Continuous Production of Barium Titanate Nanopowder by Hydrothermal Synthesis

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Continuous production of barium titanate fine particles were performed by hydrothermal synthesis process using a green reaction system. The mechanism of particle formation and growth and the feasibility of continuous production of barium titanate particles were also discussed. The separation solution had been reclaimed and recycled as a base solution, after the hydrothermal reaction in this study. This recycled process has been studied at least 9 cycles. The effect of the mineralizer and Ti-precursor material on particle size and its morphology was investigated.

Keywords: Hydrothermal synthesis, Barium titanate, Ammonia, Poly(ethylene glycol).

INTRODUCTION

Barium titanate is one of the most useful dielectric materials and has been intensively researched[1]. In particular, nanosized barium titanate powder has become attractive and has received growing attention, used for multilayer ceramic capacitors (MLCC), positive temperature coefficient (PTC) thermistors and electro-optic devices[1-4]. Simple and effective preparation methods can also contribute to the enhancement of the application possibilities of barium titanate nano-particles.

Various methods used to preparing barium titanate particles have been reported, such as solid-state reaction[2,4], solvothermal[3], hydrothermal[5-7], microwave synthesis[8] and different chemical routes[9-12]. Because each method has its own advantages and disadvantages like particle agglomeration, energy intensive, expensive chemicals and generation of toxic wastes, some of the preparation methods have been industrialized, such as solid-state reaction and hydrothermal processing, while other methods are still used at the laboratory level. Hydrothermal synthesis is one of the most important techniques that has been previously reported[7,13-16], because of the following reasons: (a) The production of fine particles with a narrow size distribution. (b) Direct preparation of crystalline productions without high-temperature calcinations compare with solid-state reaction. (c) The presence of powders not needed to be milled before sintering, thus avoiding contamination. (d) The production of spherical morphology particles. Previous reports have focused on the reaction of a barium precursor such as barium hydroxide and a titanium source such as titanium alkoxide[4,5,9], titanium tetrachloride[11], or a titanium

oxide gel [Ti(OH)$_4$][13]; additionally used strong basicity potassium hydroxide[14] or sodium hydroxide[15] as alkaline mineralizer. However, these raw materials may cause pollution. In order to meet the requirements and exponentially growing technological demand, there is a need to develop an eco-friendly approach for nanomaterials hydrothermal synthesis avoiding of using toxic chemicals in the synthesis protocol.

A simple reaction of Ba(OH)$_2$ with crystalline or hydrous titania (TiO$_2$) in an aqueous solution is suitable for the eco-friendly synthesis, because the product of this reaction contains only water and barium titanate[10,16]. Accordingly, in this study, we have tried to explore and developed a cost-effective, eco-friendly and continuous hydrothermal synthesis route of barium titanate fine powders. The synthesis route is by the Ba(OH)$_2$ and TiO$_2$ reaction and with ammonia solution as mineraliser and poly(ethylene glycol)-2000 as additive.

EXPERIMENTAL

The preparation process of continuous hydrothermal synthesis barium titanate particles is schematically shown in Fig. 1. First, a mixture of distilled water (100 mL), PEG-2000 (2 mL) and ammonia water (25 %, 6 mL) was added to a 120 mL Teflon-lined autoclave to get a base solution. At the first synthesis process, Ba(OH)$_2$·8H$_2$O and TiO$_2$ with Ba/Ti = 1.2 molar ratio was added to this base solution and have a concentration of 0.1 M. The system was sealed, heated rapidly to the reaction temperature (450 K) and left for given time (2 h to 24 h). After the hydrothermal reaction, the obtained precipitate was centrifuged at 3000 rpm for 5 min. The
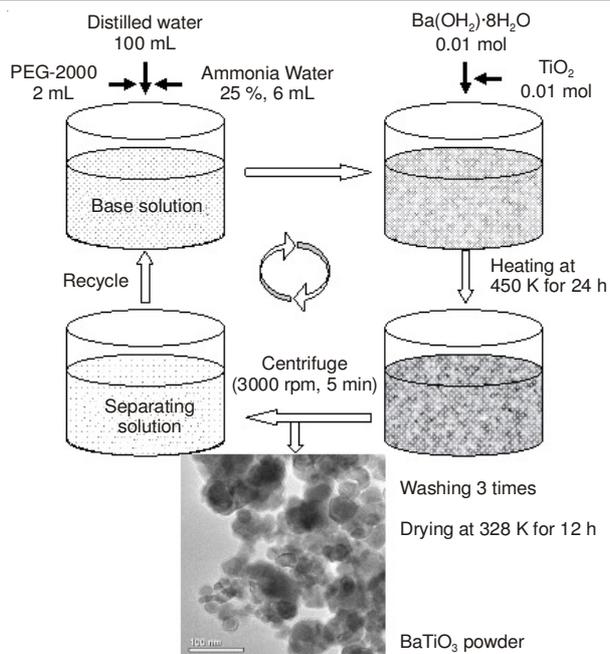
Fig. 1. Schematic representation of the preparation process of BaTiO₃ particles

separation solution consisted mainly of PEG, Ba(OH)₂ and ammonia water reclaimed and recycled as a base solution. At the next synthesis process, Ba/Ti molar ratio Ba/Ti = 1 was added to the base solution as mineralizer. The synthesis process has been studied at least 9 cycles.

Then, the obtained precipitate was dispersed into 100 mL of distilled water and centrifuged again. This washing process of the obtained precipitate was repeated three times. The obtained precipitate was dried in an oven at 328 K for 12 h. All of the chemicals used in this preparation were of reagent grade. In this study, we studied the effect of Degussa P25-TiO₂ (70 % anatase and 30 % rutile), anatase TiO₂ (AR) and the effect of ammonia water as alkaline mineralizer. The X-ray diffraction (XRD) patterns of the samples were measured by using Mac-Science M18X-HF-SRA equipment. The particle shape was observed by field emission-secondary electron microscope (FE-SEM) and Transmission electron microscope (TEM).

RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the product that hydrothermally synthesized at 450 K for 24 h with different reaction conditions: (a) using P25-TiO₂, (b) using commercial TiO₂ (AR) as titanium source with PEG-2000 and ammonia water as mineralizer, (c) using P25-TiO₂ only with ammonia water as alkaline mineralizer, respectively. The inset represents the enlarged XRD patterns of the (111) peaks around 2θ = 38.7 °C and of the (002) peaks around 2θ = 45.2 °C of the sample powders. All XRD diffraction peaks in Fig. 2 with different reaction conditions can be assigned to the well-crystallized barium titanate. As shown in Fig. 2a,b, cubic phase barium titanate nano-crystals can be hydrothermally synthesized by using ammonia water as mineralizer and using PEG-2000 as additive. Generally, barium titanate powder was synthesized through the hydrothermal synthesis route, with smaller particle size, better particle size distribution and dispersity, using PEG

as surfactants[10,17]. The coverage of PEG on the surface of particles resulted in alleviating of agglomeration because of the steric hindrance. As shown in Fig. 2c, it was observed that barium titanate nanocrystals can be hydrothermally synthesized using only ammonia water as mineralizer. Generally, the use of aqueous ammonia solution in place of strong basicity solution (NaOH or KOH) can be advantageous because: (a) ammonia does not have a tendency to get incorporated into the oxide matrix and (b) any residual ammonia entrained in barium titanate powder can be easily driven off during drying the powder at low temperature[4-6,14]. But, as shown in Fig. 2c, the split of the (002) peak around 2θ = 45.2 °C in the inset means the product is a mixture with cubic and tetragonal phase of barium titanate[6].
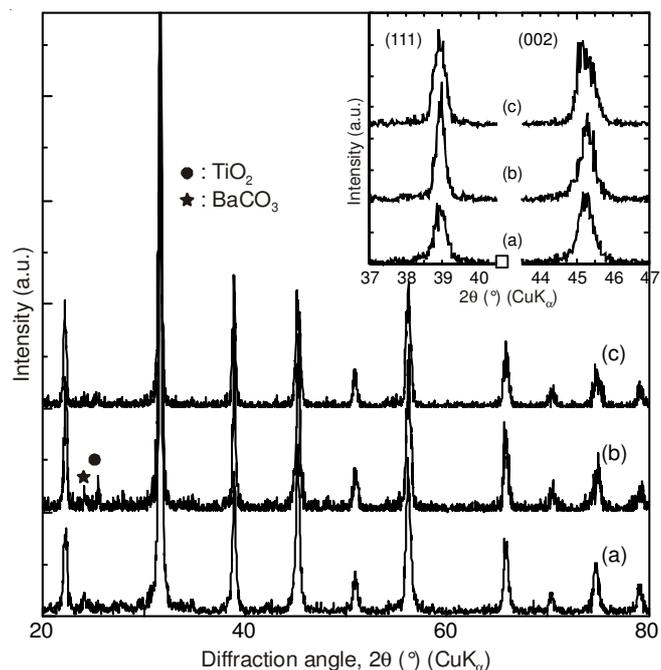

Fig. 2. XRD patterns of the different reaction conditions: (a) TiO₂ (P25) and (b) anatase TiO₂ (AR) with PEG-2000 and ammonia water as mineralizer, (c) TiO₂ (P25) only with ammonia water 25 % as mineralizer, corresponded to 24 h at 450 K, respectively

The SEM images and the EDS analysis of the product that hydrothermally synthesized at different reaction conditions are shown in Fig. 3. As shown in Fig. 3a,b, the average diameters of the particles are about 20 and 40 nm, respectively. The electron diffraction pattern identifies that the particles are cubic phase barium titanate as shown in Fig. 3a,b inset, where the diffraction rings correspond well to the perovskite structure. Only using ammonia water as mineralizer, as shown in Fig. 3c, the average diameters of the particle is about 100 nm and the shape and size of the particles also becomes uneven, the product is a mixture with cubic and tetragonal phase. As shown in Fig. 3a inset, detected by high-resolution TEM (HRTEM) imaging of the particles prepared at 450 K for 24 h, the cubic barium titanate particles had an interplanar spacing of 2.78 Å which corresponded with a crystal orientation of (110)[10]. It has been established that the crystal growth rate along a crystallographic orientation is proportional to the surface attachment energy and poly(ethylene glycol) polymer molecules would
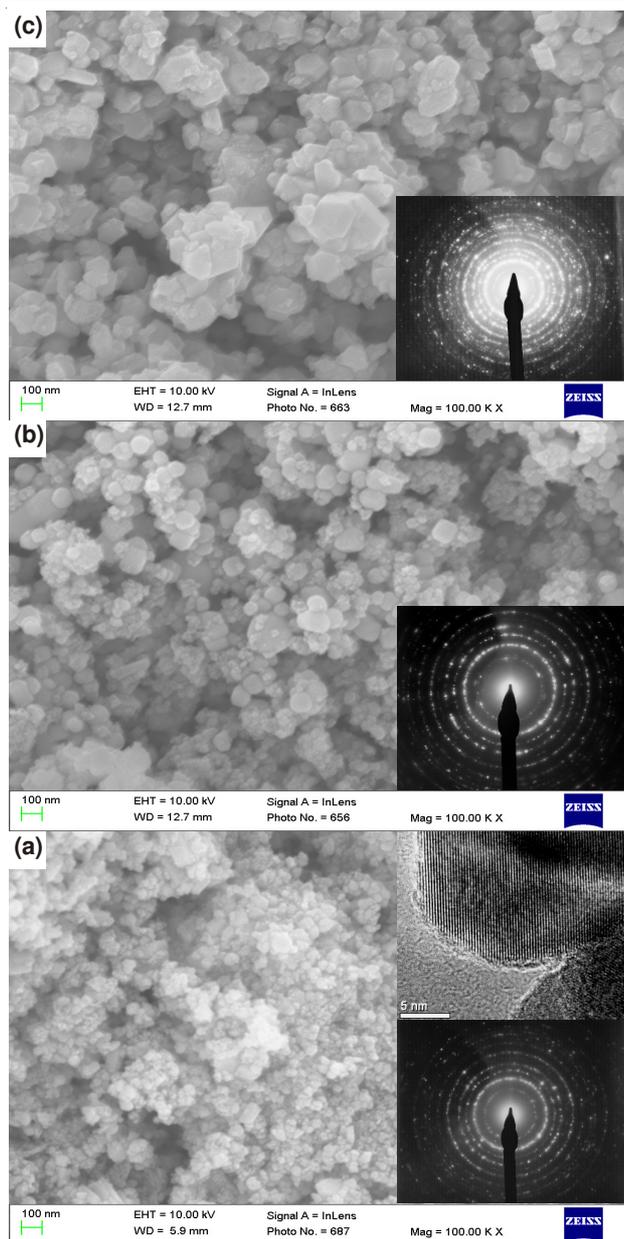
Fig. 3. SEM images of the different reaction conditions: (a) TiO$_2$ (P25) and (b) anatase TiO$_2$ (AR) with PEG-2000 and ammonia water as mineralizer, (c) TiO$_2$ (P25) only with ammonia water 25 % as mineralizer, corresponded to 24 h at 450 K, respectively
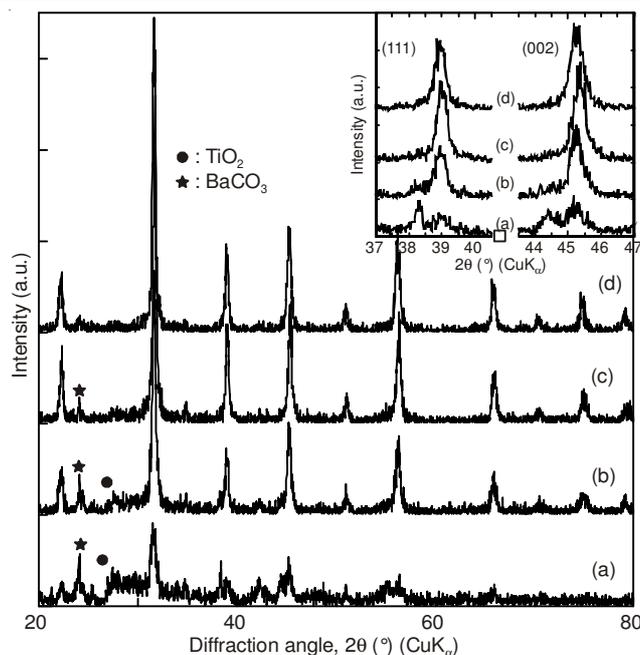

Fig. 4. XRD patterns of BT nanocrystals hydrothermally synthesized at 450 K for 2 h (a), 4 h (b), 8 h (c) and 24 h (d), respectively. The insert represents the enlarged XRD patterns of the (111) peaks around 2θ =37~40 and of the (200) peaks around 2θ = 45° of the sample

have a strong interaction with the crystals[17]. Although PEG can be adsorbed on all surfaces of the crystals, the coverage on the (110) surfaces would be much higher than that on the (100) surfaces, since the density of metal atoms in the (110) planes is higher. This selective adsorption of PEG results in a protective layer on the (110) surfaces, significantly suppressing the crystal growth along the (110) zone axes.

Fig. 4 shows the XRD patterns of barium titanate nano-crystals hydrothermally synthesized at 450 K for 2, 4, 8 and 24 h, respectively. The XRD patterns indicate that the peak of the synthesized powders, as shown in Fig. 4a, is not recognized with barium titanate crystal characteristics for 2 h. While at 450 K for 4 h, the cubic phase barium titanate nanocrystal's peak has been observed. At 8 h and above, the peak intensity, which corresponds to barium titanate, increased. All the peaks

of the synthesized powders shown in Fig. 4 were consistent with the barium titanate phase and no split of the (002) peak around 2θ = 45.2° in the insert, which means the well-crystallized cubic phase.

The XRD patterns of barium titanate nanocrystals continuous hydrothermally synthesized: (a), (b), (c), (d) and (e) corresponded to the recycle times 1, 3, 5, 7 and 9, respectively are shown in Fig. 5. It was observed that cubic phase
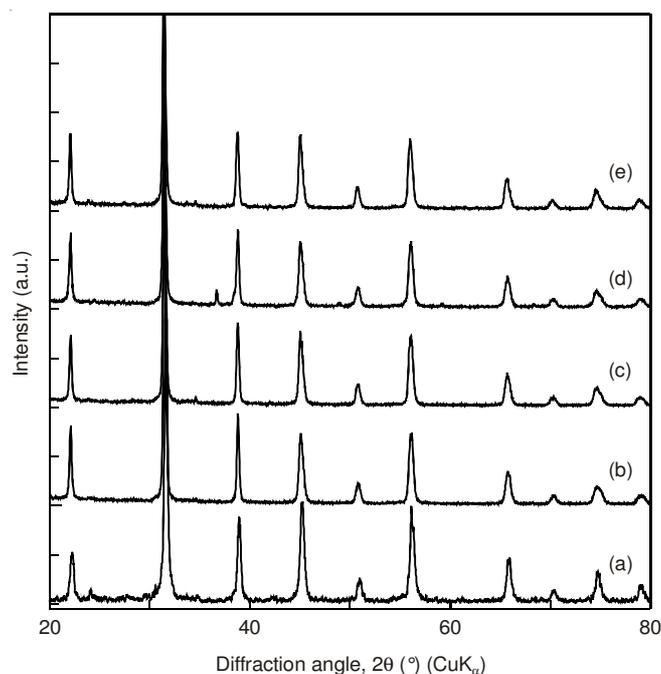

Fig. 5. XRD patterns of BT nanocrystals hydrothermally synthesized at 450 K for 24 h, recycled using the separation solution as a base solution, (a), (b), (c), (d) and (e) corresponded to the recycle times 1, 3, 5, 7 and 9, respectively

barium titanate nanocrystals can be continuous hydrothermally synthesized by using the separation solution after the hydrothermal reaction as a base solution. The particle size and morphology were dependent on the Ti-precursor material and the mineralizer, the cycle synthesis times has no significant influence on this study. As reported, in the presence of poly-(ethylene glycol), Titanium precursor aggregated with PEG-2000 to form spherical colloidal particles and multiple nucleation of barium titanate takes place on the surface of these colloidal particles. For this reason, the barium titanate particle can be better controlled of the crystallite size and crystal morphology becomes uniform by this process. Furthermore, the poly(ethylene glycol) is soluble in water, no toxicity and the high boiling point > 500 K. Accordingly, using PEG-2000 and ammonia water as mineralizer, it is a cost-effective, eco-friendly and continuous hydrothermal synthesis route.

Conclusion

The well-crystallized cubic phase barium titanate fine particles were prepared by a continuous, green and sustainable hydrothermal synthesis process. The shape and size of the prepared particles were uneven when using ammonia solution as mineralizer. The barium titanate particle can be better controlled not only the crystallite size but also crystal morphology by using PEG-2000 as additive. By cycle using the separation solution as a base solution, morphology and size of the barium titanate fine particles is not affected by the number of cycles.

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