Synthesis of Barium Ferrite Powder by the Coprecipitation Method using Iron Pickling Waste Acid

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ABSTRACT

Barium ferrite powders were synthesized by the coprecipitation method using iron-pickling waste acid (IPWA) and $BaCl_2 \cdot 2H_2O$ as raw materials. Fe^{2+} ions in the IPWA, which contains both Fe^{2+} and Fe^{3+} ions, were oxidized into Fe^{3+} ions using H_2O_2. Proper amount of $BaCl_2 \cdot 2H_2O$ was dissolved into the oxidized IPWA. Using NaOH, Ba^{2+} and Fe^{3+} ions were coprecipitated as $Ba(OH)_2$ and $Fe(OH)_3$. The coprecipitated $Ba(OH)_2$ and $Fe(OH)_3$ were washed and dried. Barium ferrite powders were obtained by calcining the dried $Ba(OH)_2$ and $Fe(OH)_3$ mixture from 400°C to 1000°C with a 100°C interval. Barium ferrite powders were characterized by X-ray diffraction, SEM, and VSM. It was found that barium ferrite powders could be synthesized at around 630 °C. The synthesized barium ferrite powders showed hexagonal plate shapes with a fairly uniform size. The barium ferrite powder calcined at 900 °C showed good magnetic properties, saturation magnetization of 67 emu/g and maximum coercivity of 5000 Oe.

Key words : Barium ferrite powder, Coprecipitation, Iron-pickling waste acid

1. Introduction

A s barium ferrites ($BaO \cdot 6Fe_2O_3$) display extremely uniform magnetic properties and have a high coercive field strength, they are used in permanent magnets, in high density digital storage media and as antiforgery devices in the magnetic strips of cheque and identity cards.[1] Traditionally most of the barium ferrites were prepared by the solid state reaction of $BaCO_3$ and Fe_2O_3.

Recently wet chemical methods were used frequently to control the particle size and size distribution of ceramic powders. Especially since the coprecipitation method is simple and easy to control the particle characteristics in the synthesis of the ceramic powders, it is one of the most widely used among wet chemical methods. Barium ferrite can also be made by the coprecipitation method by adding an aqueous solution of NaOH into an aqueous solution of metallic chlorides containing Ba^{2+} and Fe^{3+} in a ratio required for the formation of the barium ferrite.[2]

Though IPWA is a good source for the preparation of various types of iron oxides[3], it has not been reported yet to make the barium ferrite using IPWA. In this paper, we studied the possibility of barium ferrite synthesis using IPWA as a source of Fe^{3+} ion and analyzed the characteristics of thus-prepared powders.

2. Experimental Procedures

IPWA and 99% purity $BaCl_2 \cdot 2H_2O$ (Aldrich Co.), the

sources of the Fe and Ba^{2+} ions, respectively, were used as raw materials for the coprecipitation of barium ferrite powder. To oxidize Fe^{2+} ions in the IPWA to Fe^{3+} state, H_2O_2 was used. 99% purity NaOH (Merck Co.) was used to coprecipitate the $Ba(OH)_2$ and $Fe(OH)_3$ from a solution containing Fe^{3+} and Ba^{2+} ions.

The amount of Fe ions in the IPWA was determined using ICP(Thermo Jarrel Co. AS-25 model). The chemical composition of the IPWA is shown in Table 1. The amount of total Fe ions, i.e., Fe^{2+} and Fe^{3+} ions, in the IPWA was 115.30 g/l, i.e., 2.06 mol/l. IPWA was diluted with a distilled water to make the 1 M Fe ion solution. Fe^{2+} ions in the IPWA were oxidized to Fe^{3+} ions with H_2O_2 according to the Eq. (1).

$$H_2O_2(aq) + 2\ Fe^{2+}(aq) + 2\ H^+(aq) \rightarrow 2\ H_2O + 2\ Fe^{3+}(aq) \quad (1)$$
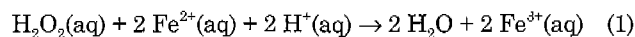
Then $BaCl_2 \cdot 2H_2O$ was dissolved into a distilled water. The proper amount of Fe^{3+} ion and Ba^{2+} ion solutions were mixed according to the barium ferrite composition of $BaO \cdot 6Fe_2O_3$. $Ba(OH)_2$ and $Fe(OH)_3$ were coprecipitated by adding a 2 M NaOH solution with the rate of 10 ml/min into the mixed solution of Fe^{3+} and Ba^{2+} ions. The solution was stirred continuously with magnetic stirrer throughout the coprecipitation process.

After the completion of coprecipitation, the precipitate was washed several times until the pH of the suspension reaches to 7. During this washing process, it is believed that the unprecipitated metal ion impurities are removed. The coprecipitate was filtered and dried in the oven at 30 °C for 24 h. Mixture powder of $Ba(OH)_2$ and $Fe(OH)_3$ was calcined from 400°C to 1000 C with a 100°C intervals for 12 h.

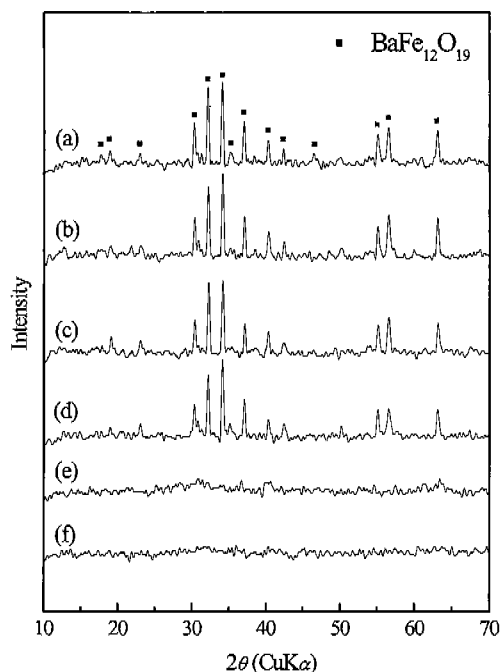[†]Corresponding author : yjshim@nongae.gsnu.ac.kr

Table 1. Chemical Composition of the IPWA   (unit: ppm)

T. Fe*	T. Mn	Ca^{2+}	Al^{3+}	Mg^{2+}	Na$^+$	T. Cr	T. Ti	K$^+$	T. Si
2.06	246	22.5	56.9	5.2	1.3	79.8	1.4	5.3	54.3

*content of total Fe ion is expressed in molarity unit
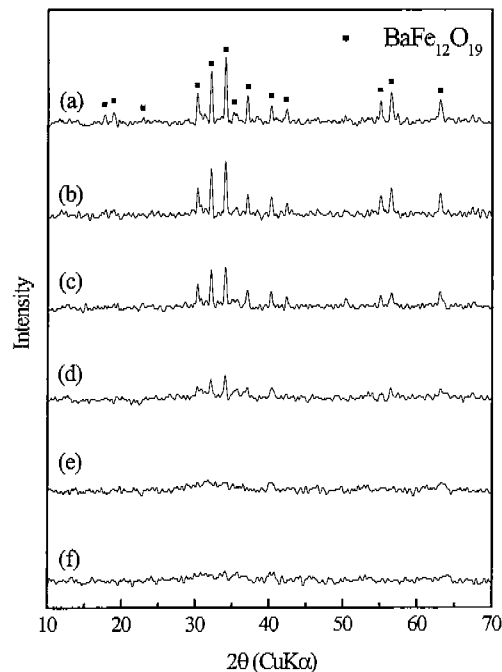

Fig. 1. X-ray diffraction patterns of barium ferrite calcined at (a) 1000°C, (b) 900°C, (c) 800°C, (d) 700°C, (e) 600°C and (f) 400°C.

Fig. 2. X-ray diffraction patterns of barium ferrite calcined at (a) 650°C, (b) 640°C, (c) 630°C, (d) 620°C, (e) 610°C and (f) 600°C.

Characterization of the calcined barium ferrite powder were carried out using X-ray diffractometer (Rigaku Co. D-max 3), SEM (Philips Co. L-30S), and VSM (Micromag Co. 3900).

3. Results and Discussion

The IPWA used in this experiment seems to be pre-treated to remove impurities. As the total amount of Fe ions, i.e., Fe^{2+} ions and Fe^{3+} ions, is about 99.6 wt% (Table 1), the IPWA is a very good source for the synthesis of barium ferrite powder. The chemical composition of IPWA used in this study is similar to that of reported in ref 4.

From the X-ray diffraction patterns of the calcined powder as a function of calcination temperature of Fig. 1, barium ferrite was completely synthesized above 700 °C without formation of other phases. When barium ferrite is synthesized by the solid state reaction of BaCO$_3$ and Fe$_2$O$_3$, BaO·6Fe$_2$O$_3$ begins to appear around 800 °C [5,6] and the reaction is completed around 1000°C. According to the BaO-Fe$_2$O$_3$ phase diagram, various forms of BaO-Fe$_2$O$_3$ solid solution may appear during the calcination process depending on the mole ratio of BaO and Fe$_2$O$_3$.[7] To know the exact formation

temperature of barium ferrite, the precipitated powders were calcined from 600 °C to 650°C with a 10°C interval and the resultant X-ray diffraction patterns are shown in Fig. 2. From the result of Fig. 2, it was found that barium ferrite synthesis temperature is around 630 °C. Therefore, it is possible to decrease considerably the synthesis temperature of barium ferrite using IPWA compared to that of the solid state reaction method. Also the synthesis temperature of barium ferrite from the coprecipitated precursor using IPWA was comparable or lower than those of other wet chemical methods.[8-10]

As such a low temperature synthesis of barium ferrite without formation of secondary phases indicates that Ba and Fe ions are mixed well in an atomic scale in the coprecipitated precursor using the IPWA, it is expected that the size and shape of the barium ferrite particles can be controlled by heat-treatment at relatively low temperatures. This in turn means that the magnetic properties of the barium ferrite powder, which are closely related to the size and shape of the particles, can be controlled efficiently by controlling calcination temperatures.

Figure 3 shows the morphology of precursor particle before calcination and the size and shape changes of the
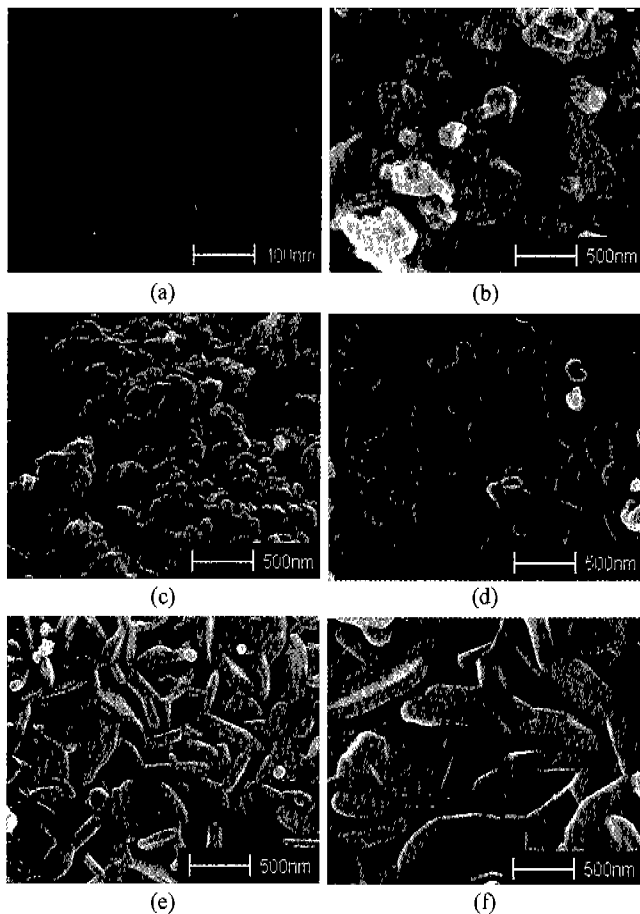
Fig. 3. SEM photographs of precursor particle (a) and barium ferrite powders calcined at (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C and (f) 1000°C.

Fig. 4. Coercivity of barium ferrite powder as a function of calcination temperature.

Fig. 5. Saturation magnetization and remanent magnetization of barium ferrite powder as a function of calcination temperature.

barium ferrite particles as the calcination temperature changes from 600°C to 1000°C. Although the precursor was agglomerated, it was observed that particles were consisted of nanoscale particles. The size increases steadily with the increase of calcination temperature. Although barium ferrite phase was identified by X-ray diffraction patterns at calcination temperatures of 700°C and 800°C (Fig. 1), a hexagonal-shaped barium ferrite particles were not seen at these calcination temperatures and barium ferrite particles seemed to be agglomerated. At a calcination temperature of 900°C, barium ferrite particles showed well-developed hexagonal shapes and nearly uniform size. The size and thickness of the barium ferrite particles calcined at 900 °C were around 0.5 μm and 0.1 μm, respectively. As the calcination temperature was increased to 1000°C, barium ferrite particles grew further in the size and thickness. It is well known that well-developed hexagonal shapes having low thickness-to-length ratio are necessary for good magnetic properties.

Figure 4 shows the coercivity of the barium ferrite powders as a function of calcination temperature. The coercivity increases steadily as the calcination temperature increases from 650°C to 900°C and then decreases abruptly at 1000 °C. Maximum coercivity is around 5 kOe at the calcination
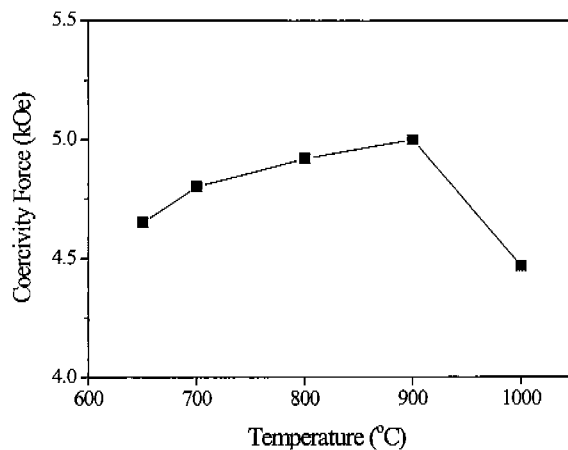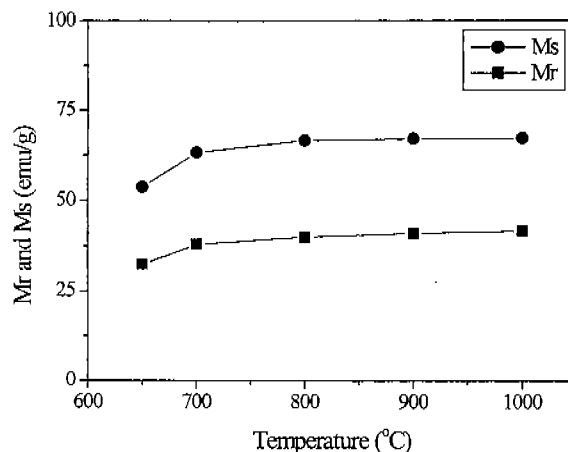
temperature of 900°C. By comparing SEM morphology (Fig. 3), the coercivity seems to be closely related to the particle characteristics of barium ferrite. It has been reported that coercivity increases with increasing particle size of the barium ferrite below single domain size and then decreases abruptly as its particle size grows above the single domain size.[10-12] As the maximum coercivity of the barium ferrite was obtained at the calcination temperature of 900 °C, single domain size of the barium ferrite in this study is believed to be around 0.5 μm.

Figure 5 shows remanence and saturation magnetization of the barium ferrite powders as a function of calcination temperature. The saturation magnetization, about 55 emu/g at the calcination temperature of 650 °C, increases steadily as the calcination temperature increases to 800 °C, and then remains around 67 emu/g regardless of the increase of calcination temperature. Saturation magnetization of the barium ferrite prepared by the coprecipitation method using IPWA was about 93% of the theoretical value of saturation magnetization.[13]

Barium ferrite powders, with good particle characteristics and satisfactory magnetic properties, were prepared by the coprecipitation method using IPWA. Synthesis of the barium ferrite powder using the IPWA can be a promising method in the powder preparation. As the possibility of preparing barium ferrite by coprecipitation using IPWA was demonstrated, a research on the powder morphology for improvement of the magnetic properties are under way by controlling calcination process.

4. Conclusions

Barium ferrite ($BaO \cdot 6Fe_2O_3$) could be synthesized by the coprecipitation method using IPWA at relatively low temperature around 630°C. It was demonstrated that the control of particle shape and size is possible thorough calcina - tion of nanoscale precursor particles prepared by the coprecipitation method. Synthesized barium ferrite powders had a 67 emu/g saturation magnetization and 5000 Oe coercive force. As the magnetic properties are closely related to the particle shapes, the properties could be substantially im - proved by controlling the calcination process.

Acknowledgement

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