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Effect of polarization and synthesis process on crystal structure and ferroelectric and piezoelectric properties of $BaTiO_3$

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INTRODUCTION

$Pb(Zr,Ti)O_3$ has been widely used as a piezoelectric ceramic due to excellent piezoelectric and temperature properties. Due to growing concern about environmental problems in recent years, the development of lead-free piezoelectric ceramics becomes urgent business because $Pb(Zr,Ti)O_3$ contain a toxic element. $BaTiO_3$(BT) is one of the candidate materials. In this study, we prepared BT by three synthesis processes – i.e, solid state reaction (SD), polymerized complex method (PC), hydrothermal synthesis method (HT) – in order to improve dielectric and piezoelectric properties. Two-step sintering has been reported as efficient for preparing nano-grain ceramics because this method enables a sintering without grain growth in the final-stage[1)]. Therefore, we performed a two-step sintering to synthesize BT with high-performance. By carrying out powder neutron diffraction (iMATERIA, J-PARC) and synchrotron X-ray diffraction (BL02B2, SPring-8) measurement, we examined a relation among the dielectric and piezoelectric properties and the synthetic process from the viewpoint of the crystal structure. Additionally we examined an influence of a polarization process on this relation.

EXPERIMENTAL

In the solid state reaction, we performed wet mixing of $BaCO_3$ and TiO_2 at specific ratios. After wet mixing, the materials were calcined and then sintered. In the PC method, metal-citrate complex was formed by reacting $Ti[OCH(CH_3)_2]_4$, $BaCO_3$ and anhydrous citric acid in ethylene glycol. The solution was heated to promote polymerization and to obtain a polymeric gel. The obtained gel was pyrolyzed to form a powder precursor, and then heat-treated to yield the single-phase of BT powder. In hydrothermal reaction, BT powders were synthesized by reacting TiO_2 powder with $Ba(OH)_2$ at 180 ^{o}C for 30 h. The powder obtained by the synthesis was then molded into pellets, and the bulk ceramics were made by sintering. As for all the synthetic process, sintered processes were carried out in air at 1350^{o}C for 8 h in the case of the “single-step” method. We also applied a “two-step” sintering as well[2)].

The identification of the phases and the evaluation of the lattice parameters were carried out by XRD. The compositions of metal constituents were measured by ICP. Relative densities of the ceramics were estimated by the Archimedes method, and the morphologies of the samples were observed by SEM. P-E hysteresis loop measurements were carried out at various frequencies using a TF-2000FE device (aixACCT). The temperature dependences of the dielectric permittivities (ε_s) and dielectric losses ($\tan\delta$) of the samples were measured by a LCR meter (HP-4284A). The piezoelectric constants d_{33} were measured using a piezoelectric d_{33} meter. In order to investigate the crystal structures in detail, we performed Rietveld analysis(Z-Rietveld, RIETAN-FP) using neutron diffraction data. The electron densities were determined by the maximum entropy method using Dysnomia.

RESULTS AND DISCUSSION

It was found by the powder XRD that the obtained BT ceramics could be identified as a single phase regardless of the synthetic process. From observations of the surface morphologies of the sintered bodies by SEM, the particle size could be controlled uniformly and the pellets were sufficiently dense in all the prepared compounds. As an example, Fig. 1 shows the P-E hysteresis loop of BT prepared by the PC method with a single-step sintering before and after the prepolarization (25^{o}C, 0.0−4.0kV/mm, 180sec). The higher remanent polarization (Pr) was obtained in the specimen by the prepolarization. The same tendency was observed not only the PC method, but also the other synthesis methods. Figure 2 shows the poling-field dependence of the piezoelectric constant d_{33}. The specimen prepared by the SD method exhibited the high d_{33} to be superior to that of the other specimens.

As described above, it was demonstrated that the synthetic method and/or the polarization affected the ferroelectric and piezoelectric properties of BT. In order to clarify the origin of these features, we carried out the Rietveld analysis using neutron diffractions, and investigated the structural changes. From the result, a good fitting was obtained by using a two-phase model of the tetragonal (P4mm) and cubic (Pm-3m) structures.

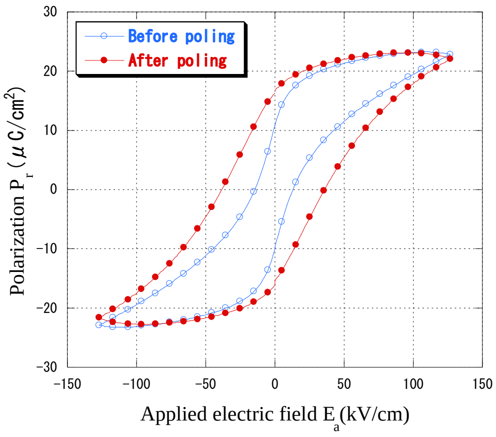

Fig.1 Hysteresis loops of BT prepared by the polymerized complex method before and after prepolarization treatment.

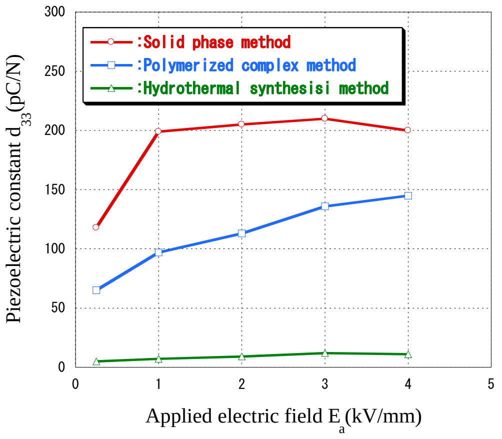

Fig.2 Relationship between the piezoelectric constant d_{33} and applied electric field.

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2) Y. Idemoto, M. Tashiro, N. Kitanura, Powder and Powder Metallurgy, **59**, 101 (2012).