

## Barium Ferrite Powders Obtained by Co-Precipitation

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(Received by J. R. Leite October 20, 2000; in revised form March 6, 2001;  
accepted March 13, 2001)

Subject classification: 61.43Gt; 75.50.Dd; 75.50.Ww; S11.2

Barium ferrites are usually produced by the ceramic method. On the other hand, very fine particles with high chemical homogeneity can be obtained by wet methods, such as co-precipitation. In this work, barium ferrite powders were obtained by co-precipitation. The effects of Fe/Ba molar ratio, reagent addition order, pH, temperature calcination and the presence of NaCl during calcination were investigated. The products were characterized by differential thermal analysis, X-ray diffractometry and scanning electron microscopy. The magnetic properties were evaluated by a vibrating sample magnetometer. The presence of a large amount of NaCl during calcination had a detrimental effect on the magnetic properties. Very fine particles with intrinsic coercivities up to 440 kA/m (5.50 kOe) and saturation magnetization  $\sigma_s$  up to 71 Am<sup>2</sup>/kg (71 emu/g) were achieved.

### 1. Introduction

Co-precipitation is a simple method to produce barium ferrite (BaFe<sub>12</sub>O<sub>19</sub>) powders with high intrinsic coercivity [1, 2] and is an alternative method to the ceramic process. It does not require sophisticated instrumentation and low cost raw materials can be used. Very fine particles with high chemical homogeneity and high reactivity can be obtained, so that calcination and sintering temperatures are lower than in the ceramic method [1]. Many aspects of the production steps of BaFe<sub>12</sub>O<sub>19</sub> powders by co-precipitation can interfere on the final product microstructure and magnetic properties, such as molar ratio, reagent addition order and the presence of NaCl [3, 4]. In order to obtain the stoichiometric compound BaFe<sub>12</sub>O<sub>19</sub> the Fe/Ba molar ratio must be defined previously, considering three aspects: the pH during precipitation, the solubility of the precipitated barium hydroxide, and the effects of the washing steps on the final Ba content. To overcome the Ba depletion it is usual to define an initial molar ratio lower than the stoichiometric one. Two different precipitation routes can be pointed out, considering the addition order, either to drop the salt solution into the alkaline solution or opposite. Different calcined products, related with different precursors, were obtained by these two different routes. There is a relationship between magnetic properties and precipitation route. The NaCl formed during precipitation acts as a catalyst to synthesize BaFe<sub>12</sub>O<sub>19</sub> during calcination [4], especially in processes where the washing step is carried out after calcination.

The aim of this work was to investigate the effects of these aspects on the magnetic properties of barium ferrites obtained by co-precipitation.

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## 2. Experimental Procedure

Pure iron chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Merck), and pure barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck), were used as raw materials. Fe/Ba molar ratios between 10 and 12 were investigated. The pH was controlled between 11 and 13.

Two precipitation routes were investigated: addition of alkaline solution ( $\text{NaOH}/\text{Na}_2\text{CO}_3$ ) into the salt solution ( $\text{FeCl}_3/\text{BaCl}_2$ ) (A\_S) and addition of salt solution into the alkaline solution (S\_A). The obtained co-precipitate was divided in two groups: for the first one, the washing was carried out after calcination (denominated here as “unprewashed”) and for the second group, the co-precipitate was washed only before calcination until the elimination of  $\text{NaCl}$  (denominated here as “prewashed”). The dried powders (“prewashed” and “unprewashed”) were calcined in a tubular furnace under dynamic oxygen atmosphere at temperatures ranging from 800 to 1100 °C for 1.5 h.

The samples were characterized by differential thermal analysis (DTA), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The magnetic properties were measured using a vibrating sample magnetometer (VSM) with a maximum applied field of 1600 kA/m.

## 3. Results and Discussion

### 3.1. Addition order

Figure 1 shows the XRD patterns of as-precipitated and calcined samples considering S\_A and A\_S routes (“prewashed”). S\_A precipitated powders showed  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{BaCO}_3$  peaks, whereas A\_S samples showed peaks of  $\beta\text{-FeOOH}$  and  $\text{BaCO}_3$ . All calcined samples showed the formation of  $\text{BaFe}_{12}\text{O}_{19}$ , but  $\alpha\text{-Fe}_2\text{O}_3$  was only detected in S\_A samples. The formation of phases other than  $\text{BaFe}_{12}\text{O}_{19}$  in the calcined samples can be related with the reactivity of the different phases formed during co-precipitation, considering the two different routes investigated.

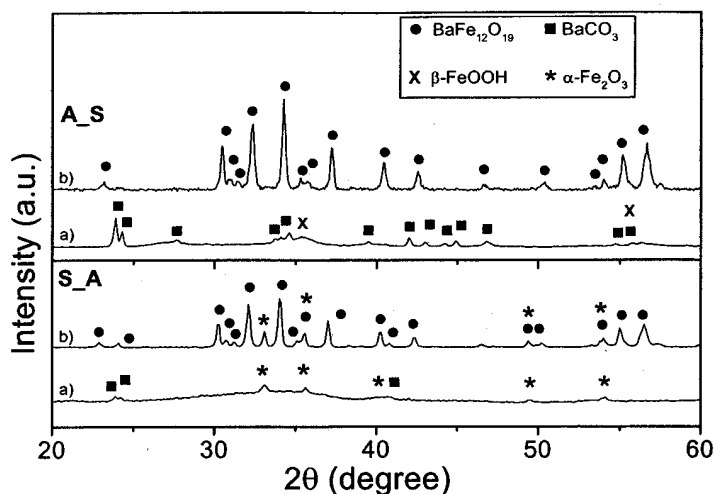


Fig. 1. XRD patterns of the “prewashed” samples; (a) as-precipitated and (b) calcined at 800 °C

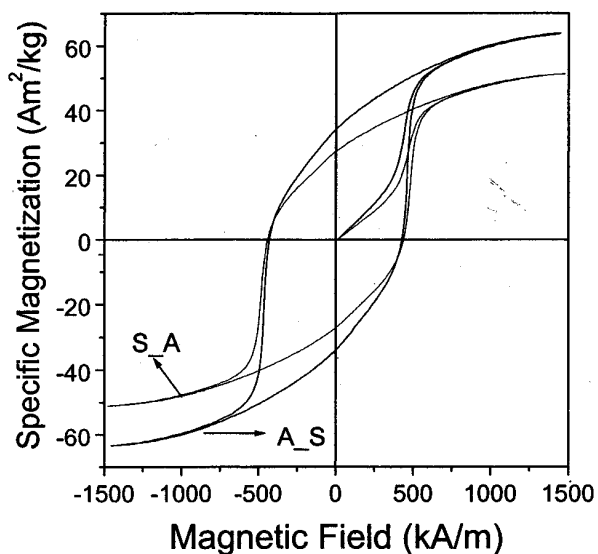


Fig. 2. Hysteresis curves of "pre-washed" samples produced by A\_S and S\_A routes calcined at 800 °C

The presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> affected the magnetic properties (Fig. 2). Higher values of saturation magnetization  $\sigma_s$  were observed for the sample obtained by the A\_S route, where the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was not observed after calcination.

Since the A\_S route resulted in better magnetic properties the effects of washing steps, molar ratio, pH and calcination temperature were investigated only in samples obtained by this route.

### 3.2. Washing steps (NaCl presence)

The DTA curves of as-precipitated A\_S samples (Fig. 3) show the washing effect. The "unprewashed" sample showed a sharp exothermic peak at 650 °C, attributed to barium ferrite crystallization. A sharp endothermic peak at 770 °C due to the melting of NaCl was observed for the "unprewashed" sample, too. As described in literature, barium ferrite formation occurs at temperatures around 760 °C [3], but the presence of NaCl decreases this temperature to 638 °C [4]. For the "prewashed" samples, these transitions were not well defined.

The XRD patterns of "prewashed" and "unprewashed" samples, calcined at 920 °C are shown in Fig. 4. No NaCl was detected in the final products. BaFe<sub>12</sub>O<sub>19</sub> was the only phase formed in the "prewashed" sample. The XRD pattern of the "unprewashed" sample showed the crystallization of the antiferromagnetic Ba<sub>2</sub>Fe<sub>6</sub>O<sub>11</sub> phase besides the formation of BaFe<sub>12</sub>O<sub>19</sub>. Sloccari [5] also observed the formation of this antiferromagnetic phase in the subsystem BaO · Fe<sub>2</sub>O<sub>3</sub>–BaO · 6Fe<sub>2</sub>O<sub>3</sub>. The presence of a large amount of NaCl in our "unprewashed" samples during calcination can be the principal responsible for the formation of Ba<sub>2</sub>Fe<sub>6</sub>O<sub>11</sub>.

Figure 5 shows the effect of washing in the magnetic properties of the samples calcined at 920 °C. The presence of Ba<sub>2</sub>Fe<sub>6</sub>O<sub>11</sub> in the "unprewashed" samples decreased  $\sigma_s$ . The saturation magnetization  $\sigma_s$  of the "prewashed" sample (71 Am<sup>2</sup>/kg) was nearly

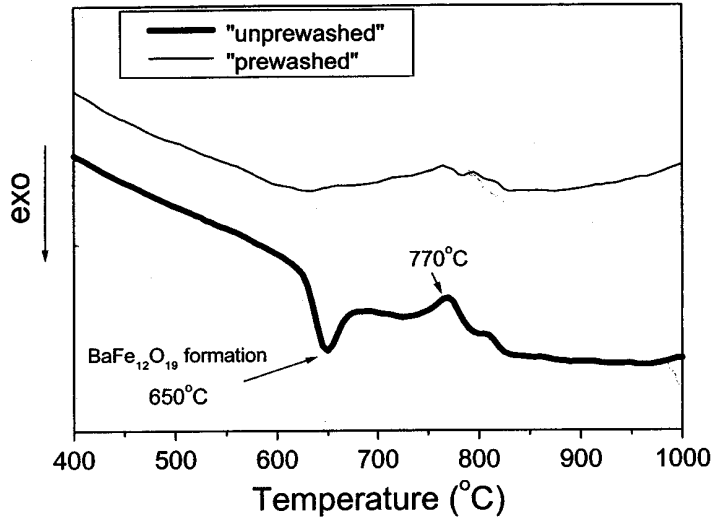


Fig. 3. DTA curves of as-precipitated A\_S samples obtained with  $n = 11$  and  $\text{pH} = 12.5$  (heating rate 10 K/min/dynamic oxygen)

the theoretical value predicted for pure barium ferrite ( $72 \text{ Am}^2/\text{kg}$ ) [6]. In this work, the  $\sigma_s$  values were obtained by applying the law of approach to saturation ( $1/H^2$ ) [7].

The washing also had some effect on the intrinsic coercivity (Fig. 5). For the samples obtained with  $n = 10$  and  $\text{pH} = 12.5$ , the coercivity increased from 345 kA/m for the “unprewashed” sample, to 427 kA/m for the “prewashed” one. This effect can be explained by the difference of NaCl concentration. A large amount of NaCl (“unprewashed” samples)

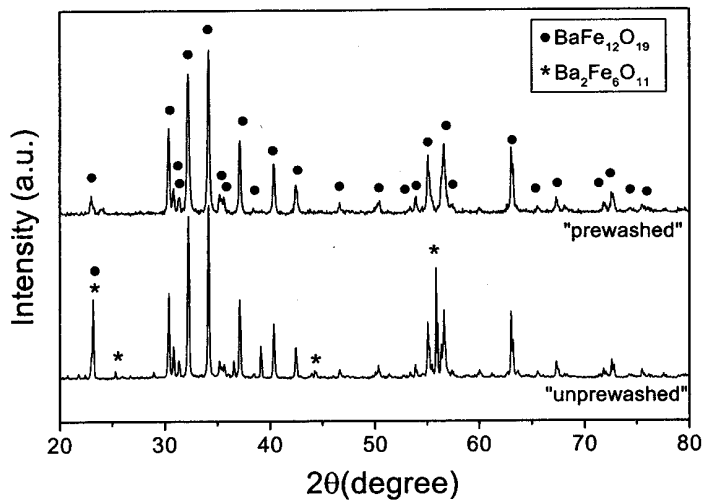


Fig. 4. XRD patterns of “prewashed” and “unprewashed” samples obtained by the A\_S route ( $n = 10$ ,  $\text{pH} = 12.5$ ,  $T = 920^\circ\text{C}$ )

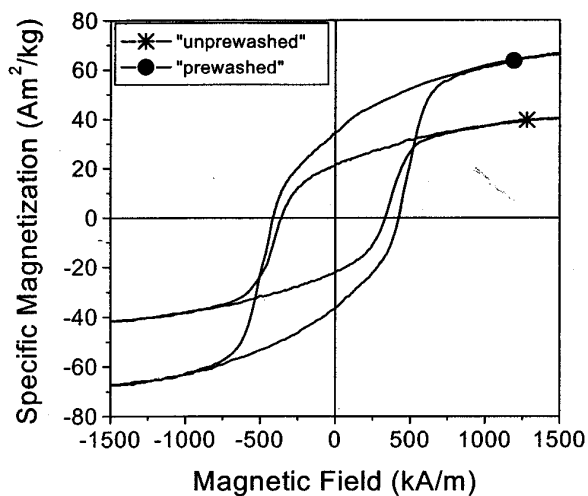


Fig. 5. Hysteresis curves of calcined A<sub>S</sub> powders ( $n = 10$ , pH = 12.5), showing the washing effect

during calcination tends to particle agglomeration inducing the grain growth and leading to a decrease in intrinsic coercivity. Washing reduces considerably the NaCl concentration ("prewashed" samples) and consequently the grain growth after calcination.

### 3.3. Molar ratio

Figure 6 illustrates the effect of solution molar ratio (for different pH values) on  $\sigma_s$  for the "unprewashed" samples. In a general way, the increase of the solution molar ratio to the stoichiometric value of 12 was not accompanied by an expected increase in  $\sigma_s$ . Different pH

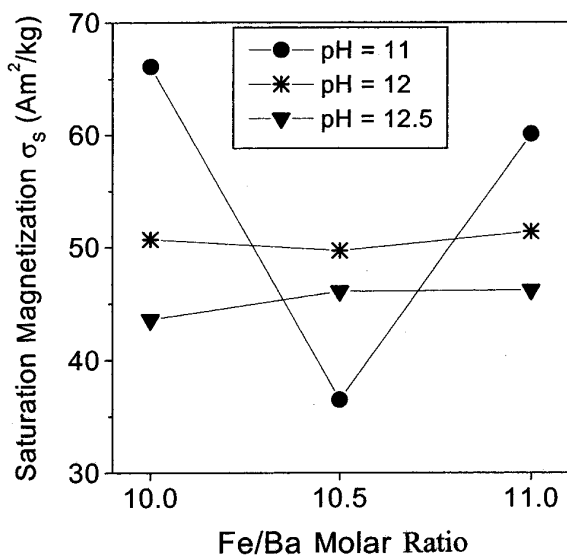


Fig. 6. Relation between molar ratio and  $\sigma_s$  (A<sub>S</sub> samples,  $T = 920^\circ\text{C}$ )

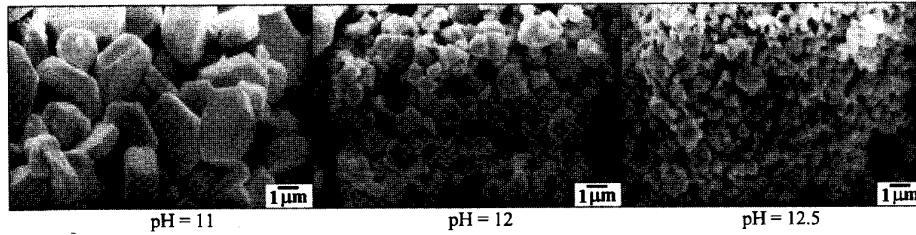


Fig. 7. SEM micrographs of “unwashed” A\_S samples (Fe/Ba = 11, 920 °C) at different pH values

and washing procedures can modify the precipitated molar ratio (pH and molar ratio are not independent variables). In Fig. 6 we considered the nominal values of the molar ratios.

### 3.4. pH

The particle size decreased with increasing pH for samples obtained with  $n = 10$  (Fig. 7), while for higher molar ratios (10.5, 11 and 12) the behavior was inverse. The presence of a liquid phase (NaCl) during calcination probably can be related with the ferrite particle size.

Figure 8 shows the effect of pH on magnetic properties. The  $\sigma_s$  decreased with pH increase in all “unwashed” samples, regardless of molar ratio and calcination temperature. Latorre et al. [8] observed a similar effect of pH on the magnetic properties of barium ferrite obtained by oxi-co-precipitation.

The NaCl formation during co-precipitation increases with increasing pH (higher NaOH contents). The presence of a large amount of NaCl, during calcination can cata-

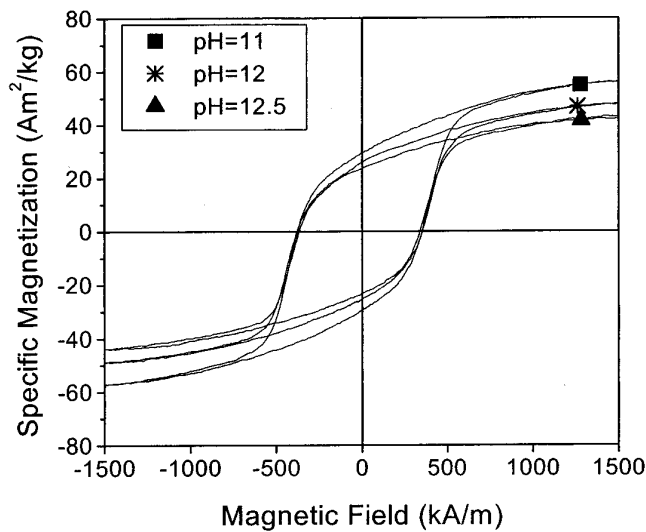


Fig. 8. Hysteresis curves of A\_S samples obtained with  $n = 11$  and calcined at 920 °C

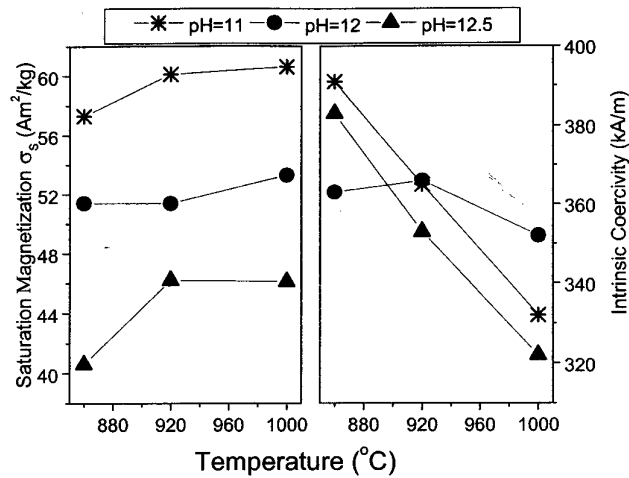


Fig. 9. Relation between temperature and magnetic properties for "unprewashed" samples (A\_S samples)

lyze the formation of phases other than  $\text{BaFe}_{12}\text{O}_{19}$ , as  $\text{Ba}_2\text{Fe}_6\text{O}_{11}$  (Fig. 4), which cannot be removed by washing. As discussed before, the presence of  $\text{Ba}_2\text{Fe}_6\text{O}_{11}$  decreased  $\sigma_s$ .

### 3.5. Calcination temperature

Figure 9 shows that the intrinsic coercivity decreased when the temperature was increased. This effect is related to the increasing grain size with the increase of calcination temperature. The calcination temperature had only a small effect on  $\sigma_s$  (Fig. 9), considering a constant value of pH.

## 4. Conclusions

The addition of alkaline solution into the salt solution (A\_S route) resulted in samples with better magnetic properties than the S\_A route.

The higher was the pH during precipitation the lower was  $\sigma_s$ .

The presence of large amounts of NaCl during calcination had a detrimental effect on the magnetic properties.

The calcination temperature had a small effect on the saturation magnetization  $\sigma_s$ , but affected the coercivity.

**Acknowledgement** We would like to thank FAPESP for financial support.

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