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LETTER TO THE EDITOR

Soft magnetic nanoparticles of $\text{BaFe}_{12}\text{O}_{19}$ fabricated under mild conditions

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Abstract

Nanoparticles of barium hexaferrite, with an average size of 12 nm, were prepared by a hydrothermal route at relatively low temperatures (140–180 °C). The effects of reaction temperature and time on the particle size and magnetic properties were discussed. The nanoparticles show a soft magnetic feature with a saturation magnetization of 1.1 emu g⁻¹ and coercivity of 221.0 Oe, rather than the hard magnetic characteristic that the corresponding bulk material exhibits. Annealing treatment in air at 800 °C led to an order-of-magnitude increase of the saturation magnetization (67.3 emu g⁻¹) and coercive force (4511 Oe). It is suggested that the oxygen vacancies should be responsible for the soft magnetic characteristic that appeared for the as-prepared barium hexaferrite nanoparticles.

1. Introduction

Since its first preparation by Philips [1], hard magnetic barium hexaferrite has been widely used as a permanent magnet because of its fairly large magnetocrystalline anisotropy and high Curie temperature, together with its relatively large saturation magnetization, excellent chemical stability, and corrosion resistivity. Fine particles are suitable for use in high-density perpendicular magnetic recording. For example, one factor that limits the performance of high-density recording media is the media noise, which results from coupling between the magnetic grains, and it is generally believed that the grain interaction should become less significant with very small grain size [2]. In ultrahigh-density recording, magnetic grains <50 nm are desirable for obtaining a reasonable signal-to-noise ratio (SNR) [3].

Various methods such as co-precipitation [4, 5], glass crystallization [6], hydrothermal synthesis [7, 8], sol-gel techniques [9], organometallic precursor methods [10], microemulsion

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synthesis [11, 12], spray deposition (for magnetic recording thin films) [2], and other processes [13] have been developed for preparing this material. However, all these methods require two basic production operations: mixing of initial components either mechanically or chemically, and a subsequent heat treatment of the obtained mixture: the temperature usually ranges from 700 to 1400 °C. Because of the annealing at high temperatures, the grain size of the barium ferrite is usually larger than 50 nm, which limits the possibilities of obtaining ultrafine particles for the desired applications, especially basic research. On the other hand, it is reported that the saturation magnetization for magnetic materials decreases with decreasing particle size [14, 15], which will also limit the applications of nanosized magnetic materials in magnetic recording. Non-magnetic layers on the surfaces of fine particles and a fraction of finer particles in the superparamagnetic range have been suggested to be responsible for the decrease of the saturation magnetization in nanosized magnetic materials [14].

It is the purpose of this letter to report the development of a hydrothermal process for preparation of nanoparticles of barium hexaferrite under mild conditions and study the magnetization in the nanoparticles of a hard magnetic ferrite.

2. Experimental details

The starting materials for the present synthesis include iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), barium hydroxide [$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$], and barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). The hydrothermal synthesis was carried out in a 45 ml Teflon-lined stainless-steel autoclave. The barium hydroxide was dissolved in distilled water, and then iron chloride solution was added to it while stirring. The barium chloride solution was also added to increase the concentration of Ba^{2+} to aid the formation of barium ferrite. The molar ratio of $\text{Ba}(\text{OH})_2$ to FeCl_3 is 3:1, the concentration of Fe^{3+} is 0.1 mol l^{-1} , and that of barium chloride is 0.3 mol l^{-1} for typical reactions. Then, the autoclave was heated to 140, 160, 180 °C for 12, 24, 48 h, respectively. The products were washed with distilled water, dried at 80 °C, then washed with HCl aqueous solution (0.1 M) and distilled water three times, and dried at 80 °C again for 6 h.

The samples were characterized by means of x-ray diffraction (XRD) using an x-ray diffractometer with high-intensity Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The magnetic properties were measured on a BHV-55 vibrating sample magnetometer (VSM) at room temperature.

3. Results and discussion

The XRD patterns of the products derived for different reaction temperatures are shown in figure 1. It is clear that the product is the pure phase of hexagonal $\text{BaFe}_{12}\text{O}_{19}$, and broadening of the peaks is obvious, indicating significant decreasing of the particle size. With increasing of the reaction temperature, the peaks got narrower and sharper, manifesting the particle size increase and crystallinity improvement. Generally, longer reaction time results in better crystallinity of the product. However, no further changes in particle size and crystallinity were observed when the reaction time was longer than 12 h. It is interesting to find that the (110) and (220) peaks became much stronger than those on the JCPDS card (JCPDS, 84-0757), indicating (110) orientation present in the sample. The TEM image (figure 3(A)) reveals that the sample consisted of a large number of plane-like particles. Their cleavage faces might be (110), leading to (110) orientation of the sample. This is different from the case for barium ferrite thin film, in which a strong *c*-axis perpendicular orientation was observed [16].

As shown in figure 3(A), the particles appear to be plane-like in shape, reflecting the characteristic feature of single crystal. The size of the particles was, measured from the TEM

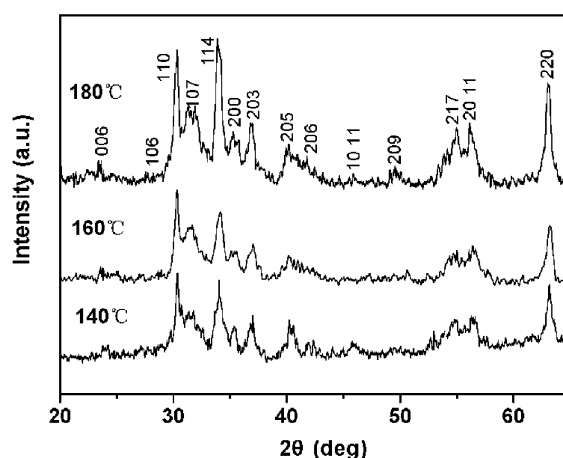


Figure 1. XRD patterns of barium ferrite synthesized at 140, 160, and 180 °C, respectively.

image, around 12 nm for the sample formed at 140 °C and around 30 nm for the sample prepared at 180 °C.

The synthesis of magnetic barium ferrite at relatively low temperatures is rather difficult. We found that if we co-precipitated Fe^{3+} and Ba^{2+} ions (1:1, mole ratio) with sodium hydroxide or ammonia solution and treated the resulting substance in an autoclave at 180 °C, no barium ferrite was formed. It is found that the higher $\text{Ba}^{2+}/\text{Fe}^{3+}$ ratio is favourable for the formation of $\text{BaFe}_{12}\text{O}_{19}$. Therefore, during the preparation, the ratio of Ba^{2+} is far more excessive than the stoichiometry ratio in $\text{BaFe}_{12}\text{O}_{19}$. XRD studies show that barium ferrite was not the only phase, no matter what conditions were imposed. The main impurity phases identified were Fe_2O_3 and its hydrate, but they could be eliminated easily by washing the product with HCl. When the $\text{Ba}^{2+}/\text{Fe}^{3+}$ ratio was higher than 5:1 or lower than 3:1, the crystallization of barium ferrite was more difficult than that with a $\text{Ba}^{2+}/\text{Fe}^{3+}$ ratio of 4:1. A possible explanation is that iron hydroxide would form more easily when the alkalinity of the solution was very strong, which is not beneficial for the formation of barium ferrite. On the other hand, when the concentration of Ba^{2+} was too low, the content of Ba^{2+} ions was insufficient for the formation of a stable barium hexaferrite phase.

The hysteresis loops of the samples prepared at 140 °C are shown in figure 4. Although the values of the saturation magnetization (1.1 emu g^{-1}) and coercive force (221.0 Oe) for these samples are much lower than those for the corresponding bulk material and the samples prepared at high temperatures or after high-temperature annealing, they provide us with an opportunity to establish the magnetic characteristic of barium hexaferrite on the nanometre scale. It is interesting to find that nanoparticles exhibit the soft magnetic feature; this has not been reported previously for this material. Non-magnetic layers on the surfaces of nanoparticles were usually suggested as being responsible for the lowering of the magnetization [14, 15]. However, the reduction of the crystalline size to nanometres usually causes lowering of the saturation magnetization by up to 10–20%. In order to study the mechanism leading to the soft magnetic feature, the magnetization of a sample annealed in air at 800 °C for an hour was measured. The inset of figure 4 shows that the saturation magnetization (67.3 emu g^{-1}) and coercive force (4511 Oe) increase significantly. Figure 2 shows the XRD patterns of the sample annealed at 800 °C. It is observed that the (107) and (114) reflections became stronger compared to those for the product freshly prepared at 140 °C, indicating improvement

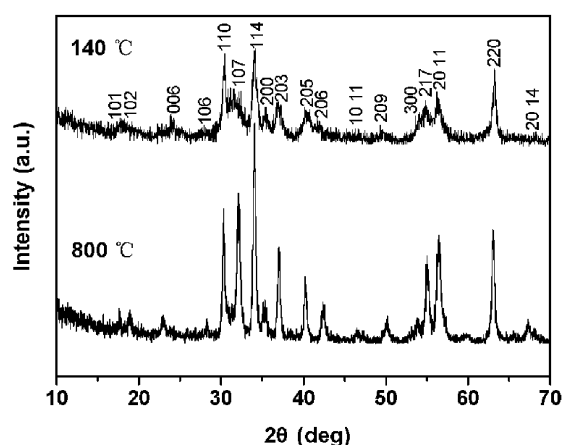


Figure 2. XRD patterns of barium ferrite synthesized at 140 °C and annealed at 800 °C.

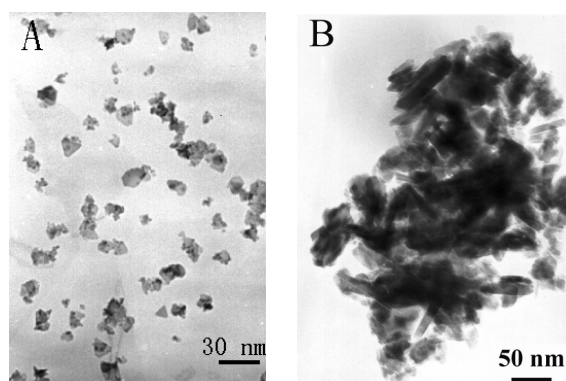


Figure 3. TEM images of the samples freshly prepared at 140 °C (A) and annealed at 800 °C (B).

of crystallinity and grain growth to some degree. Figure 3(B) shows the TEM morphology of the annealed sample; the particles are rod-like in shape with a size of 18 nm × 55 nm. The annealing process did not increase the particle size dramatically. It is, therefore, suggested that the annealing process decreased the concentration of oxygen vacancies and strengthened the $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ exchange interaction, and as a result improved the magnetic properties of the barium hexaferrite. This suggestion was also supported by the data on the saturation magnetization of the sample annealed at 800 °C under argon shielding. The sample had saturation magnetization (20.7 emu g^{-1}) and coercive force (2543 Oe) much lower than those for the sample annealed in air (67.3 emu g^{-1} , 4511 Oe).

4. Conclusions

Nanoparticles of $\text{BaFe}_{12}\text{O}_{19}$ were hydrothermally prepared at 140 °C, which is the lowest temperature reported so far for barium hexaferrite fabrication. The particle size was 12 nm on average, much smaller than those reported in the literature. It was found that the nanoparticles exhibit a soft magnetic characteristic rather than the hard one that the corresponding bulk material shows. Annealing of the sample in air can improve the magnetic properties dramatically. It is suggested that if the concentration of oxygen vacancies were decreased, this

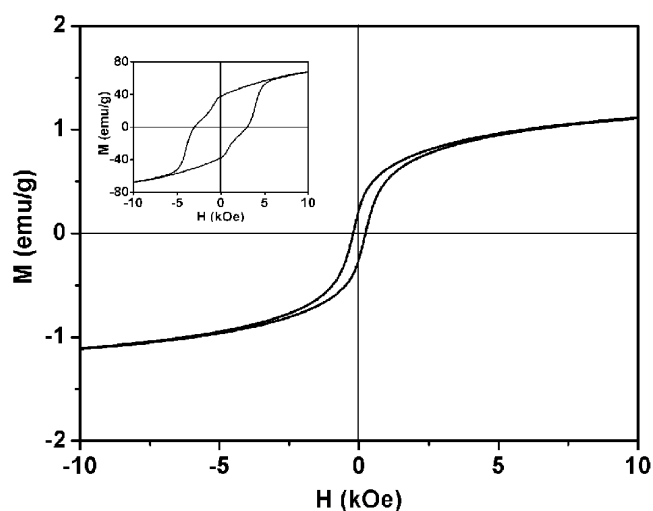


Figure 4. The hysteresis loop of the sample prepared at 140 °C. The inset shows the hysteresis loop for the sample annealed at 800 °C.

could enhance the $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ superexchange interaction, and as a result improve the magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles. The result also suggests that in addition to non-magnetic layers on the surfaces of nanoparticles, the oxygen vacancies in the lattice play a key role in determining the magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles.

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