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Research Article

Two-Step Hydrothermal Synthesis of Well-Dispersed $(Na_{0.5}Bi_{0.5})TiO_3$ Spherical Powders

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$(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) powders that have well-dispersed, uniform particle size and well-developed spherical shape were successfully prepared by a two-step hydrothermal synthesis method. Nanosized TiO_2 powders were firstly synthesized by a hydrothermal method, and then the TiO_2 particles are used as a raw material to synthesize NBT powders. It was found that by using the TiO_2 nanoparticles as Ti source, the well-dispersed spherical NBT powders with about 200 nm in size could be obtained at 200°C for 4 h with a low mineralizer concentration of 6 mol/L NaOH in the second step. The formation of spherical NBT powders can be explained by first generating nuclei on the surface of TiO_2 nanoparticles via in situ crystallization mechanism and then crystal growing and agglomerating by dissolution-recrystallization mechanism.

1. Introduction

Piezoelectric ceramics have been widely used in electrical devices such as actuators, accelerators, ultrasonic generators, piezoelectric transducers, filters, and sensors [1–3]. Lead-based piezoelectric ceramics such as lead zirconate titanate (PZT) are the first-choice material because of their superior ferroelectric, piezoelectric, and pyroelectric properties [4, 5]. However, owing to the environmental pollution caused by PbO that is contained in lead-based piezoelectric devices, more and more efforts have been made to develop high-performance lead-free piezoelectric ceramics [6–13]. As one of the typical lead-free candidates, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), that was discovered by Smolenski in 1960, possesses an a-site complex perovskite structure and exhibits excellent piezoelectric and ferroelectric properties [14–18]. It is a trigonal system at room temperature and has a Curie temperature of 320°C. NBT ceramics have strong ferroelectricity ($Pr = 38\ uc/cm^2$), large electromechanical coupling coefficient (about 40% to 50% for kt and k33), small dielectric constant (240 to 340), and good acoustic performance ($NP = 3200\ Hz \bullet m$). Such characteristics give NBT ceramics unique advantages in the production of high-frequency ultrasonic transducers and surface-acoustic wave devices. Preparation of ceramic precursor powder in the ceramic industry is a very important processing, and the particle size of powders has a great impact on the sintering process of ceramics. In addition, due to size and special shape effects, nanosized ceramics exhibit fascinating and applicable performance [19–21]. Compared with the conventional solid-state reaction method, there are many wet chemical methods for the synthesis nanosized NBT powders, such as the sol-gel method, coprecipitation method, and hydrothermal method [22–26]. Among these methods, the hydrothermal method is considered to be remarkably advantageous in the preparation of fine crystalline powders with a high purity due to the direct precipitation of crystals from solutions, controllable rate, and homogeneity of nucleation and growth of crystals. Hydrothermal reaction is usually performed under a moderate condition and does not require expensive precursors or equipments. It offers a low-temperature (below 300°C) direct route to obtain ceramic powders with a fine size and uniform morphology, which can prevent undesirable changes in stoichiometry when compounds contain volatile elements such as Bi and alkali metals in many lead-free piezoelectrics. Recently, hydrothermal synthesis has been used in the

synthesis of NBT powders with different sizes and shapes [27–31]. For example, Kanie et al. [27] and Zhang *et al.* [28] have synthesized cubic-shaped NBT particles and found that the NBT particle size could be controlled by changing the initial NaOH concentrations. Ghasemian et al. have reported that well-crystallized NBT nanofibers with 150–200 nm diameters and 5 mm length were obtained at 200°C for 20 h with a NaOH concentration of 20 mol/L. [29] Lu *et al.* have also reported that NBT nanostructures including nanoplates, nanotubes, and nanowires could be synthesized by adjusting the reaction time and NaOH concentration [30]. The above results clearly indicate that the size and shape of NBT powders are strong correlation with synthesis conditions, especially the NaOH concentration. However, in these studies, the NBT powders were synthesized by using a higher NaOH concentration, and the prepared NBT powders rarely have well-dispersed, uniform particle size and well-developed spherical shape.

In this study, we attempt to prepare spherical NBT nanosized powders using a two-step hydrothermal method. Namely, nanosized TiO_2 powders are firstly synthesized by a hydrothermal method, and then the TiO_2 particles are used as a raw material to synthesize NBT powders under the conditions of a low concentration of mineralizer and a short reaction time. We investigate the influences of mineralizer concentration, reaction temperature, and time on the crystalline structure and particle shape. The crystal growth mechanism in the hydrothermal reaction process is also discussed.

2. Experimental

All reagents used in this work are commercially available in analytical grade without further purification. Titanium sulfate ($Ti(SO_4)_2$, Sinopharm, China, ≥96.0%), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, Sinopharm, China, ≥99.0%), sodium hydroxide (NaOH, Sinopharm, China, ≥96.0%), and ammonia ($NH_3{\cdot}H2O$, Sinopharm, China, 25-28.0%) were used as raw materials for hydrothermal reactions.

2.1. Hydrothermal Synthesis of TiO_2 Powders. A certain amount of $Ti(SO_4)_2$ was dissolved in 30 mL of distilled water and stirred for 10 minutes until completely dissolved. Then, ammonia was dropwise added to the solution until the solution pH = 10, producing a white suspension. The white suspension was transferred to a Teflon-lined 50 mL stainless steel autoclave and reacted at 200°C for 2 h, followed by a natural furnace cooling to room temperature. The final products were filtered, washed with distilled water several times until the pH value of supernatant approached to 7, and obtained wet TiO_2 particles. In the next step, the wet TiO_2 particles will be used to hydrothermally synthesize NBT powders.

2.2. Hydrothermal Synthesis of NBT Powders. NBT powders were synthesized via hydrothermal method, in which NaOH was used as both the sodium source and the mineralizer. The specific procedure was shown in Figure 1. Firstly, NaOH was dissolved in distilled water with concentrations of 4, 5, or 6 mol/L. The stoichiometric amount of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 10% nitric acid solution, and then the solution

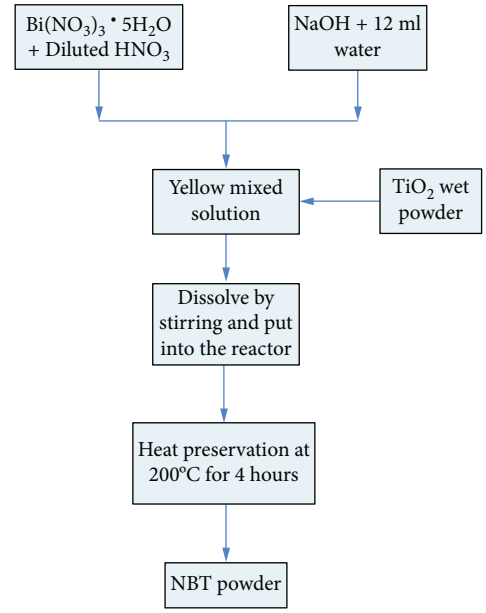


Figure 1: Scheme of NBT powder hydrothermal synthesis.

was added into the NaOH solution to give a yellow suspension. Subsequently, according to the $Bi(NO_3)_3{\cdot}5H_2O : TiO_2$ molar ratio of 1 : 2, the wet TiO_2 particles obtained above were introduced to the yellow suspension. After stirring 30 minutes, the as-prepared mixture was poured into a Teflon-lined 50 mL stainless steel autoclave with a filling capacity of 80% and then heated at a certain temperature for several hours. After the hydrothermal reaction, the autoclave was cooled down to room temperature in air. Finally, the products were filtered and washed by distilled water and dried at 80°C for 24 h.

2.3. Structural Characterization. The crystalline structure of the samples was investigated by X-ray diffraction (XRD, XRD-7000, SHIMADZU) with Cu-Kα radiation ($\lambda = 1.5406$ Å) at room temperature. The particle size and morphology were observed by scanning electron microscopy (SEM, S-3400N, HITACHI). The crystalline structure, size, and shape of the samples were also studied by transmission electron microscopy (TEM, Tecnai G2 F20, FEI).

3. Results and Discussion

3.1. The Hydrothermal Synthesis of TiO_2. Figure 2(a) shows XRD patterns of the TiO_2 particles hydrothermally synthesized at 200°C for 2 h. All diffraction peaks belong to the anatase phase of TiO_2 (PDF card no. 21-1272). The TEM image shows that most of the TiO_2 particles have a rodlike shape with the average size of 50 nm in length and 25 nm in width (Figure 2(b)). Figure 2(c) shows a HRTEM image of a TiO_2 particle and Figure 2(d) shows FFT patterns of the single TiO_2 particle, indicating that it crystallized in to the anatase phase and its crystallinity is very good. The interplanar spacing of the (101) planes is about 0.351 nm, which is in accordance with the XRD results. The well-crystallized

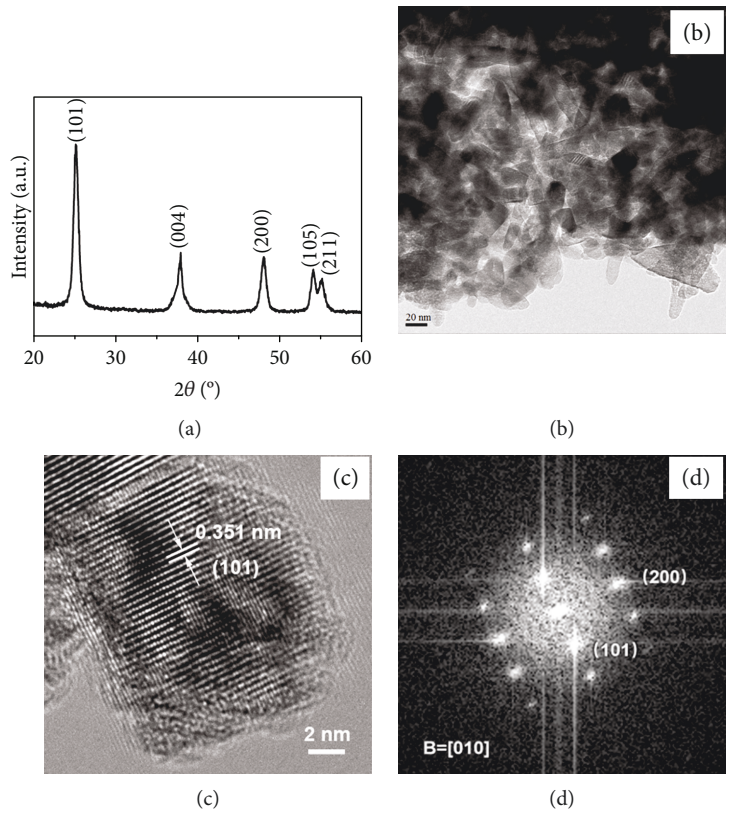


Figure 2: (a) XRD patterns of TiO_2 particles hydrothermally synthesized at 200°C for 2 h. (b) TEM photograph of TiO_2 particles. (c) HRTEM image of a single TiO_2 particle. (d) FFT patterns of the single TiO_2 particle.

TiO_2 particles with the nanoscale size are used as a raw material in the hydrothermal synthesis of NBT powders.

3.2. The Hydrothermal Synthesis of NBT. In a hydrothermal synthesis process, the mineralizer concentration has a great effect on the crystalline structure and morphology of powders. Therefore, we first investigated the effects of the NaOH concentration on the crystallization and morphology of NBT particles by varying the NaOH concentrations in the starting solution from 4 to 6 mol/L. Figure 3(a) shows XRD patterns of the NBT powders hydrothermally synthesized at 200°C for 4 h with different NaOH concentrations. When the NaOH concentration is 4 and 5 mol/L, the main diffraction peaks correspond to the perovskite phase of $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) (PDF card no. 46-0001), but a weaker diffraction peak of the second phase of $Bi_4Ti_3O_4$ (PDF card no. 35-0088) can still be detected. With increasing the NaOH concentration to 6 mol/L, the NBT powders with the single perovskite phase are obtained. The results imply that a higher NaOH concentration is required to ensure well-crystallized NBT powders with the single perovskite phase. According to Setinc et al. [32], the increase of the NaOH concentration raises the pH value of the system and improves the solubility of initial reactants such as TiO_2 and $Bi(NO_3)_3{\cdot}5H_2O$, which favors an in situ mechanism of NBT formation. Therefore, the appropriate NaOH concentration is required to make the initial reactants have a sufficient solubility to improve the crystallization of the NBT perovskite phase and avoid the emergence of second phase of $Bi_4Ti_3O_4$. Considering that the solubility of NaOH solution with a concentration more than 6 mol/L in water at room temperature may decrease and it is difficult to form a clear solution, thus we chose 6 mol/L as the concentration of mineralizer in the following experiment.

The reaction rate in the hydrothermal reaction process is related to the reaction temperature. To investigate of the effect of hydrothermal temperature on the structure and morphology of the NBT powders, the hydrothermal temperature is set at 140°C, 160°C, 180°C, and 200°C for 4 h, respectively. As shown in Figure 3(b), when the reaction temperature is between 140°C and 180°C, although the perovskite phase dominates in the powders, a weaker diffraction peak of the second phase $Bi_3Ti_4O_{12}$ is also observed. When the hydrothermal temperature reaches 200°C, all the diffraction peaks match well with those of the perovskite phase of NBT, and no second phase can be detected. The results indicate the higher reaction temperature leads to the higher activity of the Ti^{4+}, Bi^{3+}, and Na^+ in the crystal, resulting in an increase of the number of effective collisions in these ions and the increase of the reaction activation energy. The autoclave used in our experiment is equipped with a Teflon liner that cannot be more than 200°C, thus the choice of the reaction temperature at 200 degrees is more appropriate.

In the hydrothermal synthesis process, the reaction time controls the degree of nucleation and crystal growth of the perovskite NBT. Figure 3(c) shows the XRD patterns of NBT samples hydrothermally synthesized at 200°C for different reaction times. In the powders synthesized for 2 h, the

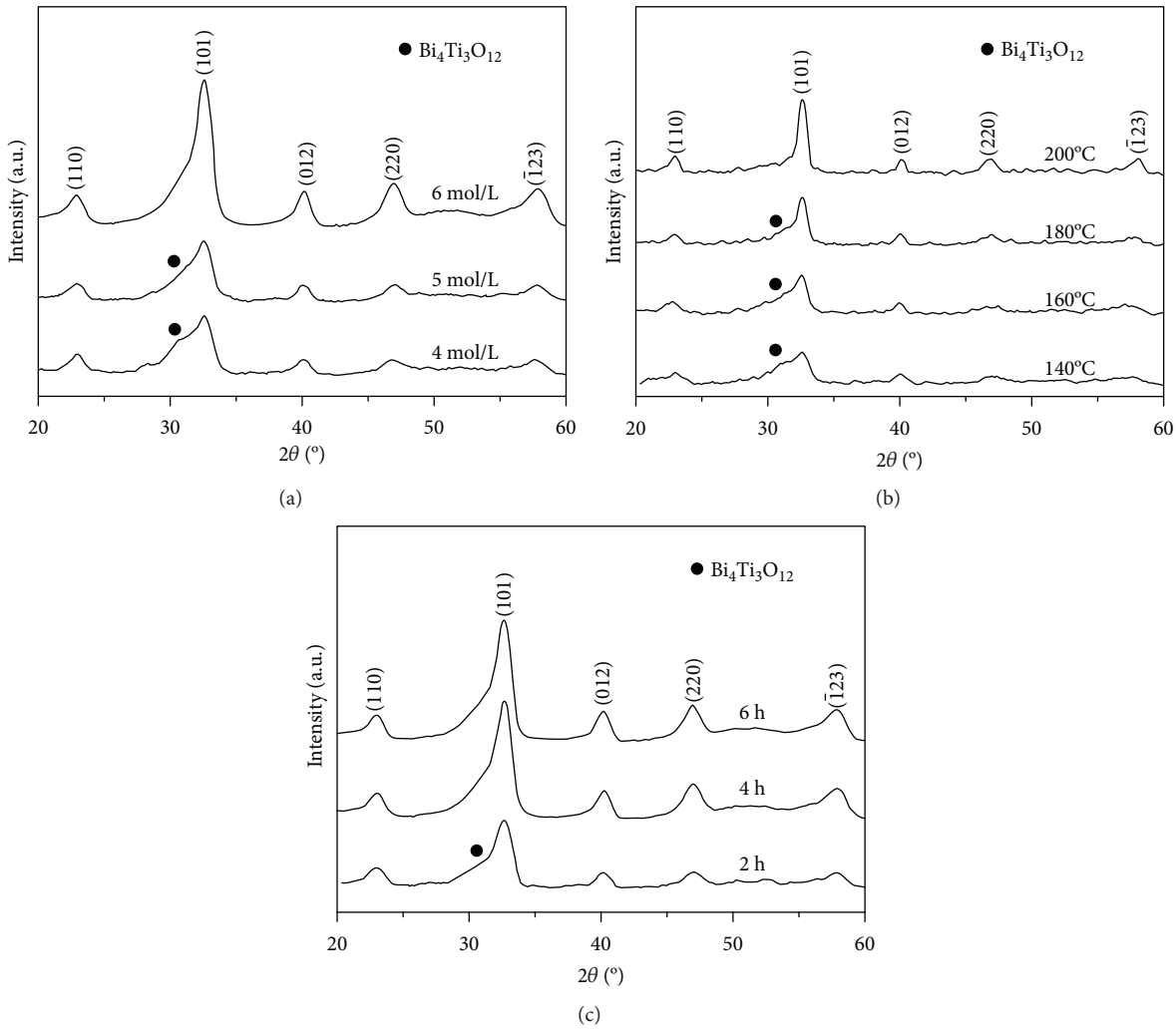


Figure 3: XRD patterns of NBT powders obtained under different hydrothermal conditions: (a) at 200°C for 4 h with different NaOH concentrations, (b) at different reaction temperatures for 4 h with a NaOH concentration of 6 mol/L, and (c) at 200°C for different reaction times with a NaOH concentration of 6 mol/L.

diffraction peaks can be indexed to the perovskite phase of NBT with a small peak of the second phase $Bi_4Ti_3O_{12}$. When the synthesis time was extended to 4 h, the secondary phase disappears and single perovskite NBT powders are obtained. When the synthesis time was further extended to 6 h, the diffraction peaks of NBT perovskite phase become sharper and stronger, indicating that a long reaction time can improve the crystallinity of perovskite NBT powders. However, considering the efficiency and cost, the reaction time can be determined for 4 h.

Figure 4 shows SEM images of the NBT powders obtained at 200°C for 4 h under different NaOH concentrations. It can be seen from Figure 4(a) that the shape of NBT powders synthesized with the NaOH concentration of 4 mol/L is irregular spherical-like shape and its size is not uniform due to the existence of the second phase $Bi_4Ti_3O_4$, as indicated by XRD results (Figure 3(a)). By increasing the mineralizer concentration to 5 mol/L, the NBT powders synthesized with the NaOH concentration of 5 mol/L show a spherical shape with several sheet agglomerates mixing therein (Figure 4(b)). However, the NBT powders synthesized with the NaOH concentration of 6 mol/L have well-dispersed, clear, and uniform spherical shape with the size of 200 nm in diameter (Figure 4(c)). Clearly, the mineralizer NaOH concentration not only affects the crystallinity but also decides the final morphology of the powders. At the low NaOH concentration, the powders with the poor crystallinity are obtained, which may be due to the decreased solubility of the initial reactants TiO_2 and $Bi(NO_3)_3{\cdot}5H_2O$. A sufficient solubility of the starting material enables the dissolution of the precursor species and can lead to a perfect crystallization.

Figures 5 and 6 show SEM images of the NBT powders obtained at different temperatures and times. It can be seen from Figure 5 that several sheet agglomerates mix in the NBT powders synthesized at 160 and 180°C for 4 h, and the spherical morphology is not fully developed, which may be due to the presence of the second phase of $Bi_3Ti_4O_{12}$ (Figure 3(b)). By increasing the synthetic temperature to 200°C, the NBT powders have well-dispersed uniform

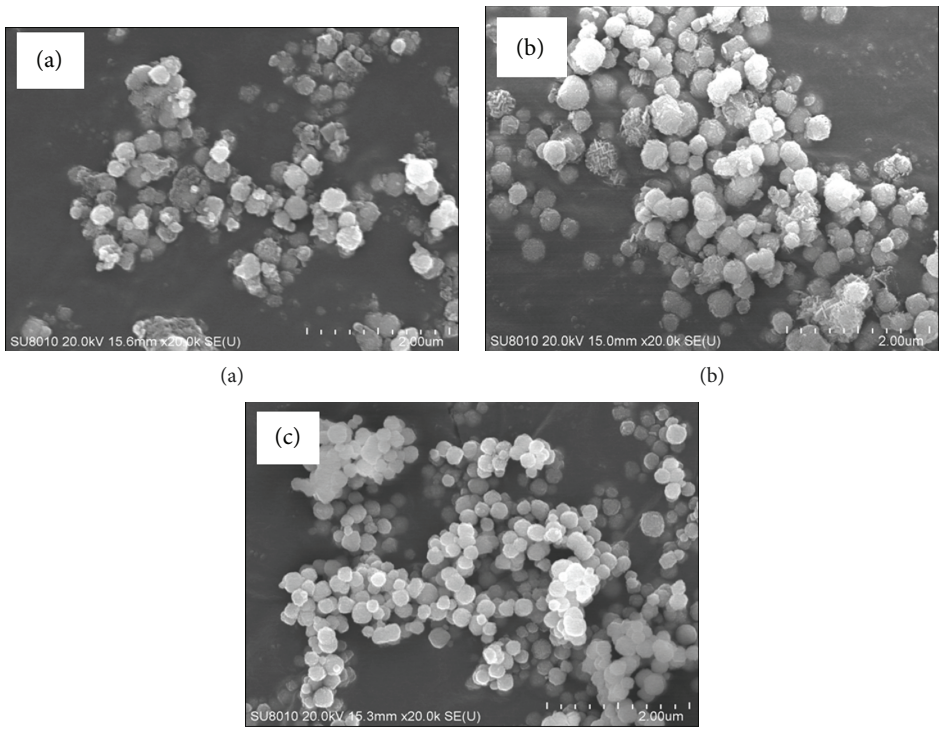


FIGURE 4: SEM photos of NBT powders obtained at 200°C for 4 h with different NaOH concentrations: (a) 4 mol/L, (b) 5 mol/L, and (c) 6 mol/L.

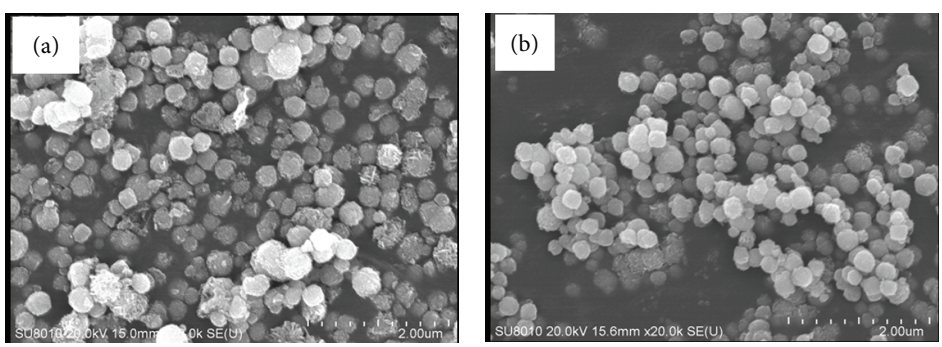


FIGURE 5: SEM photos of the NBT powders obtained at temperatures of (a) 160°C and (b) 180°C for 4 h with 6 mol/L NaOH.

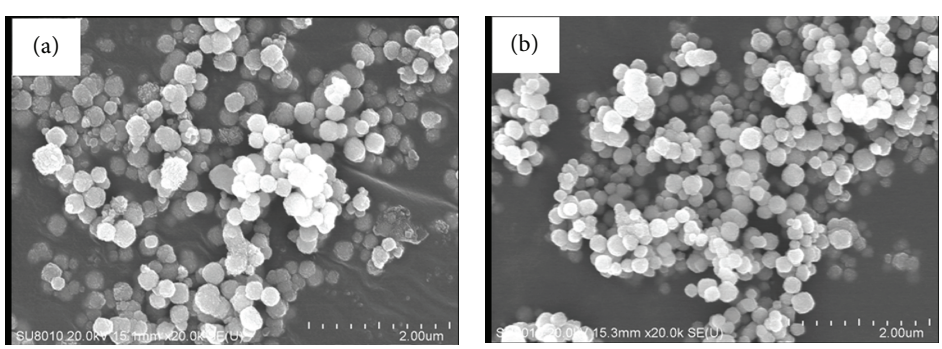
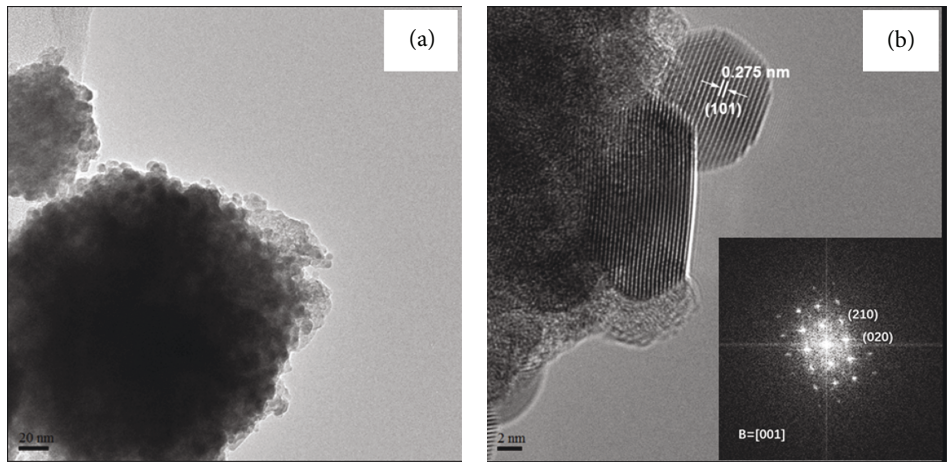


FIGURE 6: SEM photos of the NBT powders obtained at 200°C for (a) 2 h and (b) 6 h under 6 mol/L NaOH.



(a) (b)

Figure 7: (a) TEM photograph of NBT powders obtained at 200°C for 4 h under 6 mol/L NaOH. (b) HRTEM image of a single NBT particle. Inset: the FFT patterns of the single NBT particle.

spherical shape, as shown in Figure 4(c). The synthesis time also obviously influences the morphology and distribution of the NBT powders. Compared to Figures 6(a), 6(b), and 4(c), perovskite NBT powders with well-dispersed and spherical shape could be obtained at 200°C for 4 h under 6 mol/L NaOH, which can be considered as the most appropriate hydrothermal synthesis condition in this work.

To further characterize the crystallinity of NBT powders, TEM study on the particles was conducted. The typical TEM images of the NBT particles are shown in Figure 7. A spherical particle exhibited spherical agglomerates with the size of 200 nm in diameter which were consisted of smaller primary nanoparticles with the average size of 10~20 nm from Figure 7(a). The corresponding HRTEM image and fast Fourier transform (FFT) patterns of the single NBT particle are given in Figure 7(b). The interplanar spacing is about 0.275 nm, which matches well with the (101) lattice spacing (0.274 nm) of the perovskite NBT, demonstrating good crystallinity and the single crystal structure of the particle.

3.3. Formation Mechanism of NBT Powders. The hydrothermal chemical reaction process for the NBT powders can be described in the following chemical equation:

$$\mathrm{Ti(SO_4)_2 + NH_3 \cdot H_2O \longrightarrow TiO_2 + H_2O + NH_4^{+} + SO_4^{2-}} \quad (1)$$

$$\begin{aligned} \mathrm{TiO_2 + H_2O} &\longrightarrow \mathrm{TiO_2 \cdot nH_2O} \\ &\longrightarrow \mathrm{Ti^{4+} + OH^-} \end{aligned} \quad (2)$$

$$\begin{aligned} \mathrm{Bi(NO_3)_3 \cdot 5H_2O} &\longrightarrow \mathrm{Bi_2O_3 \cdot nH_2O + NO_3^-} \\ &\longrightarrow \mathrm{Bi^{3+} + OH^- + NO_3^-} \end{aligned} \quad (3)$$

$$\mathrm{NaOH \longrightarrow Na^{+} + OH^-} \quad (4)$$

$$\mathrm{Na^{+} + Bi^{3+} + Ti^{4+} \longrightarrow (Na_{0.5}Bi_{0.5})TiO_3} \quad (5)$$

In the first step (reaction (1)), with $Ti(SO_4)_2$ and ammonia as raw materials, hydrothermal reaction was carried out at 200°C for 2 h, resulting in 10 nm of TiO_2 nanopowder. In the second step, TiO_2 and H_2O was formed $TiO_2 \cdot nH_2O$ and Ti^{4+} successively, while $Bi(NO_3)_3 \cdot 5H_2O$ hydrolyzed into $Bi_2O_3 \cdot nH_2O$ and Bi^{3+}, NaOH dissolved into Na^+ and OH^- (reaction (2)-(4)). Then, Na^+, Bi^{3+}, and Ti^{4+} react to form NBT (reaction (5)).

In a hydrothermal reaction, the crystal growth mechanism usually has two ways including in situ crystallization and dissolution-recrystallization [30, 31]. Based on the NBT crystal growth and morphology discussed above, it is believed that these two growth mechanisms are included in this study. The formation mechanism of NBT spherical particles is illustrated in Figure 8. As shown in Figure 8, due to the solubility of $Bi_2O_3 \cdot nH_2O$ in solution (4.0×10^{-31}) is much larger than that of $TiO_2 \cdot nH_2O$ (1.0×10^{-40}), the $Bi_2O_3 \cdot nH_2O$, Bi^{3+}, Ti^{4+}, Na^+, and OH^- in the solution were absorbed on the surface of TiO_2 particles to form nuclei clusters and reduce the surface energy, leading to a stable NBT crystal developing via in situ growth mechanism. As the reaction proceeds, the poorly soluble $Bi_2O_3 \cdot nH_2O$ and $TiO_2 \cdot nH_2O$ precursors dissolve in a hydrothermal medium and enter the solution in the form of Bi^{3+}, Ti^{4+}, and OH^- to form individual growth units. Then, nucleation begins when the concentration of growth units is supersaturated than that of precursors, while the concentration of growth elements becomes lower than the solubility of the precursors, thus the precursors begin to dissolve. So repeated, the precursors are gradually dissolved completely; meanwhile, the corresponding NBT crystal grains were precipitated out in the solution. At this point, the dissolution-recrystallization mechanism plays a major role in causing the NBT crystal nucleuses agglomerated into spherical agglomerates and finally forming the NBT particles.

4. Conclusion

In summary, spherical NBT powders are successfully synthesized by a simple two-step hydrothermal method. Firstly, 10 nm-sized TiO_2 powders were hydrothermally synthesized with $Ti(SO_4)_2$ and ammonia as raw material at 200°C for 2 h.

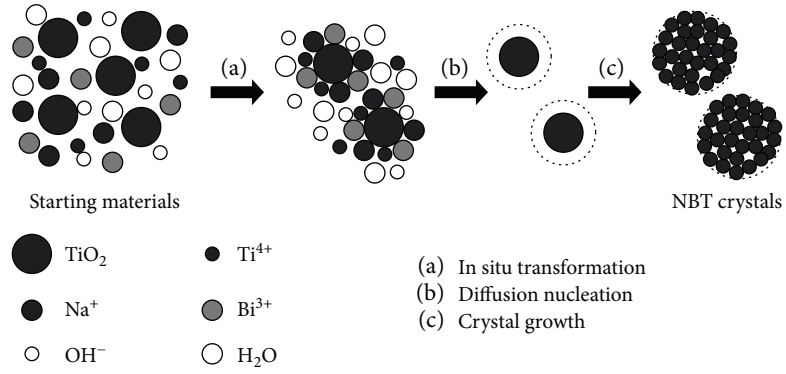


Figure 8: Schematic of the formation mechanisms for NBT spherical particles.

Then, hydrothermal reaction was carried out by adding $Bi(NO_3)_3{\cdot}5H_2O$ and NaOH mixed solution with wet TiO_2 powders obtained above at a certain temperature for several hours to get NBT powders. It was found that the hydrothermal conditions such as the mineralizer NaOH concentration, hydrothermal treatment temperature, and time have significant influences on the structure and morphology of the synthesized NBT powders. The NBT powders with a single perovskite phase were prepared at 200°C for 4 h with NaOH conditions of 6 mol/L. The NBT powders had a spherical morphology with uniform particle size about 200 nm and no agglomeration. The formation mechanisms of NBT nanosized powders can be summarized that nuclei clusters grew up on the surface of 10 nm-sized TiO_2 obtained in the first step via in situ growth mechanism, and then NBT crystal nucleuses agglomerated into spherical particles formed by the dissolution-recrystallization mechanism. The simple two-step hydrothermal method under the low mineralizer concentration and short reaction time is offered for uniform spherical NBT powders, which further has applications in the field of lead-free piezoelectric ceramics. Moreover, it is believed that the well-dispersed NBT powders with spherical shapes will be widely applied in high-frequency ultrasonic transducer and acoustic surface wave device.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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