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Facile synthesis of nanorods of tetragonal barium titanate using ethylene glycol

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Abstract

Tetragonal barium titanate ($BaTiO_3$) nanorods were synthesized from hydroxide precursor by a hydrothermal/solvothermal method with 10 vol% ethylene glycol as solvent. The hydroxide precursor slurry was prepared by the addition of 10 M NaOH to a mixed solution of $BaCl_2$ and $TiCl_4$. When the above aqueous slurry was heated with water only at 200 °C, cubic $BaTiO_3$ nanocrystals formed, whereas tetragonal $BaTiO_3$ nanorods were obtained when heated with 10 vol% ethylene glycol. The crystallization of cubic $BaTiO_3$ via dissolution–reprecipitation of precursor could be suppressed by the addition of ethylene glycol, resulting in the formation of tetragonal $BaTiO_3$ under hydrothermal treatment at 200 °C.

Keywords: Tetragonal barium titanate; Hydrothermal synthesis; Nanorod

1. Introduction

Since the discovery of ferroelectricity in $BaTiO_3$ during the 1940s, numerous studies of $BaTiO_3$ ceramic have been carried out because of its excellent dielectric, piezoelectric, and ferroelectric properties. One of the typical uses of $BaTiO_3$ is the application to multi-layer ceramic capacitors (MLCCs). The miniaturization and capacity enlargement of MLCCs are required for the next generation of electronic devices, which means the necessity to produce thinner dielectric layers. Thus, it is important to synthesize the $BaTiO_3$ nanoparticles with high tetragonality.

It is well known that highly crystalline $BaTiO_3$ could be obtained by hydrothermal or solvothermal treatment of the mixture of $Ba(OH)_2$ and $Ti(OH)_4$ prepared by using alkoxide source or salts such as $BaCl_2$ and $TiCl_4$, and NaOH as precipitant [1–12]. With the hydrothermal process, the cubic $BaTiO_3$ nanoparticles with stoichiometric composition are easily formed because of the following two reasons: (a) the stabilization of cubic phase by incorporation of hydroxide groups into a $BaTiO_3$ structure during hydrothermal reaction and (b) the particle size effect. The crystalline $BaTiO_3$ particles have a core–shell structure such as tetragonal phase as core and cubic phase as shell [13]. As the particle size becomes small, the surface to volume ratio increases, leading to the stabilization of cubic $BaTiO_3$.

Generally, the tetragonal $BaTiO_3$ is prepared by calcination or dry heat treatment at over 1000 °C, resulting in significant particle growth. However, conventional- and microwave-hydrothermal methods have been used by several researchers to prepare tetragonal $BaTiO_3$ powders at much lower temperatures than the solid state process as described below. Glycothermal synthesis with 1,4-butanediol solution was used at 220 °C by Jung et al. [14] to synthesize tetragonal powders, while a facile hydrothermal synthetic strategy was implemented to obtain nanosized barium titanate ($BaTiO_3$) powders with tetragonal structure by Lee et al. [15]. Hydrothermal synthesis of $BaTiO_3$ at

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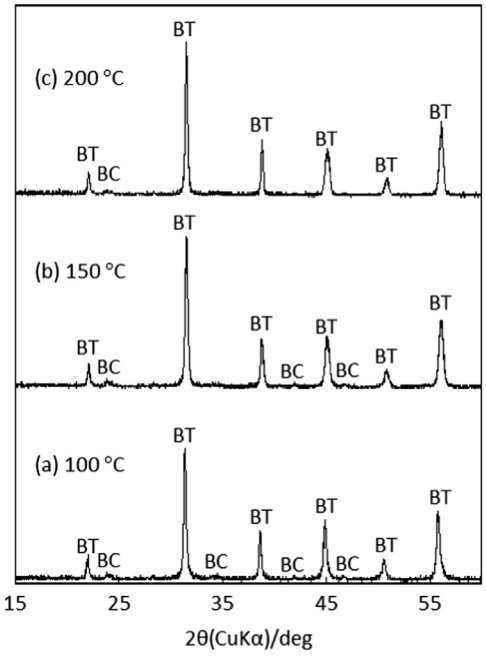

Fig. 1. XRD patterns of the products formed at 100 °C (a), 150 °C (b) and 200 °C (c); BT: $BaTiO_3$, BC: $BaCO_3$.

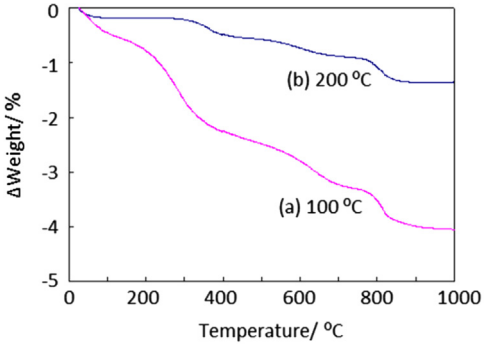

Fig. 2. TG curves of $BaTiO_3$ products formed at 100 °C (a) and 200 °C (b).

240 °C in the presence of chloride ions led to the formation of the tetragonal polymorph upon cooling through the Curie temperature as reported by Dutta and Gregg [16]. Tetragonal $BaTiO_3$ powders were prepared hydrothermally, using Ba $(OH)_2 \cdot 8H_2O$ and TiO_2 (anatase), in the absence of anions such as chloride ions, at a temperature of 220 °C for several days by Wu et al. [17]. Microwave-hydrothermal synthesis of tetragonal nanoparticles was achieved at 240 °C for 12 h, previously [18]. Nanocrystalline tetragonal $BaTiO_3$ with particle sizes ranging from 30 to 100 nm was synthesized via microwave-hydrothermal routes at various fixed microwave frequencies and also using variable frequency by Nyutu et al. [19] at 170 °C for many hours. Thus, many studies showed that tetragonal $BaTiO_3$ powders could be easily synthesized. On the other hand, there are only few reports for the synthesis of tetragonal $BaTiO_3$ nanorods. There is an urgent need to produce tetragonal $BaTiO_3$ nanorods with high dielectric constant for preparing polyvinylidene fluoride (PVDF) nanocomposites for low temperature applications. Joshi et al. [20] reported that $BaTiO_3$ nanorods were apparently

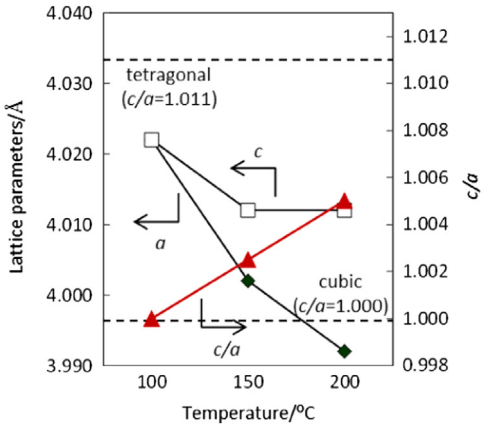

Fig. 3. Change in the lattice parameters of $BaTiO_3$ with the process temperature. The lattice parameters of *a* and *c* axes were determined from (200) and (111) planes using Si powder as standard.

synthesized at 170 °C with a surfactant-free hydrothermal method; however, this procedure could not be reproduced by us. Therefore, our objective in this study was to synthesize the tetragonal $BaTiO_3$ nanorods by low temperature hydrothermal treatment. It is well known that the formation of crystalline $BaTiO_3$ proceeds by dissolution–reprecipitation of hydroxide precursors. Here, the effect of ethylene glycol addition was investigated in the facile synthesis of tetragonal $BaTiO_3$ nanorods by controlling the dissolution of hydroxide precursors which depend on the dielectric constant of solvent. The effects of reaction temperature and time were investigated on the formation of crystalline $BaTiO_3$ nanorods. Here, we found that the crystal growth of tetragonal $BaTiO_3$ nanorods occurred with ethylene glycol during hydrothermal treatment at 200 °C although the stable crystalline phase of $BaTiO_3$ is cubic over 120 °C. Furthermore, the obtained tetragonal $BaTiO_3$ nanorods showed higher tetragonality than that of single crystal after cooling to room temperature.

2. Experimental

2.1. Preparation

$BaTiO_3$ was synthesized by a precipitation-aging method of Ba–Ti–OH precursor followed by a conventional-hydrothermal (C-H) process. Hydroxide precursor was prepared by using $BaCl_2 \cdot 2H_2O$ (99%, Kishida Chemical Co., Ltd.), $TiCl_4$ solution (16–17%Ti, Wako Pure Chemical Industries, Ltd.) and NaOH (96.0%, NACALAI TESQUE, INC.) as follows. The concentrations of Ba and Ti in the starting solution were set at 0.3 M and 0.2 M, respectively. 15 ml of 0.3 M $BaCl_2$ aqueous solution and 5 ml of 0.2 M $TiCl_4$ solution were mixed together at room temperature. 10 ml of 10 M NaOH aqueous solution was then added to the Ba–Ti aqueous solution, leading to precipitation of Ba–Ti–OH. Hydrothermal treatment was carried out with either adding only 20 ml of deionized (DI) water or adding first 5 ml of ethylene glycol (99.5%, Kishida Chemical Co., Ltd.) followed by the addition of 15 ml of DI water to the Ba–Ti–OH slurry solution in order to adjust the total volume of starting precursor slurry to 50 ml. Only two concentrations i.e., 5 (10 vol%)