Hydrothermal Synthesis and Characterization of $Bi_2Fe_4O_9$ Nanoparticles

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Sheet-like $Bi_2Fe_4O_9$ nanoparticles were successfully synthesized by a rather facile hydrothermal process. Transmission electron microscopic (TEM) and selected area electron diffraction (SAED) studies show that the particles are sheet-like, about 30 nm in the direction of thickness. X-ray diffraction (XRD) analysis indicated that the as-prepared particles were pure $Bi_2Fe_4O_9$, but after storing at room temperature for half a year, γ-Fe_2O_3 appeared. The magnetic properties of the nanoparticles before and after storing were characterized by a vibration sample magnetometer (VSM).

In the 1960s, the crystalline and magnetic structures of $Bi_2Fe_4O_9$ had been investigated by neutron diffraction and Mössbauer measurements.[1–4] Moreover, its catalysis for ammonia oxidation to NO is of current interest 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.[5,6]

During the past decades, nanoscale materials have sparked a worldwide interest for their unique electronic, optic, catalytic, and magnetic properties and their potential application in the next generation nanodevices.[7–10] Early in the 1964, solid-state sintering at temperatures over 850 °C has been used to synthesize $Bi_2Fe_4O_9$.[1] However, for its disadvantages such as high temperature, impurity readily present with other compounds, large dimension, and condition not to be easily controlled, new methods of the preparation have been investigated until now. It is well known that hydrothermal processing, for its low cost, simple process, low temperature synthesis and high monodispersion of product, has been developed for the synthesis of various nanocrystals, which have a narrow distribution of particle size, phase homogeneity, and controlled particle morphology.[11–14] Since the catalytic activity increases with the surface-to-volume increase, the nanocrystals obtained by mild hydrothermal conditions are expected to have more application in the field of the catalysis. In our present work, $Bi_2Fe_4O_9$ nanoscale powders were prepared at 180 °C via a hydrothermal process.

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) and iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) were used as starting materials. The typical synthesis condition was briefly described as following: 5 mmol of bismuth nitrate pentahydrate and 5 mmol of iron nitrate nonahydrate were dissolved into 5 mL dilute nitric acid (1 M) together to make solution A. Then, 6.20 g of sodium hydroxide (NaOH) was dissolved into 20 mL distilled water to make solution B. The solution B was dropwise added to the solution A with vigorous stirring. After 10 min, the reaction mixture was transferred to a Teflon-lined stainless autoclave till 80% of its volume was filled. Then, the autoclave was sealed and maintained at 180 °C for 24 h. After the reaction completed, the autoclave was cooled to room temperature on standing. The saffron products was collected by filtration, and washed several times with distilled water and ethanol, and then dried at 60 °C for 6 h in air. The as-synthesized sample was characterized by X-ray powder diffraction (XRD) using a Rigaku D/max-rA diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å.), Transmission electron microscopic (TEM) and selected area electron diffraction (SAED) studies were carried out by a Hitachi Model H-800 instrument with a tungsten filament using an accelerating voltage of 200 kV. Room temperature M–H loops were measured on a vibration sample magnetometer (VSM, BHV-55) up to H = 10 kOe for magnetization measurements.

The XRD pattern of the newly prepared $Bi_2Fe_4O_9$ powders was shown in Figure 1(a). All diffraction peaks in Figure 1(a) can be perfectly indexed to the orthorhombic $Bi_2Fe_4O_9$ [space group: *Pbam*] with lattice constants of $a = 7.995$ Å, $b = 8.440$ Å and $c = 5.994$ Å (JCPDS 25-0090). The average particle sizes are 27, 23 and 22.6 nm calculated by using the Debye–Scherrer formula from the reflection of (211), (121), and (130), respectively. Also, we find that the relative intensity of the reflection of (211) to other peaks is much stronger than those of bulk materials in the JCPDS card, indicating the presence of (211) orientation in the sample. The XRD pattern of the $Bi_2Fe_4O_9$ sample placed for six months under ambient conditions is shown in Figure 1(b). All diffraction peaks can be indexed to the pure $Bi_2Fe_4O_9$, but a very weak peak ($d = 2.9396$ Å) in the diffraction can be indexed of γ-Fe_2O_3. We conjecture that the impurity results from the slow decomposition of a small quantity $Bi_2Fe_4O_9$. The possible reaction is shown as following:

$$Bi_2Fe_4O_9 \rightarrow Bi_2O_3 + 2\gamma\text{-}Fe_2O_3 \tag{1}$$

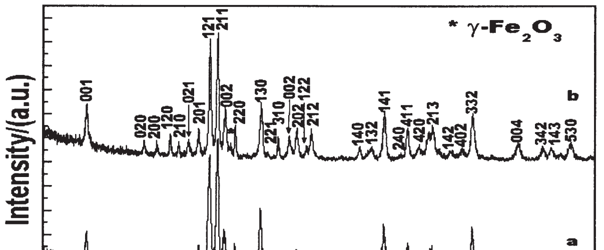

Figure 1. XRD patterns of the $Bi_2Fe_4O_9$ via a hydrothermal process, (a) fresh sample; (b) sample placed six months at ambient conditions. A very weak peak in (b) was assigned to γ-Fe_2O_3, which resulted from the decomposition of $Bi_2Fe_4O_9$.

Figure 2 shows a typical TEM image of the as-prepared sample. The TEM image reveals that the sample consists of a large number of sheet-like particles and the selected area elec-

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tron diffraction (SAED) of one typical particle confirms the single crystal feature of the particles. The above results reveal that the orientation growth of the particles occurs in the process of the synthesis, which agree with the results of the X-ray diffraction.

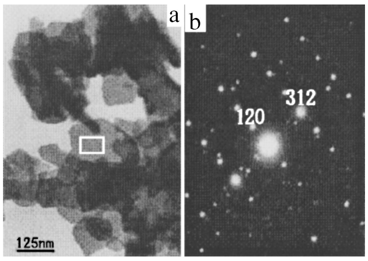

Figure 2. A typical TEM image (a) and select area electron diffraction (SAED) (b) of an as-prepared sample.

The magnetic measurement results of the samples before and after storing for half a year were shown in Figure 3. It showed that the fresh sample is paramagnetic in agreement with previous neutron diffraction and Mössbauer measurements.[3,4] The permeability χ of the products is equal to 6.99×10^{-6} H/m. But it is surprising that we could observe the magnetic hyteresis loop in the sample placed for six months under ambient conditions, as shown in the inset of Figure 3.

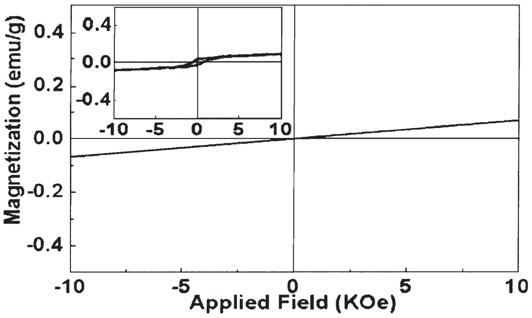

Figure 3. The magnetization curves versus external magnetic field of the fresh sample, showing a distinct paramagnetism. The inset shows a magnetic hysteresis loop for the sample placed for six months at ambient condition, which arised from the impurity of γ-Fe_2O_3.

We note that the coercive force of the measured sample (Hc = 699Oe) is very close to that of the pure γ-Fe_2O_3 ($Hc =$ 714Oe).[15] Furthermore, combined with the X-ray diffraction of the sample placed for six mouths under ambient condition, we believe that the magnetic hysteresis loop, characteristic of the ferromagnetic materials, was atlributed to the impurity of γ-Fe_2O_3, formed from $Bi_2Fe_4O_9$ by decomposition, as shown in the Eq 1.

We find that the concentration of the metal ions, alkalinity in the precursor solution, and temperature play key roles in preparing the pure $Bi_2Fe_4O_9$, while the molar ratio of the Bi^{3+}/Fe^{3+} seems to be less important. When the concentration of metal ions ($[M^{3+}]$) was 0.02 and 0.1 mol/L, pure $BiFeO_3$ and $Bi_2Fe_4O_9$ were obtained, respectively. A mixture of the two compounds was formed if the $[M^{3+}]$ was higher than 0.02 mol/L and lower than 0.1 mol/L. Moreover, it is found that the higher concentration favoured the formation of pure $Bi_2Fe_4O_9$. In our experimental process, it was necessary that the molar ratio of the hydroxide ions to the sum of metal ions ($N = OH^-/(Bi^{3+} + Fe^{3+})$) in the precursor solution should be kept very high; otherwise $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{25}FeO_{40}$ would coexist (Figure 4a). The lower N in the solution, the more quantities of the $Bi_{25}FeO_{40}$ would form. The pure $Bi_{25}FeO_{40}$ could not be prepared until the pH decreased to 8.5, and pure $Bi_2Fe_4O_9$ would be formed if the value of N was up to 15. The influence of the phase components was not evidenced when the value of N exceeded 15. Furthermore, the experiments were carried out at 120, 150, and 180 °C for 24 h. When the precursor solution in an autoclave was treated at 120 and 150 °C (Figure 4b), no $Bi_2Fe_4O_9$ was formed and the product was almost pure $Bi_{25}FeO_{40}$. As the temperature increases to 180 °C, the pure well-crystallized $Bi_2Fe_4O_9$ could be obtained. When the molar ratio of the Fe^{3+} and Bi^{3+} ions ($m = Fe^{3+}/Bi^{3+}$) was in the range of 1 and 2 and the other conditions were the same, no impurities were formed, which was different from the previous results in Ref. 1.

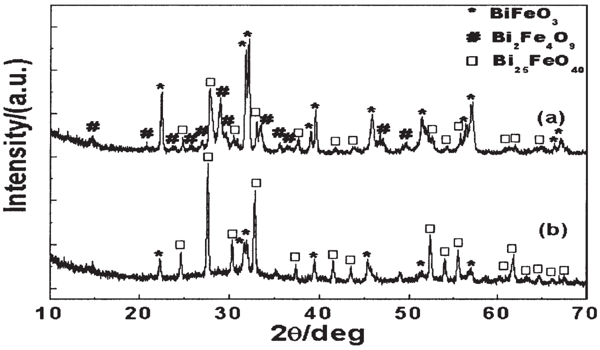

Figure 4. The XRD patterns of the samples formed at different conditions. (a) N = 9, $[M^{3+}] = 0.1$ M and 180 °C. (b) N = 15, $[M^{3+}] = 0.1$ M and 150 °C.

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