FULL PAPER

Synthesis of Sr substituted BaTiO₃ nanoparticles by hydrothermal treatments with maintaining the source material form and particle size

Hidetoshi MIYAZAKI^{1,†}, Katsumi YAMADA¹, Yuta KITANO¹, Yuki MAKINOSE¹, Takeshi KUBOTA¹, Kohji OMATA¹ and Shinya TSUKADA²

¹Graduate School of Natural Science Technology, Shimane University, 1060 Nishikawatsu, Matsue 690–8504, Japan

²Faculty of Education, Shimane University, Matsue 690–8504, Japan

Ion exchange of Ba to Sr was carried out for spherical BaTiO₃ particles (particle size of 600 to 700 nm) by hydrothermal method using strontium nitrate aqueous solution, and the hydrothermal conditions were at 200 °C for 0.5 to 1.5 mol/L for 24 h. After hydrothermal treatment, all samples remained the form and particle size of the source materials. The Sr substituted BaTiO₃ sample obtained by hydrothermal treatment with strontium nitrate at 1.5 mol/L showed the composition of Sr_{0.14}Ba_{0.86}TiO₃ by elemental analysis by EDX, and the Curie temperature was confirmed to be 90 °C by Raman spectra, respectively.

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1. Introduction

BaTiO₃ (hereinafter, BT) has a high dielectric constant and is widely used in multi layered ceramic capacitors¹⁾ and ferroelectric random access memories.²⁾ The Curie temperature of BT is approximately 130 °C,³⁾ and exhibits a paraelectric property with a cubic structure at a temperature of T_c or higher, and exhibits a ferroelectric property with a tetragonal structure at a temperature of T_c or lower.⁴⁾ Because a temperature dependence of a relative permittivity of BT shows a sharp peak near T_c , thereby; the addition of a shifter agent such as Sr⁵⁾ or a depressor agent such as La⁶⁾ reduces the T_c and temperature dependence.

BT can control the Curie temperature T_c and the temperature dependence of the dielectric constant by substituting Sr for Ba in BT.⁵⁾ (Ba,Sr)TiO₃ in which Sr is substituted into BT is synthesized by a solid-state reaction method, a hydrothermal method,⁷⁾ a sol–gel method,⁸⁾ and so on. The solid-phase reaction method makes it easy to control the composition, but it is difficult to control the particle size and form. In addition, although it is possible to synthesize nano-sized particles with the various fabrication methods, it is difficult to remove impurities such as metal residues. In previous, we have reported the application of a hot water treatment or a hydrothermal treatment to remove Na from glass,⁹⁾ and to exchange Ca ion to Na ion in bentonite clay.¹⁰⁾ On the other hand, the diffusion of Sr in BaTiO₃ has been studied at temperatures as high as 1200 °C.¹¹⁾ Therefore, based on our previous reports, we expected ion

exchange Sr to Ba in BaTiO₃ by hydrothermal treatment (soft chemical process) with maintaining the source material form and particle size.

In this study, we tried to exchange Ba and Sr in BT while maintaining the particle size and shape by hydrothermal treatment of monodispersed BT particles in a strontium nitrate aqueous solution. The Sr substitution amount was evaluated from the lattice constant and elemental analysis, and the T_c of the Sr doped BT sample obtained by Raman spectrum measurement was estimated.

2. Experimental procedure

Strontium nitrate Sr(NO₃)₂ (FUJIFILM Wako Pure Chemical Corp., Japan) and BaTiO₃ (BT-05, mean particle size 660 nm, Sakai Chemical Industry Co.Ltd., Japan) were used as starting materials. Strontium nitrate was added to distilled water to prepare a 0.5 to 2.0 mol/L strontium nitrate aqueous solution. This strontium nitrate aqueous solution of 80 mL and BaTiO₃ of 1.0 g were mixed in a Teflon container and carried out a hydrothermal treatment at 200 °C. The treated suspension was centrifuged at 3500 rpm for 15 min, and the obtained powder was dried at 60 °C for 12 h. This centrifugaion was repeated twice to wash the strontium nitrate adhering to the sample.

The crystal structure of the sample was measured using an X-ray diffractometer (XRD, Rigaku Miniflex, Rigaku, Japan) with Cu K α radiation (30 kV, 15 mA). The morphology of the particles was observed using a scanning electron microscope (SEM, JCM-6000, JEOL, Japan). Raman spectrum measurement was performed by a single monochromator (Lucir, Japan) with a 532 nm line from an Nd:YAG laser at RT–550 °C and the instruments described

[†] Corresponding author: H. Miyazaki; E-mail: miya@riko.shimane-u.ac.jp

in the previous report.¹²⁾ The composition of the specimens was performed using an energy dispersive fluorescent X-ray analyzer (Shimadzu EDX-700HS).

3. Results and discussion

Commercial BaTiO₃ (BT) particles were hydrothermal treated at 200 °C for 24 h with varying strontium nitrate concentration. When the treatment temperature was less than 200 °C, almost no ion exchange was observed. A few ion-exchange was observed in the treatment times of 12 h or less, and the sample treated for 40 h or more was close to the sample treated for 24 h.

Figures 1 and 2 illustrate the XRD patterns for the powders synthesized by hydrothermal treatment with varying the strontium nitrate concentration between 0.5 to 2.0 mol/L. Figure 1 presents the spectrum of 2θ in a wide angle (10–70°), and Fig. 2 represents the spectrum around (110) (011) peaks (31.2–32.0°). All the powders assigned as tetragonal BaTiO₃ with JCPDS 83-1875. From Fig. 1, it was confirmed that the structure of BT was not changed by the hydrothermal treatment and that strontium nitrate residue was not observed in the hydrothermal-treated powders. From Fig. 2, it was observed that the (110) and (101) peaks were shifted to higher angle with increase of the strontium nitrate concentration. From the XRD pattern, the peak (Fig. 2) is slightly obscured in the BST sample. We will discuss this result later, but Sr ions assumed not to be sufficiently diffused into the BT particles. Ota et al. reported that the XRD peak shifted to a wide angle with increase of Sr-doped amount in (Ba,Sr)TiO₃.¹³⁾ Our results agreed well with the reported results. These results suggested that Ba in BaTiO₃ was substituted to Sr and that the amount of Sr substitution changed depending on the strontium nitrate concentration. For the powder treated with strontium

nitrate concentration of 2.0 mol/L or more, the XRD peak was almost the same as that of the sample treated with 1.5 mol/L concentration. Because the XRD peak shift was the largest in the powder hydrothermal treated with the strontium nitrate of 1.5 mol/L, we performed SEM observation, Raman evaluation, and composition analysis by EDS for this sample. Hereafter, we call this sample BST in this paper.

Figure 3 depicts the SEM images of the source BT powder and the hydrothermal treated BST powder. The source BT powder was spherical form and had a mean particle diameter of 660 nm, and BST after the hydrothermal treatment was also spherical form and the mean particle diameter was 630 nm. As can be seen from the SEM image, the particle form was almost unchanged before and after the hydrothermal treatment, and the particle size was also maintained. These results revealed that hydrothermal treatment can substitute Ba to Sr while maintaining the form and size of the BaTiO₃ particles.

Figure 4 demonstrates the results of Raman spectra for BT and BST powders at room temperature. The spectra of those were in good agreement with the Raman spectra of BaTiO₃ samples reported in previous investigations.^{14),15)} For the Raman spectrum signal of BaTiO₃, Dobal et al. have reported that the intensity of E(TO1) mode decreases drastically above the Curie temperature T_c .¹⁵⁾ We evaluated the temperature dependence of E(TO1) mode in Raman spectra of BT and BST in order to estimate the T_c of those powders. The inset in Fig. 4 also demonstrates the temperature dependence of E(TO1) mode of Raman spectra of BT and BST. The intensity of the E(TO1) mode decreased significantly at about 130 °C for BT and at 90 °C for BST. From these results, the T_c of BT and the obtained BST was estimated to be 130 and 90 °C, respectively. However, the intensity of E(TO1) was not a critical change comparison with that of the non-doped BT. The Sr concentration in BT particle assumed to be inhomogeneous from the XRD

Fig. 1. The XRD patterns for the source BaTiO₃ powder and the hydrothermal treated BaTiO₃ powders using strontium nitrate aqueous solution with the concentration of 0.5–1.5 mol/L. The 2θ angle was between 10 to 70°.

Fig. 2. The XRD patterns for the samples, ibid of Fig. 1. The 2θ angle was between 31.2 to 32°.

Fig. 3. The SEM images of the source BT and the resulting BST powders.

measurement results. Similarly, the moderate intensity change of the E (TO1) peak in the temperature dependence of the Raman spectra assumed to be attributed to inhomogeneity of Sr distribution in the BT particles. It was confirmed that the T_c of the hydrothermal treated BST powder decreased about 40 °C. It was suggested that ion exchange Ba in BT to Sr was caused by hydrothermal treatment, and the composition of the hydrothermal treated BST powder was estimated to be $\text{Sr}_{0.11}\text{Ba}_{0.89}\text{TiO}_3$ from the result of T_c decrease.¹⁵⁾ The elemental analysis of the BST sample by EDS revealed $\text{Sr}_{0.14}\text{Ba}_{0.86}\text{TiO}_3$, and the composition calculated from Raman spectroscopy was slightly smaller than the elemental analysis value. We also evaluated the lattice constant from the XRD measurement for the BST samples, and the lattice constants of the BST were $a = 3.993 \text{ \AA}$, $c = 4.030 \text{ \AA}$. In previous, the correlation between the substitution amount x in $\text{Sr}_x\text{Ba}_{1-x}\text{TiO}_3$ and the lattice constant of $\text{Sr}_x\text{Ba}_{1-x}\text{TiO}_3$ has been reported.¹⁶⁾ We calculated the composition from the previous report and the lattice constants in the present study and the composition was $\text{Sr}_{0.03}\text{Ba}_{0.97}\text{TiO}_3$. The composition calculated from this lattice constant was smaller than those obtained from EDS and Raman results. Sr diffusion into the BT particles was

Fig. 4. The Raman spectra for the source BT and the resulting BST powders.

assumed to be insufficient. Furthermore, because BST was synthesized by Sr diffusion into BT under hydrothermal conditions, the composition of the particle surface and the particle center assumed to be different slightly. Therefore, it shall be necessary to study hydrothermal conditions such as solvent and temperature in the future works.

4. Conclusion

We successfully synthesized Sr-doped BaTiO_3 by BaTiO_3 nanoparticles to hydrothermal treatment using an strontium nitrate aqueous solution, and the particle size (around 600 nm) and the form (spherical) of the source BaTiO_3 were maintained after hydrothermal treatment. It was confirmed that Ba in BT was substituted Sr from the composition analysis by EDS and temperature dependence of Raman spectra. In conclusion, it was proved that Sr-substituted BaTiO_3 particles could be easily obtained by hydrothermal treatment of source BaTiO_3 spherical nanoparticles (particle size of sub hundreds nanometer) with maintaining the form and particle size of the source material. Furthermore, ion exchange assumed to be possible by extending this method for materials those undergo phase changes due to slight composition changes and materials with various shapes such as needle-shaped particles and thin films.

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