

Bi₂Fe₄O₉ 纳米粉体: 水热法制备及表征

于志伟 苗鸿雁* 谈国强

(陕西科技大学材料科学与工程学院, 西安 710021)

关键词: Bi₂Fe₄O₉; 纳米粉体; 水热法

中图分类号: O614.81*1; O614.53*2; TQ135.3*2

文献标识码: A

文章编号: 1001-4861(2008)03-0483-04

Bi₂Fe₄O₉ Nanoparticles: Preparation by Hydrothermal Method and Characterization

YU Zhi-Wei MIAO Hong-Yan* TAN Guo-Qiang

(School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi an 710021)

Abstract: Bi₂Fe₄O₉ nanoparticles were prepared at low temperature via a facile, one-step hydrothermal synthesis process using iron(III) nitrate nonahydrate(Fe(NO₃)₃·9H₂O) and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) as starting materials and sodium hydroxide (NaOH) as the precipitant and mineralizer. XRD results indicate that the as-prepared nanoparticles are pure Bi₂Fe₄O₉. SEM images reveal that the as-prepared Bi₂Fe₄O₉ nanoparticles have a sheet-like morphology. The Bi₂Fe₄O₉ nanoparticles thus obtained are paramagnetic at room temperature as shown by magnetic measurements.

Key words: Bi₂Fe₄O₉; nanoparticles; hydrothermal

In the 1960s, the crystalline and magnetic structures of Bi₂Fe₄O₉ were investigated by neutron diffraction and Mössbauer measurements^[1,2]. Bi₂Fe₄O₉ is one of ferroelectric materials, which has not only potential applications in magnetic and ferroelectric devices, but also possesses the ability to couple the electric and the magnetic properties, providing an additional degree of freedom in device design^[3]. Moreover, its catalysis for ammonia oxidation to NO is of the current interests because it will possibly replace the high-cost, deficiency, and unrecoverable loss of commercial catalysts (platinum, rhodium, and palladium alloys) in the industrial process of nitric acid manufacturing^[4,5].

In 1964, solid-state sintering at over 850 °C was

used to synthesize Bi₂Fe₄O₉^[1]. However, for its disadvantages such as high synthesizing temperature, impurity readily to present with other compounds, large dimension and preparation conditions not to be easily controlled, new methods have to be developed. It is well-known that hydrothermal process includes methods which involve water both as a catalyst and occasionally as a component of solid phases in the synthesis at pressures (>a few atmospheres) and high temperatures (>100 °C). Hydrothermal method, as one of the best methods to produce pure fine oxide powders for its low cost, simple process, low temperature and high monodispersity, has been developed for synthesizing various nanocrystallites requiring a narrow distribution

收稿日期: 2007-10-17。收修改稿日期: 2007-12-15。

国家自然科学基金(No.50672055)资助项目。

* 通讯联系人。E-mail: mhy@sust.edu.cn

第一作者: 于志伟, 男, 25 岁, 硕士; 研究方向: 功能材料及薄膜。

of particle size, phase homogeneity and controlled particle morphology^[6,7].

In the present work, $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles were prepared via a hydrothermal synthesis method. The effect of hydrothermal conditions on the preparation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles was investigated.

1 Experimental

1.1 Preparation of precursor

Before the hydrothermal synthesis procedure, precursor was prepared. In a typical process: the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (250 g/A.R., Xi an Chemical Reagent Company) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (250g/A.R., Xi an Chemical Reagent Company) without further purification were used as raw materials, and in all of reaction solutions $C_{\text{Fe}}=0.025 \text{ mol} \cdot \text{L}^{-1}$, $n_{\text{Fe}}/n_{\text{Bi}}=2$. A mixture of 10 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 5 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved into 20 mL glycol, after the stock solution stirred for 30 min, 200 mL distilled water was added to the solution with stirring and a faint yellow emulsion was gained, then ammonia was dropped into the solution until the pH value 9~10 to form the precursor. The as-prepared precursor was washed with distilled water several times until the precursor solution was neutral.

1.2 Hydrothermal synthesis procedure

The precursor was transferred into a Teflon container with a capacity of 40 mL kept in a stainless steel autoclave, and the filling ratio was fixed at 75%. The analytically pure NaOH was used as the precipitant and mineralizer with a concentration (C_{NaOH}) range from 0.1 to 1.0 $\text{mol} \cdot \text{L}^{-1}$. Then the autoclave was sealed and heated at 180~240 °C for 24 h. The products were collected at the bottom of the autoclave after it was furnace-cooled to room temperature. Yellow powders were obtained after the filtrates were washed several times with distilled water and dried at 60 °C for 6 h.

1.3 Characterization

X-ray diffraction (XRD) data of Powder were collected with a Rigaku D/max2200PC X-ray diffractometer (Cu K α , $\lambda=0.15418 \text{ nm}$, DS-RS-SS=1 °0.3 mm $^{-1}$; Graphite monochromator, Solid detector, 40 kV \times 40 mA), it was operated under the stepping scanning mode in a scanning range of 2 θ =10°~70° with steps of

0.02° at a scanning speed of 8°·min $^{-1}$. The morphologies and microstructures of the samples were taken with a scanning electron microscope (SEM, FEI Quanta 200: 200 V ~30 kV, 6 $\times 10^{-4}$ Pa, resolution of 3.5 nm). Room temperature magnetic property was measured with a vibration sample magnetometer (VSM, BHV-55) up to H=10 kOe.

2 Results and discussion

Fig.1 shows XRD patterns of the samples prepared at different heating temperatures (T_{heating}). All the samples are phase-pure without any observable impurities. All diffraction peaks can be perfectly indexed to the orthorhombic $\text{Bi}_2\text{Fe}_4\text{O}_9$ (JCPDS:20-0836) with space group Pbam. The lattice constants for a typical sample prepared at 180 °C are obtained as $a=0.7905 \text{ nm}$, $b=0.8448 \text{ nm}$ and $c=0.5988 \text{ nm}$. As Fig.1 obviously shows, with T_{heating} rising from 180 to 240 °C, the peak intensities increase gradually, indicating the improvement of crystallization. In addition, the relative intensity along (001) and (002) directions increase with T_{heating} quickly, which infers that the crystallites possibly exhibits an over growth along the (001) or (002) plane.

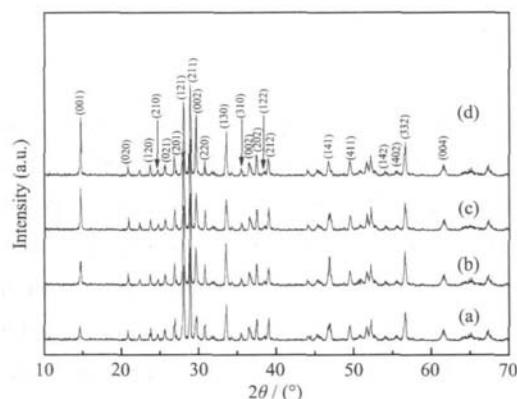


Fig.1 XRD patterns of the samples prepared at different heating temperatures (T_{heating}) with $C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$: (a)180 °C, (b)200 °C, (c)220 °C, and (d)240 °C

Fig.2 shows XRD patterns of the samples prepared at 180 °C for 24 h with different concentrations of NaOH (C_{NaOH}). From XRD results, it is found that the pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ can be obtained only when C_{NaOH} is over 0.25 $\text{mol} \cdot \text{L}^{-1}$. When C_{NaOH} is lower than 0.15 $\text{mol} \cdot \text{L}^{-1}$, the as-prepared products are pure BiFeO_3 (PDF:20-0169). When $C_{\text{NaOH}}=0.2 \text{ mol} \cdot \text{L}^{-1}$, not only main phase

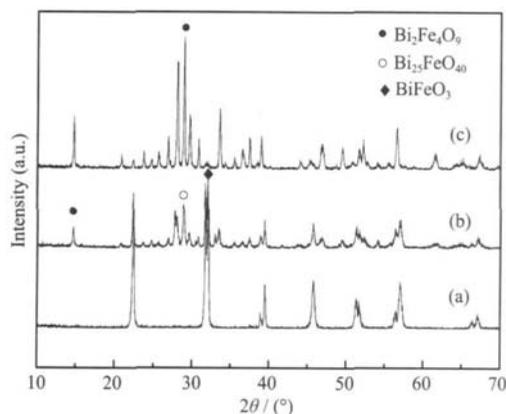


Fig.2 XRD patterns of the samples prepared at 180 °C for 24 h with different concentration of NaOH (C_{NaOH}): (a) 0.15 mol·L⁻¹, (b) 0.20 mol·L⁻¹, (c) 0.25 mol·L⁻¹

BiFeO_3 , but also a scale of $\text{Bi}_{25}\text{FeO}_{40}$ (PDF:46-0416) and

$\text{Bi}_2\text{Fe}_4\text{O}_9$ are formed in the products.

Fig.3(a~d) shows the morphologies and microstructures of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples synthesized at different heating temperatures (T_{heating}) with $C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$. It can be seen that size and shape of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles are strongly dependent on temperature. Fragment-like particles with a shaggy appearance can be obtained if $T_{\text{heating}}=180$ (Fig.3(a)). With $T_{\text{heating}}=200$, particles exhibit flat faces and irregular sheet shape (Fig.3(b)). When T_{heating} increases to 220, the samples have a laminar shape with an average thickness about 200 nm (Fig.3(c)). Higher temperature ($T_{\text{heating}}=240$) results in smaller, thinner and smoother particles, which are uniform and regular square nanocrystallites with a size of about 450 nm and thickness around 100 nm (Fig.3(d)).

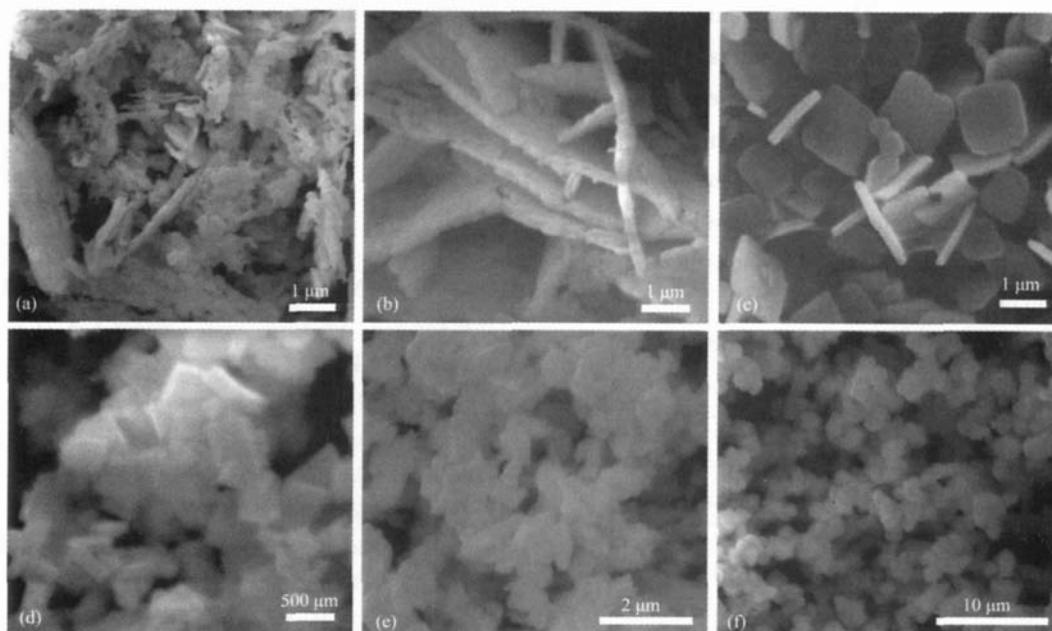


Fig.3 SEM images of $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples synthesized at different temperatures $C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$, with precursor: (a) 180 °C, (b) 200 °C, (c) 220 °C, and (d) 240 °C; without precursor: (e) 220 °C, and (f) 240 °C

The formation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles can be ascribed to a typical hydrothermal ripening process. Generally, the hydrothermal process is controlled by the dissolution/recrystallization mechanism^[8-10]. When the reactants are heated, hydrolyzation will occur. During this process, the precursors are dissolved in the aqueous solution to form anisotropic $\text{Bi}_2\text{Fe}_4\text{O}_9$ nuclei. It is believed that two-dimensional growth occurs only when the chemical potential of two surfaces is much higher than others. The size, morphologies and microstructures

are affected by the probabilities of crystal nucleation and crystal growth. If the probability of the crystal nucleation is higher than that of the crystal growth, the crystallites will be small; otherwise the large one will be obtained. Evidently, when T_{heating} increases from 180 to 240 with $C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$, the dissolution/recrystallization during the hydrothermal reaction process becomes more vigorous, facilitating a fast nucleating process and hence the formation of large numbers of crystal nuclei, resulting in smaller and regular $\text{Bi}_2\text{Fe}_4\text{O}_9$

particles.

Fig.3 (e and f) shows SEM pictures of powders produced without preparing precursor before hydrothermal synthesis. We can see that the as-prepared powders are rough and irregular, and the size of the particles is more than 1 μm . Comparing to the same synthesizing conditions (c, d and e, f), the products prepared with precursor are well crystallized and more uniform, and also have a smaller particle size. It can be seen that the precursor plays an important role in hydrothermal synthesis of $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanoparticles.

The magnetic measurement result of the sample prepared at 240 $^\circ\text{C}$ with $C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$ is shown in Fig.4. It displays that the fresh sample is paramagnetic in agreement with previous neutron diffraction and Mössbauer measurements. The fundamental paramagnetic studies on Fe metal particles^[11] indicate that size is the only factor to control their paramagnetic properties and paramagnetic state usually exists in metal particles within a few size nanometers ranges. The as-prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles are nanometer sized, well crystallized and uniform square crystallites, therefore have a good characteristic of paramagnetism.

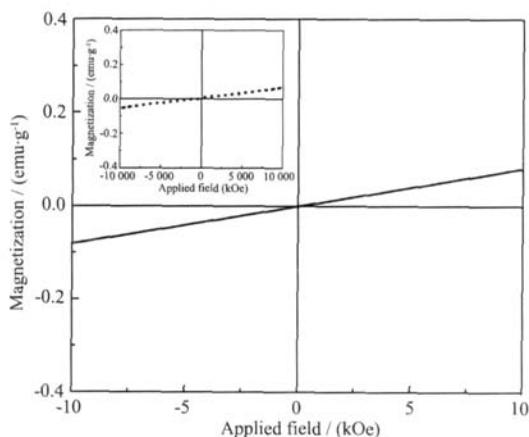


Fig.4 Magnetization curve versus external magnetic field of the fresh samples. The inset shows the true test data. ($C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$, $T_{\text{heating}}=240 \text{ }^\circ\text{C}$, 24 h)

3 Conclusions

Crystalline and uniform $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles with different morphologies were selectively synthesized by tuning hydrothermal conditions. The heating temperature and the alkaline concentration both have influences on the morphologies, microstructures and growth orientations of the final crystallites. The high-quality square nanocrystallites were obtained at the heating temperature of 240 $^\circ\text{C}$ with $C_{\text{NaOH}}=0.5 \text{ mol} \cdot \text{L}^{-1}$ in the precursor solution. The magnetic measurement indicates that the as-prepared samples exhibit a paramagnetic order at room temperature.

In conclusion, the concentration of alkalinity in the precursor solution and heating temperature play important roles in the preparation of pure $\text{Bi}_2\text{Fe}_4\text{O}_9$.

Acknowledgement: This work was supported by National Science Foundation of China (Grant Nos. 50672055).

References:

- [1] Koizumi H, Niizeki N, Ikeda T. *J. Appl. Phys.*, 1964,3:495~496
- [2] Bokov V A, Novikov G V, Trukhtanov V A, et al. *Phys. Solid State*, 1970,11:2324~2326
- [3] Salje E K H. *Phase Transitions in Ferroelastic and Co-elastic Crystals*. Cambridge University Press, Cambridge, 1990
- [4] Zakharchenko N I. *J. Appl. Chem.*, 2000,73:2047~2051
- [5] Zakharchenko N I. *Kinet. Catal.*, 2002,43:95~98
- [6] Somiya S, Roy R. *Bull. Mater. Sci.*, 2000,23:453~460
- [7] Yanagisawa K. *J. Ceram. Soc. Jan.*, 2005,113:565~572
- [8] Yu SH, Liu B, Mo M S, et al. *Adv. Funct. Mater.*, 2003,13:639~647
- [9] Hirano M, Kato E. *J. Am. Ceram. Soc.*, 1996,79:777~780
- [10] Hirano M, Kato E. *J. Am. Ceram. Soc.*, 1999,82:786~788
- [11] CHEN Xing(陈兴), DENG Zhao-Xiang(邓兆祥), LI Yu-Beng(李宇鹏), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, 2002,18:460~464