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Short communication

Hydrothermal synthesis and characterization of $Na_{0.5}Bi_{0.5}TiO_3$ microcubes

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Abstract

$Na_{0.5}Bi_{0.5}TiO_3$ microcubes with smooth faces and clear, well-defined edges have been successfully prepared for the first time by a simple hydrothermal method without any surfactants. The as-prepared $Na_{0.5}Bi_{0.5}TiO_3$ microcubes showed an obvious emission band compared with nanoparticles, which is attributed to the different NBT morphology and size.

Keywords: Hydrothermal; $Na_{0.5}Bi_{0.5}TiO_3$ microcubes; Luminescence

1. Introduction

It is well known that materials' physical and chemical performances are greatly dependent on their composition, crystal phase, as well as surface properties that are strongly related to the particle shape and grain size [1–4]. Therefore, much effort has been devoted to synthesizing functional materials with controllable shape and size [1–4]. Uniformly cubic shaped nano- or microcrystals have attracted special interest due to their unique properties arising from the exposing well-defined crystal planes and their advantages in serving as building block for the further construction of multifunctional devices [1]. So far, a variety of cubes, such as Co_3O_4 nanocubes, Ag nanocubes, $KMnFe(CN)_6{\cdot}2H_2O$ microcubes and $ZnSn(OH)_6$ microcubes, have been successfully synthesized [5–8]. Bismuth sodium titanate $Na_{0.5}Bi_{0.5}TiO_3$ (abbreviated to NBT) has been considered to be an excellent candidate for a key material of lead-free ferroelectric materials [9,10]. Therefore, the fabrication of well-crystallized NBT crystallites with different morphologies is of fundamental importance in investigating the correlation between morphology and basic physical properties. NBT nano-sized whiskers and micron-sized plates have been synthesized by a hydrothermal process [11] and molten salt method [12]. However, there are few reports on the synthesis of NBT microcubes. In this paper, we first report the hydrothermal synthesis of NBT microcubes, furthermore, the PL property of the as-obtained NBT microcubes was also investigated for the first time, which is significant in investigating the correlation between morphology and basic physical properties.

2. Experimental

The chemical reagents used in the work were bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), titanium (IV) sulfate [$Ti(SO_4)_2$], sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH). All the chemicals were analytical grade purity and were used as received without further purification.

The hydrothermal process included the following steps: 0.005 mol $Bi(NO_3)_3$ and 0.01 mol $Ti(SO_4)_2$ were dissolved in 30 ml diluted HNO_3 (10%) to form aqueous solutions. Then, Na_2CO_3 solution was slowly added to the above solution to coprecipitate Ti^{4+} and Bi^{3+} ions by constant stirring and precipitate was formed. The precipitate was filtered, and washed with distilled water to remove NO_3^-, SO_4^{2-}, CO_3^{2-}, and Na^+ ions. Then, the precipitate was mixed with NaOH

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solutions under constant magnetic stirring for 5 min. The suspension solution was poured into the stainless-steel Teflon-lined autoclave for the hydrothermal treatment. The autoclave was sealed and maintained at 200 °C for 24 h. Finally, it was cooled down to room-temperature naturally. The products were filtered, washed with distilled water and absolute ethanol for several times, and then dried at 90 °C for 4 h for characterization.

X-ray diffraction was performed on a Rigaku X-ray diffractometer with high-intensity Cu Kα radiation. Scanning electron microscope (SEM) images were obtained from SIRION field-emission scanning electron microscope. The room-temperature luminescent spectra were performed on Hitachi F-4500 fluorescence spectrophotometer under excitation of Xe lamp.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples synthesized at 200 °C for 24 h with different NaOH concentrations. When the NaOH concentration was 4 M, the NBT phase was readily obtained. All XRD peaks can be indexed to a perovskite structure (JCPDS: 46-0001), and no other impurities could be detected. When further increasing NaOH concentration to 8 M, crystallization was more perfect. It is obvious that the diffraction peaks became stronger and sharper as NaOH concentration was increased to 10 M, which suggested that high NaOH concentration would favor the crystallization and evolution of NBT phase.

Fig. 2 shows SEM images of the NBT samples synthesized by the hydrothermal method with different NaOH concentrations. As presented in Fig. 2(a), agglomerated and irregular particles with an average size of about 50 nm were prepared as NaOH concentration was 4 M. When the NaOH concentration was increased to 8 M, as depicted in Fig. 2(b), the cubic-like NBT particles with a mean size of ca. 60 nm could be obtained and severe agglomeration was also observed. Remarkably, NBT microcubes with smooth faces and clear, well-defined edges were prepared in the case of further increasing NaOH concentration to 10 M, as exhibited in Fig. 2(c).

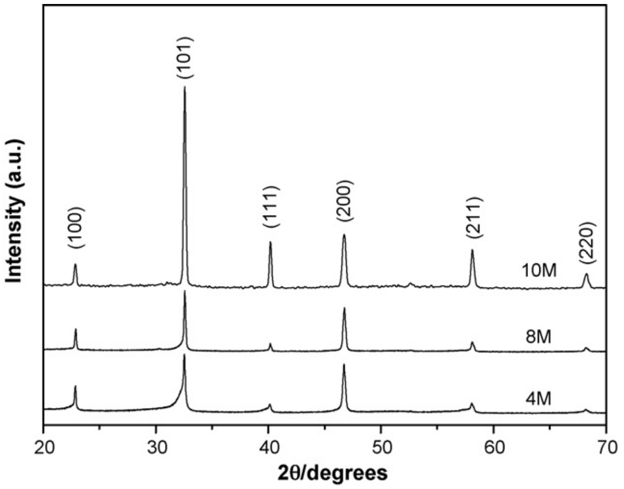

Fig. 1. XRD patterns of the samples prepared by the hydrothermal process at 200 °C for 24 h with different NaOH concentrations.

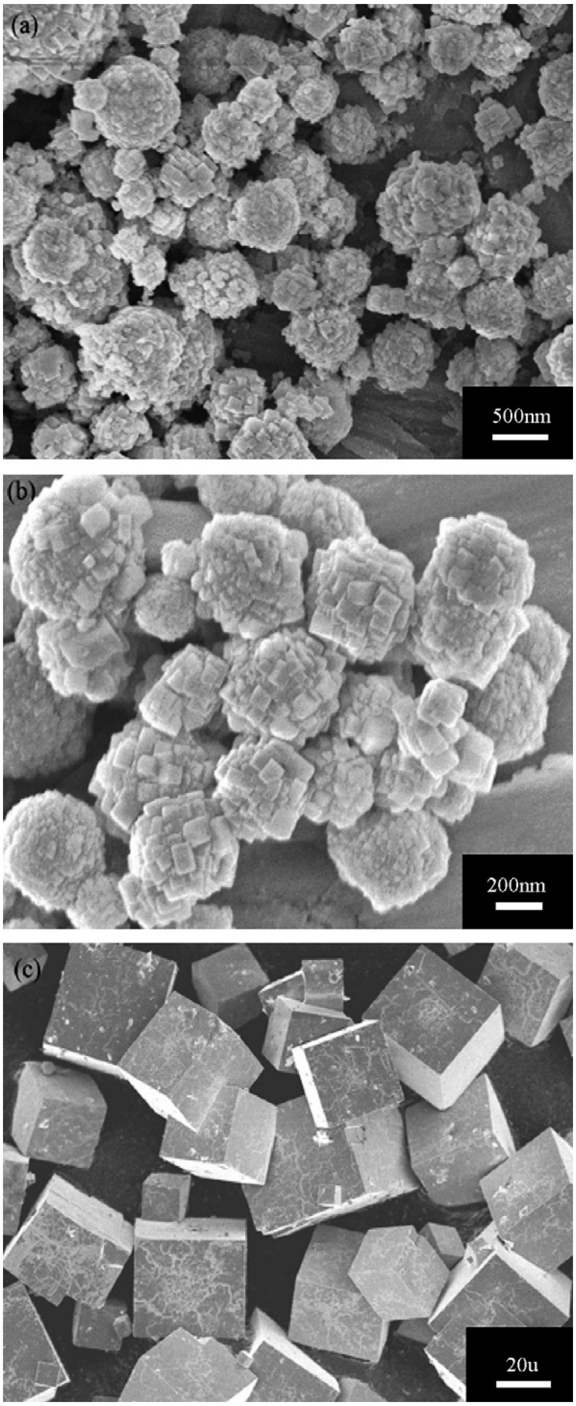

Fig. 2. SEM images of the samples prepared by the hydrothermal process at 200 °C for 24 h using NaOH concentration of (a) 4 M, (b) 8 M, and (c) 10 M, respectively.

As we know, during the hydrothermal process, the competition between crystal nucleation and crystal growth determines the size of the products [13]. The crystal size will be small on condition that the rate of crystal nucleation is greater than that of crystal growth. So in our experiment, NaOH concentration played a key role in adjusting the rate of crystal nucleation and crystal growth. We conjecture that the rate of

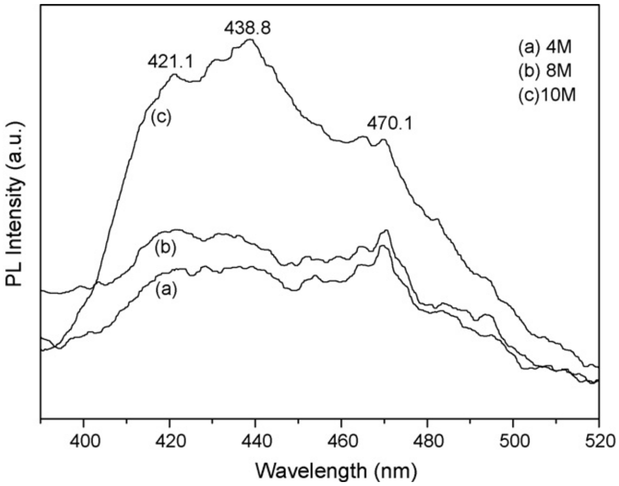

Fig. 3. Room-temperature PL spectra (with the excitation wavelength 350 nm) of the as-prepared NBT crystallites obtained by the hydrothermal process using NaOH concentration of (a) 4 M, (b) 8 M, and (c) 10 M, respectively.

crystal growth must be lower than that of crystal nucleation in the case of low NaOH concentration, so the nuclei of NBT crystals could grow only to nanometer size. However, when NaOH concentration increased up to 10 M, the rate of crystal growth must be highly greater than that of crystal nucleation, and NBT nuclei could easily grow up to micrometer size.

Room-temperature photoluminescence (PL) properties of the as-prepared NBT crystallites were studied. No obvious emission band of the obtained NBT nanoparticles was detected, as shown in Fig. 3(a and b), however, the NBT microcubes exhibited a broad emission band (Fig. 3c, peaking at ca. 421.1, 438.8, and 470.1 nm), which may be attributed to the different NBT morphology and size. The mechanism of the size- and morphology-dependent PL properties of NBT crystallites are in progress.

4. Conclusion

NBT microcubes have been successfully prepared for the first time by a hydrothermal method. It was found that NaOH concentration played an important role in the formation of size- and morphology-controlled NBT crystallites. Remarkably, the as-prepared NBT microcubes exhibited an obvious emission band (peaking at ca. 421.1, 438.8, and 470.1 nm) compared with NBT nanoparticles, which is of fundamental importance in investigating the correlation between morphology and basic physical properties. Further work is under way to study the growth mechanism of these microcubes and the possibility of synthesizing other related materials.

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