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Low-temperature synthesis of $Bi_2Fe_4O_9$ nanoparticles via a hydrothermal method

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Abstract

$Bi_2Fe_4O_9$ (BFO) nanoparticles were successfully synthesized by a hydrothermal method at a temperature as low as 100 °C. The as-prepared powders, characterized by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), transmission electron microscope (TEM) and physical property measurement system (PPMS), exhibited a pure BFO phase about 100 nm size with uniform sheet-like shape and exhibited an AF order at room temperature. It was found that high alkali concentration and alkali ion Na^+ played a key role in the formation of BFO nanoparticles at a low temperature of 100 °C.

Keywords: Hydrothermal; $Bi_2Fe_4O_9$ nanoparticles; Low temperature

1. Introduction

$Bi_2Fe_4O_9$ (BFO), is an important functional material because of its potential applications as a semiconductor gas sensor [1] and a good catalyst, which will possibly replace the high-cost, shortage and unrecoverable loss of catalysts (platinum, rhodium, and palladium alloys) for oxidizing ammonia to NO in the industrial process of nitric acid [2,3].

Early in the 1964, $Bi_2Fe_4O_9$ powders have been prepared by a traditional solid-state reaction [4] which needed high temperature (>850 °C) and harsh reaction conditions. $Bi_2Fe_4O_9$ powders prepared by this method are always relatively large in particle size and with impurities. Recently, single-crystalline $Bi_2Fe_4O_9$ cubes and nanowires have been successfully synthesized by the molten salt method [5] and template-induced sol–gel route [6], respectively, which still needed a high synthesis temperature of >800 °C. The hydrothermal process has been known to be one of the most important synthetic methods, which has advantages of low cost, simple process and well-controlled morphology. However, previous works [7,8,3] showed that a hydrothermal synthesis temperature of >180 °C must be required. Therefore, a method to obtain ultrafine $Bi_2Fe_4O_9$ powders by a hydrothermal process under a milder condition has been a goal for many researchers in this field.

In our previous work, our group has successfully synthesized $BiFeO_3$ nanoparticles by a hydrothermal technique at low temperature [9]. In this paper, we report the synthesis of pure $Bi_2Fe_4O_9$ nanoparticles by a hydrothermal method at a low temperature of 100 °C, which is so far the lowest synthetic temperature of $Bi_2Fe_4O_9$ crystallites.

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 hydroxide (KOH) 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 $Fe(NO_3)_3$ 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

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precipitate was formed. The precipitate was filtered, and washed with distilled water to remove NO_3^- and K^+ ions. Then, 2 g precipitate was mixed with 30 ml NaOH solutions (2, 7 and 12 M, respectively) 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 100 °C for 9 h, respectively. Finally, they were cooled down to room temperature naturally. The products were filtered, washed with distilled water and absolute ethanol for 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. EDS data were obtained with Oxford INCA in the high-resolution TEM (HRTEM). Magnetization was measured by using physical property measurement system (PPMS-9T, quantum design).

3. Results and discussion

The effect of alkali concentration on the formation of BFO was investigated. Fig. 1a–c shows the XRD patterns of the as-prepared powders, synthesized at 100 °C for 9 h using deferent NaOH concentrations of 2, 7 and 14 M, respectively. As shown in Fig. 1a, BFO began to crystallize at 100 °C with 2 M NaOH concentration, and the crystallization became a little better when the NaOH concentration increased to 7 M. Well-crystallized BFO crystallites with orthorhombic structure could be successfully synthesized at 100 °C when NaOH concentration was increased to 14 M, suggesting that high alkali concentration played an important role in the synthesis of BFO and could decrease obviously the synthesis temperature of BFO crystallites. Furthermore, the relative intensity of the reflection of (2 1 1) was much stronger than that of bulk materials in the JCPDS card (JCPDS: 25-0090), indicating the

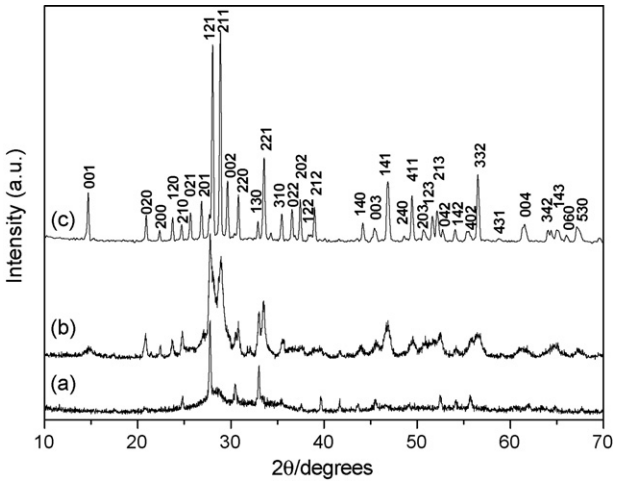

Fig. 1. XRD patterns of the as-prepared samples synthesized at 100 °C for 9 h using deferent NaOH concentrations of (a) 2 M, (b) 7 M and (c) 14 M, respectively.

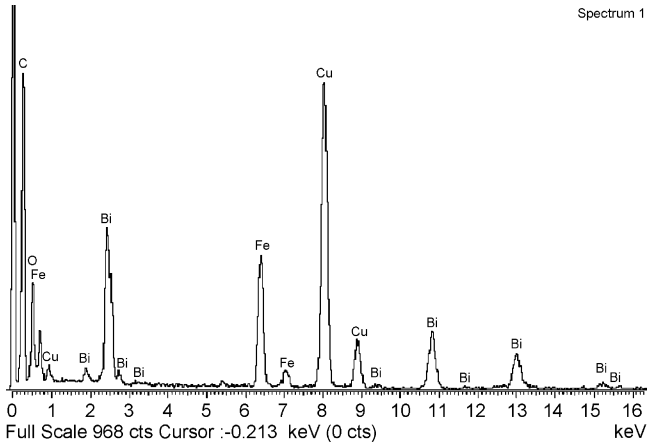

Fig. 2. EDS data of a single grain chosen randomly. The Cu and C peaks originate from the TEM grid.

presence of (2 1 1) orientation in the as-prepared powders. As shown in Fig. 2, the ratio of Bi and Fe, determined by EDS taken on a single grain chosen randomly in the high-resolution transmission electron microscope, approximately equals to 1:2, further demonstrating that $Bi_2Fe_4O_9$ crystallites have been synthesized successfully. The Cu and C signals arise from the TEM grids.

The effect of alkali metal Na^+ and K^+ ions on the formation of BFO was also investigated. The contrast experiment, in which 12 M NaOH was replaced by equimolar amount of KOH and other reaction conditions were unchanged, was done. As shown in Fig. 3, well-crystallized BFO crystallites could be obtained with 12 M NaOH, but not with 12 M KOH, indicating that the formation of BFO crystallites was affected by the type of alkali cations. It is well known that the alkali cations behave as structuring ions favoring the formation of certain zeolitic structures [10,11]. Similarly, Na^+ ions as structuring ions also had a pronounced effect on the synthesis of orthorhombic BFO.

Fig. 4 shows the TEM micrographs of the as-prepared BFO crystallites. It was remarkable that the BFO crystallites prepared at 100 °C for 9 h with 12 M NaOH were sheet-like

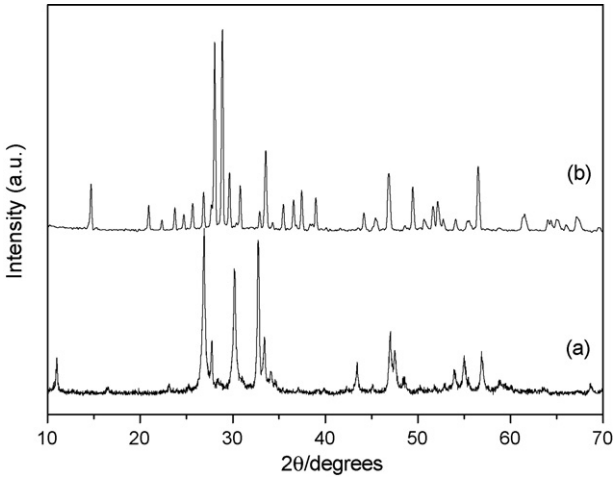

Fig. 3. XRD patterns of the as-prepared samples synthesized at 100 °C for 9 h with (a) 12 M KOH and (b) 12 M NaOH.

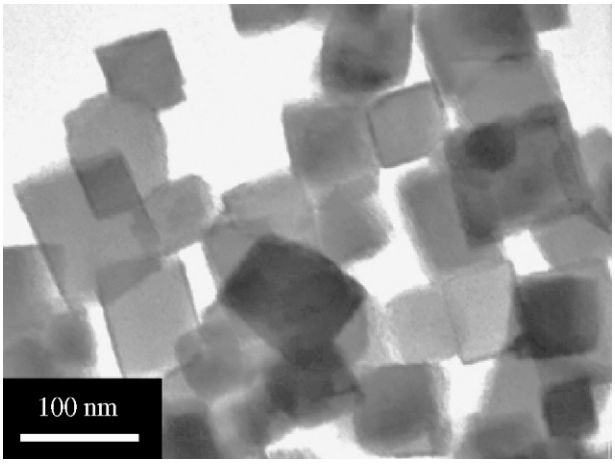

Fig. 4. Transmission electron microscope images of the as-prepared samples synthesized at 100 °C for 9 h with 12 M NaOH.

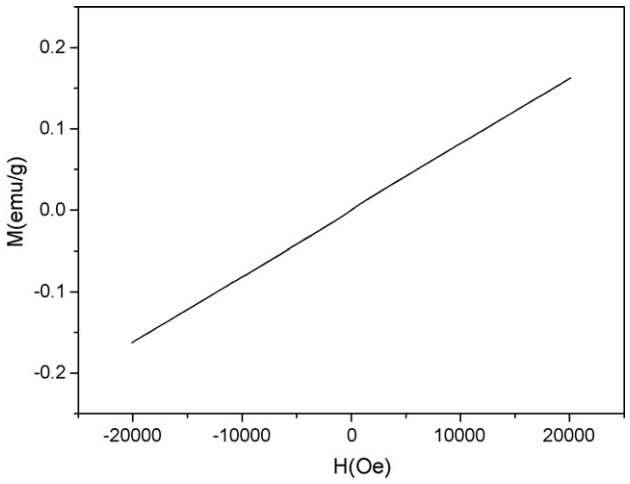

Fig. 5. The *M–H* curve measured at room temperature for the as-prepared samples synthesized by the hydrothermal process at 100 °C for 9 h with 12 M NaOH.

in morphology with a side length of about 100 nm, demonstrating that the orientation growth of the BFO crystallites existed during the present synthesis procedure, which was consistent with the above XRD results.

The magnetization of the as-prepared nanoparticles with an applied magnetic field at room temperature was also investigated in this paper. As shown in Fig. 5, the magnetic hysteresis loop showed a almost linear field dependence, similar to the report [7], and clearly demonstrated that the sample exhibited an antiferromagnetic (AF) order at room temperature. The AF order came from the superexchange interactions between the iron ions, which occupied sites of octahedral and tetrahedral coordination in equal amounts.

4. Conclusion

In conclusion, BFO nanoparticles were successfully synthesized by hydrothermal method at a low temperature of 100 °C. It is found that high alkali concentration can efficiently lower the BFO synthesis temperature and alkali cations Na^+ also have a key effect on the formation of BFO. It is rational to expect that some other nanoscale materials may be synthesized by this method on a milder condition.

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