The Effects of Fe_3O_4 or $\delta\text{-FeOOH}$ Precursor on Magnetic Properties of Barium Ferrite Particles Prepared by the Salt-Melt Method

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Abstract—Barium ferrite particles were prepared by coprecipitation and calcination in NaCl flux, called the salt-melt method. Three different compositions for preparing barium ferrite particles were designed. Right after coprecipitation, the composition I contained $\alpha\text{-Fe}_2\text{O}_3$, $\delta\text{-FeOOH}$, Fe_3O_4 , $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, NaCl, the composition II $\alpha\text{-Fe}_2\text{O}_3$, $\delta\text{-FeOOH}$, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, NaCl, and the composition III $\alpha\text{-Fe}_2\text{O}_3$, $\delta\text{-FeOOH}$, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, NaCl. When calcined at 600 °C, all the compositions contained the same ingredients, $\alpha\text{-Fe}_2\text{O}_3$, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, NaCl, $\text{BaFe}_{12}\text{O}_{19}$. When calcined at 900 °C, the compositions I and II gave hexagonal platelets of barium ferrite but the composition III did not. Also, the composition II, resulting in the hexagonal platelets of 0.1-0.5 μm in size, presented the highest values of saturation magnetization (σ_s), 71 emu/g, and intrinsic coercivity (H_c), 5.3 kOe, since its particle size distribution before calcination was narrowest as well as smallest and thus attained the highest reactivity.

I. INTRODUCTION

Barium ferrite (BF) particles are magnetic material with high uniaxial anisotropy, chemical stability and mechanical durability, which are potential properties for applications in high density magnetic recording media, permanent magnets and microwave etc. [1,2]. For applications in permanent magnets, the suitable mean particle size of BF is about 1 μm . By contrast, for applications in high-density recording media, the mean particle size of less than 0.1 μm is desirable.

Finely divided $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ particles can be prepared by the glass-crystallization method, the hydrothermal method, the coprecipitation method and the flux method [3-7]. The advantage of the coprecipitation method is that coprecipitates are very fine and the constituents can be fully mixed on the atomic scale; thus the reaction temperature can be lower. It has the following disadvantages: difficult filtration, loss of barium during washing of the filtrate, and particle agglomeration during calcination.

In the present paper, BF particles were prepared by coprecipitation without filtering and washing to avoid the above disadvantages and calcination in NaCl flux, called the salt-melt method [8]. Three different compositions (i.e. the different ratios of the added constituents) for preparing BF particles were designed. Attempts were made to investigate the possible reaction routes and morphological changes during those preparation processes.

II. EXPERIMENTAL

The preparation procedures were described below.

Composition I:

- (1) The addition of barium chloride into a ferrous chloride aqueous solution with a predetermined

Fe/Ba molar ratio, 8/1.

- (2) Coprecipitation by a NaOH solution, with a molar amount equivalent to that of total cations in the solution. An extra amount of NaCl was also added to adjust the flux ratio (Na/Fe) at 4.67.
- (3) Heating at 260 °C until completely dry (without filtering).
- (4) Calcining at 600 °C or 900 °C for 4 h.
- (5) Crushing, washing with deionized water, filtering and drying.

Composition II:

- (1) and (2) were the same as those for the composition I.
- (3) 35 wt% $\text{H}_2\text{O}_2(\text{aq})$ was dropped into the resulting suspension until no reaction was observed.
- (4) Drying at 40 °C until completely dry (without filtering).
- (5) Calcining at 600 °C or 900 °C for 4 h.
- (6) Crushing, washing with deionized water, filtering and drying.

Composition III:

- (1) The addition of barium chloride into a mixed solution of FeCl_3 and FeCl_2 at a $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ molar ratio of 1.98, with a predetermined Fe/Ba molar ratio, 8/1.
- (2) to (5) were the same as those for the composition I.

The particle morphology was examined by a transmission electron microscope (TEM) operated at 100 kV. The crystal structure was identified by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation or TEM electron diffraction method. The differential scanning calorimetry (DSC) measurement was carried out under a nitrogen atmosphere at a scanning rate of 10 °C/min.

The magnetic properties were measured using a vibrating-sample magnetometer (VSM) with a maximum field of 2T at room temperature.

III. RESULTS AND DISCUSSION

Fig. 1 shows the DSC curve derived from the composition III right after coprecipitation, in which the endothermic peak at about 220 °C corresponds to the transformation of the dihydrate of $\text{Ba}(\text{OH})_2$ to the monohydrate [9] and all the possible melting peaks are located below 100 °C [10], implies that the added BaCl_2 was transformed to $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. The DSC curves obtained from the compositions I and II were difficult to be analyzed due to the transformation of $\delta\text{-FeOOH}$ also occurring in the range of 100-200 °C. According to the XRD analyses, right after coprecipitation, the composition I resulted in $\alpha\text{-Fe}_2\text{O}_3$, $\delta\text{-FeOOH}$, Fe_3O_4 , $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, NaCl , the composition II resulted in $\alpha\text{-Fe}_2\text{O}_3$, $\delta\text{-FeOOH}$, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, NaCl , and the composition III resulted in $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 , $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, NaCl . Their magnetic properties are presented in Table I. Basically, the values reflect the relative amount of Fe_3O_4 produced.

Fig. 1. DSC curve of coprecipitates of the composition III

Table I Magnetic properties of samples before calcination

Composition	I	II	III
σ_s (emu/g)	12.53	3.43	6.43
σ_r (emu/g)	2.51	0	0.75
H_c (Oe)	160	0	40

When the compositions were calcined at 600 °C, all iron oxides were normally transformed to $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ to $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ [9]. Interestingly, in the composition II $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ formed long platelets owing to recrystallization which did not take place in the compositions I and III, as shown in Fig. 2, in which the corresponding electron diffraction was taken with the zone axis of [110] for $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ crystal [11] on the up right corner of the figure. It is noted that this particular TEM sample was prepared by rapidly washing after calcination to preserve $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$. In Fig. 3, XRD pattern shows the formation of barium ferrite for the composition II calcined at 600 °C. However, it was not able to find any

hexagonal platelets of barium ferrite by means of TEM observation. It indicates that the reaction to form barium ferrite is quite slow at 600 °C and 4 h heat treatment would be too short for the formation of hexagonal platelets. From the XRD analyses, when calcined at 600 °C, all the compositions were found to contain the same ingredients, $\alpha\text{-Fe}_2\text{O}_3$, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, NaCl , $\text{BaFe}_{12}\text{O}_{19}$, however at different proportions. Table II lists the magnetic properties of the resulting particles (after filtering) derived from the compositions I, II and III. Basically, the magnetic properties are strongly related to the formation of barium ferrite. From Table II, it is evident that the composition II resulted in the largest amount of barium ferrite and the particle size should be large enough to show high coercivity value.

Fig. 2. TEM of the composition II calcined at 600 °C

Table II Magnetic properties of samples after calcination

Composition	I		II		III	
Calc. Temp.	600 °C	900 °C	600 °C	900 °C	600 °C	900 °C
σ_s (emu/g)	27.78	66.49	41.39	70.99	2.23	14.64
σ_r (emu/g)	7.53	35.22	12.87	38.01	0	1.49
H_c (kOe)	0.18	4.53	3.07	5.30	0	0.27

Fig. 3. XRD pattern of the composition II calcined at 600 °C

When calcined at 900 °C, as shown in Fig. 4(a), the typical hexagonal platelets obtained from the compositions I and II can be clearly observed, while only unreacted α -Fe₂O₃ and BaO particles are observed for the composition III (confirmed by XRD, since the particles were too large to perform electron diffraction), as shown in Fig. 4(b). Table II lists their magnetic properties of the resulting particles. Among those calcined at 900 °C, the sample derived from the composition II possesses the largest values of σ_s and H_c . By contrast, the σ_s and H_c values derived from the composition III are quite small. It is thus suggested that since Fe₃O₄ particles tended to agglomerate during coprecipitation and formed large particles of α -Fe₂O₃ during calcination, only very little barium ferrite (difficult to be detected by XRD or TEM method) formed at the interface between α -Fe₂O₃ and BaO particles.

Fig. 4. (a) typical hexagonal platelet of samples calcined at 900 °C, and (b) calcined product of the composition III at 900 °C

Fig. 5. TEM of the composition I right after coprecipitation

It should be noted that, according to Table II, the σ_s and H_c values derived from the composition II after calcination are always larger than those derived from the composition I. Actually, the composition II contained the largest amount of δ -FeOOH and formed very fine and superparamagnetic particles during oxidation by H₂O₂. As can be observed in Figs. 5 and 6, the finest

homogeneously dispersed particles are derived from the composition II, while the randomly distributed largest particles about 0.3 μ m are derived from the composition III, which was due to heating at 260 °C and led to grain growth before calcination, and so did the composition I. Since finer particles have higher reactivity, the composition II can thus form appreciable amount of barium ferrite even when calcined at 600 °C and has the highest values of σ_s and H_c when calcined at 900 °C.

Fig. 6. TEM of the coprecipitates (a) from the composition II, and (b) from the composition III

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