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Short communication

Hydrothermal synthesis of single-crystal bismuth ferrite nanoflakes assisted by potassium nitrate

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Abstract

Well-crystallized single-crystal $BiFeO_3$ (BFO) nanoflakes have been successfully synthesized for the first time by the hydrothermal method assisted by KNO_3. The as-prepared samples were characterized by X-ray powder diffraction (XRD), transmission electron microscope (TEM), high-resolution TEM (HRTEM), and physical property measurement system (PPMS). It was found that KNO_3 played a key role in the formation of BFO nanoflakes. The as-prepared BFO nanoflakes were single-crystal in structure and showed super paramagnetic behavior at room temperature. It is expected that this process may be extended to the synthesis of other kinds of nanostructure materials, which will be beneficial to their detailed experimental investigation of the size- and morphology-dependent properties.

Keywords: Hydrothermal synthesis; Bismuth ferrite nanoflakes

1. Introduction

Multiferroic materials, which exhibit a coexistence of simultaneous ferroelectric and magnetic order parameters, have attracted increasing attention due to their fascinating fundamental physical properties and their potential applications in multifunctional devices [1–4]. However, there is a scarcity of single-phase materials in nature possessing multiferroic behavior. Among the currently studied single-phase compounds, $BiFeO_3$ (BFO) is the most outstanding, since it exhibits obvious ferroelectromagnetism at room temperature. The perovskite BFO is ferroelectric (T_C = 1103 K) and antiferromagnetic (T_N = 643 K) [5].

Various techniques, such as conventional solid-state reaction [6], co-precipitation [7], soft chemical route [8], ferrioxalate precursor method [9], micromulsion technique [10], hydrothermal route [11,12] and sol–gel process [13], have been developed to synthesize BFO micrometer- and nanometer-sized crystallites. And one-dimensional polycrystal BFO nanowires and nanotubes have also been successfully prepared by a template-based technique [14–16]. However, there is no report on the synthesis of two-dimensional BFO crystallites, which is of fundamental importance in investigating the correlation between morphology and basic physical properties.

In our previous work, our group has successfully synthesized single-crystal perovskite $PbZr_{0.52}Ti_{0.48}O_3$ nanowires by polymer-assisted hydrothermal method [17]. In this paper, we report the hydrothermal synthesis of two-dimensional single-crystal BFO nanoflakes.

2. Experimental

The chemical reagents 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), and potassium hydroxide (KOH). All the chemicals were analytical grade purity and were used as received without further purification.

0.005 mol $Bi(NO_3)_3$ and 0.005 mol $Fe(NO_3)_3$ were dissolved in diluted HNO_3 to form aqueous solutions. Then, the KOH solution was slowly added to the above solution to coprecipitate Fe^{3+} and Bi^{3+} ions by constant stirring and then a brown precipitate was formed. The precipitate was filtered, and

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washed with distilled water to remove NO_3^{-1} and K^+ ions. Then, the precipitate was mixed with 40 ml KOH solution (12 M), followed by adding 10 g KNO_3 under constant 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, 36 h, and 48 h, respectively. Finally, they were cooled down to room temperature naturally. The products were filtered and washed with distilled water for several times, and then dried at 70 °C for 4 h for characterization.

X-ray diffraction was performed on a Rigaku X-ray diffraction meter 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. High-resolution TEM (HRTEM) images were obtained on a JEOL-2010 HRTEM using an acceleration voltage of 200 kV. Magnetization was measured using physical property measurement system (PPMS-9T, quantum design).

3. Results and discussion

Fig. 1 shows the XRD patterns of the sample synthesized by the potassium nitrate-assisted hydrothermal process at 200 °C for 24 h. It can be found that all the diffraction peaks in the XRD pattern can be indexed to a pure phase BFO with a perovskite structure, well consistent with the literature values (JCPDS: 73-0548). The samples, synthesized via the same hydrothermal route at 200 °C for 36 h and 48 h, have above similar XRD patterns. These XRD patterns indicate that well-crystallized BFO crystallites can be obtained under the current synthetic conditions.

Previous report [11] showed that BFO powders hydrothermally prepared without the addition of KNO_3 consisted of uniform rectangle crystallites in the submicron range. Fig. 2 displays TEM photographs of the samples synthesized by the potassium nitrate-assisted hydrothermal process at 200 °C for 24 h, 36 h and 48 h, respectively. It is worth pointing out that the morphology of the as-prepared BFO nanaocrystallites was sensitive to the holding time and varied obviously with the

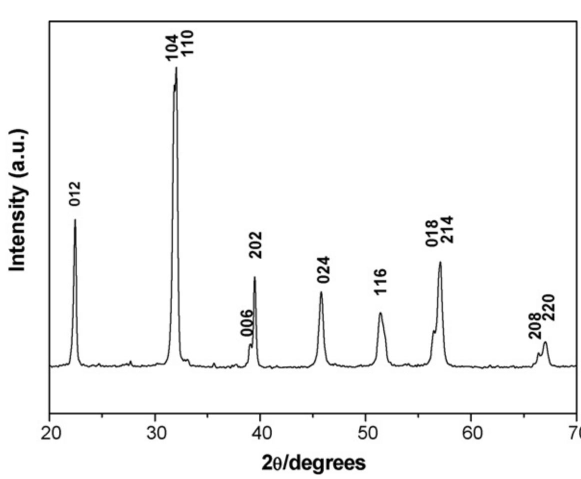

Fig. 1. XRD patterns of the as-prepared sample synthesized by the potassium nitrate-assisted hydrothermal process at 200 °C for 24 h.

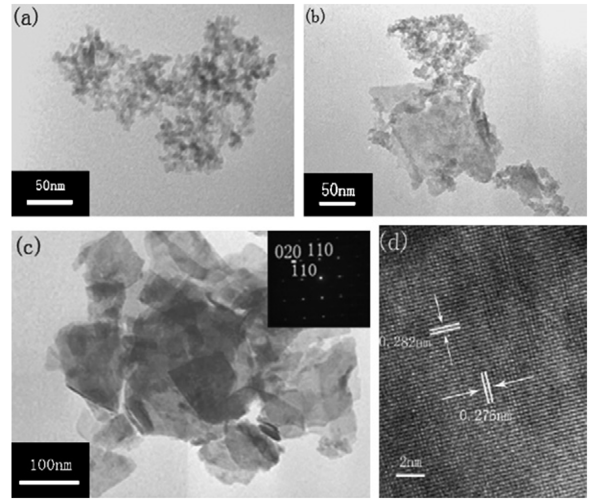

Fig. 2. Transmission electron microscope images of the as-prepared samples synthesized by the potassium nitrate-assisted hydrothermal process at 200 °C for (a) 24 h, (b) 36 h, and (c) 48 h, respectively, and electron diffraction pattern of a chosen randomly nanoflake (inset). (d) High-resolution TEM (HRTEM) image of one randomly chosen BFO nanoflake.

holding time. The BFO sample prepared at 200 °C for 24 h consisted of nanoparticles with average sizes of 5 nm, as shown in Fig. 2(a). However, a small quantity of nanoflakes began to appear when the holding time was increased to 36 h (Fig. 2(b)). When the holding time was further protracted to 48 h, the as-obtained crystallites were entirely composed of nanoflakes with a side length of about 100–200 nm, as depicted in Fig. 2(c). No significant preferred orientation is detected from the XRD patterns due to the random arrangement of these nanoflakes. Furthermore, it is reasonable that the as-prepared BFO crystallites with different morphologies exhibit similar XRD patterns [18–20]. The corresponding electron diffraction pattern (inset of Fig. 2(c)), taken from a randomly chosen single-nanoflake, confirmed that the as-prepared BFO nanoflakes are single-crystal in structure. The HRTEM image (Fig. 2(d)) of one randomly chosen BFO nanoflake shows clear crystal domain with a uniform interplanar spacing of 0.282 nm and 0.276 nm, corresponding to the (1 1 0) and $(\bar{1}\,1\,0)$ plane. Combined with above XRD results, it can be concluded that well-crystallized single-crystal BFO nanoflakes have been synthesized successfully by the present hydrothermal process assisted by KNO_3.

In this process, BFO nanoflakes possibly grew at the cost of nanoparticles. This phenomenon may be explained by the Ostwald ripening process [21], in which crystal growth is described in terms of growth of nanoflakes at the expense of nanoparticles. Reduction in surface energy is the primary driving force for crystal growth and morphology evolution. Nanoparticles would be gradually consumed when the reaction time was further prolonged. Finally, as shown in Fig. 2(c), well-crystallized single-crystal nanoflakes were obtained.

The variation of the magnetization of the as-prepared samples with an applied magnetic field at room temperature was also investigated in this paper. As shown in Fig. 3, the as-prepared BFO nanoflakes showed super paramagnetic behavior

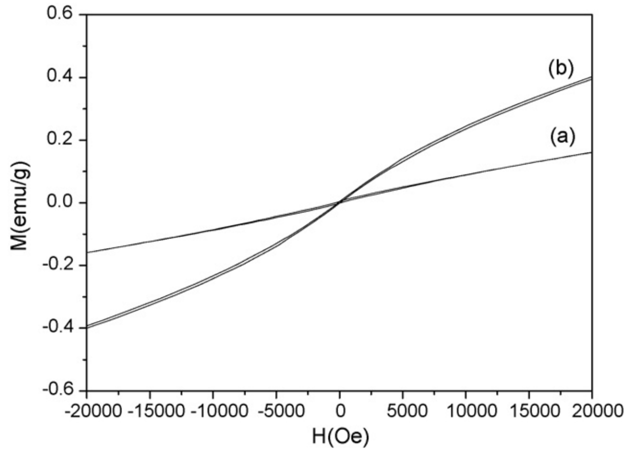

Fig. 3. The *M–H* curve measured at room temperature for the BFO (a) nanoflakes and (b) nanoparticles synthesized by the hydrothermal process.

at room temperature (Fig. 3(a)), and the magnetism of BFO nanoflakes was weaker than that of BFO nanoparticles (Fig. 3(b)). The variation of the magnetization of the as-prepared BFO samples may be ascribed to the effect of different morphology.

4. Conclusions

Well-crystallized single-crystal BFO nanoflakes have been successfully synthesized for the first time by the hydrothermal method assisted by KNO_3. It was found that KNO_3 played an important role in the formation of BFO nanoflakes and BFO nanoflakes possibly grew at the cost of nanoparticles. The as-prepared BFO nanoflakes showed super paramagnetic behavior at room temperature. It is expected that this process may be extended to the synthesis of other kinds of nanostructure materials, which will be beneficial to their detailed experimental investigation of the size- and morphology-dependent properties.

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