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Barium zirconate titanate nanoparticles synthesized by the sonochemical method

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Abstract

A new route for preparing barium zirconate titanate nanoparticles ($BaZr_{0.3}Ti_{0.7}O_3$ (BZT)) has been developed by ultrasonication of $BaCl_2 \cdot 2H_2O$, $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$ precursors in a high concentration of NaOH aqueous solution. The as-prepared powders were identified by X-ray diffraction (XRD) as cubic perovskite BZT. The phase formation was confirmed by FT-IR and Raman spectroscopy. The increase of NaOH concentration resulted in BZT powders with smaller particle size and less $BaCO_3$ contamination. The microstructure of BZT powders prepared in 20 M NaOH examined by scanning electron microscopy (SEM) showed nanosized spherical morphology with the average particle sizes of 51 ± 6 nm.

Keywords: A. Powders chemical preparation; Barium zirconate titanate

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1. Introduction

In recent year, environmentally friendly lead-free barium zirconate titanate ceramics ($Ba(Zr_xTi_{1-x})O_3$ (BZT)) have been extensively studied due to their potentiality for tunable microwave applications e.g. phase shifters, resonator, antennas, MEMS based sensors and actuators [1–3]. BZT has great benefits for such applications as it exhibits high dielectric constant, low dielectric loss and particularly high tunability. BZT with perovskite structure (ABO_3) is formed by a complete solid solution of ferroelectric $BaTiO_3$ and paraelectric $BaZrO_3$. Substitution of Ti^{4+} ions (ionic radius = 0.745 Å) by chemically more stable Zr^{4+} ions (ionic radius = 0.860 Å) on the B-sites leads to stability of the system and single diffuse phase transition temperature [3,4]. The dielectric properties of $Ba(Zr_xTi_{1-x})O_3$ ceramics are found to depend on Zr concentration. It has been reported that for $Ba(Zr_xTi_{1-x})O_3$ with x in the compositional range of $0.26 \leq x \leq 0.42$, the solid solution exhibits typical relaxor-like behavior in both bulk and thin film materials [4,5].

BZT powders can be prepared by various methods including solid state reaction [1] auto-combustion [6], sol–gel [7], hydrothermal [8] and co-precipitation [9] techniques. For the wet chemical processes, it has been suggested by Reddy et al. [9] that a strong alkaline condition (≥ 15 M NaOH) is favored for the chemical equilibrium of reaction of the BZT formation. In addition, precipitation of oxides in highly basic solution was found to increase the purity of products [10]. In order to improve sinterability and dielectric properties, BZT powders are expected to be nanosized with homogeneous distribution of the composition [4,9]. Among the various preparing methods, sonochemical synthesis based on irradiation of high-intensity ultrasound (20 kHz to 10 MHz) into a liquid medium seems to be an interesting method to fulfill the requirements. Sonochemistry yields the benefits of an acoustic cavitation phenomenon i.e. the formation, growth and implosive collapse of the bubbles stimulated by ultrasonication. This phenomenon can create an extreme condition (intense

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local heat ~5000 K, high pressure ~20 MPa and rapid heating and cooling rates $>10^{10}$ K s^{-1}) [11,12] initiating a wide range of chemical reactions and resulting in novel materials with unique properties. To the best of our knowledge, the study on preparation of $BaZr_{0.3}Ti_{0.7}O_3$ nanoparticles by a sonochemical method in a highly basic solution has not been reported yet. Therefore, the effects of ultrasound irradiation and concentration of alkaline solution on the phase formation and morphology of BZT were investigated in this work.

2. Material and methods

The stoichiometric amounts of barium chloride dihydrate ($BaCl_2 \cdot 2\,H_2O$, Fluka, 99% purity), zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8\,H_2O$, Sigma-Aldrich, 99.5% purity) and titanium chloride ($TiCl_4$, Waka, 99% purity) were dissolved in de-ionized water. The mixed solution was added into a sonication chamber containing 15 or 20 M (mol/l) sodium hydroxide solution (NaOH, Carla Erba, 97% purity). A pH of the synthesis solution was maintained at pH ≈ 14 during the reaction. The irradiation process was carried out by direct immersion of a high-intensity ultrasonic probe (Ti-horn (Sonic and Material Inc., VC 750), 2.5 cm diameter, 20 kHz, 150 W/cm^2) into the reaction solution under flowing of argon gas for 30 min. After the reaction finished and cooled down to room temperature, products were separated and washed with de-ionized water until the washed solution was neutralized (pH ~ 7) followed by drying in an oven at 100 °C for 24 h. Phase characterization was carried out using an X-ray diffractometer (XRD, Bruker D8 Advance, CuKα radiation 1.5418 Å, $2\theta = 20$–$80°$), Fourier-transform infrared spectrometer (FT-TR, Perkin-Elmer GX 8500, KBr mixing, measuring in the range of 400–4000 cm^{-1}) and a Raman spectrometer (Thermo scientific DXR, measuring in the range of 100–1000 cm^{-1}). The microstructure was examined by a scanning electron microscope (SEM, Hitachi 54700).

3. Results and discussion

XRD patterns of as-prepared powders obtained after ultrasonication in different concentrations of NaOH solution for 30 min are shown in Fig. 1. The XRD patterns showed well-defined diffraction peaks and the major peaks were identified to cubic perovskite BZT phase (JCPDS no. 31-0174) indicating that well-crystallized BZT powders can be achieved by ultrasonication in ≥ 15 M NaOH solution. Diffraction peaks assigned to $BaCO_3$ phase were also detected in the XRD patterns. The formation of $BaCO_3$ was probably a result of the open-air synthesis system. This contamination was suggested to be eliminated by using a closed system or washing the products with formic acid [13]. The calculated crystallite sizes using Debye–Scherrer equation were 13.9 ± 0.02 nm and 16.1 ± 0.02 nm for BZT powders prepared in 15 M and 20 M NaOH, respectively.

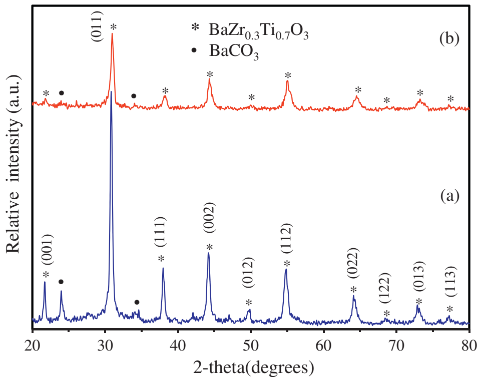

Fig. 1. XRD patterns of as-prepared BZT powders obtained from ultrasonication in (a) 15 M NaOH and (b) 20 M NaOH aqueous solution for 30 min.

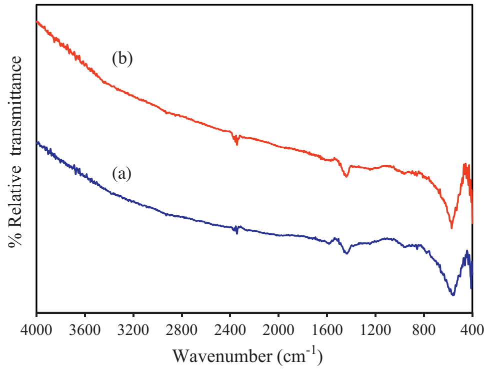

Fig. 2. IR spectra of BZT powders prepared using (a) 15 M NaOH and (b) 20 M NaOH solution.

The phase identification of BZT powders prepared by the sonochemical method was further investigated by FT-IR and Raman spectroscopy. IR spectra of BZT powders prepared using 15 M and 20 M NaOH (Fig. 2) showed strong absorption bands at 540 cm^{-1} corresponding to the characteristic absorption bands of the perovskite phase (vibration of BO_6 octahedra, when B = Ti or Zr) [6] along with absorption bands of the carbonate phase at 1450 cm^{-1} [14].

Room temperature Raman spectra of BZT powders prepared by ultrasonication in different NaOH concentrations (Fig. 3) compared well with literature reports [4,15]. The characteristic Raman modes of BZT were observed at 185, 220, 300 and 512 cm^{-1} (A_1(TO) modes) associating with the asymmetry within the BO_6 octahedra along with the modes at region 600–800 cm^{-1} assigned to the locally distorted ZrO_6 octahedra and a signature of the ferroelectric relaxor phase. The bands related to $BaCO_3$ were also observed at 135, 155 and 694 cm^{-1} [14,16]. As shown in Fig. 3, these bands exhibited less intensity in the spectra of BZT prepared using the higher NaOH concentration. This observation is in good agreement with the XRD investigation (Fig. 1) in which low intensity of $BaCO_3$ diffraction peaks was detected in the XRD pattern of BZT prepared from 20 M NaOH. These results suggest that

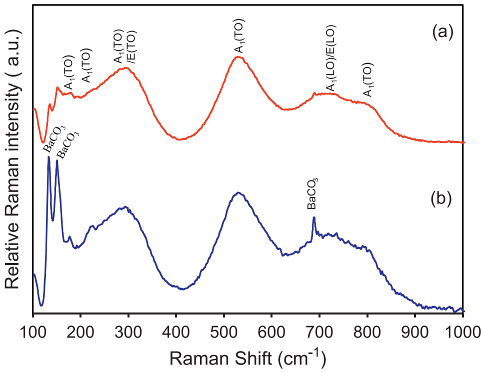

Fig. 3. Room temperature Raman spectra of BZT powders prepared using (a) 15 M NaOH and (b) 20 M NaOH solution.

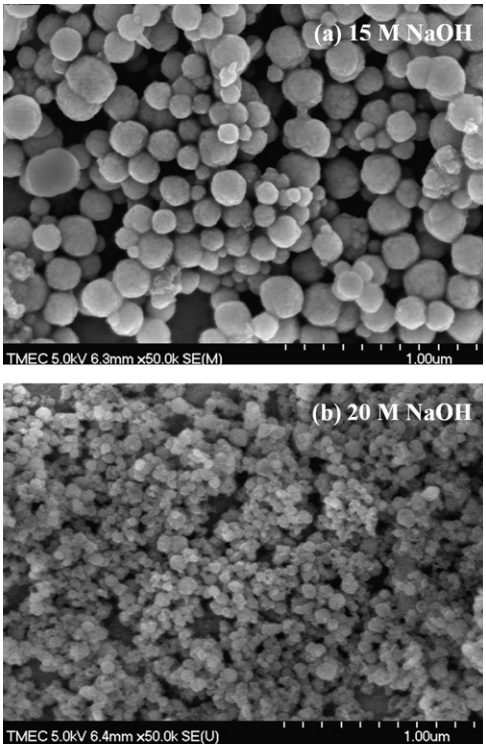

Fig. 4. SEM images of BZT powders prepared using (a) 15 M NaOH and (b) 20 M NaOH solution.

using higher concentration of NaOH (20 M) can reduce the formation of $BaCO_3$ impurity and it could be due to the effect of pH condition. Since at high hydroxide ion (OH^-) concentration, the chemical equilibrium of the reaction favors the BZT formation over the carbonate formation [9].

Fig. 4 shows SEM images of BZT powders prepared using different NaOH concentrations. The BZT powders showed spherical morphology with the average particles sizes of 137 ± 14 nm and 51 ± 6 nm for the powders prepared using 15 M and 20 M NaOH solution, respectively. As can be seen in Fig. 4, especially for the powders prepared using 15 M NaOH, the BZT particles were aggregates formed by epitaxial growth of primary nanocrystals. This result is consistent with the calculated crystallite size obtained from the XRD study (13.9 ± 0.02 nm for 15 M NaOH and 16.1 ± 0.02 nm for 20 M NaOH). Similar observations have been reported by Dang et al. in the preparation of $BaTiO_3$ by the sonochemical method [17,18]. The unique morphology of the oxides was suggested to be due to the effect of ultrasonic irradiation. The smaller particle size obtained from BZT powders prepared using 20 M NaOH is consistent with the lower intensity of XRD peaks shown in Fig. 1. The decrease of particle size observed in BZT prepared using 20 M NaOH solution could be a result of the higher concentration of hydrolyzed metal species leading to supersaturated solution, thus the nucleation process is more favorable than the grain growth process [10].

4. Conclusions

Barium zirconate titanate nanoparticles ($BaZr_{0.3}Ti_{0.7}O_3$) were successfully prepared by a sonochemical method in a strong alkaline environment (15 M and 20 M NaOH aqueous solution) using $BaCl_2 \cdot 2H_2O$, $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$ as precursors. The as-prepared powders were characterized to cubic perovskite BZT with a nanosized spherical shape. The concentration of NaOH solution was found to affect the phase formation and morphology of the BZT products in which using higher NaOH concentration resulted in BZT with smaller particle size and less $BaCO_3$ contamination. BZT powders prepared by ultrasonication in 20 M NaOH showed well-crystallized materials with the average particle sizes of 51 ± 6 nm and the crystal sizes of 16.1 ± 0.02 nm. These results indicate that the sonochemical method could offer a new approach to produce BZT nonoparticles.

Acknowledgments

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