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Ultrasonic assisted synthesis of $BaTiO_3$ nanoparticles at 25 °C and atmospheric pressure

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ABSTRACT

Barium titanate ($BaTiO_3$) nanoparticles were successfully synthesized *via* a sonochemical method (25 kHz) at a constant temperature of 25 °C and atmospheric pressure without a calcination step. Barium hydroxide $Ba(OH)_2$ and diisopropoxytitanium bis(acetylacetonate) ($C_{12}H_{28}O_6Ti$) were used as the starting materials. The effects of the concentration of NaOH used and ultrasonic reaction time were investigated. The phase composition, functional groups and morphology of synthesized powders were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Fourier transform Raman spectroscopy (FT-Raman) and transmission electron microscopy (TEM). The XRD and FT-Raman results revealed the cubic structure of $BaTiO_3$. The optimal NaOH concentration and ultrasonic reaction time for producing a narrow particle size distribution and the bowl-like structure of $BaTiO_3$ nanoparticles were 10 M and 1 h, respectively. TEM imagery showed their morphology as a monodispersed bowl-like structure with a size of 54.90 ± 18.18 nm. After longer ultrasonic contact times, the bowl-like structure tended to fracture forming irregularly shaped nano-sized $BaTiO_3$ particles.

1. Introduction

It is well established that $BaTiO_3$ is a dielectric and has been widely used for the preparation of multilayer ceramic capacitors (MLCCs), embedded capacitors in printed circuit boards [1], positive temperature coefficient devices [2], dynamic random access memory, electromechanics, and nonlinear optics [3]. Additionally, $BaTiO_3$ nanocrystals have promising biomedical applications, such as in *in vitro* imaging (as a contrast marker), in the formulation of bone cement and as a piezoelectric dopant in smart prosthetic implants [4]. Their ferroelectric, piezoelectric, and dielectric properties are dependent on their structure and finite size [5]. For example, the efficiency of MLCCs depends on the number and the thickness of their ceramic layers (2–3 nm) [6]. Therefore, many attempts have been made to synthesize nano-sized $BaTiO_3$ particles. Nano-sized $BaTiO_3$ powders have been synthesized by various techniques such as solid-state reactions [6,7], hydrothermal methods [1,2], sol–gel methods [8,9], a combination of sol-gel and hydrothermal methods [10], spray pyrolysis [11,12] and sonochemical techniques [13–18]. The main advantages of sonochemical methods in the synthesis of metal oxides (compared with other methods) are that the resulting materials have a uniform size distribution, higher surface area, faster reaction times, and improved phase purity [19]. According to the report of Wirunchit et al. [20], nanocrystals of perovskite $Ba(Zr,Ti)O_3$ were formed directly before being oriented and aggregated into larger particles in an aqueous solution under ultrasonic irradiation. They also suggested that the nucleation in the sonocrystallization process was accelerated by the implosive collapse of bubbles, while the crystal growth process was inhibited or delayed by shock waves and turbulent flow created by ultrasonic radiation. Recently, Moghtada and Ashiri [16] found that the tetragonality of $BaTiO_3$ nanopowders increased with increasing sonication time and sonication (bath) temperature. Additionally, Akbas et al. [17] found that high-intensity ultrasonic waves could enable a significant improvement in the production of high-purity $BaTiO_3$ ceramics with no carbonate impurities and with a small dielectric loss. From the literature, sonication has been conducted without cooling so that the temperature of the solution increased gradually to 50 °C [21], 60 °C [16,18,21], 80 °C [13,14], 85 °C [22] by the end of the reaction. In the current study, the effects of sodium hydroxide (NaOH) concentration and ultrasonic reaction time on the properties of $BaTiO_3$ nanoparticles were investigated by means of Fourier transform infrared spectroscopy (FTIR), Fourier transform Raman spectroscopy (FT-Raman), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Our work is differentiated from previous studies in that temperature as well as the ultrasonic

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frequency for synthesizing $BaTiO_3$ was controlled at 25 ± 1 °C (25 kHz) [23,24] at atmospheric pressure. The sonochemical efficiency value (SE-value) for KI oxidation of the reaction was 5.52×10^{-10} J/mol [23]. Additionally, no calcination process was used in this work.

2. Materials and methods

2.1. Materials

Anhydrous barium hydroxide ($Ba(OH)_2$ (95.0% purity, Fisher Chemical), diisopropoxytitanium bis(acetylacetonate) ($C_{12}H_{28}O_6Ti$, 75 wt% in isopropanol, Sigma-Aldrich) and anhydrous sodium hydroxide (NaOH) (99.8% purity, Merck) were used as the starting materials. An ethanol solution (99.8% purity, Merck) and deionized water (DI) were used as washing solutions. All chemical reagents were of analytical grade and used without further purification.

2.2. Synthesis of $BaTiO_3$ nanoparticles

To study the effect of NaOH concentration, 2.05 g $Ba(OH)_2$ was completely dissolved in DI (40 mL) to prepare a solution of Ba^{2+}. 4.5 mL of $C_{12}H_{28}O_6Ti$ was slowly added to the $Ba(OH)_2$ solution with continuous stirring at room temperature for 1 h in a closed container. Then, 40 mL of an aqueous solution of NaOH (2, 6 and 10 M) was slowly added into the $Ba(OH)_2$ solution to study the effects of NaOH concentration on $BaTiO_3$ phase formation. The pH value of the solution pH value reached 14 during the process. Next, the mixed starting solution was transferred into a 100 mL Schlenk flask (diameter 5.0 cm). After that, the Schlenk flask was placed in the ultrasonic reactor of our previous work [23,24] and sonicated for 4 h. The ultrasonic rotors consisted of an ultrasonic probe (diameter = 5.0 cm, 200 W) which generated ultrasonic waves at a frequency of 25 kHz, at a constant temperature of 25 ± 1 °C in a circulating thermostatically controlled water bath (10 L). The gap between the ultrasonic horn and the sample flask was maintained at 0.5 cm. During ultrasonic irradiation, temperature was monitored by means of a thermocouple probe (AgilentU1185A; J-Type) immersed in the top half of the solution and connected to a microcomputer. After desired time, the suspension was centrifuged at 1000 rpm (Allegra X-30 R, Beckman Coulter) for 10 min to separate the solids from the solution. Next, the precipitate was transferred into a 2000 mL beaker. DI water was added with continuous stirring until the pH was reduced to 7. A 200 mL aliquot of an ethanol solution was then added to the mixture and stirred overnight at room temperature. Finally, the synthesized precipitate was centrifugally separated and washed with DI water twice, then dried at 40 °C for 5 h. The resulting powder was stored in a desiccator for further analysis. The above procedure was repeated under the same conditions (10 M NaOH) and the mixtures were irradiated for 0.5, 1 and 4 h to study the effect of ultrasonic reaction times on $BaTiO_3$ phase formation.

2.3. Characterization techniques

X-ray diffraction (XRD, PW3710, the Netherlands) was used to determine the crystalline structure and identify crystallographic phases of the powders. The Reitveld method was used to calculate the structure of $BaTiO_3$. Structural refinement of the $BaTiO_3$ nanoparticles was performed using X'Pert High Score Plus software [25]. The crystallite size of synthesized $BaTiO_3$ was calculated using the Scherer equation from the full-width at the half-maximum of the 110 plane in the XRD pattern [21]. The chemical functional groups of the powder were determined using FT-Raman spectrometry (BrukerVertex70 with a Raman module Bruker RAM II) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer model Spectrum GX). The morphology of the synthesized $BaTiO_3$ was observed using transmission electron microscopy (TEM, TECNAI G^2 20S-TWIN). The particle sizes of $BaTiO_3$ were evaluated by analysis of TEM images using ImageJ software [24].

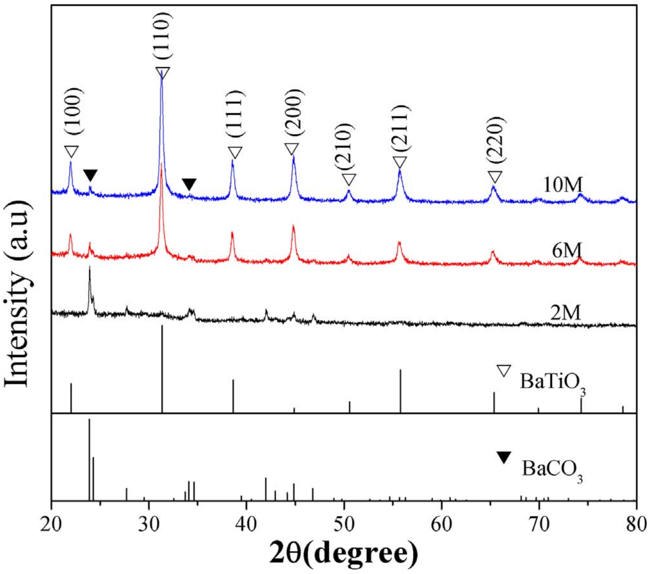

Fig. 1. Effect of NaOH concentration on XRD patterns of $BaTiO_3$.

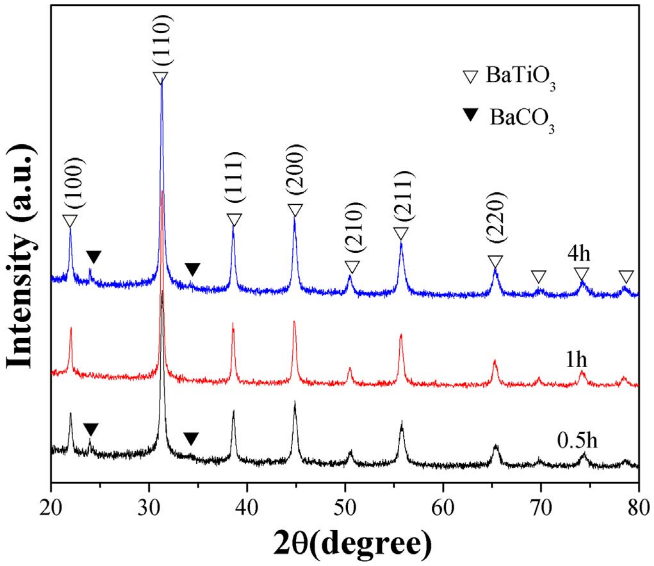

Fig. 2. Effect of sonication times on XRD patterns of $BaTiO_3$.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the as-synthesized nanoparticles formed at different NaOH concentrations with an ultrasonic reaction time of 4 h. At a NaOH concentration of 2 M, the as-synthesized sample formed only a $BaCO_3$ phase (JCPDS No. 05-0378). This finding suggests that reaction was still incomplete, similar to the findings of Wirunchit et al. [20]. They also found that at a lower concentration of NaOH (5 M), $BaCO_3$ and $Ba(OH)_2(H_2O)_3$ was still observed when synthesizing barium zirconated titanate using a sonochemical reaction for 1 h. With increasing NaOH concentrations such as 6 M and 10 M, a perovskite phase was obtained and could be indexed as a cubic structure corresponding to JCPDS No. 75-0213 of $BaTiO_3$. However, the $BaCO_3$ phase could be also detected and was reduced with increasing NaOH concentrations. The highest intensity of a perovskite phase occurred when using 10 M NaOH. Therefore, a 10 M NaOH concentration was selected