

Preparation and characterization of BaTiO₃ particles coated with yttrium compound

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Barium titanate (BaTiO₃) particles were homogeneously coated with yttrium compound by the decomposition of yttrium nitrate with urea in aqueous solution. The morphologies of the yttrium compound-coated BaTiO₃ particles were controlled by varying the initial concentration of yttrium nitrate for a fixed reaction temperature and time. The relationship between the initial yttrium concentration and the coating layer thickness was confirmed by transmission electron microscopy (TEM) images. Electron probe microanalyzer (EPMA) and XRD data showed that the BaTiO₃ particles were homogeneously coated with yttrium compound.

Key words: BaTiO₃, yttrium compound, coating, morphology, TEM, Electron Probe Microanalyzer.

Introduction

Barium titanate (BaTiO₃) is a typical representative of an oxide crystallized with the perovskite structure. Due to its outstanding ferroelectric and dielectric properties, BaTiO₃-based materials have many applications in electronic devices such as multilayer ceramic capacitors (MLCCs), high-capacitance capacitors, positive temperature coefficient (PTC) thermistors, electro-optic devices, piezoelectric sensors and humidity sensors. In MLCCs, BaTiO₃ has to be incorporated with other dopant materials to overcome its severe capacitance variance with temperature for application as MLCCs. There are two kinds of MLCCs using BaTiO₃ as a starting material. One is Y5V MLCCs (capacitance variation between -82% and +22% in the -25 °C to 85 °C) and the other is X7R MLCCs (capacitance variation within ± 15% from -55 °C to 125 °C) [1]. In general, Sr and Ca-doped powder for application in the Y5V MLCCs is utilized, whereas powder, with Ca and Zr doping are used in the X7R MLCCs. In addition, the lifetime of MLCCs is also a critical factor to be considered in the fabrication of MLCCs. Y₂O₃ has been considered the most effective element for improvement in the reliability of MLCCs [2].

In the shape forming process, BaTiO₃ and additives such as SrCO₃, CaCO₃, ZrO₂, and Y₂O₃ are mixed by a mechanical milling method, but in the mechanical milling, a homogeneous distribution of these additives is difficult to achieve, which causes a segregation of additives. This leads to an adverse impact on the elec-

trical properties because the electrical properties are attributed to a uniform distribution of components after sintering. In addition, segregation of additives readily occurs from the difference in settling rates between different particles in multi-component dispersions [3]: which results in variations of the particle packing structure. Adsorption of counter ions onto the particle surface, one of the alternative methods, utilizing charge differences between particle surface and ions, can overcome the non-uniformity of components and the difference in the settling rates. However, this method causes a decrease in the surface potential of oxide particles, which decreases the dispersion stability [4]. Bleier *et al.* attempted to obtain co-dispersion in a Al₂O₃-ZrO₂(CeO₂) composite by manipulation of the surface potential of each component [5]. Every particle must have the same charge sign to obtain a sufficiently homogeneous particle distribution of each particle. However, this method can be utilized in a dispersion system, which has similar conditions of particle size and density. Another concept, which utilizes the surface charge of each particle, for multi-component dispersion is hetero-coagulation. However, this only occurs at a suspension pH between the isoelectric points of the two different particles. Thus, there are limitations that wet processing has to be performed at a certain suspension pH. In addition, it is well known that certain ceramic particles, such as BaTiO₃ and Y₂O₃, are easily dissolved in an acidic pH region, which limits the available processing window. The dissolution of surface ions has a significant impact on the dispersion stability of the suspension [6]. A significant limitation, the suspension pH in the BaTiO₃ and Y₂O₃ system, in the processing window comes due to the dissolution of surface ions from components. Therefore, many attempts have been

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made to coat the particle surface with doping components to improve the dispersion stability in multi-component systems.

Many researchers have attempted to prepare core/shell composites. Park *et al.* [7] synthesized zinc sulfide phosphors coated with yttrium oxide using a sol-gel process. In this process, yttrium iso-propoxide was used as the precursor materials in a toluene/iso-propanol solution. Matijević and coworkers [8-14] synthesized various combinations of core/shell particles, including cores like hematite, silica, titania, chromium oxide, polystyrene latex and coatings like aluminum, zirconium, and yttrium carbonates. In their method, the core particle was varied in morphology from a sphere to an elongated shape. In recent studies, Plaza *et al.* [15-17] fabricated and characterized hematite particles coated with yttrium compounds to obtain a stable dispersion. They studied the various properties of the coated hematite by varying the composition and reaction time. In this study, the method described by Aiken and Matijević [11], was applied to obtain barium titanate (BaTiO_3) particles coated with yttrium basic carbonate (Y(OH)CO_3). Because barium titanate is unstable in water, hydroxide ions at the surface of particles are dissolved and nuclei of yttrium hydroxides are formed on the surface of barium titanate. The growth of yttrium compounds occurs at elevated temperature, because urea decomposes and offers carbonating ions above 60°C [18]. Formation of core/shell particles was confirmed by electron microscopy and the yttrium content and the loss of yttrium ions in the particles obtained were analyzed by an electron probe microanalyzer.

Experimental

Materials

Barium titanate powders (BT-04B, Sakai Chemical Industry Co Ltd., Japan, average diameter = $0.4\ \mu\text{m}$) were used as core particles and yttrium nitrate hexahydrate ($\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich, 99.9%) was used to form a shell coating. Urea (Aldrich, 99+%) was used to offer the sources of carbonating ions for the synthesis of metal basic carbonates. Polyvinyl pyrrolidone (PVP, Mw = 40,000, Aldrich) are used as a stabilizer.

Preparation of Y(OH)CO_3 -coated BaTiO_3 particles

Yttrium basic carbonate was prepared on the BaTiO_3 particles with the following procedure. First, two aqueous solutions were prepared. Solution I contained $\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and urea, whereas solution II contained PVP. Then, barium titanate powders were added into solution I to prepare a BaTiO_3 dispersion and this dispersion was sonicated for 5 minutes to disaggregate the BaTiO_3 aggregates and to form the nuclei of yttrium hydroxides on the surface of the barium titanate (Details are given in Table 1). Finally, solution II was added to solution I and suspension obtained was aged

Table 1. Specific concentrations and thickness of coating layer (before calcination)

Sample	BaTiO_3 (mM)	$\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (mM)	Layer thickness (nm)
S1	10	0.5	-
S2	10	1.0	5
S3	10	2.0	20
S4	10	3.0	25

PVP: 2.5 wt%, Urea: 0.1

Reaction temperature: 90°C , Reaction time 6 h

in a convection oven at 90°C for 6 hours. PVP, unreacted compounds and yttrium compounds in the bulk solution were removed by centrifuging the sample at 3000 rpm and replacing the supernatant with fresh water and ethanol.

Characterizations

Particle size and morphology were investigated by Transmission Electron Microscopy (TEM, JEOL model, JEM2000-EX II). Samples were prepared by dropping highly diluted dispersions on to carbon-coated copper grids and dried in a desiccator at room temperature. The chemical composition of particles was measured to the depth of $1\ \mu\text{m}$ by an electron probe microanalyzer (EPMA, JEOL model, JXA-8900R). Aggregated particles were analyzed because the diameter of each particle was below $1\ \mu\text{m}$. Because yttrium basic carbonates are amorphous, the particles obtained were calcined at 800°C for 3 h to convert Y(OH)CO_3 to Y_2O_3 to obtain the crystalline structure of yttrium oxide. X-ray diffraction measurements were performed on a Rigaku D/MAX RINT 2000 X-ray diffractometer, and the detector was moved stepwise ($\Delta 2\theta = 0.05^\circ$) between 10° and 100° .

Results and Discussion

Morphology and Structure

Figure 1 shows the TEM images of the coated particles. The shapes of the bare particles are irregular and the average diameters of them are $400\ \text{nm}$ (the diameters of some particles are about $150\ \text{nm}$). The yttrium compounds formed in bulk were not observed by TEM because yttrium compounds formed in the bulk were removed by washing and centrifugation. Concerning the relationship between the initial concentration of yttrium nitrate and the coating-shape, the thickness of the coating layer increases with an increase in the initial concentration of yttrium nitrate. If the initial concentration of yttrium nitrate is insufficient to form a homogeneous coating layer on the barium titanate, a coating layer is not formed or a non-homogeneous coating layer is formed. In the case of S1 (see Table 1), Y(OH)CO_3 islands were formed on the barium titanate particles. S2 had a thin coating layer, but the coating

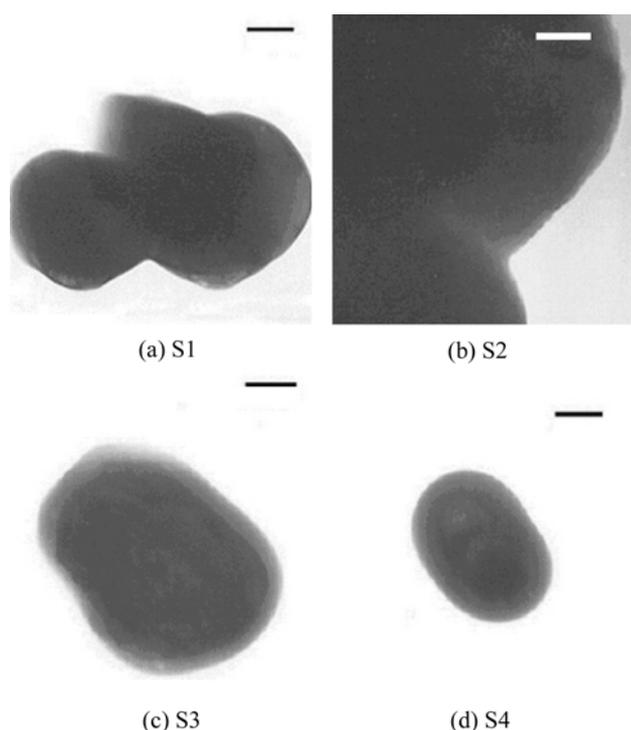
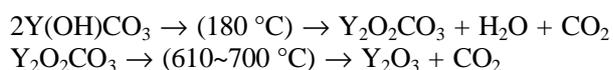


Fig. 1. TEM images of BaTiO₃ coated with yttrium compound (before calcinations; bar: 100 nm) (a) S1; (b) S2; (c) S3; (d) S4.

shell was not homogeneous. The coating layers of S3 and S4 were very homogeneous compared with the layer on S2. However, a concentrated aged solution of barium titanate (0.1 M) and yttrium nitrate (20 mM, Ba/Y = 10:2) produced large Y(OH)CO₃ particles in the bulk solution. It is suggested that a high initial concentration of yttrium ions caused a nucleation of Y(OH)CO₃. Y(OH)CO₃ bridges between the barium titanate particles show that the distance between particles were small and core particles were connected by yttrium basic carbonates.

Figure 2 shows TEM images of samples calcined at 800 °C for 3 h. During the calcination, yttrium carbonates are converted to yttrium oxides. Other authors have demonstrated that yttrium basic carbonates were converted to yttrium oxides by thermogravimetric analysis [9-13]. The following is the mechanism of converting yttrium basic carbonates to yttrium oxides. At about 180 °C, the weight loss is associated to water loss and decomposition of the hydroxycarbonate to the oxycarbonate occur. When the temperature reaches 610~700 °C, vaporization is complete, and an amorphous oxycarbonate transforms into crystalline cubic yttrium oxide.



After calcination, the thickness of the coating layer decreases, because H₂O and CO₂ are removed during the calcination. However, the thickness of the coating layer is not uniform. The coating layer of yttrium basic carbonate was converted to particle-like coatings of

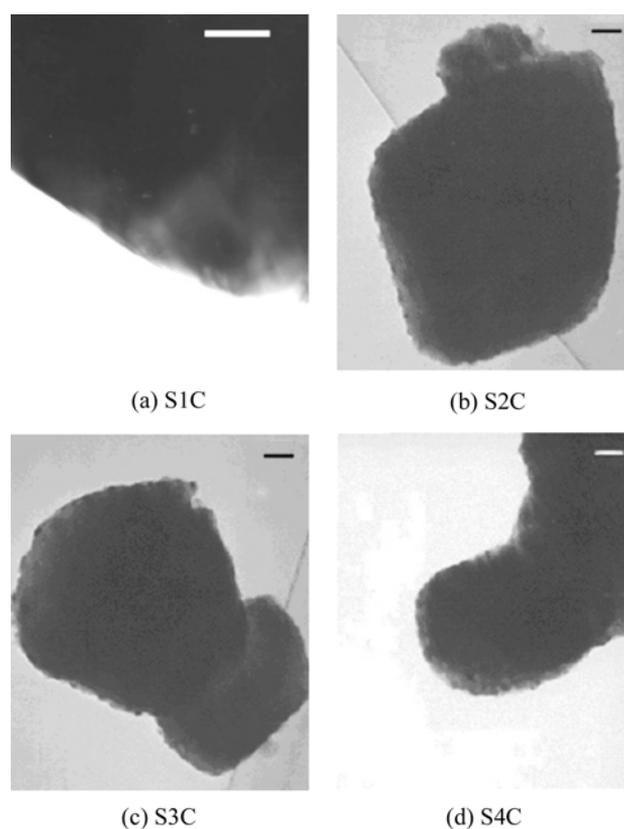


Fig. 2. TEM images of BaTiO₃ coated with yttrium compound (after calcinations, bar: 50 nm) (a) S1C; (b) S2C; (c) S3C; (d) S4C.

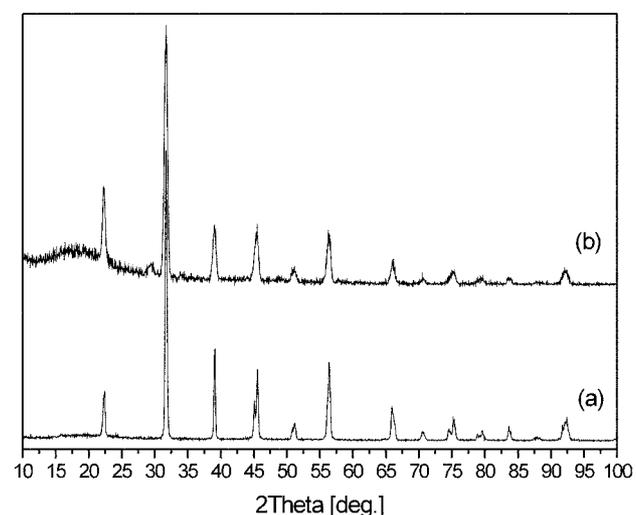


Fig. 3. XRD spectra of bare BaTiO₃ particles (a) and S4C (b).

yttrium oxides during the calcination.

X-ray diffraction data are shown in Fig. 3. X-ray diffraction patterns of the Y₂O₃-coated BaTiO₃ (S4C) particles are compared with the bare BaTiO₃ particles. X-ray diffraction patterns of the other samples were the same.

Chemical composition

For calculating the amounts of yttrium in samples,

Table 2. Initial and final atomic ratio of barium to yttrium

Sample	Initial atomic ratio of Ba:Y	Final atomic ratio of Ba:Y	Loss of yttrium (%)
S1	100:5	100:4.04 [96.12:3.88]	19.19
S2	100:10	100:9.66 [91.19:8.81]	3.43
S3	100:20	100:17.29 [85.26:14.70]	13.54
S4	100:30	100:21.86 [82.06:17.96]	27.15

atomic ratios of barium to yttrium were measured by EPMA analysis. Data were taken in five different positions from each sample. Table 2 shows the average atomic ratio of barium to yttrium, and the atomic loss of yttrium. Barium titanate particles were coated with yttrium to above 80% of the initial concentration of yttrium except for S4. An increase in the initial concentration of yttrium nitrate leads to an increase in the yttrium atoms in the sample obtained. But, an optimum composition exists for minimizing the loss of yttrium ions. In the case of S2, 96.57% of yttrium covered barium titanate was used to form yttrium basic carbonates and the loss of yttrium atoms was smaller than any other samples. When the initial yttrium concentration was above 1.0 mM, the loss of yttrium ions increased with an increase in the initial yttrium concentration. In order to reduce the loss of yttrium ions, the initial molar ratio of barium titanate to yttrium nitrate must be optimized.

Conclusions

BaTiO₃ particles were coated with yttrium compounds using a method described by Aiken and Matijević. Yttrium compounds were homogeneously distributed around BaTiO₃ particles and the thickness of the coating layer was related to the initial concentration of yttrium nitrate. It was confirmed that an optimized

composition is required to obtain a coating layer which is sufficient.

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