

Hydrothermal Synthesis and Structural Characterization of BaTiO₃ Powder

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ABSTRACT

The main purpose of the present study was to synthesize and characterize the structural morphology of barium titanate (BaTiO₃) powder. The synthesis of BaTiO₃ powder was carried out by hydrothermal process using barium hydroxide (Ba(OH)₂) and titanium dioxide (TiO₂) as precursors in a high-pressure stirred reactor autoclave for a 7-hour reaction time at various temperatures (100, 150 and 180 °C). The physical appearance of the synthesized BaTiO₃ powder was white crystalline. X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) were used to characterize the BaTiO₃ powder. Raman spectroscopy and XRD techniques confirm the formation of cubic-phase BaTiO₃. Raman peaks at 305 and 516 cm⁻¹ confirmed the formation of BaTiO₃. SEM micrographs showed different shapes and a highly dispersed size distribution of particles. The crystal structure of BaTiO₃ powder changed as the reaction temperature changed during the synthesis process. The morphological properties of the BaTiO₃ powder prepared at 100 °C clearly indicated spherical, irregular, and cubic rod-like structures. The particle size of BaTiO₃ powder was very fine at higher reaction temperatures of 150 and 180 °C. Cubic-phase BaTiO₃ was obtained in all the synthesized samples. Barium carbonate (BaCO₃) and residual unreacted TiO₂ phases as impurities were detected in the BaTiO₃ powder. The purity of BaTiO₃ powder was high at 180 °C under these synthesis conditions.

Keywords: Cubic Phase, Powder, Hydrothermal Synthesis, X-ray Diffraction, Raman Spectroscopy, Scanning Electron Microscopy

1. Introduction

Barium titanate (BaTiO₃) is the most widely used perovskite structure ceramic material due to its excellent dielectric, piezoelectric, pyroelectric, and ferroelectric properties. It has commercial applications in piezoelectric and optoelectronic devices, pyroelectric sensors, lasers, nonlinear optical devices, image processing, pattern recognition, dielectric amplifiers, and manufacturing of multilayer ceramic capacitors (MLCs) due to the high dielectric constant and low dielectric loss [1-3]. BaTiO₃ nanoparticles showed antibacterial activity [4] and therapeutic applications such as cancer therapy and drug delivery due to their biocompatibility [5-9]. The demand of non-conducting dielectric ceramic materials is increasing continuously and attempts are being made to reduce the size of communication devices as much as possible. Barium titanate (BaTiO₃) has become more and more important in ceramic materials due to its high dielectric constant and photocatalytic characteristics.

For the synthesis of high-purity BaTiO₃ powder, various chemical methods were used, such as barium tetanyl oxalate [10, 11] hydrolysis of barium titanium alkoxide [12, 13], coprecipitation [14-16], one-step sol-gel [17-19], molten salt [20] and hydrothermal process [21-26]. Hydrothermal synthesis process proceeds in a strong alkaline solution to prepare high-purity homogeneous and ultrafine BaTiO₃ powder at low-temperature (60-180 °C) chemical reactions. This process involves the chemical reaction of barium hydroxide (Ba(OH)₂) or barium chloride (BaCl₂·2H₂O), or barium acetate (C₄H₆BaO₄) as barium (Ba) source and titanium dioxide (TiO₂), titanium tetrachloride (TiCl₄) or titanium alkoxide (C₁₂H₂₈O₄Ti) as titanium (Ti) source at 85-250 °C during a couple of hours reaction time. The reaction

temperature has a pronounced effect on the synthesis of BaTiO₃ [27-30]. The formation of BaTiO₃ at room temperature was not experimentally observed even after 12 12-hour reaction time due to slow kinetics. BaTiO₃ (pseudo-cubic phase) was produced at 60 °C and above with a small amount of BaCO₃ as the secondary phase [31]. This method has been widely used for the synthesis of BaTiO₃ powders, nanotubulars, and nanowires. The formation of cubic or tetragonal phase BaTiO₃ depends on temperature, the presence of counter-anions, and the characteristics of powders (size of crystallites and presence of defects) [32]. The present study is focused on synthesizing nanosized BaTiO₃ powder using a hydrothermal process in a stirred reactor autoclave at various reaction temperatures.

2. Experimental

Titanium dioxide powder (TiO₂; >99.90%, Merck) and barium hydroxide octahydrate (Ba(OH)₂·8H₂O; 98%; Sigma-Aldrich) were used for the synthesis of BaTiO₃ nanopowder. Formic acid (HCOOH; 85%; Merck) was used to wash the synthesized BaTiO₃ powder. All the chemicals were reagent-grade and used without further purification.

For hydrothermal synthesis of BaTiO₃ powder, a weight of 19.0 g Ba(OH)₂·8H₂O and 3.40 g TiO₂ powder were mixed in a 250-mL Teflon reaction vessel containing 60 mL deionized water. The Teflon reaction vessel was kept in a laboratory high-pressure stirred autoclave (Model limbo li, Büchi AG, Switzerland) to operate at 100, 150 and 180 °C for 7 hours with a stirring speed of 60 rpm. After the hydrothermal reaction, the contents of the Teflon vessel were cooled to room temperature and the soluble impurities and adsorbed ions were removed with a dilute (0.25 M) formic acid solution (9.50 mL of 85% formic acid in 250 ml deionized water). The contents of the

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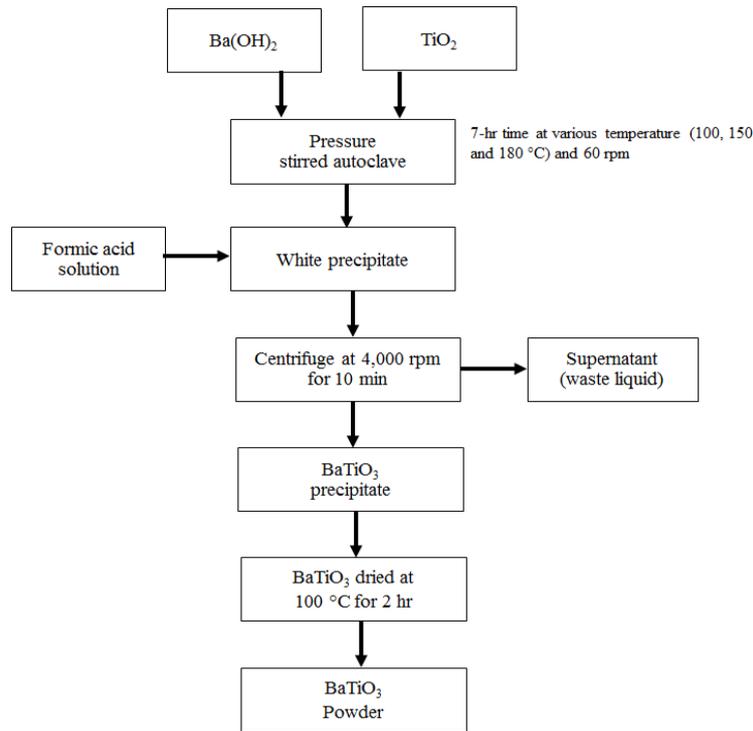


Fig. 1: Flow chart of the step-wise procedure for the synthesis of BaTiO₃ powder by hydrothermal process

Teflon reaction vessel were transferred into centrifuge bottles to separate the BaTiO₃ precipitate. After centrifugation at 4,000 rpm for 10 min, the supernatant was decanted and the yellowish-white precipitate was washed initially with a dilute formic acid solution and then with deionized water. Finally, the washed precipitate and residue were dried in an oven at 100 °C for 2 hours.

The structural properties of the BaTiO₃ powder samples were characterized by X-ray diffraction (Bruker D8 Advance X-ray Diffractometer, Germany). A scanning electron microscope (Model JEOL JSM-6490A, Japan) was used to characterize the microstructure and particle morphology of BaTiO₃ powders. The powder samples were mounted on Cu stubs and sputter-coated with Au for 90 s using JFC-1500 ion sputtering device operated at an accelerating voltage of 20 kV. The Raman spectra of BaTiO₃ powders were recorded using a Micro Raman Spectrophotometer (Dongwoo Optron Co., Ltd. Korea) with a laser (532 nm) power of 150 mW equipped with a CCD detector and monochromator M320. The flow chart of the hydrothermal process of BaTiO₃ powder is shown in Fig. 1.

3. Results and Discussion

3.1 Synthesis of BaTiO₃ powders

Barium titanate (BaTiO₃) powders were prepared using a stirred-reactor autoclave using 19.0 g Ba(OH)₂·8H₂O and 3.40 g TiO₂ powder as precursors in 250-ml Teflon reaction vessel containing 60-ml deionized water at 100, 150, and 180 °C for 7-hour reaction time by the hydrothermal method according to the following chemical reactions:



According to the above chemical reaction equilibrium, an increase in OH⁻ and Ba²⁺ ion concentration resulted in the formation of BaTiO₃ products (equations 2 and 3). An increase in the Ba-to-Ti ratio as precursors during the synthesis process resulted in the formation of BaTiO₃. So, the overall net chemical reaction for BaTiO₃ synthesis is described below:



The formation of BaTiO₃ (equation 4) is controlled by the solubility of Ba(OH)₂. If the limit of solubility of Ba(OH)₂ is reached before completion, the reaction stops and the yield is stabilized [33]. The hydrothermal process involves a simple chemical reaction between Ba(OH)₂ and TiO₂ in an aqueous solution in a stirred autoclave to produce BaTiO₃ precipitate and water. The kinetics of BaTiO₃ formation from Ba(OH)₂ and TiO₂ were studied by Hertl [30], reporting that Ba²⁺ or Ba(OH)⁺ ions react chemically with titanium precursors to form BaTiO₃ by heterogeneous nucleation on its surface. The hydroxide ions (OH⁻) play a vital role in the nucleation of BaTiO₃ crystals and act as a catalyst by promoting the growth of BaTiO₃ under hydrothermal conditions [34]. The dynamic nature of the interaction between TiO₂, Ba²⁺, and OH⁻ leads to a crystallization mechanism involving nucleation, growth, and crystal dissolution. The role of OH⁻ could be to facilitate the hydrolysis of Ti-O-Ti bonds [35].

3.2 Characterization of BaTiO₃ powder

The typical XRD patterns of the BaTiO₃ powders synthesized at 100, 150, and 180 °C are shown in Fig. 2. The XRD patterns of BaTiO₃ powders exhibited that X-ray diffraction peak intensities at 2 θ = 22.00° (100), 31.35° (110), 38.65° (111), 44.95° (200) and 55.80° (211) increased with an increase in reaction temperature during synthesis process (Fig. 2).

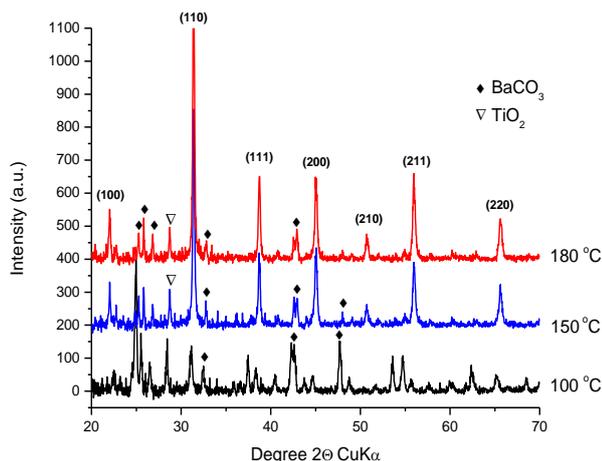


Fig. 2: XRD patterns of BaTiO₃ powder synthesized at 100, 150 and 180 °C by the hydrothermal process.

The unit cell parameter for the crystalline BaTiO₃ was determined to be $a=3.994$ Å and $c=4.035$ Å, which fit well with the peak positions of standard cubic-phase BaTiO₃ [JCPDS no. 01-089-1428]. It is clear that the X-ray diffraction peak (110) becomes sharper and stronger with an increase in reaction temperature. When the reaction temperature increased from 100 °C to 150 °C and then 180 °C, the XRD patterns became sharp-edged, which represents the crystallinity of BaTiO₃ powders. The temperatures higher than about 130 °C (Curie temperature), BaTiO₃ exists in the cubic perovskite structure. In this crystal structure, the Ba⁺² ions occupy the corners of the elementary cell, the Ti⁺⁴ ions are in the volume center and the O⁻² ions are in the surface center. Below the Curie point, the crystal structure transforms from the cubic phase to the distorted tetragonal structure with a displacement of the center of positive and negative charges within the sub-lattice [35]. The crystallinity of BaTiO₃ (cubic) was estimated by measuring the XRD intensities of cubic BaTiO₃ (100) peak at 2 θ = 22.160 ° with few by-products of BaCO₃ [36]. The XRD patterns of BaTiO₃ powders synthesized at 100, 150, and 180 °C clearly showed shifting of reflections around 2 θ = 45° (200) (Fig. 3). XRD patterns exhibited an appreciable increase in peak intensities and small shifting of peak positions at 150 and 180 °C that presumably due to small particle size, which confirmed the cubic structure of BaTiO₃ powder. The single peak reflection around 2 θ = 45° (200) region matched well with the typical XRD peaks of cubic BaTiO₃ [37].

The presence of BaCO₃ and unreacted TiO₂ phases was also identified in the products as impurities (Fig. 2). The concentration of BaCO₃ in the product decreased with the increase in reaction temperature (Fig. 4). Newalkar et al. [32] reported the formation of barium carbonate (BaCO₃) as a

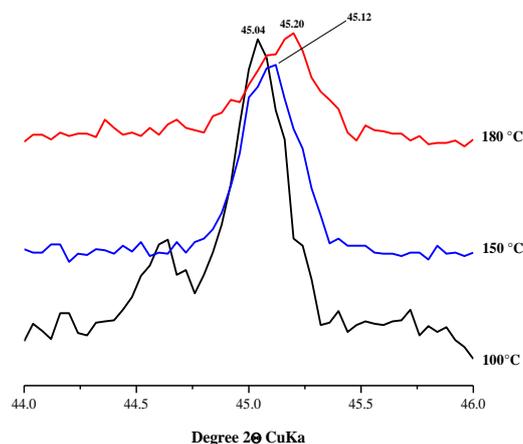


Fig. 3: XRD pattern of BaTiO₃ powders synthesized at 100, 150, and 180 °C showing clear reflections (200) of the cubic phase BaTiO₃

minor impurity in BaTiO₃ powder synthesized in the temperature range of 60-160 °C during the microwave hydrothermal process. Guo et al. [21] observed that the grain size of BaTiO₃ powder increased due to the agglomeration of fine particles with the increase in reaction time during the microwave hydrothermal process. BaTiO₃ crystallizes in the perovskite structure as a cubic lattice with barium ions occupying the corners of the unit cell, oxide ions occupying the face centers, and titanium ions occupying the centers of the unit cells. BaTiO₃ has a cubic structure above 120 °C.

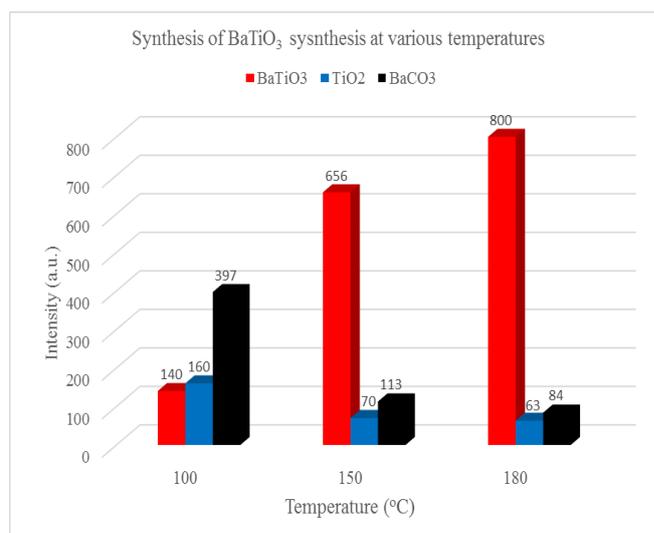
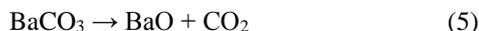


Fig. 4: XRD peak intensities show concentrations of BaTiO₃, BaCO₃ and unreacted TiO₂ in BaTiO₃ powders synthesized at 100, 150 and 180 °C by hydrothermal processes.

Barium carbonate (BaCO_3) might be decomposed to barium oxide (BaO) and carbon dioxide (CO_2) at a higher reaction temperature during the hydrothermal process and its reaction with TiO_2 could produce BaTiO_3 , as stated by the following chemical reactions:



The decomposition reaction of BaCO_3 (solid) = BaO (solid) + CO_2 (gas) was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) methods [38]. Nanocrystalline BaTiO_3 was prepared by solid-state reaction of TiO_2 with BaCO_3 of different particle sizes (650, 140, and 50 nm) [39].

The Raman scattering spectra of the BaTiO_3 powders synthesized at 100, 150, and 180 °C are shown in Fig. 5. The frequency range covered is from 100-1000 cm^{-1} . Raman spectra clearly showed sharp bands at 145, 160, 197, 397, 516, and 637 cm^{-1} , a sharp small band at 980 cm^{-1} and two small broad bands at 305 and 797 cm^{-1} in all the products (Fig. 5). Two broad shoulder bands at 792 and 984 cm^{-1} are also appeared in the sample obtained at 7-hour reaction time. It is clear from the Raman spectra of both samples that they contained bands of predominantly cubic-phase BaTiO_3 identified by the bands around 166, 196, 394, 512, and 636 cm^{-1} . It was observed that the peak intensities decreased with an increase in the reaction temperature of the synthesis process. The frequencies near 190 and 516 cm^{-1} modes come from the $F1u$ cubic phase modes, the 303 cm^{-1} mode comes from the breaking of the cubic silent $F2u$ mode [33]. Ávila et al. [34] suggested that the peaks at 639, 396, and 144 cm^{-1} correspond to the anatase shape of TiO_2 .

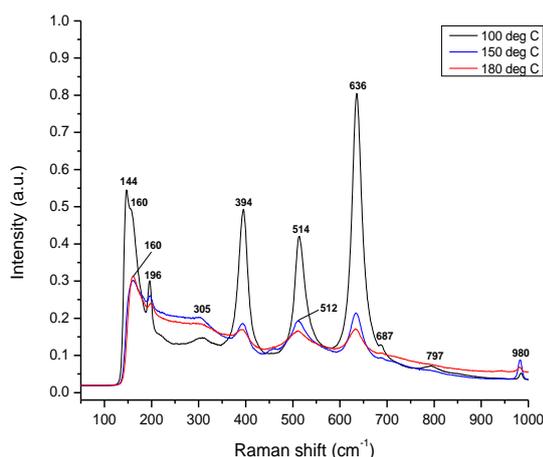


Fig. 5: Raman spectrum of BaTiO_3 powder prepared at 100, 150, and 180 °C by hydrothermal process. * = denotes Raman peaks at 305 and 516 cm^{-1} , which correspond to BaTiO_3 .

The experimental data shows that the chemical reaction between Ba(OH)_2 and TiO_2 was incomplete after 7-hour reaction time. The presence of unreacted TiO_2 coexisted in all the synthesized BaTiO_3 powders (Fig. 4). The concentration

of unreacted TiO_2 corresponding to peak intensities decreased with an increase in reaction temperature during the synthesis process. Frey and Payne [37] suggested that the spectral peak at 193-195 cm^{-1} represents the existence of an orthorhombic BaTiO_3 phase. In this study, the Raman spectra showed a sharp band around 195-198 cm^{-1} in BaTiO_3 powders. The Raman spectra clearly showed the cubic distortion of BaTiO_3 structure coexisting with unreacted TiO_2 at 394 and 635 cm^{-1} . Raman bands near 630 cm^{-1} correspond to BaCO_3 phase, anatase TiO_2 , or hexagonal BaTiO_3 , which is stabilized at room temperature by high surface energy [40-42]. Cubic phase BaTiO_3 showed Raman spectrum at 166, 196, 394, 512, and 636 cm^{-1} [43]. It is clear from the Raman spectra that the synthesized powders contained bands of predominantly cubic phase BaTiO_3 at 166, 196, 394, 512, and 636 cm^{-1} . The intense Raman spectra near 144, 394, 514, and 636 cm^{-1} correspond to unreacted anatase TiO_2 phase in the BaTiO_3 powders as an impurity which is attributed to the increase of peak intensities near 394, 514, and 636 cm^{-1} due to coexistence with cubic phase BaTiO_3 spectral lines (Fig. 5).

SEM micrographs of BaTiO_3 powders are shown in Fig. 6. The BaTiO_3 particles showed irregular, sphere-like, cube-like particles and cube-rod structures. The average particle sizes of BaTiO_3 powders are 38-92, 45-63, and 28-52 nm at 100, 150, and 180 °C, respectively. The shape and particle size distribution in BaTiO_3 powder showed agglomeration due to nano-sized particles. BaTiO_3 powders synthesized at 100 °C appeared heterogeneous morphology (cube, hexagonal and rod-shaped) (Fig. 6A), whereas powder synthesized at 150 °C appeared to be very uniform spherical morphology (Fig. 6B) and cube-shaped (Fig. 6C).

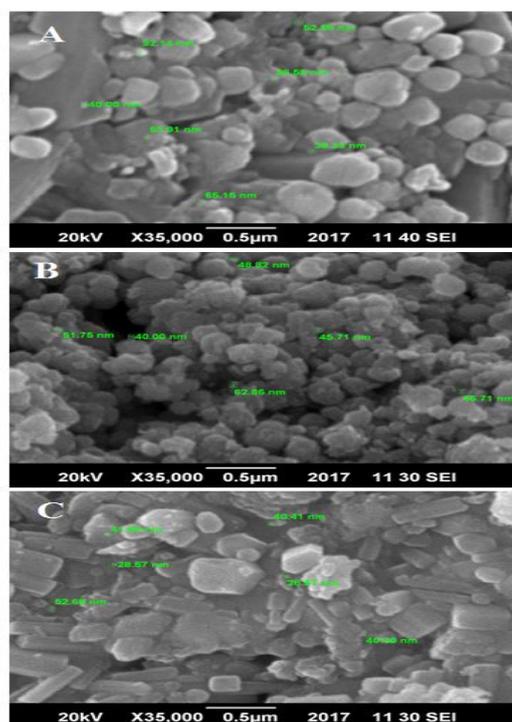


Fig. 6: SEM micrographs of BaTiO_3 powders synthesized at 100 °C (A), 150 °C (B), and 180 °C (C) by hydrothermal process

4. Conclusions

Hydrothermal method is the most promising route to synthesize ceramic oxide powders with controlled morphology, and high crystallinity in a one-step process. XRD and Raman spectroscopy data revealed that cubic-phase BaTiO₃ powders were successfully synthesized by hydrothermal processes. It is clear that cubic-phase BaTiO₃ nanocrystalline powder was directly crystallized by using Ba(OH)₂·8H₂O to TiO₂ at a ratio of (4:1) as a starting material in a stirred reactor autoclave by hydrothermal process. The hydrothermal synthesis process offers a promising approach to producing high-purity crystalline BaTiO₃ powder.

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