

Preparation of magnetic barium ferrite powders by microwave hydrothermal method

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Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) particles were prepared using microwave hydrothermal synthesis with $\text{Fe}(\text{NO}_3)_3$ and $\text{Ba}(\text{NO}_3)_2$ as starting materials. The phase composition, crystallography and morphology of $\text{BaFe}_{12}\text{O}_{19}$ were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), differential scanning calorimetry (DSC), FT-IR spectra and vibrating-sample magnetometer (VSM). The results showed that nanosized hexagonal barium ferrite was synthesized when Ba/Fe ratio molar was 1 : 8 and annealed at 900 °C for 30 minutes. Meanwhile the different morphologies of $\text{BaFe}_{12}\text{O}_{19}$ could be influenced by Ba/Fe molar ratio and reaction time. For sample, the saturation magnetization (σ_s) was 61 emu/g, coercive force (H_c) was 4800 Oe.

Key words: Microwave hydrothermal, Barium ferrite, Magnetic property.

Introduction

Hexagonal barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) is one of the most commonly used material in permanent magnets, magnetic recording media and microwave devices owing to its high saturation magnetization, large coercivity, good chemical stability, corrosion resistance, etc [1-4]. The magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$ originate from the Fe^{3+} of the barium hexaferrite structure [5]. In magnetoplumbite structure, the arrangement of the twelve iron ions in the unit cell is two in the tetrahedral sites (four nearest O^{2-} neighbors), nine in the dodecahedral sites (six nearest O^{2-} neighbors) and one in the hexagonal site (five nearest O^{2-} Neighbors) [6].

Until now, there are many ways to prepare $\text{BaFe}_{12}\text{O}_{19}$ powders, such as glass crystallization [7], gel-to-crystalline conversion [8], sono-chemical synthesis [9], aerosol pyrolysis [10], ester-derived synthesis [11], ammonium nitrate melts [12], solid state synthesis [13], chemical precipitation [14], precipitation in alcohol [15], reverse micelle based method [16], low temperature combustion synthesis [17], mechanical alloying synthesis [18], citrate precursor synthesis [19], aerosol-derived synthesis [20] and hydrothermal synthesis [21-23]. But many of those methods lead to the formation of intermediate phase such as $\alpha\text{-Fe}_2\text{O}_3$ and Fe_2O_4 . In recent years, there are several reports where conventional hydrothermal preparative techniques have been substituted by the microwave hydrothermal method because this method offers rapid heating, faster kinetics, homogeneity, higher yield, better reproducibility, and is economical

and energy saver. Therefore, this work aims to synthesize single phase, nanosized, $\text{BaFe}_{12}\text{O}_{19}$ particles, with narrow size distribution, by microwave hydrothermal method, under mild conditions.

Experimental Procedure

The starting materials for the synthesis were barium nitrate $\text{Ba}(\text{NO}_3)_2$ (purity 99.5%), iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purity 98.5%), sodium hydroxide NaOH (purity 98.0%) and distilled water. The concentration of Ba^{2+} was optimized at 0.01 mol/L, while the Fe^{3+} was adapted to 0.08 mol/L. Barium nitrate and iron nitrate were first dissolved in distilled water completely with Ba/Fe = 1 : 8. NaOH was added dropwise to the above solution until pH = 13. The resultant solution in a sealed tetrafluorometoxil (TFM) vessel was heated and reacted at 200 °C for 30 min while the reaction pressure increased to 25 atm, and then cooled it to room temperature. After washing thoroughly with distilled water and drying at 80 °C, the precipitate was annealed at 900 °C for different time in air.

The phase composition of the powder was characterized with powder X-ray diffraction (XRD, D/MAX 2200pc, Japan). Their diffraction patterns were obtained by using Cu K α radiation of wavelength $\lambda = 0.15418$ nm. The infrared spectra were recorded using FT-IR instrument for samples between the range 400 to 4000 cm^{-1} (Bruker V70, German). The thermal behavior of the powder was measured by differential scanning calorimetry (DSC, Netzsch STA 409 PC/PG). The size and morphologies were characterized by scanning electron microscope (SEM, JSM-6390). The magnetizations of the sample were measured using a vibrating-sample magnetometer (VSM, Lakeshore 665).

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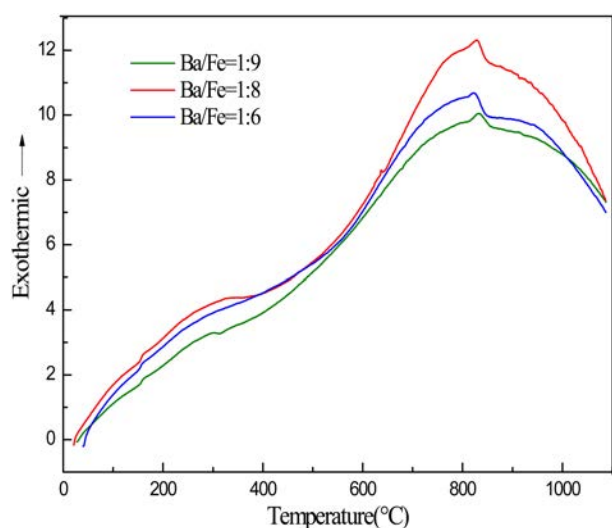


Fig. 1. The DSC curves of $\text{BaFe}_{12}\text{O}_{19}$ with different molar ratio

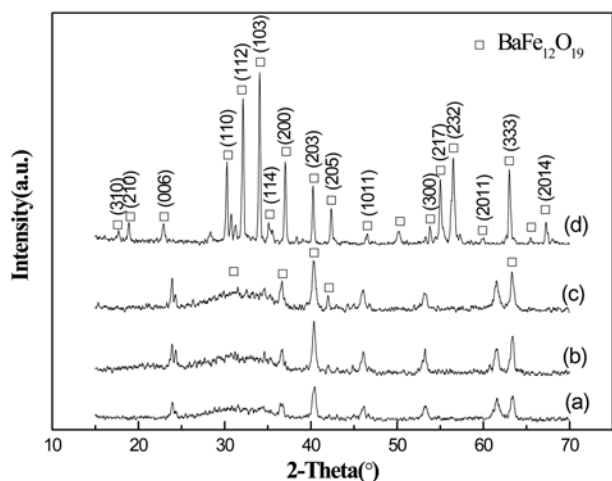


Fig. 2. X-ray diffraction patterns of $\text{BaFe}_{12}\text{O}_{19}$ powder with different molar ratio (a) $\text{Ba/Fe} = 1:6$ (b) $\text{Ba/Fe} = 1:8$ (c) $\text{Ba/Fe} = 1:9$ and (d) $\text{Ba/Fe} = 1:8$, annealed at 900°C

Results and Discussion

Phase transformation of as-prepared barium ferrite powders were examined using DSC measurements, their DSC curves are presented in Fig. 1. There are no obvious differences between three DSC curves. An endothermic reaction is observed at around 300°C corresponds to the evaporation of water and absorbed -OH of surface in the samples. The large exothermic peak at the onset temperature of around 820°C in the DSC curve corresponds to the crystallization of the phase transformation.

Fig. 2 shows the XRD patterns of barium ferrite samples as prepared. For un-annealed samples, broad peaks and high background in both of the XRD powder patterns suggest the small crystallite size and low degree of the crystallinity of samples. Some observed peaks correspond to the barium ferrite structure. However, their relative intensities differ from those of the standard

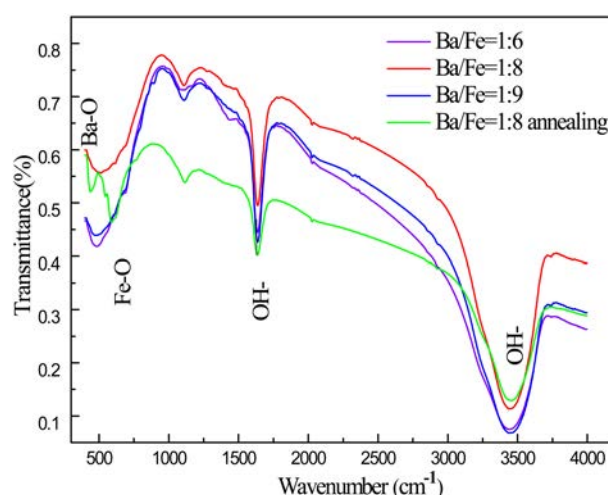


Fig. 3. The FT-IR graphs of $\text{BaFe}_{12}\text{O}_{19}$ samples with different molar ratio (a) $\text{Ba/Fe} = 1:6$ (b) $\text{Ba/Fe} = 1:8$ (c) $\text{Ba/Fe} = 1:9$ and (d) $\text{Ba/Fe} = 1:8$, annealed at 900°C

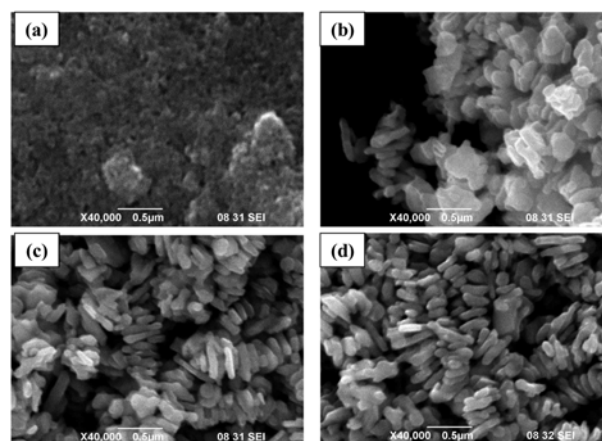


Fig. 4. The SEM micrographs of samples annealing at 900°C (a) $\text{Ba/Fe} = 1:8$, $T_c = 30$ min and un-annealed, (b) $\text{Ba/Fe} = 1:8$, $T_c = 60$ min, (c) $\text{Ba/Fe} = 1:8$, $T_c = 30$ min, and (d) $\text{Ba/Fe} = 1:9$, $T_c = 30$ min.

diffraction pattern. This can be explained on the basis of small particles with a high aspect ratio. The synthesized particles grow extensively in the ab -plane, while a limited growth was observed in the c -direction. Consequently, only a few unit cells grew in the c -direction and the peaks of the respective planes show unusually low intensity. Some complex compounds were formed with cells that result in low crystallinity.

The crystal ordering and growing of $\text{BaFe}_{12}\text{O}_{19}$ were possible during the annealing at 900°C when enough energy for the diffusion in solid state was available. The relative intensities of the peaks in the corresponding XRD powder patterns in Fig. 2(d) are the same as those of the standard. At the same time the width of the peaks decreased and intensity of peaks increased after the annealing.

Functional groups exhibited by $\text{BaFe}_{12}\text{O}_{19}$ are investigated by FT-IR spectroscopy and the resultant spectra are presented in Fig. 3. For un-annealed samples,

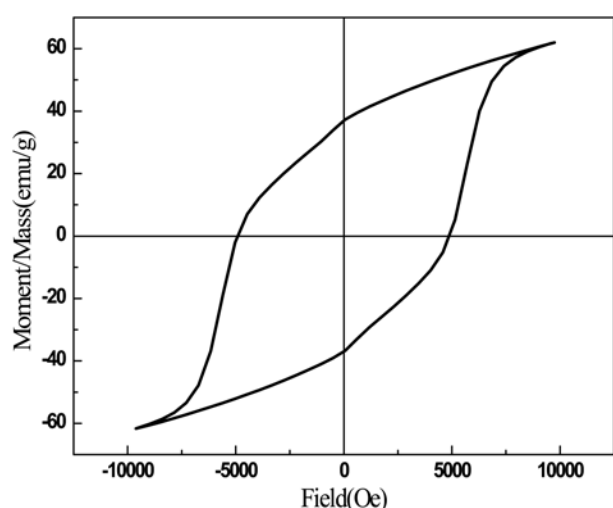


Fig. 5. Hysteresis loop of BaFe₁₂O₁₉ sample with Ba/Fe = 1 : 8 and annealed at 900 °C.

the broad band in the range of 3430 ~ 3440 cm⁻¹ corresponds to stretching vibration of -OH groups. The band at 1635, 1636, 1637 cm⁻¹ are caused by flexural vibrations of -OH groups. It is suggested that the surface of the samples exist active -OH groups. At low wave numbers, the frequency bands in the range of 470 ~ 520 cm⁻¹ correspond to the vibration of Fe-O. For annealed sample with Ba/Fe = 1 : 8, the IR band at 3455 and 1637 cm⁻¹ can be assigned to the vibration of -OH groups. But there are significantly change at 590 and 439 cm⁻¹ before and after annealing, corresponding to vibration of the tetrahedral and octahedral sites for BaFe₁₂O₁₉. The IR bands of the samples have some migration. Meanwhile, the relative strength of peak has also changed. This may be caused by -OH removed through annealing.

Fig. 4 shows SEM micrographs of the synthesized particles. It is observed that the grain is small and not fully growth in Fig. 4(a) and the particles possess flat planes in shape, and 200 nm in width while only 10 nm in thickness (Fig. 4(b)). As a result, the aspect ratio is unusually large ($l/d=20$). Small size and rod-like structure of barium ferrite can be attained according to Figs. 2(c) and 2(d). There is observably difference between Figs. 2(b) and 2(c) in grain morphology. With the increasing of reacted time (T_r) and Ba/Fe ratio the rod-like grains formed, which caused by more energy and a larger concentration of Fe³⁺. Therefore different morphologies can be obtained through extending reacted time or changing Ba/Fe ratio. Hexagonal barium ferrite was synthesized through annealing with Ba/Fe = 1 : 8 at 900 °C for 30 min.

The magnetization versus magnetic field plot at 25 °C for the sample with Ba/Fe = 1 : 8 and annealed at 900 °C is shown in Fig. 5. It is found that the saturation magnetization (σ_s) is 61 emu/g and coercive force (H_c) is 4800 Oe. The high value of H_c and σ_s comparing with hydrothermal method [24] indicates that these barium

ferrite particles are essentially single domain and improve crystallinity of sample by calcination, which can be obtained from SEM. However, the magnetization parameters of BaFe₁₂O₁₉ are lower compared to the theoretically estimated values ($\sigma_s=72$ emu/g and $H_c=6700$ Oe). The reduction of coercive force is attributable to the transition from single to multi-domain structure with the rise of sintering temperature due to increasing grain size. The mechanism of magnetization reversal changes from coherent rotation to domain wall motion that can explain the reduced coercive force [25]. The decrease of the saturation magnetization in parallel with the decrease in the particle size of the magnetic particles is a generally known phenomenon and is a consequence of many factors. One is certainly the large surface area of the particles and the incomplete coordination of atoms at the particle surface leading to a noncollinear spin configuration, which reduces the magnetization of small particles. The second reason is connected to the energy of the magnetic particles, which depends, in an external field, on the size of the particles via the number of magnetic molecules in a single magnetic domain. This has a consequence that the thermal fluctuation will significantly diminish the total magnetic moment at a given magnetic field.

Conclusion

The pure barium ferrite powders were successfully prepared by a microwave hydrothermal method within a relatively short time. The molar ratio of precursors and annealing temperature of the media on the nucleation at low temperature govern the formation of BaFe₁₂O₁₉ particles and the morphology of grains. Optimized methods can be confirmed for preparation of barium ferrite through various test analyses. It was also found that the saturation magnetization (σ_s) was 61 emu/g, coercive force (H_c) was 4800 Oe.

Acknowledgements

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