, d_{33} was measured by a d_{33} meter (ZJ-6B, Institute of Acoustics Chinese Academy of Science, China).

3. Results and discussion

Figure 1 shows HT-XRD patterns for the $BaCO_3$ and anatase TiO_2 mixed powder. Up to 600°C, the XRD patterns were substantially unchanged (except the slight peak shift by thermal expansion). At 700°C, an XRD peak at $2\theta = 31°$ corresponding to cubic $BaTiO_3$ phase was detected. The phase transition temperature of $BaCO_3$ from orthorhombic to hexagonal phase was reported as 811°C (or 806°C),[18] and some peaks corresponding to unreacted hexagonal $BaCO_3$ were found at 900°C. At 1000–1200°C, XRD peaks of only cubic $BaTiO_3$ phase were detected. After cooling, only the peaks of tetragonal $BaTiO_3$ phase were obtained.

Relative density of the reactively-sintered $BaTiO_3$ bulk ceramics is shown in **Fig. 2**. Although the reactive sintering in this study was accompanied with CO_2 gas emission from the starting $BaCO_3$, relative density reached to ~85% at the sintering temperature of ≥1250°C. **Figure 3** shows XRD patterns of pulverized samples of reactively-sintered $BaTiO_3$ at each sintering temperature. All samples were composed of single-phase tetragonal $BaTiO_3$. **Figure 4** demonstrates SEM images of the fractured surface of reactively-sintered $BaTiO_3$ ceramics. Due to the CO_2 gas emission from starting $BaCO_3$, the sample sintered at 1200°C had an open-porous structure, however, the samples sintered at ≥1250°C contained closed pores as well as some open pores. The microstructures were in good agreement with the density evaluation (Fig. 2). The grain size of the sample increased with increasing sintering temperature: typically ~1–2 μm small grains (but porous) at 1200°C, ~1–2 μm small grains as

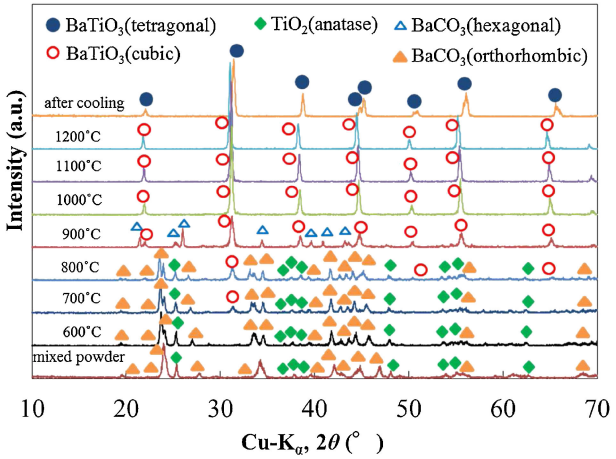

Fig. 1. HT-XRD patterns for the $BaCO_3$ and TiO_2 mixed powder.

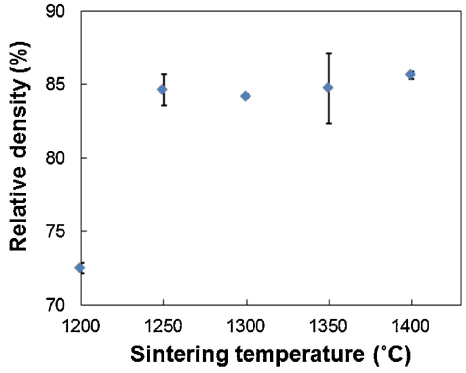

Fig. 2. Relative density of reactively-sintered $BaTiO_3$ ceramics.

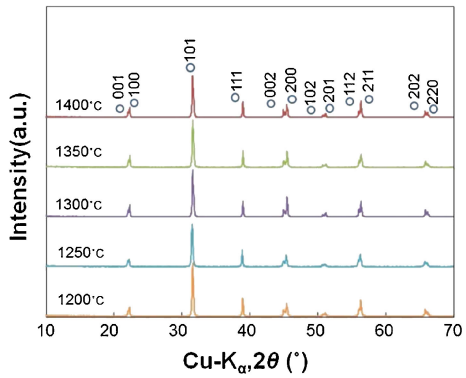

Fig. 3. XRD patterns of reactively-sintered $BaTiO_3$ at each sintering temperature.

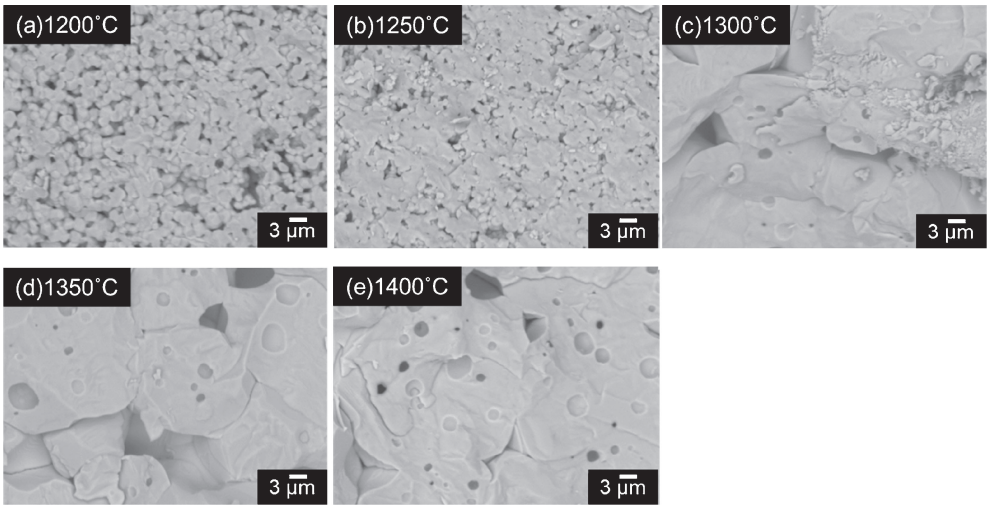

Fig. 4. SEM images of the fractured surface of reactively-sintered $BaTiO_3$ ceramics: (a) 1200°C, (b) 1250°C, (c) 1300°C, (d) 1350°C and (e) 1400°C.

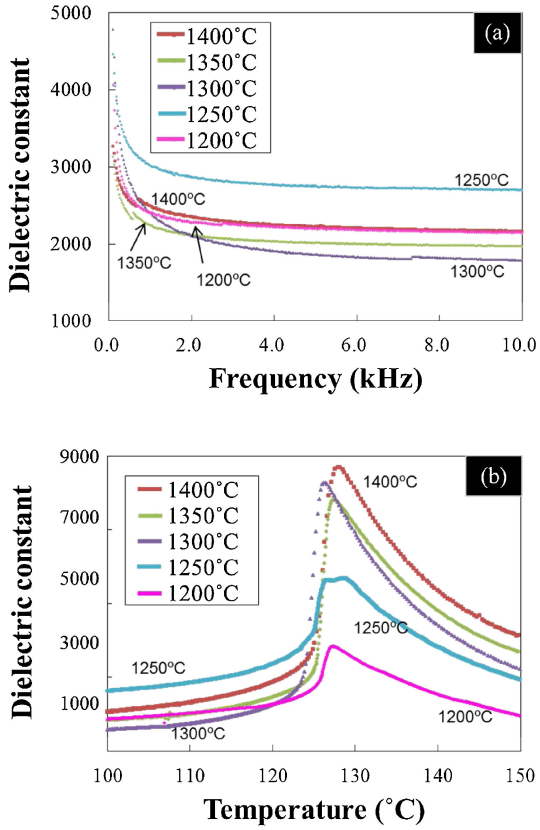

Fig. 5. Dielectric constant dependences with (a) frequency and (b) temperature.

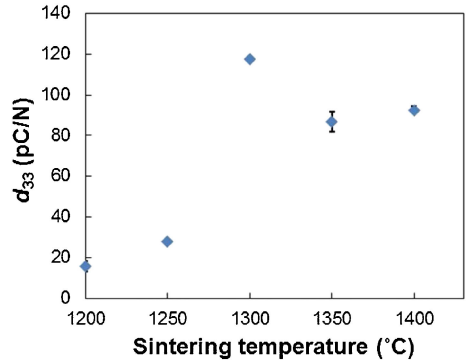

Fig. 6. Piezoelectric constant d_{33} as a function of sintering temperature.

well as 3–5 µm intermediate grains at 1250°C (i.e., bi-modal microstructure), and several tens µm at 1300–1400°C.

Figure 5(a) shows dielectric constant dependences with frequency. The sample sintered at 1250°C exhibited the highest values. As reported by Hoshina,[3] the dielectric constant of $BaTiO_3$ becomes large with the grain size of ~1.0 µm,. Although the sample sintered at 1200°C also consisted of small grains of ~1.0 µm, its low relative density (~72%, see Fig. 2) decreased the dielectric constant. At higher sintering temperatures, the dielectric constant became smaller due to the grain growth as shown in Fig. 4. Figure 5(b) shows dielectric constant dependences with temperature at the frequency of 10 kHz. The Curie temperature was ~125–128°C. Two peaks were found for the sample sintered at 1250°C, which were attributable to the bi-modal microstructure as shown in Fig. 4(b).[19] **Figure 6** shows d_{33} as a function of sintering temperature. The d_{33} steeply increased at 1300°C, and it decreased at higher temperatures. As can be seen from Fig. 2, the density values of the samples sintered at 1250 and 1300°C were similar to each other. Hence, the steep increase of d_{33} at 1300°C can be attributed to the microstructural change (grain growth) as shown in Fig. 4.[12]

4. Conclusions

$BaTiO_3$ ceramics have been prepared by reactive sintering. The high-temperature reaction behavior of $BaCO_3$ and anatase TiO_2 mixed powder was analyzed by HT-XRD. The HT-XRD confirmed the formation of transient hexagonal-phase $BaCO_3$ (~900°C) and the formation of cubic $BaTiO_3$ at ≥1000°C. The grain growth at 1300°C showed a positive effect to give relatively high d_{33} value of ~120 pC/N.

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