Solvothermal Synthesis of Barium Titanate Nanocubes with Narrow Size Distributions

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Barium titanate (BaTiO_3) nanocubes were synthesized by solvothermal reaction. The synthesis was performed using barium hydroxide [$\text{Ba}(\text{OH})_2$], barium acetate [$\text{Ba}(\text{CH}_3\text{COO})_2$], and titanium dioxide (TiO_2) as starting materials, with Ba / Ti atomic ratio of 2.0 and Ti concentration of 0.04 mol / l. A mixture of ethanol, 2-methoxyethanol and water was added to the starting materials and this mixture was heated at 240°C for 18h in an autoclave. X-ray diffraction measurements confirmed the formation of BaTiO_3 with a perovskite structure. The water served as an oxygen source for synthesis BaTiO_3 . Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations revealed cube-shaped BaTiO_3 . In order to synthesize the small-scale BaTiO_3 nanocubes, various reaction conditions such as the amount of water addition, kind of barium source, and amount of barium source were investigated. BaTiO_3 nanocubes with sharp-edged corners were formed by increasing the proportion of $\text{Ba}(\text{CH}_3\text{COO})_2$ used as a raw material for the barium source.

Key words: BaTiO_3 , nanocube, solvothermal method, perovskite oxide

1. Introduction

Perovskite oxides have an important role in the fabrication of electric devices such as multilayer ceramic capacitors (MLCCs), piezoelectric actuators for micro electro mechanical systems, electro-optics [1]. In recent years, there are strong demands to miniaturize the devices and to enhance electric properties of the constituent components. The miniaturization of these electric devices is reaching a limit because the constituent materials which are synthesized by conventional solid state reaction method are too large to miniaturize these devices. Nowadays, these materials are down-sized by milling process, which is called “top-down” method. However, the materials often undergo chipping and contamination through milling and electric properties can’t be optimized. Therefore, it is necessary to establish an entirely-new method for the fabrication of these devices or to create new functional materials in the near future. The “bottom-up” process from nano-sized materials is a key engineering to achieve these demands [2-11]. The assembled and ordered structure prepared from nanocrystallites building blocks is well-known as one of the bottom-up processes. These assemblies have lots of advantages such as high surface area, quantum size effect, and utilization of specific properties which depend on the shape of the nanocrystals as well as the configuration of the nanocrystals assembled structure.

Barium titanate (BaTiO_3 , BT) and strontium titanate (SrTiO_3 , ST) are the most popular perovskite oxides for electronic device application such as MLCCs, positive temperature coefficient (PTC) thermistor. Recently, the morphology control of the perovskite oxide such as BT was studied with a liquid phase reaction in order to fabricate functional materials. In particular, nanocubes

has been attractive attention in the field of electroceramic materials. It has been reported that BT/ST artificial superlattice thin film which consists of a few unit cells per layer has ferroelectricity and enhanced dielectric properties [12-13]. The origin of these high dielectric and ferroelectric properties in the superlattices is traced to the lattice strain which is induced at the hetero-interfaces due to lattice mismatch such as BT/ST interfaces. In other words, hetero-interface is key point for the electroceramic materials. Checkerboard structure which is built by nanocubes has many hetero-interfaces, so that improvement of physical properties further can be expected in the field of electroceramic materials [14-18]. For this purpose, the synthesis of nanocubes with narrow particle size distribution is required, and to continue with the synthesis of BT nanocubes in this study [7-8]. We have focused on the interface of nanocubes with perovskite oxides in order to develop electroceramic materials. The interface of particles is a very important factor in development of enhanced materials. It is necessary for the interface of nanocubes to be bare, so we do not use dispersants or surfactants when synthesizing nanocubes. In this study, synthesis of BaTiO_3 nanocubes was investigated by solvothermal method. In particular, raw materials were examined in order to obtain BaTiO_3 nanocubes.

2. Experimental Method

First of all, water was used at solvothermal reaction as reaction medium. BT was prepared by the solvothermal method. As raw materials, 20 mmol $\text{Ba}(\text{OH})_2$ (Ube Materials Industries Co., Ltd.; > 99.9%) and 10 mmol TiO_2 (Ishihara Co., Ltd.) (Ba : Ti = 2.0) were added into mixed solvent (150 ml of ethanol and 100 ml 2-methoxy

ethanol). The solution was transferred into a 500 ml autoclave, and then 10 ml of distilled water was added into the solution. The sealed autoclave was heated at 240 °C for 18 h, and then cooled at room temperature. After the synthesis, the precipitate was collected centrifugal separator and washed twice with water and once with ethanol. The product was dried in a dryer 80 °C overnight. Finally the product was washed to elimination impurity by acetic acid aqueous solution.

Next barium source was chosen less reactive than $\text{Ba}(\text{OH})_2$. BaCO_3 , BaC_2O_4 and $\text{Ba}(\text{CH}_3\text{COO})_2$ were chosen as the barium source candidates. As raw materials, 1 mmol barium source and 0.25 mmol TiO_2 (Ishihara Co., Ltd.) ($\text{Ba} : \text{Ti} = 4.0$) were added into 12.5 ml 0.08M KOH aqueous solution. The solution was transferred into a 25 ml autoclave. The sealed autoclave was heated at 230 °C for 18 h, and then cooled at room temperature. After the synthesis, the precipitate was collected centrifugal separator and washed twice with water and once with ethanol. The product was dried in a dryer 80 °C overnight. Finally the product was washed to elimination impurity by acetic acid aqueous solution.

BT was synthesised to mix barium source $\text{Ba}(\text{OH})_2$ and $\text{Ba}(\text{CH}_3\text{COO})_2$. As raw materials, (20-x) mmol $\text{Ba}(\text{OH})_2$ (Ube Materials Industries Co., Ltd.; > 99.9%), x mmol $\text{Ba}(\text{CH}_3\text{COO})_2$ (Kanto Chemical Co., Ltd.; > 99.0 %) and 10 mmol TiO_2 (Ishihara Co., Ltd.) ($\text{Ba} : \text{Ti} = 2.0$) were added into mixed solvent (150 ml of ethanol and 100 ml 2-methoxy ethanol). The solution was transferred into a 500 ml autoclave, and then 10 ml of distilled water was added into the solution. The sealed autoclave was heated at 240 °C for 18 h, and then cooled at room temperature. After the synthesis, the precipitate was collected centrifugal separator and washed twice with water and once with ethanol. The product was dried in a dryer 80 °C overnight. Finally the product was washed to elimination impurity by acetic acid aqueous solution.

3. Results and Discussion

Figure 1 shows XRD pattern and SEM images of the product obtained in the synthesis with the solutions containing various amounts of water. Reduction in peak of TiO_2 could be confirmed from the result of XRD pattern, it is gradually increased the amount of water added, it was confirmed single phase BT in the system was added 10 ml of water. However, it was supposed to form the particles is like as spherical by SEM observation. TiO_2 was completely dissolved in the solvent solubility is increased by adding water to the solvent, TiO_2 is easily dissolved, and 10 ml water is added, but with the increase in solubility, nucleation is shifted to the lower temperature side. It is believed that nuclei were formed isotropically due to the shape of the particles and it became spherical.

Figure 2 shows XRD pattern of the product obtained in the synthesis with BaC_2O_4 , BaCO_3 and $\text{Ba}(\text{CH}_3\text{COO})_2$. From XRD pattern, It was able to confirm that formation of BT only system using a $\text{Ba}(\text{CH}_3\text{COO})_2$ to barium source. Synthesis of BT can't be confirmed in the system of the other, only the peak of the raw material

could be confirmed. That considered BT has not been generated for BaC_2O_4 and BaCO_3 were not dissolved in the solvent as the cause.

Fig.1 XRD patterns and SEM images of the obtained BT powder.

$\text{Ba}(\text{OH})_2$: 20 mmol, TiO_2 : 10 mmol,
Temperature: 240°C, Time: 18 h, H_2O / ml:
(a) 0, (b) 10.

○ : BaTiO_3 , ● : TiO_2 .

Fig.2 XRD patterns of the obtained BT powder.

TiO₂: 0.25 mmol, Temperature: 230°C, Time: 18 h, Barium source (1 mmol): (a) BaC₂O₄, (b) BaCO₃, (c) Ba(CH₃COO)₂.

○: BaTiO₃, ●: TiO₂.

Figure 3 shows XRD pattern and SEM images of the product obtained in BT synthesis with mixture of Ba(OH)₂ and Ba(CH₃COO)₂. From XRD pattern, an increase of the peak of TiO₂ was confirmed ratio of Ba(CH₃COO)₂ to be used for the Ba source and increases the proportion of Ba(CH₃COO)₂ in the system of more than 50 %. Ratio of Ba(CH₃COO)₂ was confirmed a single phase of BT in the system of 40 % or less. The ratio of Ba(CH₃COO)₂ could be observed spherical particles in the system of more than 20 % from the SEM, it was possible to observe the particles cubes in the system of more than 40%. The ratio of Ba(CH₃COO)₂ which could be observed particles cubes and BT single phase was observed by TEM systems 40 %. The observations was shown in Fig.4. It is a single crystal and suggested that the presence of particles particles cubes can be confirmed on the whole, was obtained by the electron diffraction pattern in the range of (c) from (d). It can see from these results, the shape of the particles obtained as the ratio of Ba(CH₃COO)₂ to be used for the barium source is increased is likely to be a cube shape, the titanium oxide is less soluble as the ratio of Ba(CH₃COO)₂ is increased, which results it is believed to be due to the nucleation, nucleus growth is shifted to the high temperature side, the crystal growth occurred more regularly.

4. Conclusions

BT nanoparticles single phase were prepared using a solvothermal reaction at 240 °C for 18 h from solutions containing various amounts of water. Water was identified to be important for the dissolution for TiO₂. Furthermore, a new approach based on a mixture of raw materials as barium sources was investigated. BT nanocubes were successfully prepared using this approach and solvothermal reaction at 240 °C for 18 h. with Ba(OH)₂ and Ba(CH₃COO)₂ as barium source. The size of BT

Fig.3 XRD patterns and SEM images of the obtained BT powder.

TiO₂: 10 mmol, Temperature: 240°C, Time: 18 h, Ba(OH)₂ / mmol, (a) 20, (b) 16, (c) 12, (d) 10, (e) 8, (f) 4, Ba(CH₃COO)₂ / mmol, (a) 0, (b) 4, (c) 8, (d) 10, (e) 12, (f) 16.

○: BaTiO₃, ●: TiO₂.

Fig.4 TEM images of the obtained BT powder.

TiO₂: 10 mmol, Temperature: 240°C, Time: 18 h, Ba(OH)₂: 12 mmol, Ba(CH₃COO)₂: 8 mmol. (a) and (b) Bright-field TEM images, (c) Selected-area bright-field TEM image and (d) its selected-area electron diffraction image.

particles increases with the Ba(CH₃COO)₂ concentration, suggesting the nucleation rate of BT decreased with the Ba(CH₃COO)₂ concentration. Ba(CH₃COO)₂ could have a role of generating nuclei of nanocubes and Ba(OH)₂ could have a role of growing nanocubes. The proposed technique allowed for shape control in the present study, and prepared BT nanocubes that may enable the creation of new electroceramic materials with enhanced properties.

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