Synthesis and characterization of barium titanate-based solid solution nanocubes

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Ba(ZrxTi1−x)O3 nanocubes (BZT NCs) were synthesized by hydrothermal reaction with titanium and zirconium aqueous compounds and surfactants. The nanocubes were assembled on the substrates by dropping-drying method. The microstructures of the nanocube were evaluated by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The ordered assemblies of the NCs were yielded on the substrate when Zr contents were below 0.2. BZT0.2 NCs had narrow size distribution about 20 nm observed by FE-SEM and TEM. On the other hand, BZT0.5 and BaZrO3 NCs were attached each other and they formed large cube above 100 nm. Perovskite phase was characterized by Raman spectroscopy under various measurement temperatures. The ordered assemblies of the NCs were yielded on the substrate when Zr contents were below 0.2. BZT0.2 NCs had unique structure showed the piezoelectric d33-E hysteresis loops at frequency dependance. Moreover, the authors also fabricated three-dimensional (3D) BT NC assemblies by using capillary-force-assisted self-assembly method. The 3D BT NC assemblies have high packing density. Surprisingly, after sintering at 850°C, the NCs were remained in the assembly while keeping their shapes and packing density. Especially, we focused on this effect to apply to the BT NC system.

1. Introduction

Dielectric devices such as multilayer ceramic capacitors (MLCCs) have been miniaturized with high performances to satisfy with the demands for high-specification computers and mobile phones in past years. BaTiO3 (BT) particles, which were used in dielectric layers of MLCCs, were also miniaturized with high dielectric properties. However, when the particle size of BT became below 50 nm, dielectric constant of BT decreased significantly. The cubic phase of BT which appears at particle surface affects to dielectric properties. It is well-known the negative nano-size effect of the dielectric materials. Recently, cubic-shaped single-crystalline nanocrystals, so-called nanocubes (NCs) attract a great deal of attention to use as the new electrical materials. Especially, the authors have already synthesized BT NCs by hydrothermal method with aqueous compounds and organic surfactants. They highly qualified BT NCs with 15 nm in a size were obtained by this method. Moreover, the authors also fabricated three-dimensional (3D) BT NC packing structures by using capillary-force-assisted self-assembly method. The 3D BT NC assemblies have high packing density. Surprisingly, after sintering at 850°C, the NCs were remained in the assembly while keeping their shapes and ordering structures without any grain growth. Resulantly, the assembly had a lot of interfaces conjugated each other. This unique structure showed the piezoelectric d33-E hysteresis loops and high dielectric constant of 4000 at room temperature with relatively low loss below 7% and flat frequency dependences. It was also revealed that BT NC assemblies were able to be fabricated on desired area by using the micro-patterned substrates. As mentioned above, BT NC assembly has a great potential to become the entirely new dielectric materials for the future dielectric devices.

On the other hand, there are a lot of issues to overcome for the robust applications of dielectrics. The most important issue is tuning the dielectric properties of the materials. The simple and useful approach is doping or substitution other elements in the host material. In general, BT bulk has maximum dielectric constant at Tc around 120°C due to the paraelectric-ferroelectric phase transition. As some dielectric devices are used in the adequate temperature range, the dielectric properties are required to be independent of environmental temperature change. Recently, high performance dielectric devices in a relatively-high temperature range up to 150°C are demanded for power electronics fields. Substitution of Ti ions by Zr ions on BT to control the stoichiometry of Ba(Zr0.5Ti0.5)O3 (BZT) is well-known method to flatten the temperature dependence of dielectric properties. Especially, it has been reported that the flat temperature dependence of dielectric constant and dielectric constant at room temperature were yielded at the ratio of Zr:Ti = 0.2:0.8 in both case of ceramics and thin films. The authors focused on this effect to apply to the BT NC system.

In this study, the solid-solution BZT NCs with various Zr/Ti ratio were synthesized by using advanced hydrothermal method using both Ti and Zr aqueous compounds mixtures and surfactants. Especially, we focused on x = 0.2. Microstructures, compositions and crystallographic phase of BZT, NCs were clarified by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) observations, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

2. Experimental procedure

A typical synthesis process was similar to the previous report and summarized in Fig. 1. All reagents were used...
Experimental procedure of BZT NCs by hydrothermal synthesis using aqueous compounds mixtures and surfactants.

without any purifications. 3 mmol of Ba(OH)2·8H2O was completely dissolved into 22.8 ml of H2O under stirring for 10 min in a 50 ml Teflon-lined autoclave. Titanium(IV) bis(ammonium lactate) dihydroxide (TALH) and zirconium ammonium lactate hydroxide compounds (ZALH) were mixed with desired Zr/Ti ratio. Zr/Ti mixed aqueous compounds (total amount of 3 mmol) were added to Ba(OH)2 aqueous solution. The solution became cloudy. 7.2 ml of 5 M NaOH aqueous solution was added under stirring. And then, tert-butylamine (t-BA) and oleic acid (OLA) (Ba:t-BA:OLA = 1:12:12 in molar ratio) were added into the solution. The sealed autoclave was heated to 220–230°C for 72 h. After the reaction, the viscous white slurry was yielded. By centrifugation, the precipitates were separated and washed twice by ethanol, and they were ultrasonically dispersed into toluene. The precipitates were separated and washed twice by centrifugation, the precipitates were separated and washed twice. When the temperature increased to 230°C and the time was elongated to 96 h, BZT0.5 NCs were obtained but they became large cubes above 100 nm terminated by rough surfaces with coexistence of irregular shaped fine particles [Fig. 2(c)]. It suggested that the crystallization speed of BZT NCs decreased with increasing Zr contents with respect to BT NCs.

The BZT NCs were observed as shown in Fig. 3(a). Figures 3(b) and 3(c) were obtained by FFT. These results insisted that highly-quali-
sed single-crystalline BZT NCs were obtained. Edge length of the NC was measured as 21 nm. The length was corresponding to the narrow size distribution of BZT0.1 and BZT0.2 NCs. However, Zr contents increased to 0.5, 20 nm sized NCs could not be obtained at 220°C for 72 h. When the temperature increased to 230°C and the time was elongated to 96 h, BZT0.5 NCs were obtained but they became large cubes above 100 nm terminated by rough surfaces with coexistence of irregular shaped fine particles. Therefore, OLA desorbed from Zr ions of NCs and then the BZ framelike structure. It should be noticed that the framework has been already formed in the starting compound. Therefore, the structural difference might have significantly affected the reaction to build up the crystal structure. On the other hand, BaZrO3 (BZ) NCs (x = 1.0) with 20 nm in a size were conjugated each other and formed large cubes as shown in Fig. 2(d). This result supported that the capping ability of OLA at Zr and Ti ions-terminated surfaces was quite different. It is considered that OLA capping to Zr ions was unstable compared with that to Ti ions. Therefore, OLA desorbed from Zr ions of NCs and then the BZ NCs attached each other under the hydrothermal condition. As a result, they were assembled in large cubes. When Zr content was below 0.2, BZT NCs with narrow size distribution and sharp edges were able to be synthesized. However, there is increased difficulty to synthesize the homogeneous and isolated BZT NCs with increasing Zr contents due to the difference of reactivity of the Ti and Zr compounds. As a result, longer reaction time and higher temperature were required to obtain the BZT phase in the case of x ≥ 0.5.

Figure 3 shows TEM images of BZT NCs. Sharp-edged NCs were observed as shown in Fig. 3(a). Figures 3(b) and 3(c) show high resolution (HR) image of BZT NC and fast Fourier transferred (FFT) pattern of Fig. 3(b). No voids and defects were observed by HR-TEM image. Moreover, regular spot pattern was obtained by FFT. These results insisted that highly-qualified single-crystalline NCs were obtained. Edge length of the NC was measured as 21 nm. The length was corresponding to the
average size observed from Fig. 2(b).

Figure 4(a) shows XRD profiles of BZT, NCs dropped on Si substrates. Perovskite phase was obtained in all composition of BZT, NCs. However, small amount of BaCO₃ existed in BZT₀.₅ and BZ NCs. This result also suggests that the reactivity of the starting compounds decreased with increasing Zr contents. It is noteworthy that intensity of {100} diffraction was higher that of {110} in the case of BT, BZT₀.₁ and BZT₀.₂ NCs. These assemblies had {100} preferred orientation. This means self-assembly of these NCs occurred due to the narrow size distribution even when the NC colloidal solution was simply dropped and dried on the substrate. The lattice constants of BZT, NCs were calculated by diffraction peaks of XRD profiles and summarized in Fig. 4(b). All of the NCs assumed as pseudocubic structure. The lattice constants increased linearly with increasing Zr contents in accordance with Vegard’s law. The lattice constant of BZ NCs (a = 4.19 Å) was similar to those of BZ ceramics (a = 4.18 Å, JCPDS No. 04-005-4212) and the hydrothermally synthesized BZ particles reported by Kanie et al.²⁶ These results supported that Zr ions were substituted to Ti sites with the desired ratios through the present synthesis method due to the homogeneous aqueous mixtures of Zr and Ti lactate compounds.

Figure 5 shows XPS spectra of BZT₀.₂, NCs and commercial BT nanoparticles (BT NPs) which was synthesized by hydrothermal method with average particle size of 100 nm. Of course, Zr₄d spectra was only obtained in the case of BZT₀.₂ NCs as shown in Fig. 5(a). This means there are no Zr contaminations in BT NCs and BT NPs. To analyze the actual composition of BZT₀.₂ NCs, the area of the Ba, Ti and Zr peaks were calculated. The relative atomic concentrations of Ba, Ti, Zr and the ratio normalized by Ba were also listed in Table 1. The composition of Zr seemed to be slightly low compared with the other elements from Table 1. The deviation is considered to stem from the following reasons. The detection sensitivity is dependent of each elements, and the peak area is calculated by using a coefficient of sensitivity. Therefore, the accuracy of the composition analysis by XPS is not so high. On the other hand, since it has been

Table 1. Composition of BZT₀.₂ NCs calculated by XPS spectra

| Element | Atomic conc. (%) | Normalized ratio by Ba |
|---------|------------------|------------------------|
| Ba      | 51.5             | 1.0                    |
| Ti      | 40.9             | 0.79                   |
| Zr      | 7.65             | 0.15                   |
temperature range. On the other hand, BZT0.2 NCs had no peak This suggested that local lattice strain is maintained at high phase at room temperature. The intensity of this peak decreased with increasing temperature but shoulder remained at 150°C. Raman spectra of BT NCs were calculated by XRD profiles and increased linearly with increasing Zr contents. The composition of BZT0.2 NCs was considered to be nearly equal to nominal ratio by XPS and XRD analysis. Moreover, the amount of physisorbed OH was confirmed by binding energy of O1s and found to be relative low in the case of BT NCs and BZT0.2 NCs. OLA-derived carboxylate capping to the NCs was also confirmed by O1s, small peak around 530.5 eV. Raman spectra of BT NCs showed a sharp peak around 305 cm⁻¹ which was assigned to tetragonal phase at room temperature. Intensity of this peak decreased with increasing temperature but the shoulder was remained at 150°C. On the other hand, Raman spectra of BZT0.2 NCs had no change over wide temperature range and they had no phase transition. This result indicated that the flat temperature dependence of dielectric constant of BZT0.2 NCs was expected over the wide temperature range.

4. Conclusions
BZTₙ (ₙ = 0.1, 0.2, 0.5, 1.0) NCs were synthesized by hydrothermal method with mixtures of Zr and Ti aqueous compounds and surfactants. The NCs in the BT-BZ solid-solution system were successfully synthesized by modification of hydrothermal condition and using the aqueous compounds. Especially, in the case of ₙ ≤ 0.2, 20 nm NCs with a narrow size distribution were synthesized. Highly-qualified single-crystalline BZT₀.₂ NCs without any voids and defects were confirmed by HR-TEM. Lattice constants of BZT NCs were calculated by XRD profiles and increased linearly with increasing Zr contents. The composition of BZT₀.₂ NCs was considered to be nearly equal to nominal ratio by XPS and XRD analysis. Moreover, the amount of physisorbed OH was confirmed by binding energy of O₁s and found to be relative low in the case of BT NCs and BZT₀.₂ NCs. OLA-derived carboxylate capping to the NCs was also confirmed by O₁s, small peak around 530.5 eV. Raman spectra of BT NCs showed a sharp peak around 305 cm⁻¹ which was assigned to tetragonal phase at room temperature. Intensity of this peak decreased with increasing temperature but the shoulder was remained at 150°C. On the other hand, Raman spectra of BZT₀.₂ NCs had no change over wide temperature range and they had no phase transition. This result indicated that the flat temperature dependence of dielectric constant of BZT₀.₂ NCs was expected over the wide temperature range.

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