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Short communication

Low temperature polymer assisted hydrothermal synthesis of bismuth ferrite nanoparticles

Yonggang Wang, Gang Xu, Zhaohui Ren, Xiao Wei, Wenjian Weng, Piyi Du, Ge Shen, Gaorong Han *

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

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Abstract

BFO nanoparticles were successfully synthesized by a polymer assisted hydrothermal method at a temperature as low as 160 °C. The as-prepared powders, characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM), exhibited a pure BFO phase about 10 nm size and uniform sphere-like shape. It was found that the added polymer played a key role in decreasing the growing speed of BFO nuclei and resulted in the formation of BFO nanoparticles.

Keywords: Hydrothermal; Nanoparticles; Low temperature; Polymer

1. Introduction

Recently, a great deal of attention has been given to multiferroics, in which more than one of ferroelectric, ferromagnetic, and ferroelastic properties exhibit simultaneously, owing to the potential applications in new devices design as well as interesting fundamental physics studies [1–4]. However, such systems are rare in nature, as the usual atomic-level mechanisms driving ferromagnetism and ferroelectricity are inconsistent [5]. As one of the few multiferroic materials, $BiFeO_3$ (BFO) has been the focus of many studies, because it shows ferroelectricity and ferromagnetism at room temperature. BFO, rhombohedrally distorted perovskite structure with space group *R3c* at room temperature, is ferroelectric ($T_C = 830$ °C) and antiferromagnetic ($T_N = 370$ °C) [6].

Nanoscale materials have been widely investigated because of their unique electrical, magnetic, and optical properties arising from their low dimensionality and quantum confinement effect [7]. Since BFO was discovered in 1960, various techniques have been successfully developed to synthesize BFO nanoparticles, such as soft chemical route [8], ferrioxalate precursor method [9], microemulsion technique [10] and microwave-hydrothermal process [11]. However, these methods need a calcined process at a temperature of >400 °C, which is far from low cost and results in irregular morphology and broad distribution of particle size. So it has been considered a challenge to prepare BFO nanoparticles at a milder condition.

In our previous work, our group has successfully synthesized single-crystalline $PbZr_{0.52}Ti_{0.48}O_3$ nanowires by a hydrothermal technique assisted by polymer [12]. In this paper, we report the synthesis of BFO nanoparticles by a polymer-assisted hydrothermal method at a low temperature of 160 °C, which is so far the lowest synthetic temperature of BFO nanoparticles. The process has advantages of simplicity and energy saving.

2. Experimental

The chemical regents used in the work were bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], iron nitrate [$Fe(NO_3)_3{\cdot}9H_2O$], potassium nitrate (KNO_3), poly(vinyl alcohol) (PVA), and potassium hydroxide (KOH). All the chemicals were analytical grade purity and were used as received without further purification.

The mineralizer-assisted hydrothermal process included the following steps: 0.005 mol $Bi(NO_3)_3$ and 0.005 mol $Fe(NO_3)_3$ were dissolved in 100 ml diluted HNO_3 (10%) to form aqueous solutions. Then, the KOH solution was slowly added to the above solution to adjust its pH value to 8 by constant stirring and a brown precipitate was formed. The precipitate was

* Corresponding author. Tel.: +86 571 87951649; fax: +86 571 87952341.
E-mail address: hgr@zju.edu.cn (G. Han).

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filtered, and washed with distilled water to remove NO_3^{-1} and K^+ ions. Then, 2 g precipitate was mixed with 30 ml KOH solutions (12 M) and 15 ml PVA (4 g/l) solutions under constant magnetic stirring for 5 min. The suspension solution was poured into the stainless-steel autoclave for the hydrothermal treatment. The autoclave was sealed and maintained at 160 °C for 9 h, respectively. Finally, they were cooled to room temperature naturally. The BFO powders were also synthesized for comparison by a direct hydrothermal method without any mineralizer. The products were filtered, washed with distilled water and absolute ethanol several times, and then dried at 70 °C for 4 h for characterization.

X-ray diffraction was performed on a Rigaku X-ray diffractometer with high-intensity Cu Kα radiation. Transmission electron microscope (TEM) images were taken with a JEOL, 200CX TEM using an acceleration voltage of 160 kV.

3. Results and discussion

The XRD spectra of BFO powders synthesized by a hydrothermal method at 160 °C for 9 h with and without the addition of polymer are shown in Fig. 1(a) and (b), respectively. All the diffraction peaks in the two XRD patterns can be indexed as a pure phase BFO with a rhombohedrally distorted perovskite structure belonging to *R3c* space group, which match well with the literature data (JCPDS: 86-1518). No other phases could be detected. This means that well-crystallized BFO crystals could be obtained by the present hydrothermal process. It is worth pointing out that the samples exhibit few differences in XRD intensity with or without the addition of polymer, possibly indicating that the introduction of polymer in hydrothermal process has no effect on the crystallization of BFO crystallites.

Fig. 2 displays the transmission electron microscope images of the as-prepared samples synthesized by the hydrothermal process at 160 °C for 9 h (a) without an addition of polymer and (b) assisted by polymer. As exhibited in Fig. 2(a), micrometer-sized BFO crystals with the clear crystal facets could be observed in the BFO powders prepared by a direct hydrothermal method without any addition. The BFO crystals were nearly like "cubic sugar" in morphology, with an average side size of about 100–120 nm, similar to the previous report [13] in particle size. However, as shown in Fig. 2(b), when polymer was added, the as-prepared BFO powders consist of uniform sphere-like particles with an average diameter of about 10 nm. Although the above two XRD patterns are similar, the size and morphology of BFO crystals synthesized under different hydrothermal conditions are completely different, which is also reasonable according to the literatures [14,15].

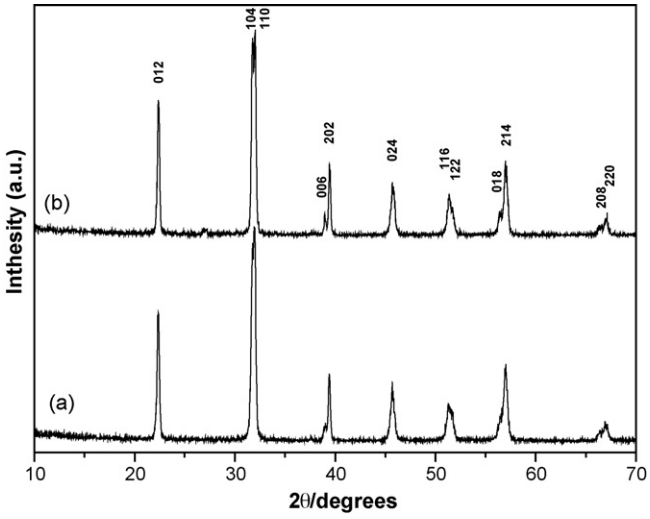

Fig. 1. X-ray diffraction patterns of the as-prepared samples synthesized by the hydrothermal process at 160 °C for 9 h (a) without any mineralizer and (b) assisted by polymer.

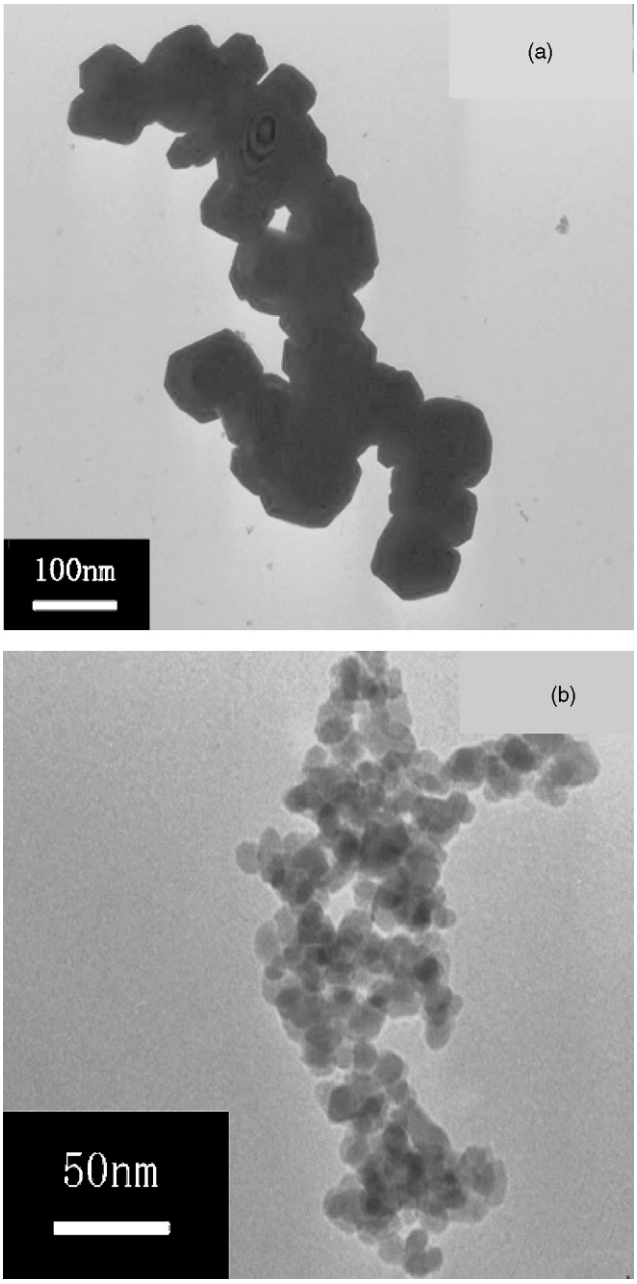

Fig. 2. Transmission electron microscope images of the as-prepared samples synthesized by the hydrothermal process at 160 °C for 9 h (a) without any mineralizer and (b) assisted by polymer.

As we known, during the hydrothermal process, the competition between crystal nucleation and crystal growth determines the size of the products [16]. 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, polymer evidently played a key role in limiting the growth speed of BFO crystals. We conjecture that the rate of crystal growth must be greater than that of crystal nucleation in case of no addition of polymer, so the nuclei of BFO crystals could grow easily up to micrometer size. However, in the presence of polymer, the polymer would attach to the surface of BFO nuclei to lower surface energy, which might noticeably decrease the growing speed of BFO nuclei and limit the size of BFO particles to the nanometer range.

4. Conclusion

Well-crystallized BFO nanoparticles, with an average diameter of about 10 nm, have been successfully synthesized by a hydrothermal method assisted by PVA at a low temperature of 160 °C. The introduced polymer has been found to play an important role in decreasing the growing speed of BFO nuclei and result in the formation of BFO nanoparticles.

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