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Synthesis of nanocrystalline BaTiO$_3$ ceramics via hydrothermal condition and structural characterization by HRTEM and SAED

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ABSTRACT

In the present work, we report a suitable approach for the preparation of BaTiO$_3$ nanostructures via the hydrothermal condition using Dolapix ET85 as surfactant. The powders were investigated by X-ray diffraction (XRD), scanning election microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX), field emission transmission electron microscopy (FETEM), selected area electron diffraction (SAED), high resolution transmission electron microscopy (HRTEM) and zetasizer measurement. As a matter of fact, the hydrothermal method guarantees the production of BaTiO$_3$ nanoparticles with desired morphology for commercial applications. In addition, uniform particles, size distribution and purity of samples are highly dependent on the applied hydrothermal condition.

Keywords: *Hydrothermal; Nanotechnology; Crystallinity; Perovskite; BaTiO$_3$.*

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INTRODUCTION

As a typical perovskite ferroelectric oxide, barium titanate (BaTiO$_3$) have been extensively investigated, affording wide applications in devices such as thermistors [1], multilayer ceramic capacitors (MLCCs) [2], electro-optic devices [3], and dynamic random access memories (DRAM) [4]. Pushed by the current trend of miniaturization of these devices with improved properties, the nanosized BaTiO$_3$ materials are desirable. For MLCCs in particular, the improved performance can be obtained by decreasing the thickness of ceramic layer with the decrease of particle size [5]. Furthermore, ceramics produced from agglomerate-free nanosized powders with narrow size distribution have shown unique consolidation and compaction properties [6].

Specially, BaTiO₃ nanostructures are also promising candidates for realizing nanoscale electronic [7], optical [8], and mechanical [9] devices because they retain wire-like connectivity despite their nanoscale radial dimension. To achieve this goal, particles with improved quality and uniform size of the order of 100 nm are highly required. However, conventional BT particles obtained by solid-state reaction between BaCO₃ and TiO₂ at high temperatures above 900 °C are generally rather coarse with uncontrolled and irregular morphologies, which are not suitable to realize very thin dielectric layers. Recent emphasis has been focused on wet chemical methods to synthesize high quality BT particles [10,11]. Among the various chemical methods developed so far, the hydrothermal method has been found to be a very promising method for synthesis of ultra-fine (<100 nm) BT particles from the viewpoint of stoichiometry control, reproducibility, purity, and particle size. The low-temperature hydrothermal synthesis of BT nanoparticles is normally carried out by suspending titania nanoparticles or titania gel in an aqueous Ba(OH)₂ solution, and then autoclaving at 150–300 °C. Up to date, the hydrothermal preparation of BT nanoparticles has been investigated extensively [12,13]. The effects of the synthesis temperature, the pH value of the reactive medium, and the Ba/Ti ratio on the particle size and morphology have also been investigated [14,15], but different results were reported by various researchers. Clearly, much remains to be done in order to establish the factors which influence and control the particle size and morphology of sub-micron BT particles synthesized by hydrothermal method. In the present work, the hydrothermal technique was developed for the formation of ultra-high crystalline BT nanopowders in different pHs and surfactants. These high-quality BT nanopowders represent well-defined nanoscale structure needed for both fundamental studies and electronic applications.

EXPERIMENTAL

All of the reagents and solvents were in analytical grade and were used without any further purification. A mixture of 14.66 g BaCl₂.2H₂O, and 4.79 g TiO₂ were put into a 500 ml glass beaker containing 400 ml distilled water. For some samples, an organic surfactant of 1.5 g Dolapix ET85 was charged in the solution. Next, 2 mL of 2 M KOH aqueous solution was added to the solution, respectively. After substantial stirring, the two optically transparent alkali solutions were mixed and stirred for another 30 min. The resulting alkali solution was then transferred into a 300 ml stainless Teflon-lined autoclave and was heated at 170 °C for 2 h. The resulting suspension was cooled to room temperature right after the heating and was then stored at a constant temperature of 50 °C. After 18 hours, samples were collected and washed several times with distilled water and then deionized water. For these experiments, a Siemens D500 powder diffractometer with the K$_{\alpha1}$, radiation of copper (λ = 1.5406 Å), was used and X-ray diffraction patterns were recorded in an angular range of 2θ = 10-80°. The obtained BaTiO₃ was characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy (SEM/EDX, XL30). The size distribution and morphology of the samples were analyzed by field emission gun (FEG) transmission electron microscope (TEM), selected area electron diffraction (SAED) observation on a Philips CM200 transmission electron microscope operated at 200 kV. TEM samples were prepared by dispersing the nanorods in ethanol and collecting them on lacey carbon, Cu mesh TEM girds. Particle size of BaTiO₃ has been monitored by a Malvern 3000 HSA zetasizer operating at wavelength of 633.0 nm at ambient temperature. The crystallite size of the powder was evaluated from the peak broadening of XRD patterns based on Scherrer's formula as follows [16]:

$$D = \frac{0.9\,\lambda}{FWHM.\cos\theta} \qquad (1)$$

in which D is the crystallite size (nm), λ is the wavelength of the monochromatic X-ray beam (λ = 0.154056 nm for Cu$_{K\alpha}$ radiation), FWHM is the full width at half-maximum for the diffraction peak under consideration (rad), and θ is the diffraction angle (deg). Table 1 shows characteristic of different samples used to investigate different conditions.

Table 1. Characteristic of different samples used to investigate different conditions.

Sample (Id)	pH	surfactant	Crystallite Size (nm)
BT3	12.5	Dolapix ET85	42
BT4	13	Dolapix ET85	39
BT6	14	Dolapix ET85	28

RESULTS AND DISCUSSION

Figure 1 shows a series of XRD patterns for 3 samples of BaTiO$_3$ synthesized in the different conditions (Table 1). For amount of different surfactants, structural change does not occur and XRD patterns with characteristic peaks of cubic perovskite structure (space group: Pm3m) of BaTiO$_3$ (JPCDS No. 31-174) are observed. Also, different pHs employed have no significant effect on the spinel structure and do not change the crystallographic structure (although some peaks of impurity are detected for the sample and BT4). However, it is obvious that the degree of crystallinity is different for various cases. This issue can be well understood from the powder morphologies. With the increase in synthetic pH (BT6: pH=14), the XRD peaks become sharp, indicating the increase in crystallinity of BT powders synthesized without peaks of impurity.
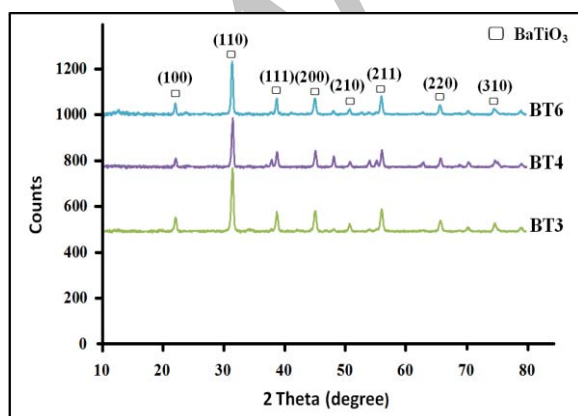
Fig. 1. XRD patterns of BaTiO$_3$ samples prepared with different pHs and surfactants (a) BT3, (b) BT4, (c) BT6.

The most important effect of surfactant can be expected in the preparation of nanostructure materials. In order to see what influence the template is having on the textural characteristics for the pH values under investigation and also to evidence whether the surfactant molecules play a role in the formation of nanostructures, we chose the same syntheses but without addition of surfactant. This is of particular interest with respect to the fact that nanomaterials obtained at higher pH values exhibit very broad size distribution, which are also encountered for compounds obtained by the hydrothermal synthesis. Furthermore, the usage of a high basic condition and surfactant are the two crucial keys in ensuring the formation of BaTiO$_3$ nanostructure under the hydrothermal condition. The formation mechanism is in situ transformation, which involves diffusion of Ba^{2+} into the undissolved TiO$_2$ oxide, resulting in an outside layer of BaTiO$_3$ with an unreacted TiO$_2$ core. However, until now the true role of different surfactants for the formation of MWCNTs is not clear. Figure 2 shows SEM images of four BaTiO$_3$ samples prepared under hydrothermal condition with different pHs. Severe structural changes of the BaTiO$_3$ morphology are obvious. The efficiency of this approach for controlling the morphology is due to the fact that there is a systematic relationship between the morphology of the BaTiO$_3$ particles with more uniformity in morphology. For the BaTiO$_3$ synthesized under hydrothermal condition (BT3: pH=12.5), the powder has a less uniform nanostructure (Figure 2a). Similar nanostructures of BaTiO$_3$ with size of ca. 90 nm (diameters ranging from 50–100 nm) have been formed. It is worth noting that better results can be achieved by changing the experimental conditions to obtain the nanostructured BaTiO$_3$. It is known that using low temperature (170 °C) and low synthesis duration would lead to an ordered morphology. This is indeed a typical path for synthesis of BaTiO$_3$, and further investigations lead to better results satisfying the requirements of nanotechnology. For higher pHs (BT6: pH=14), however, the particle size has been reduced and there is a better uniformity (Figure 2c). This suggests that the method proposed could also be used for the preparation of BaTiO$_3$ ceramics with nanostructures, which is an important task in the era of nanotechnology.
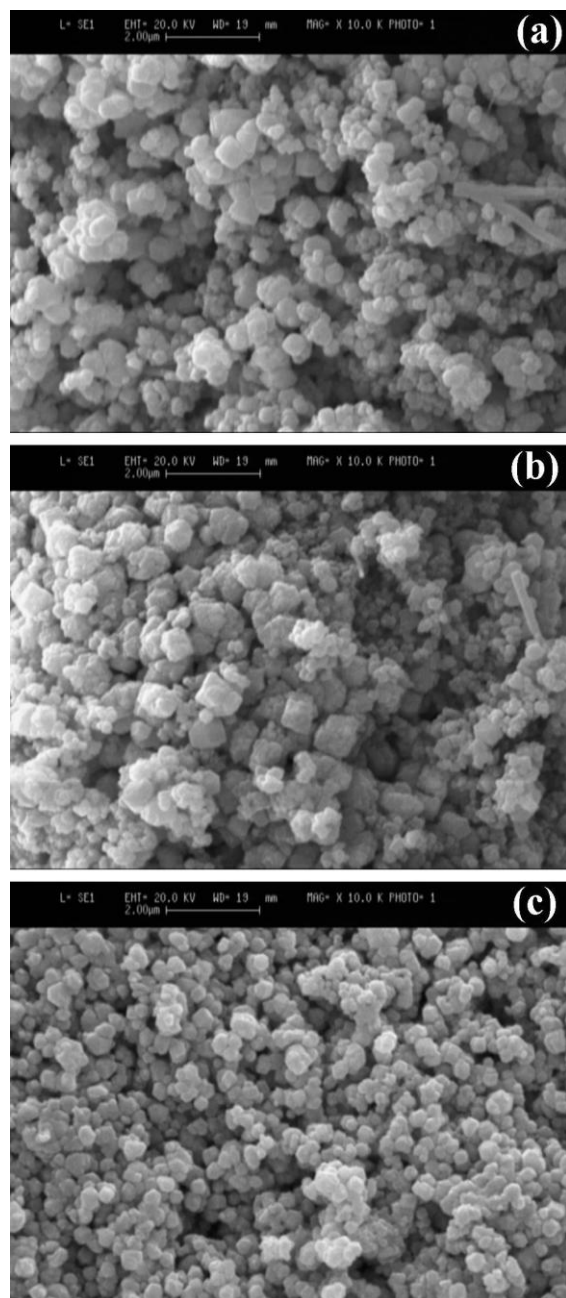
Fig. 2. SEM images of the BaTiO3 prepared under different conditions (a) BT3, (b) BT4 and (c) BT6.

Fig. 3. The nanoparticle size of BaTiO₃ measured by zeta-sizer for sample BT6 with pH=14.

The nanoparticle size of BaTiO₃ product was analyzed using by zetasizer method. These measurements reveal the particles to have highly wide distribution (Figure 3). The BaTiO₃ Powders were particles with two raging diameters from 5-40 nm and 50-100 nm for sample BT6 with pH=14. At the same time, these results are consistent with the SEM analysis.
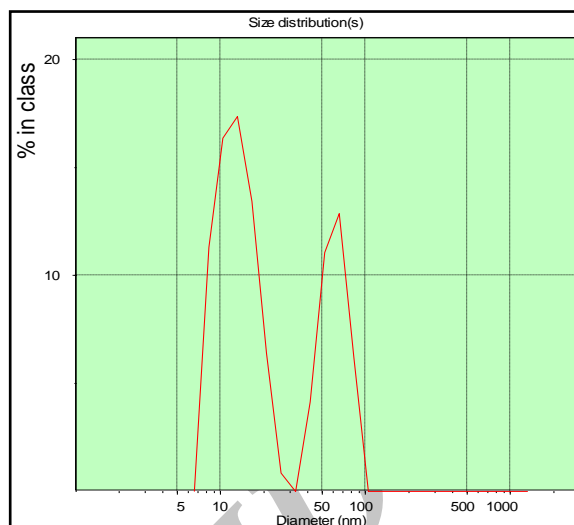
A field emission gun (FEG) CM200 transmission electron microscope was used to characterize the BaTiO₃ nanostructures, and typical TEM are shown in Figure 4(a-f). Figure 4(a-c) clearly shows that the product consists of BaTiO₃ nanostructures with 50-100 nm in diameter, which is "sub-60 nm BaTiO₃ nanostructures" in this paper. The yield of the prepared BaTiO₃ estimated by TEM observations is about 99.9 % relative to the samples on copper grids, and much less contents of the obtained product are nanoparticles (Figure 4b). Thus, the high yield efficiency of this approach for the synthesis of BaTiO₃ can be concluded, with an ultrahigh crystallinity and an excellent yield rather than previous works. In Figure 4a the as-synthesized BaTiO₃ sample shows a typical outstanding morphology, ultra-high ordered crystallinity.

In further investigation, the BaTiO₃ nanostructures were analyzed by HRTEM in detail, and all nanoparticles showed uniform lattice fringes, meaning that no amorphous product was formed. Figure 4d is the HRTEM image of BaTiO₃ nanostructure, which clearly indicates that the BaTiO₃ is structurally uniform crystalline with ultra-high crystallinity. The interplanar spacing values are calculated from Bragg's diffraction equation using the diffraction ring diameter and the camera length of the transmission electron microscope. The calculated results indicate the fringe spacing about 0.284 nm that can be observed

in Figure 4d. The SAED observations show clear spots (Figure 4e) corresponding to a perovskite structure with high crystallinity. At the same time, the SAED patterns of the samples were consistent with the ultra-high crystallinity, and the diffraction spot could be indexed as the cubic phase. This result was in good agreement with the result of XRD.

The EDS spectrum of the synthesized BaTiO$_3$ shows that these are only elemental O, Ba and Ti except the element of Cu, which comes from the supported grid for TEM measurement (Figure 4f). The atomic ratio of Ba to Ti according to EDS semi-qantitative assessment is about 1, which was

equal to the theoretical value. Those results are in good agreement with the results of ICP. In this work, the BaTiO$_3$ nanostructures were synthesized via a hydrothermal condition using the as-prepared BaCl$_2$.2H$_2$O, and TiO$_2$ as new starting materials. It is known that the crystalline perovskite phase of BT can be directly synthesized under hydrothermal conditions; however, the obtained BT powders are generally highly defective in the crystallographic structure. Their microstructures (i.e., uniform particles, size distribution, purity, crystallinity degree and so on) are characterized at atomic scale, especially by HRTEM, to achieve nanoparticles with controlled microstructural characteristics.
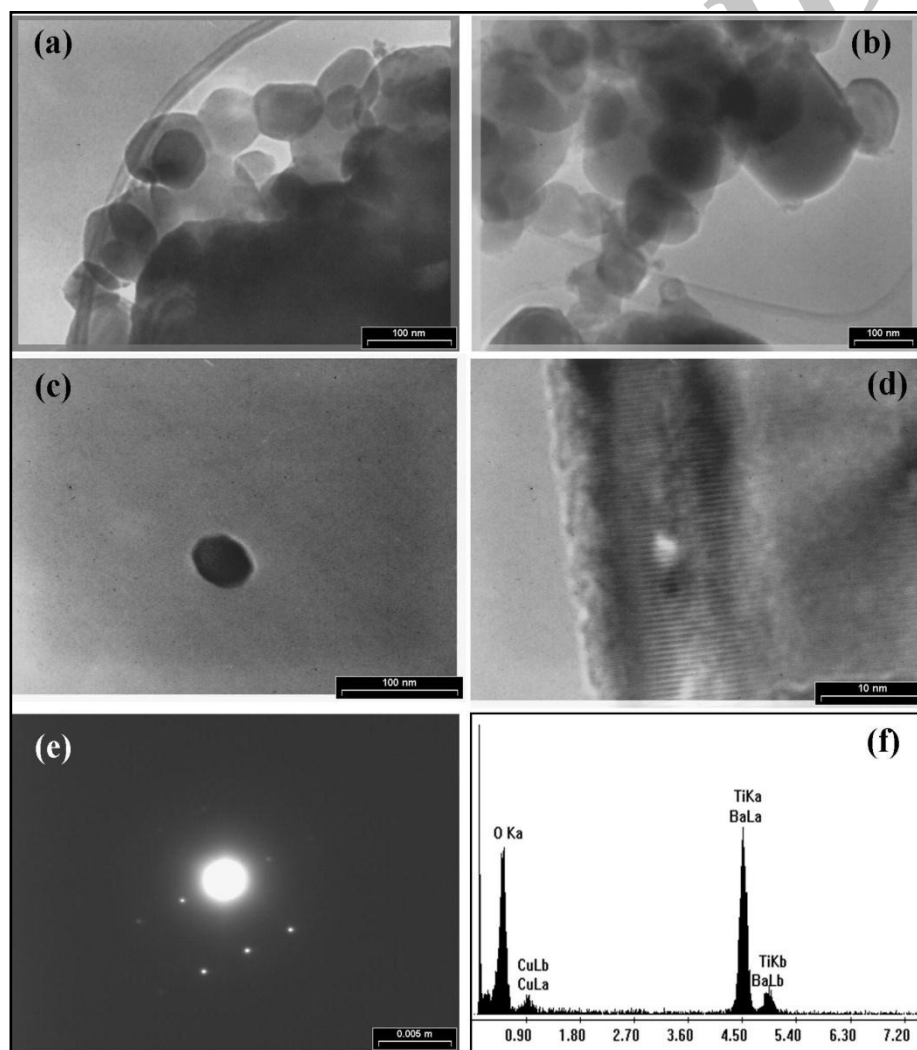

Fig. 4. as-synthesized BaTiO$_3$ obtained at hydrothermal condition, (a,b,c) TEM micrograph (d) HRTEM image, (e) SAED and (f) EDAX.

CONCLUSION

The nanostructure of BaTiO$_3$ nanocrystals prepared by the hydrothermal technique has been examined by XRD, SEM, TEM, HRTEM and SAED. XRD results indicate that the BT nanocrystals are concluded cubic phases, which is also confirmed by the electron diffraction. SEM and TEM images show that the BT nanocrystals as-prepared BaCl$_2$.2H$_2$O, and TiO$_2$ as starting materials have a fairly narrow size distribution and a spherical grain morphology, with an average grain size of 60 nm. As a matter of fact, hydrothermal method guarantees production of BaTiO$_3$ for different applications.

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