

Preparation and Magnetic Properties of Ba-Ferrite Particles Using the SuperCritical Water Crystallization Method

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Barium ferrite particles were synthesized from $\text{Ba}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and KOH mixed solutions using hydrothermal crystallization in supercritical water. The experimental apparatus for production of barium ferrite is a flow-type apparatus. Fine barium ferrite particles were produced because supercritical water causes the metal hydroxides to be rapidly dehydrated before significant growth takes place. The effects of Fe/Ba ratio and reaction time on the formation, particle size, and magnetic properties of barium ferrite were studied. When Fe/Ba ratio were varied from 0.5 to 12, single-phase barium ferrite powder was only produced in the range of $0.5 < \text{Fe}/\text{Ba} < 2$. Also, with elevating reaction time, the $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ particle size grew smaller. Especially, uniform barium hexaferrite particles of size 100-200nm were obtained at 80sec. In this study, therefore, single-phase barium ferrite particles are highly stable and can be produced continuously in a reaction time of less than 2min.

1. Introduction

Barium ferrite has the formulation of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ and shares the same hexagonal crystal structure as that of magentoplumbite ($\text{PbFe}_{7.5}\text{Mn}_{3.5}\text{Al}_{10.5}\text{Ti}_{0.5}\text{O}_{19}$). The ferrite $\text{BaFe}_{12}\text{O}_{19}$ is widely used in permanent magnets because of its large coercive force, which is derived from the large magnetocrystalline, and its fine grain structure. Additionally, the substance is chemically stable and has high electric resistance ($\sim 10^6 \Omega \text{cm}$) and low specific gravity. It is known that the substance is prone to form plate crystals as its C-axis growth is restricted and it tends to grow primarily in the basal plane. The resulting crystal, therefore, shows the hexagonal, plate-like structure, and high-density recording is possible through perpendicular magnetic recording as the easy-direction of magnetization is formed perpendicular to the plate plane. It is found that barium ferrite particles are suitable for longitudinal high-density recording as well

as for perpendicular recording media, since they have a small demagnetization loss of remanence and a low value of SFDr. It can be used for many applications such as traditional permanent magnets, high-density magnetic and magneto-optic recording media and microwave filters.[1-5]

Barium ferrite synthesis depended on the ceramic method because of manufacturing parameters such as sinter temperature, sinter environment, impurity or additive etc. In order for it to be used as a high-density magnetic recording media, however, there are delicate conditions that maybe satisfied: the formed particles must be evenly fine in size and have high dispersion in an organic matter. The substance, therefore, cannot be synthesized using conventional ceramic processes and a new process is required for good magnetic properties. As a result of studies aimed at overcoming these problems, the supercritical water crystallization method was proposed.[6-10]

In supercritical water crystallization, owing to the fact that the metal salt aqueous solution can be heated rapidly to the operating temperature, both hydrolysis and in situ refining of the generated small metal oxide nuclei can take place simultaneously. Thus, high refining rates, as well as fast hydrolysis rates can be expected and a flow type continuous process can be developed.

This paper describes the preparation and characterization of fine particles of barium hexaferrite by supercritical water crystallization. Among the various variables in supercritical water crystallization, the influence of concentration and reaction time of the feed materials are studied.

2. Experimental

The feed solution was prepared by barium nitrate($\text{Ba}(\text{NO}_3)_2$) (Junsei, 98.5%) and iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (Showa, 98%) in de-ionized water. The iron(III) nitrate concentration was fixed at 0.02mol and then the Fe/Ba molar ratio was changed between 0.5 and 12 by varying the barium nitrate concentration. Potassium hydroxide(KOH) aqueous solution was also used as a high ionization degree reagent to control the concentration of the anions in the solution. The alkali molar rate, which is the ratio of KOH concentration to total nitrate concentration, was fixed at 4.

Fig. 1 shows the experimental flow apparatus that was used in this study. Barium

and iron(III) nitrate aqueous solution was fed into mixing-point, MP1 by high pressure pump(GL Science Co., Model PUS-11) at a flow rate about 2ml/min and a degasser(Jour Research, X-ActTM) was used to remove dissolved air from the distilled water. KOH aqueous solution was pumped by another pump at a flow rate of 2ml/min. Before the injection into the preheating zone, the two solutions were combined at mixing-point MP1 at 40MPa and room temperature. The feed solution was combined with the preheated water at 350-450°C at mixing point MP2. The feed rate was at 4ml/min. At the time, the temperature was fixed at 200°C where the nuclei are formed. For the maintenance of supercritical conditions, the solutions containing the nuclei were mixed with the preheated water at 500-600°C at mixing-point MP3. The external heater was used for minimizing the temperature gradient in the reactor during the reaction. The vertical tube reactor was made of 316 stainless steel and the temperature was controlled with a K-type thermocouple and a proportional integral differential(PID) temperature controller, with the temperature distribution being within $\pm 1^\circ\text{C}$. The residence time of the solution in the reactor(τ) was evaluated via Eq. (1).

$$\tau = \frac{V\rho}{F} \quad (1)$$

Where, V : Reactor volume F : Mass flow rate

ρ : Density of the feed solution

The residence time was changed by changing the reactor volume while maintaining a constant feed flow in all experiments. The reactor volume was varied by changing the reactor length. The products after the reaction was rapidly cooled by using a heat exchanger in order to the residence time could be accurately determined. The fine particles were collected through the in-line filter(Swagelok, Model SS-8F-K4-05, 0.5 μm) and the filtered solution then passed through a back-pressure regulator was finally collected in a storage tank.

The products from the experiment was cleaned with distilled water and dried for 24 hours in the dryer (60°C). The crystal structure of the products was analyzed by X-ray diffractometry(XRD, Model D/MAX, Rigaku, CuK α graphite monochromator) at scan rate of 2° 2 θ /min and also scanning electron micrographs(SEM, Model XL-30, Philips) analyzed for the shapes and sizes of the particles. Vibrating sample magnetometer(VSM, Model 7300, Lake Shore) was used to measure the magnetic properties(coercivity and saturation magnetization) of the products. In the measuring,

the maximum applied magnetic field was 10kOe.

3. Results and Discussion

Barium hexaferrite, which has been used as the magnetic material for high density recording media, could be prepared from aqueous suspensions containing ferric nitrate, barium nitrate and potassium hydroxide by the supercritical water crystallization method. In this process, the effect of the Fe/Ba ratio and the reaction time on the size, morphology and phase of the product was investigated with a flow-type apparatus. The morphology and the phase of the fine particle produced were observed using a scanning electron microscope(SEM) and X-ray diffraction(XRD).

For the analysis of the characteristics of the particle formed with varying Fe/Ba ratio and reaction time, the reaction pressure was at 40MPa and the temperatures of MP2, MP3 were respectively fixed at 200°C and 400°C. Fine barium hexaferrite particles were obtained in the continuous hydrothermal synthesis apparatus when the alkali mole ratio of $[\text{OH}^-]/[\text{NO}_3^-]$ was 4.

Fig. 2 shows XRD patterns of the product synthesized by supercritical water crystallization as a function of Fe/Ba molar ratio. When Fe/Ba ratio were varied from 0.5 to 12, more $\alpha\text{-Fe}_2\text{O}_3$ was produced than $\text{BaFe}_{12}\text{O}_{19}$ in the range of $8 < \text{Fe}/\text{Ba} < 12$. In the range of $2 < \text{Fe}/\text{Ba} < 5$, however, single-phase barium ferrite only was produced in the range of $0.5 < \text{Fe}/\text{Ba} < 2$. Fig. 3 shows SEM photographs that imply that the mean particle size varies with Fe/Ba molar ratio. For powder derived at a Fe/Ba molar ratio of 0.5, agglomerates of ultrafine particles having only a low crystallinity are formed, though the XRD patterns appear to be $\text{BaO}\cdot 6\text{Fe}_2\text{O}_3$. At a Fe/Ba molar ratio of 2, barium hexaferrite crystals with thin hexagonal plate morphology and sizes between $0.1 \sim 0.2\mu\text{m}$ are formed. Also, the result of SEM analysis demonstrates the fact that the particle size increases with increasing a Fe/Ba molar ratio, with the particle size of produced barium hexaferrite becoming $0.5\mu\text{m}$ at a Fe/Ba molar ratio of 5.

Fig. 4 shows SEM photographs of particles obtained at various residence times at MP3 and in the reactor. Throughout the range, single-phase barium hexaferrite was found. The size of particles was reduced as the residence times increased. At residence times of 80 seconds or higher, however, the size reduction effect was little, because of the dissolution and recrystallization of formed barium hexaferrite which

caused widened distribution of particles and increase in particle sizes.

Compared with the conventional batch apparatus which requires 30-48 hours to synthesize barium hexaferrite in the hydrothermal synthesis method, the continuous process of this study remarkably minimizes the reaction time for the 1st stage hydrolytic product and the 2nd stage dehydration product.

Fig. 5 shows the magnetic hysteresis curve of a barium hexaferrite particle that was synthesized with varying reaction time. It shows a saturation magnetization of 40emu/g and a coercivity of 1,500Oe at 100sec, which are similar to the physical properties of general high density video or data storage tapes.

4. Conclusions

It was confirmed that in the supercritical water crystallization process, BaO·6Fe₂O₃ synthesis follows the nonstoichiometric reaction path. Composition and morphology of produced particles are strong functions of both Fe/Ba molar ratio and reaction time. Particle size decreases with decreasing Fe/Ba molar ratio, and with increasing reaction time. This is probably because of the influence of supersaturation followed by an increase in nuclei formation owing to the degree of Ba(OH)₂ precipitation. Thus, it is concluded that the product composition and morphology can be controlled by adjusting the reaction conditions to obtain optimum conditions of Ba(OH)₂ precipitate formation.

In the BaFe₁₂O₁₉ formation reaction, the reaction kinetics are tens of times as fast as the batch type hydrothermal synthesis method. Single-phase BaO·6Fe₂O₃ could also be synthesized in the continuous synthesis process using the supercritical water crystallization method.

References

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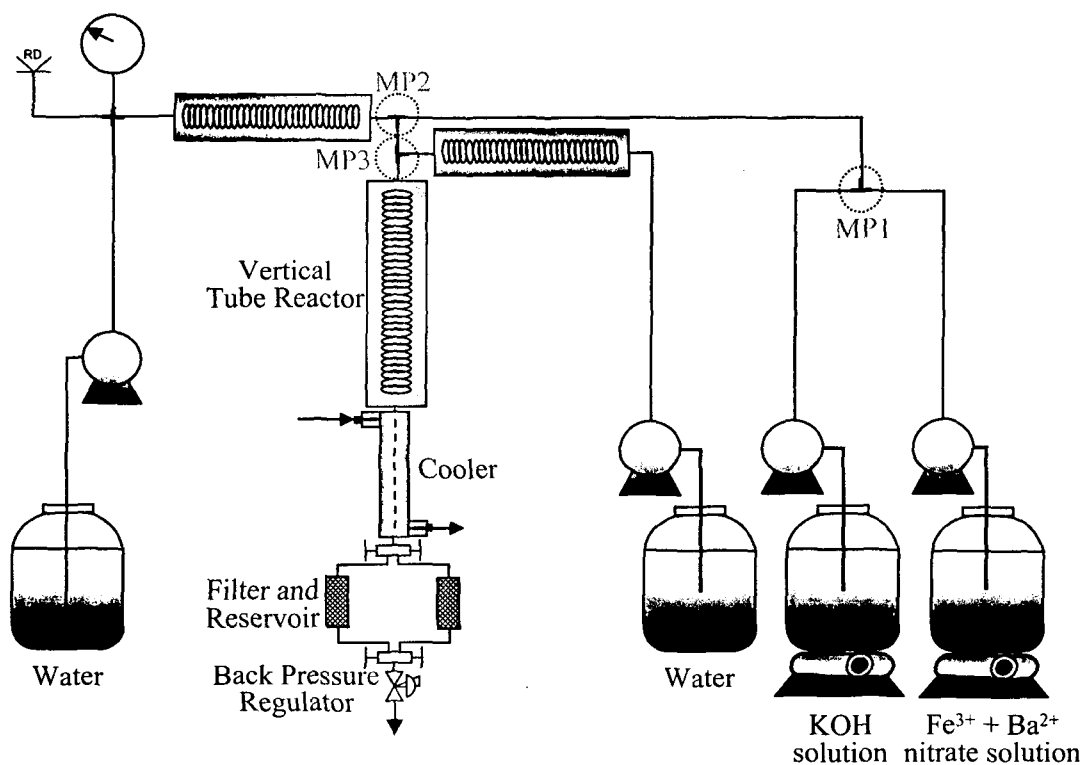


Fig. 1. Schematic diagram of the continuous synthesis apparatus by the supercritical water crystallization method

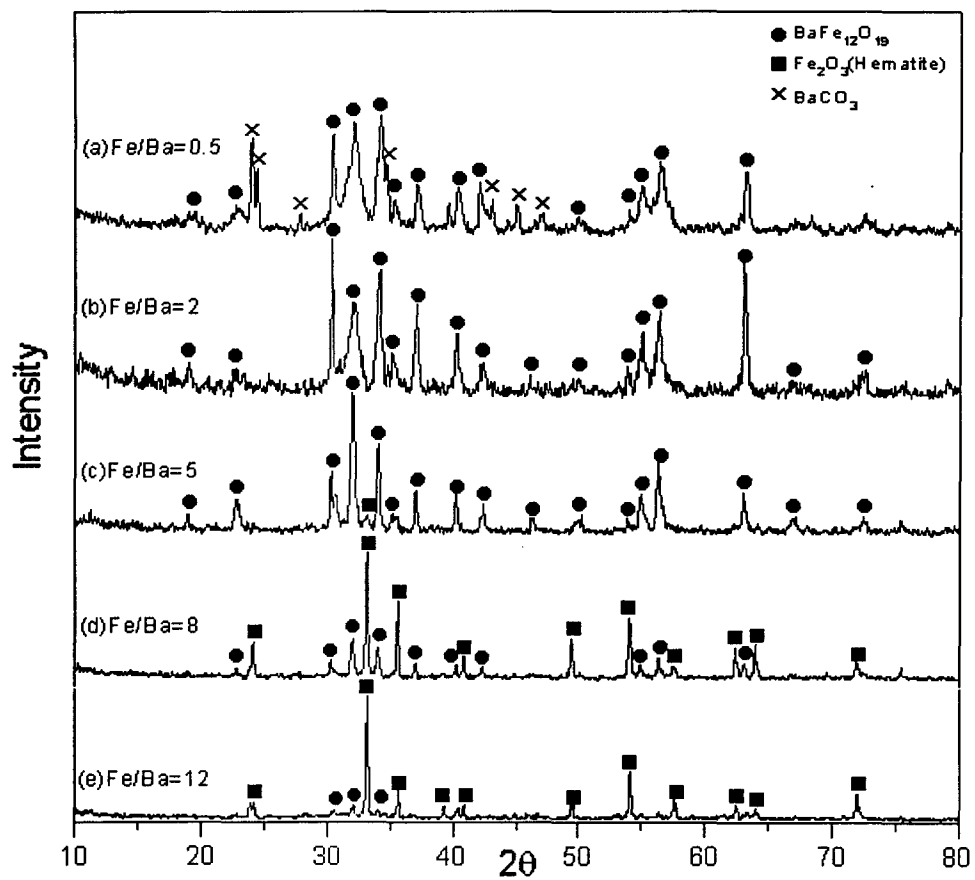


Fig. 2. XRD patterns with various Fe/Ba ratios at R=4

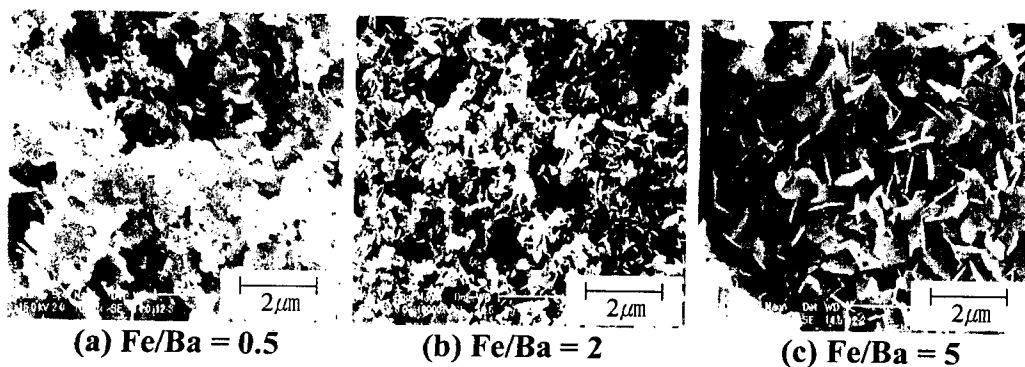


Fig. 3. SEM micrographs with various Fe/Ba ratios at R=4

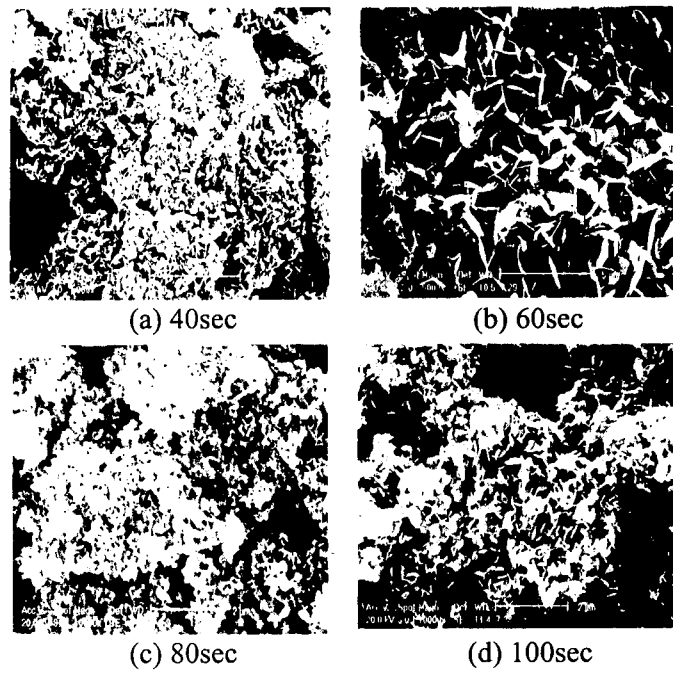


Fig. 4. SEM photographs of the products obtained with various residence time

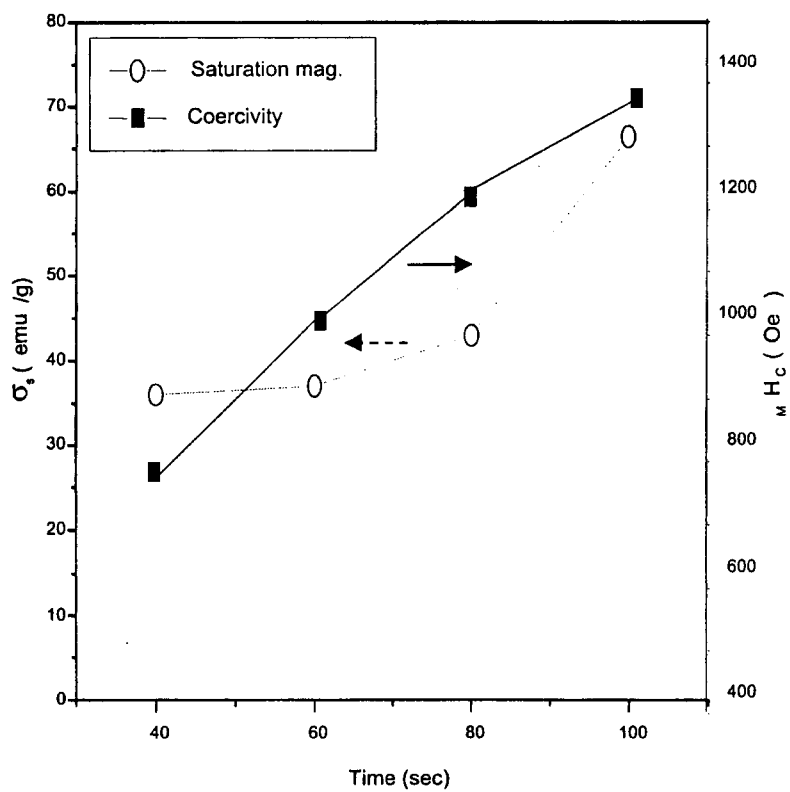


Fig. 5. Saturation magnetization and coercivity of Ba-ferrite particles with various reaction time