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

Sung-Chan Nam\textsuperscript{1}, Sang-Do Park, and Geon-Joong Kim\textsuperscript{*}

\textsuperscript{*}Department of Chemical Engineering, Inha University, Inchon 402-751, Korea
Korea Institute of Energy Research, Taejon 305-600, Korea

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Abstract: Barium ferrite particles were synthesized from Ba(NO\textsubscript{3})\textsubscript{2}, Fe(NO\textsubscript{3})\textsubscript{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 the Fe/Ba molar ratio was varied from 0.5 to 12, single-phase barium ferrite powder was only produced at Fe/Ba molar ratios of 0.5 and 2. Also, with increasing residence time from 60 to 100 s, the BaO \cdot 6Fe\textsubscript{2}O\textsubscript{3} particle size grew smaller. Especially, uniform barium ferrite particles of size 100-200 nm were obtained at 100 s. In this study, therefore, single-phase barium ferrite particles can be produced continuously in a reaction time of less than 3 min.

Keywords: barium ferrite, supercritical water, flow-type

Introduction

Barium ferrite has the formulation of BaO \cdot 6Fe\textsubscript{2}O\textsubscript{3}, and shares the same hexagonal crystal structure as that of magnetoplumbite (PbFe\textsubscript{3}Mn\textsubscript{2}As\textsubscript{10.5}Te\textsubscript{0.5}O\textsubscript{19}) [1]. BaFe\textsubscript{2}O\textsubscript{19} is widely used in permanent magnets because of its large coercive force, which is derived from its large magnetocrystalline anisotropy, and its fine grain structure. Additionally, the substance is chemically stable and has high electric resistance (\textasciitilde10\textsuperscript{9}\Omega 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 SFDi. It can be used for many applications such as traditional permanent magnets, high-density magnetic and magneto-optic recording media and microwave filters [2-6].

Flux methods and hydrothermal synthesis methods are mainly known as methods for producing such barium hexaferrite.

The coprecipitation method has merit in that the process is simple and less costly, but it has problems such as it is difficult to obtain monodisperse particles, and the coprecipitate is poor in filtration efficiency. By using the hydrothermal synthesis method, the above-mentioned problem relating to the filtration efficiency of the coprecipitate can be overcome. However, this method requires a long reaction time, and is a batch system by means of an autoclave. By the coprecipitation-flux method, a fine powder having a sharp particle size distribution can be obtained. However, a high temperature is required to melt the starting materials, and reheating treatment is required. Thus, the production process tends to be complicated and the productivity will be very low [7-10].

We have investigated a method for production of fine barium ferrite particles by hydrothermal synthesis in supercritical water. This method can continuously produce fine particles of metal oxide by reacting an aqueous

\textsuperscript{1} To whom all correspondence should be addressed.
 (e-mail: scnam@kier.re.kr)
mixed solution of metal salts at around the supercritical
temperature of water by means of a flow type reactor.
This method can selectively produce fine particles of
barium ferrite consisting of thin hexagonal crystals. The
above mentioned conventional problems are overcome
by using an aqueous mixed solution comprising an iron
compound, a barium compound and an alkaline sub-
stance [11-13].
Barium hexaferrite, which has been used as the mag-
netic material for high density recording media, could be
prepared from aqueous mixed solution containing ferric
nitrate, barium nitrate and potassium hydroxide by the
supercritical water crystallization method.
This paper describes the preparation and character-
ization of fine particles of barium ferrite by supercritical
water crystallization. Among the various variables in su-
percritical water crystallization, the influence of concen-
tration and residence time of the feed materials are
studied.

**Experimental**

The feed solution was prepared by using barium nitrate
(Ba(NO₃)₂) (Junsei, 98.5%) and iron (III) nitrate (Fe
(NO₃)₃·9H₂O) (Showa, 98%) in de-ionized water. The
iron (III) nitrate concentration was fixed at 0.02 M and
then the Fe/Ba molar ratio was changed between 0.5 and
12 by varying the barium nitrate concentration. Potas-
sium hydroxide (KOH) aqueous solution was also used
as a high ionization degree reagent to control the concen-
tration of the anions in the solution. The alkalai molar ratio (R), which is the ratio of KOH concentration to total
nitrate concentration, was fixed at 4.

The Fe/Ba molar ratio and R were expressed as follows:

\[
\frac{\text{Fe/Ba molar ratio}}{R} = \frac{[\text{Fe(NO₃)₃}]}{[\text{Ba(NO₃)₂}]} \quad (1)
\]

\[
R = \frac{[\text{KOH}]}{2[\text{Ba(NO₃)₂}]+3\text{[Fe(NO₃)₃]}} \quad (2)
\]

Figure 1 shows the experimental flow apparatus (i.e. lab
scale) which was used in this study. Barium and iron
(III) nitrate aqueous mixed solution was fed into mixing-
point, MP1 by high pressure pump (GL Science Co.,
Model PUS-11) at a flow rate about 2 mL/min and a
degasser (Jour Research, X-Act(TM)) was used to remove
dissolved air from the distilled water. KOH aqueous
solution was pumped by another pump at a flow rate of
2 mL/min. Before the injection into the preheating zone,
the two solutions were combined at mixing-point MP1 at
40 MPa and room temperature. The feed solution was
combined with the preheated water at 400 °C at mixing-point MP2. The feed rate was at 4 mL/min. At
the time, the temperature was fixed at 200 °C where the
nuclei are formed [14]. For the maintenance of su-
percritical conditions, the solutions containing the
nuclei were mixed with the preheated water at 550 °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 (length 600 cm, ID 0.32 cm, volume 48.2
cm³) and the temperature was controlled with a K-type
thermocouple and a proportional integral differential
(PID) temperature controller, with the temperature
distribution being within ±1 °C. The residence time of
the solution in the reactor (τ) was evaluated via
Equation (3).

\[
\tau = \frac{V\rho}{F} \quad (3)
\]

Where, V : Reactor volume F : Mass flow rate
ρ : Density of the mixed solution of feed and
preheated water

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

In this process, the effect of the Fe/Ba molar ratio and
the reaction time on the size, morphology and phase of
the product was investigated with a flow-type apparatus.
Figure 2. XRD patterns of particles produced at the R ratios of 0.5 and 2. (400 °C, 40 MPa, 80 s)

The morphology and the phase of the fine particle produced were observed using a scanning electron microscope (SEM) and X-ray diffraction (XRD).

The products from the experiment were cleaned with distilled water and dried for 24 h in a dryer (60 °C). The crystal structure of the products was analyzed by X-ray diffractometry (XRD, Model D/MAX, Rigaku, CuK graphite monochromator) at scan rate of 2°/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 10 kOe.

Results and Discussion

When the metal oxides are synthesized from aqueous mixed solution of metal salt with the use of supercritical water crystallization, the reaction seems to go through two stage reactions: hydrolysis and dehydration [12].

\[ \text{Step1. } M(NO_3)_x + xH_2O = M(OH)_x + xHNO_3 \]  \hspace{1cm} (4)

\[ \text{Step2. } M(OH)_x = MO_x + x/2H_2O \]  \hspace{1cm} (5)

where M is a metal.

In this process, dehydration reaction may take place before hydrolysis is completed and before the large hydrated particles can grow. Therefore, a much higher reaction rate and finer metal oxide particles are expected to be produced.

For the analysis of the characteristics of the particles formed with varying Fe/Ba molar ratios and reaction times, the reaction pressure was at 40 MPa and the temperatures of MP2 and MP3 were respectively fixed at 200 °C and 400 °C [14].

Figure 2 shows XRD patterns of product synthesized by supercritical water crystallization as a function of alkali molar ratio \((\text{OH}^-)/[\text{NO}_3^-]\).

A single phase of \(\alpha\)-Fe$_2$O$_3$ was detected at the alkali molar ratio of 0.5. This was because the low concentration of potassium hydroxide solution was insufficient converting all the nitrate to hydroxide. However, fine barium ferrite particles were obtained in the hydrothermal synthesis apparatus using supercritical water at \([\text{OH}^-]/[\text{NO}_3^-]\) \( \geq 2 \).

When the pH was 3.4 such as at the alkali molar ratio of 0.5, a single phase of hematite only was produced. When alkali molar ratio exceeds 2, however, the pH increased to over 12 and only a single phase of BaO \( \cdot \) 6Fe$_2$O$_3$ was synthesized.

From these results, hematite only was produced in the acid range and it is difficult to produce single-phase barium hexaferrite from this stable phase.

Figure 3 shows X-ray diffraction patterns of the product synthesized by supercritical water crystallization as a function of Fe/Ba molar ratio. When Fe/Ba ratios were varied from 0.5 to 12, more \(\alpha\)-Fe$_2$O$_3$ was produced than BaFe$_{12}$O$_{19}$ in the range of 5 < Fe/Ba < 12. When the Fe/Ba molar ratio was 12, which is the stoichiometric ratio for BaFe$_{12}$O$_{19}$, the main product was \(\alpha\)-Fe$_2$O$_3$. However, only single-phase barium ferrite was produced when the Fe/Ba molar ratio is between 0.5 and 2.

When the Fe/Ba molar ratio was 0.5 (i.e. barium concentration increases), BaCO$_3$ peaks were detected, because the product was not washed with the acid solution, and this was probably due to carbonation of excess barium ions by atmospheric carbonic acid gas or [CO$_3^{2-}$] in the drying step [15].

Barium ferrite particles could be selectively produced with a large excess of Ba(NO$_3$)$_2$ against Fe(NO$_3$)$_3$. Figure 4 shows SEM photographs that imply the
mean particle-face size varies with Fe/Ba molar ratio. For powder derived at the Fe/Ba molar ratio of 0.5, agglomerates of fine particles consisting only of unstable amorphous phases (low degree of crystallinity) are formed, although the X-ray diffraction patterns appear to be barium ferrite.

At the Fe/Ba molar ratio of 2, barium ferrite crystals with thin hexagonal plate morphology and sizes between 0.1-0.2 μm are formed. Also, the result of SEM analysis demonstrates the fact that the average particle size increases with increasing a Fe/Ba molar ratio, with the particle-face size of produced barium ferrite becoming 0.5 μm at the Fe/Ba molar ratio of 5.

These results suggest that stable barium ferrite was formed by a non-stoichiometric reaction which was highly dependent on the composition of the starting materials.

To examine the effect of residence time on the reaction, the following experiment was conducted. The residence time of the solution was estimated to be shorter than 180 s.

Figure 5, 6 shows X-ray diffraction patterns and SEM photographs of particles obtained at various residence times between at MP3 and at the outlet of the reactor. From the X-ray diffraction results, throughout the range, single-phase barium ferrite was found. The size of particles was reduced as the residence times increased in the range of 60 to 100 s. Figure 7 shows SEM photographs of particles produced at the residence time of 140 and 180 s. At residence times of 100 seconds or higher, however, the size reduction effect was little, because
of the dissolution and recrystallization of formed barium ferrite which caused widened distribution of particles and increase in the average particle sizes. Morphology and magnetic properties of the particles produced are equally important.

Compared with the conventional batch apparatus which requires a reaction time of several hours to synthesize barium ferrite by the hydrothermal synthesis method because of the production of intermediate materials such as BaO · xFe₂O₃ [16-18], the continuous process of this study remarkably minimizes the reaction time for the 1st stage hydrolytic product and the 2nd stage dehydration product. Thus, the results demonstrate that the reaction rate is surprisingly high.

Figure 8 shows the results of saturation magnetization (Mₛ) and coercivity (H_C) of a barium ferrite particle that was synthesized with varying reaction times. The magnetic properties of saturation magnetization and coercivity were enhanced by increasing the reaction time.

The saturation magnetization jumped up to about 65 emu/g when sample reaction time increased from 80 s to 100 s, but steadily decreased down to about 50 emu/g above 100 s. On the other hand, coercivity, which has a relatively strong dependence on crystallinity, was sensitively affected by residence time, but tended to increase to 140 s.

These properties are comparable with commercially available barium ferrite produced by the glass crystallization method. The maximum production rate of powders under the present experimental conditions was 0.54 g/hr at [Fe(NO₃)₃] of 0.02 M, Fe/Ba of 2, and alkali mole ratio of 4.

Now, a study is under way to increasing the productivity of barium hexaferrite powder through scale-up of the continuous process. It is currently possible to produce 5 g/hr of barium hexaferrite at [Fe(NO₃)₃] of 0.02 M, Fe/Ba of 2, and [OH⁻]/{NO₃⁻} of 4. Reproducibility tests were performed to confirm the reliability of the scaled-up continuous process (i.e. bench scale). The reactor and tube size was increased from 1/4inch to 1/2inch and the quantity of fluid was increased compared with the lab scale continuous process. SEM photographs of the product showed that the products consist of very small hexagonal plate-like particles with no remarkable size difference and a narrow range size distribution as shown in Figure 9. SEM photographs confirmed the consistency in each case.

Henceforth, a study for estimating the effect of reaction parameter such as concentration, temperature, pressure and residence time etc will be carried out using the bench scale process.

**Conclusions**

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 from 5 to 2, and with increasing residence time. From the results of varying the Fe/Ba molar ratio, it was confirmed that in the supercritical water crystallization process, BaO₆Fe₂O₃ synthesis follows the non-stoichiometric reaction path. The magnetic hysteresis curve of a barium hexaferrite particle that was synthesized at residence time 100 s shows the saturation magnetization of 65 emu/g and the coercivity of 1,250 Oe.

The maximum production rate of powders using the lab and bench scale continuous process was 0.54 g/hr and 5 g/hr respectively at [Fe(NO₃)₃] of 0.02 M, Fe/Ba of 2 and alkali mole ratio of 4.

We found that ultra-fine barium hexaferrite particles could be produced using short residence time (<100 s)
under supercritical conditions. In conclusion, single-phase BaO · 6Fe₂O₃ could also be synthesized in a continuous synthesis process using the supercritical water crystallization method.

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References