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 ($d_{33} \sim 120 \text{pC/N}$) was obtained for BaTiO$_3$ reactively-sintered at $1300^\circ\text{C}$ for 2 h, even with a density only of $\sim85\%$, which implies the future improvement for reactively-sintered BaTiO$_3$.

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1. Introduction

Barium titanate (BaTiO$_3$) is a lead-free piezoelectric ceramic with the perovskite-type structure. Although its relatively low Curie temperature ($\sim130^\circ\text{C}$) 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. Currently, the size and alignment effects for polycrystalline BaTiO$_3$ are intensively studied to improve the dielectric properties. Various methods, such as sol–gel, hydrothermal precipitation, co-precipitation, mechanochemical synthesis and plasma spray coating, have been investigated for the processing of BaTiO$_3$ powders and bulk ceramics. To utilize BaTiO$_3$ as a piezoelectric material, cation doping and two-step sintering are attractive techniques to improve the piezoelectric properties. Karaki et al. 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), Ba$_{1-x}$Sr$_x$TiO$_3$ and (Ba,Sr)$_{1-x}$Ti$_x$O$_3$ have been already reported. Liou et al. have synthesized relatively dense BaTiO$_3$ ceramics ($\sim95\%$) by reactive sintering at $1400^\circ\text{C}$ 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., Saiatama, 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-K$_\alpha$, 40 kV, 40 mA, Rigaku, Tokyo, Japan) up to $1200^\circ\text{C}$ in air on a Pt stage.

Green pellets with dimensions of 15 mm in diameter and $\sim2.5$ 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 $1400^\circ\text{C}$ 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–$150^\circ\text{C}$, at 10 kHz) of the dielectric constant ($\varepsilon_r$) 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 temperature.
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 $2\theta = 31^\circ$ 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 $\geq$1250°C. Figure 3 shows XRD patterns of pulverized samples of reactively-sintered BaTiO$_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 $\geq$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.](image1)

![Fig. 2. Relative density of reactively-sintered BaTiO$_3$ ceramics.](image2)

![Fig. 3. XRD patterns of reactively-sintered BaTiO$_3$ at each sintering temperature.](image3)

![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.](image4)
As can be seen from Fig. 2, the density values of the samples sintered at 1300°C, and it decreased at higher temperatures. The steep increase of 

\[ \bar{d}_{33} \] at 1300°C can be attributed to the grain growth as shown in Fig. 4. 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 \[ \bar{d}_{33} \] as a function of sintering temperature. The \[ \bar{d}_{33} \] 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 \[ \bar{d}_{33} \] at 1300°C can be attributed to the microstructural change (grain growth) as shown in Fig. 4. \(^{12}\)

4. Conclusions

BaTiO₃ ceramics have been prepared by reactive sintering. The high-temperature reaction behavior of BaCO₃ and anatase TiO₂ mixed powder was analyzed by HT-XRD. The HT-XRD confirmed the formation of transient hexagonal-phase BaCO₃ (~900°C) and the formation of cubic BaTiO₃ at \(\geq 1000°C\). The grain growth at 1300°C showed a positive effect to give relatively high \[ \bar{d}_{33} \] value of \(~120\) pC/N.

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References

1) M. M. Vijatović, J. D. Bobić and B. D. Stojanović, Sci. Sin., 40, 155–165 (2008).
2) G. H. Haertling, J. Am. Ceram. Soc., 82, 797–818 (1999).
3) T. Hoshina, J. Ceram. Soc. Japan, 121, 156–161 (2013).
4) Z. Zhao, V. Buscaglia, M. Viviani, M. T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson and P. Nanni, Phys. Rev. B, 70, no. 024107 (2004).
5) D. Guo, A. Ito, R. Tu and T. Goto, J. Asian Ceram. Soc., 1, 197–201 (2013).
6) L. Wang, L. Liu, D. Xue, H. Kang and C. Liu, J. Alloys Compd., 440, 78–83 (2007).
7) E. Ciftci, M. N. Rahaman and M. Shumsky, J. Mater. Sci., 36, 4875–4882 (2001).
8) H. S. Potdar, S. B. Deshpande and S. K. Date, Mater. Chem. Phys., 58, 121–127 (1999).
9) B. D. Stojanovic, A. Z. Simoes, C. O. Paiva-Santos, C. Javalekic, V. V. Mitic and J. A. Varela, J. Eur. Ceram. Soc., 25, 1985–1989 (2005).
10) P. Cibor, H. Ageorges, J. Sedlacek and R. Ctvrltk, Ceram. Int., 36, 2155–2162 (2010).
11) Y. V. Shvartsman and D. C. Lupascu, J. Am. Ceram. Soc., 95, 1–26 (2012).
12) Y. Huan, X. Wang, J. Fang and L. Li, J. Am. Ceram. Soc., 96, 3369–3771 (2013).
13) T. Karaki, K. Yan and M. Adachi, Jpn. J. Appl. Phys., 46, 7035–7038 (2007).
14) L. B. Kong and J. Ma, Mater. Lett., 51, 95–100 (2001).
15) Y. C. Liou and C. T. Wu, Ceram. Int., 34, 517–522 (2008).
16) Y. C. Liou, J. H. Chen, H. W. Wang and C. Y. Liu, Mater. Res. Bull., 41, 455–460 (2006).
17) Y. C. Liou, C. T. Wu and T. C. Chung, J. Mater. Sci., 42, 3580–3587 (2007).
18) I. Arvanitidis, D. Sichen and S. Seetharaman, Metall. Mater. Trans., B, 27, 409–416 (1996).
19) P. Zheng, J. L. Zhang, Y. Q. Tan and C. L. Wang, Acta Mater., 60, 5022–5030 (2012).