Hydrothermal synthesis of A-site substituted BaTiO₃ nanocubes

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A-site substituted (Ba₁₋ₓSrₓ)TiO₃ nanocubes (BΣ₄T NC; x is Sr ratio) were synthesized by hydrothermal process with surfactant and additives. X-ray diffraction profiles of BΣ₄T NCs showed single-phase of perovskite. Size of BΣ₄T NCs was decreased with increasing Sr content under same hydrothermal condition. When synthesis temperature increased, size of BΣ₄T NCs was enlarged. It revealed that the size of BΣ₄T NCs was able to be controlled by optimizing the hydrothermal conditions. However, inhomogeneous substitution was observed by scanning transmission electron microscopy with energy dispersive X-ray spectroscopy. It suggested that reaction rate of Sr ions to form perovskite structure was faster than that of Ba ions under hydrothermal condition. Three-dimensional (3D) assemblies of BΣ₄T NCs after heat-treatment at 850 °C had obscured interfaces between the NCs. Raman spectroscopy of NC assemblies revealed that symmetry of BΣ₄T NCs differed from that of BaTiO₃ (BT) NCs and did not change after heat-treatment at 850 °C. Piezoresponse curves became slim hysteresis behavior with increasing Sr ratio. These results suggested that Sr substitution of BT NCs caused phase transition from ferroelectric to paraelectric phase in 3D assemblies.

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1. Introduction

Nanocrystals have attracted much attention due to a lot of unique properties such as high surface area, anisotropy of the properties, and high performance of three-dimensional (3D) assembled nanostructures.¹⁻³ The shape of nanocrystals plays an important role to enhance their properties and packing density. Nowadays, minimum size of dielectric components with high performance such as multilayered ceramic capacitors (MLCCs) have been developed.⁴ MLCCs were one of the most important components in the integrated circuit. An implantable device that is new type devices mounted in human body will appear in near future. For example, Tokuda et al., reported the 1 mm³-sized optical neural stimulator integrated photovoltaic power receiver.⁵ They used 2.2-µF MLCC as a power supply of this implantable device. Thus, the small capacitor devices with high performance have a possibility to use as the micro-energy storages for Internet of Things (IoT) and implantable devices. Therefore, miniaturization of capacitors with high capacitance is strongly demanded for these applications. BaTiO₃ (BT)-based dielectric nanomaterials have been developed to enhance the device properties. We have already developed BT nanocube (NC) 3D assemblies which have high dielectric constant above 4000 because of high quality of crystals, preferred orientation of the assembly, and strains induced by formation of a lot of interfaces.⁹⁻¹⁰ Moreover, we have also reported that Zr substitution of Ti site of BT NCs could control the frequency and temperature dependences of dielectric property by tuning Zr/Ti ratio.¹¹,¹² On the other hand, it is well known that partial substitution of Ba by Sr plays a role of shifter which makes shifting ferroelectric-paraelectric phase transition point toward lower temperature. (Ba₁₋ₓSrₓ)TiO₃ (BS₄T) ceramics is one of the effective ways to enhance the dielectric constant at room temperature with low loss tangent.¹³,¹⁴ BS₄T NCs synthesized by hydrothermal or solvothermal methods were reported by several research groups.¹⁵,¹⁶ However, they did not report electrical properties of BS₄T NC 3D assemblies. In this paper, we synthesized BS₄T NCs by hydrothermal route using a titanium aqueous compound and discussed synthesis mechanism with respect to the reaction rate of A-site cations. The relationship of crystalline symmetry and electrical properties of BS₄T NC 3D assemblies was evaluated by Raman spectroscopy and piezoresonance force microscopy (PFM).
2. Experimental

A typical process of BS\textsubscript{x}T NCs (\textit{x} is Sr content) was hydrothermal method similar to the previous our reports of BT-based NCs.\textsuperscript{6,11} BT and SrTiO\textsubscript{3} (ST) NCs were also synthesized as the case of \textit{x} = 0 and 1. The barium hydroxide octahydrate, strontium hydroxide octahydrate, titanium bis(ammonium lactato)dihydroxide, sodium hydroxide, tert-butylamine, and oleic acid were chosen as a starting materials, additives, and surfactants, respectively. They were mixed in water, and then, the aqueous solution was kept at 220–230 °C, for 48 h with stirring. White slurry was washed by ethanol and dispersed in toluene or mesitylene using ultrasonication and centrifugation. Drop-and-dry process was carried out on the substrates or the grids to measure the microstructures by scanning electron microscopy (SEM; JEOL, JSM-6335M) and scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDX; JEOL JEM-ARM200FC with JED-2300), X-ray diffraction (XRD, RIGAKU SmartLab), and Raman spectroscopy (Horiba, XploRA). 3D assemblies of BS\textsubscript{x}T NCs were fabricated on Pt coated Si substrate for electrical measurement by dip-coating method.\textsuperscript{7} 3D assembled films were heat-treated at 400 °C for 1 h and at 850 °C for 1 h, consequently. Piezoresponses of BT and BS\textsubscript{x}T NC assemblies were measured by PFM with dual AC resonance tracking mode (DART-PFM; Asylum Research, MFP-3D) using a conductive cantilever (ASYELEC-01, force constant: 2 N/m, resonance frequency: 70 kHz, tip radius: 25 nm).\textsuperscript{17}

3. Results and discussions

Figure 1 shows XRD profiles of BT, BS\textsubscript{x}T (\textit{x} = 0.3, 0.4, 0.5) and ST NCs synthesized at 220 °C for 48 h which were prepared by drop-and-dry process on Si substrate. BT, BS\textsubscript{x}T, and ST NCs were crystallized in the single-phase of perovskite through the hydrothermal reaction. The peak position linearly shifted to higher 2\theta angle with increasing Sr contents because ion radius of Sr is smaller than that of Ba. These results suggested that Ba sites of BT NC were partially substituted by Sr.

Figure 2 shows SEM images of BT, BS\textsubscript{x}T (\textit{x} = 0.3, 0.4, 0.5) and ST NCs synthesized at 220 °C for 48 h. BT NCs had narrow size distribution around 15 nm and sharp corner of NCs. ST NCs had also narrow size distribution around 15 nm, but corner shape was slightly rounded. On the other hand, the size of BS\textsubscript{x}T NCs decreased with increasing Sr ratio. When \textit{x} = 0.5 [Fig. 2(b)], cubic shaped nanocrystals below 10 nm were obtained at this synthesis condition. In order to exclude the effect of the size of NCs to electrical properties, synthesis condition was optimized. Figure 2(f) shows SEM images of BS\textsubscript{0.4}T NCs synthesized at 230 °C for 48 h. The size of NCs increased and size distribution became narrow with rising the synthesis temperature. The results indicated that size and size distribution of BS\textsubscript{x}T NCs changed with the Sr/Ba ratio even under same synthesis condition. STEM-EDX images of BS\textsubscript{0.3}T synthesized at 220 °C and BS\textsubscript{0.4}T NCs synthesized at 230 °C were shown in Fig. 3. It is difficult to discuss the Ba/Sr ratio in BS\textsubscript{x}T NCs because the Ti\textsubscript{Kα} and Ba\textsubscript{Lα} peaks in the EDX spectra partly overlap. Here, we focused on the distribution of Sr in the NCs. Regardless of nominal ratio of Sr/Ba, Sr ions showed inhomogeneous distribution. Sr-rich phases are observed at a center of the NC. The inhomogeneity in the individual NCs implied that the reaction rate of Sr ions to crystallize perovskite structure was faster than that of Ba ions. Thus, in the first step, nucleuses of Sr-rich phase were likely to be generated, after that, Barich phase were grown on the nucleus. Resultantly, Sr-rich phase might appear at a center of the NCs. As a nucleation rate of Sr-rich phase was fast, a lot of fine nucleuses were easy to be generated with increasing Sr ratio. Thus, the size of NCs became smaller with increasing Sr ratio. Additionally, we have reported that ST NCs tended to grow to the cuboid.\textsuperscript{19} In this study, some BS\textsubscript{0.4}T NCs were grown to the cuboid, as shown in Fig. 3(b). Therefore, it also suggested that Sr/Ba ratio affected the shape of NCs. Figure 4 shows SEM images of BS\textsubscript{0.3}T and BS\textsubscript{0.4}T NC

![Fig. 1. XRD profiles of (a) BT, (b) BS\textsubscript{0.3}T, (c) BS\textsubscript{0.4}T, (d) BS\textsubscript{0.5}T, and (e) ST NCs fabricated on Si substrate.](image-url)
assemblies fabricated by dip-coating method. BS$_{0.3}$T NCs were assembled with relative dense and ordering, but BS$_{0.4}$T NC assembly had a lot of cracks. As the shape of BS$_{0.4}$T NCs was slightly rounded as shown in Fig. 2(f), cracks were generated in the assembly. It was reported that the degree of ordering of NCs were affected by shape of NCs.$^{19}$ Truncated NCs tended to assemble body-centered tetragonal structure. Highly ordered assembly with cube-on-cube closest packing structure is necessary to utilize interface of NCs for enhancement of electrical properties. Figures 4(c) and 4(d) show SEM images of BS$_{0.3}$T and BS$_{0.4}$T NC assemblies after heat-treatment at 850 °C.

Boundaries between the NCs became obscure and many voids were appeared in the surface of the assemblies. These changes were similar to those of BT NC assembly. These images indicated that the NCs had joined each other by heat-treatment at 850 °C regardless of Ba/Sr ratio. Raman spectra of BT, BS$_{0.3}$T and BS$_{0.4}$T NC assemblies before and after heat-treatment at 850 °C measured at room temperature were shown in Fig. 5. When Sr content increased from 0 to 0.4, the peaks became broad. In particular, the intensity of peak around at 300 cm$^{-1}$ [arrowed peak in Fig. 5(b)] decreased by substitution of Sr. It was reported that the same phenomenon was observed in the
Therefore, this result suggested that the crystal symmetry gradually changed from ferroelectric phase to paraelectric phase with degrees of Sr substitution. The spectra of BT and BS$_{x}$T NC assemblies had almost no change after heat-treatment at 850 °C. This result meant that the symmetries of the BT and BS$_{x}$T NC assemblies did not change through the heat-treatment.

Piezoresponse behaviors of BT and BS$_{x}$T NC assemblies were shown in Fig. 6. Thickness of BT NC, BS$_{0.3}$T NC, BS$_{0.4}$T NC assemblies measured by cross-sectional
SEM were about 250, 170 and 280 nm, respectively. BT NC assembly had a hysteresis butterfly loop under DC bias. This result indicated piezoelectricity of BT NC assembly. On the other hand, amplitude curves of BS$_x$T NC assemblies became slim with increasing Sr ratio, which was similar to the case of BS$_x$T ceramics reported by Jin et al. These results suggested that substitution of Sr worked as shifter. However, the quantitative analysis of piezoelectric constant was difficult because there were many extrinsic effects such as condition of the cantilevers, contact force, contact area of the tip, inhomogeneous substitution of Sr, degree of ordering of NCs in 3D assembly, and formation condition of the interfaces between NCs. We should optimize not only Sr-substitution condition of BS$_x$T NCs and fabrication condition of 3D assembly of BS$_x$T NCs but also the measurement condition of PFM, for precise discussion of the dielectric and piezoelectric properties of BS$_x$T NCs in near future.

4. Summary

BS$_x$T NCs were synthesized by hydrothermal reaction using titanium aqueous compound, surfactant, and additives. Size and shape of the NCs depended on Sr/Ba ratio under the same synthesis condition. When synthesis temperature raised to 230°C, size of BS$_{0.4}$T NC increased from 10 to 15 nm. It was revealed by STEM-EDX analysis that a part of Ba was locally substituted by Sr owing to the
difference of reaction rate to form the perovskite structure between Sr and Ba ions under hydrothermal condition. Raman spectra revealed that the crystal symmetry of BS,T NC assemblies differed from that of BT NC assembly. Moreover, the symmetries of BT and BS,T NC assemblies did not change through the heat-treatment. BS,T NC assembly had a slim hysteresis piezoresponse curves. This result also indicated that paraelectric phase gradually increased with degrees of Sr substitution. However, homogeneous substitution of Sr and control of the size and shape of BS,T NCs should be developed by optimization of synthesis condition and processes in near future. To evaluate quantitatively the electrical properties of BS,T NC assembly, optimization of measurement condition and assembling condition should be necessary.

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