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The effects of synthesis variables on the magnetic properties of coprecipitated barium ferrite powders

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Abstract

Barium ferrites ($\text{BaFe}_{12}\text{O}_{19}$) are largely used for permanent magnets, mostly because of the adequate combination of low cost and good magnetic properties. These ferrites are usually obtained by the ceramic method; however, many chemical methods have been investigated. Among these methods, the coprecipitation is the most suitable, mainly because of its simplicity as compared to the other ones. In this work, $\text{BaFe}_{12}\text{O}_{19}$ was prepared by coprecipitation, changing the sequence of addition of the reagents, and the calcination temperature and time. The X-ray diffraction patterns of the calcined samples show the formation of $\text{BaFe}_{12}\text{O}_{19}$ at temperatures as low as 800°C . The ferrite powders obtained by coprecipitation have better magnetic properties than those obtained by the ceramic method, with an intrinsic coercivity value of 440 kA/m (5.5 kOe). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) has been largely used in the manufacture of permanent magnets since its development by Phillips researchers, in the beginning of the 50s. The wide application of these materials is mainly due to their low cost, high-saturation magnetization, high Curie temperature and high coercivity, associated with their excellent chemical stability and resistance to corrosion [1,2].

Many wet methods have been developed for the preparation of barium ferrites to avoid the milling step [2–14]. Among these methods, coprecipitation has been considered one of the most suitable for a low-cost production of fine particles of barium ferrite because it does not require expensive production equipment as high-temperature furnaces and high-energy mills. The main advantages of this method are: chemical homogeneity, the possibility of obtaining fine particles with a narrow size distribution and good reactivity of the powder that allows the decrease in calcination and also sintering temperatures [5]. Many aspects of the production steps of $\text{BaFe}_{12}\text{O}_{19}$ powders by coprecipitation interfere with the final product

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microstructure and magnetic properties, such as molar ratio, precipitation pH, addition order, calcination temperature, and others [3–7,9]. To guarantee a good reproducibility and a good performance of the final product, a careful control of these variables is very important.

The aim of this work was to qualify and to quantify statistically the effect of some synthesis variables on the magnetic properties of barium ferrites produced by coprecipitation using a full-factorial design of experiments [15]. The magnetic properties were evaluated using a vibrating sample magnetometer. X-ray diffractometry and scanning electron microscopy were also used to characterize the barium ferrite powders.

2. Experimental procedure

Barium ferrite powders were produced by coprecipitation with Fe/Ba = 11. The investigated variables were: (1) preparation method (*M*), (2) calcination temperature (*T*) and (3) calcination time (*t*).

Method 1: By this route, an aqueous solution of ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, was added to an aqueous solution of sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3 (5:1) by vigorous stirring.

Method 2: In this route, the addition order was changed, i.e., the aqueous solution of NaOH/ Na_2CO_3 (5:1) was added to the aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, by vigorous stirring.

The resulting precipitates obtained by the two described methods were washed with deionized water and dried. These powders were calcined under static atmosphere at 800°C and 1100°C in 1.5 and 4.0 h.

The crystalline phases were identified by X-ray diffractometry, using a RIGAKU PINT-2000 diffractometer, with Cu K_α radiation. The morphology and the particle size were examined in a JEOL JSM-5200 scanning electron microscope. The magnetic properties were measured using a vibrating sample magnetometer EG&G PAR model 4500 with a maximum applied field of 1600 kA/m.

To evaluate the effects of the mentioned variables on the magnetic properties of the obtained products, a 2^3 full-factorial experiment planning was used. Eight experiments were carried out, which with replication, complete a total of 16 investigated samples. The variables, levels and the factorial are given in Table 1.

3. Results and discussion

The X-ray diffraction patterns of the as-precipitated samples (Fig. 1), show that the powders obtained by Methods 1 and 2 are different in nature, i.e., different methods produced different crystalline phases. The powder obtained by Method 1 is a mixture of non-crystalline phases and two crystalline phases: hematite ($\alpha\text{-Fe}_2\text{O}_3$) and barium carbonate (BaCO_3). In the precursor powder obtained by Method 2 (Fig. 1b), the crystalline phases were akaganeite ($\beta\text{-FeOOH}$)

Table 1
The full-factorial design of experiments

Experiment	<i>M</i>	<i>T</i>	<i>t</i>	Variable	Level (–)	Level (+)
E1	—	—	—	Preparation method (<i>M</i>)	1	2
E2	+	—	—	Calcination temperature (<i>T</i>)	800°C	1100°C
E3	—	+	—	Calcination time (<i>t</i>)	1.5 h	4.0 h
E4	+	+	—			
E5	—	—	+			
E6	+	—	+			
E7	—	+	+			
E8	+	+	+			

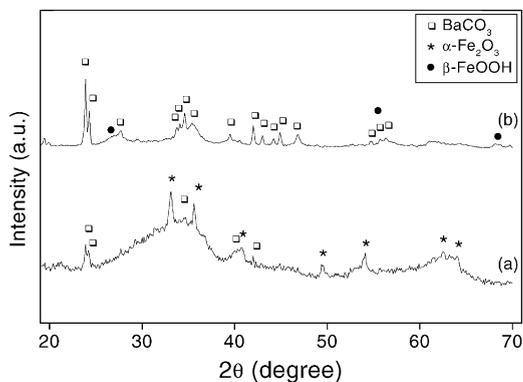


Fig. 1. X-ray diffraction patterns of the as-precipitated samples obtained by: (a) Method 1 and (b) Method 2.

and barium carbonate (BaCO_3). Sodium chloride (NaCl) peaks were not identified in these samples, indicating that the washing was efficient in the elimination of the larger amount of this product formed during the coprecipitation reaction.

The powders obtained by the two methods were subjected to different cycles of calcination and the X-ray diffraction patterns of these samples are shown in Figs. 2 and 3. It can be observed the $\text{BaFe}_{12}\text{O}_{19}$ formation even at lower calcination temperatures and the times, ($800^\circ\text{C}/1.5\text{ h}$), are independent of the preparation method. Beyond $\text{BaFe}_{12}\text{O}_{19}$, peaks of $\alpha\text{-Fe}_2\text{O}_3$ were also observed in the calcined samples obtained by Method 1. The formation of phases other than $\text{BaFe}_{12}\text{O}_{19}$ in the calcined samples can be related to the reactivity of the different phases formed during coprecipitation, considering the two different routes (Methods 1 and 2) investigated.

Fig. 4 shows the SEM micrograph of the sample obtained by Method 2, calcined at 1100°C for 1.5 h. Particles with hexagonal morphology, typical of barium ferrites produced by wet methods can be observed. The particle size is between 1 and $2\ \mu\text{m}$. Barium ferrite powders obtained by coprecipitation calcined between 860°C and 1000°C presented particle size between 0.5 and $2.0\ \mu\text{m}$ [9].

The magnetic properties of barium ferrite derived from the two preparation methods were measured at ambient temperature using a vibrating sample magnetometer. The results are sum-

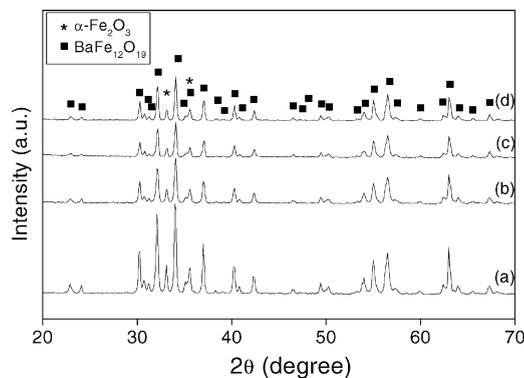


Fig. 2. X-ray diffraction patterns of the samples obtained by Method 1: (a) $800^\circ\text{C}/1.5\text{ h}$, (b) $800^\circ\text{C}/4.0\text{ h}$, (c) $1100^\circ\text{C}/1.5\text{ h}$ and (d) $1100^\circ\text{C}/4.0\text{ h}$.

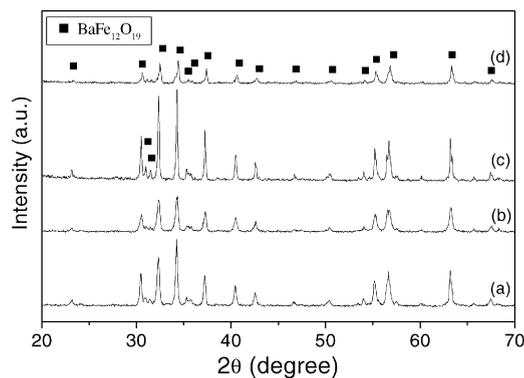


Fig. 3. X-ray diffraction patterns of the samples obtained by Method 2: (a) $800^\circ\text{C}/1.5\text{ h}$, (b) $800^\circ\text{C}/4.0\text{ h}$, (c) $1100^\circ\text{C}/1.5\text{ h}$ and (d) $1100^\circ\text{C}/4.0\text{ h}$.

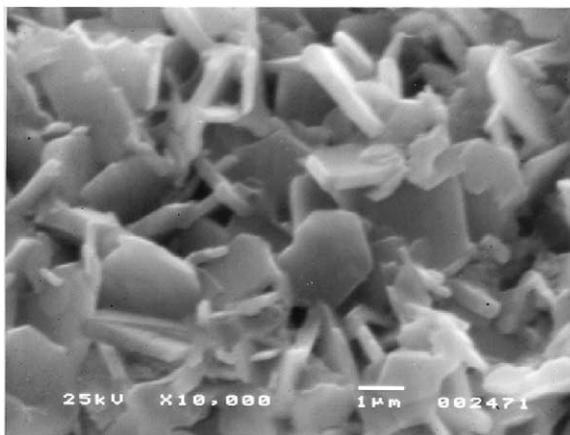


Fig. 4. SEM micrograph of the sample obtained by Method 2 calcined at 1100°C for 1.5 h.

marized in Table 2. The saturation magnetization σ_S values in Table 2 were obtained by applying the law of approach to saturation [16]. In Figs. 5(a) and (b), the hysteresis curves of the samples obtained by Methods 1 and 2, respectively, calcined at 800°C and 1100°C for 1.5 h, are shown. It is observed that the increase of the calcination temperature has a great effect in the magnetic properties of barium ferrites, mainly in the intrinsic coercivity, for both the investigated methods.

The data presented in Table 2 were statistically analyzed, using the algorithm of Yates [15]. The effect of the investigated variables in the values of iH_c and σ_S were quantitatively determined. Only the statistically significant effects were considered.

Table 2
Magnetic properties of the barium ferrite powders

Sample	iH_c (kA/m)	σ_S (Am ² /kg)
E1	440	53.8
	434 ^a	46.8 ^a
E2	430	67.5
	410 ^a	61.6 ^a
E3	162	52.6
	150 ^a	55.0 ^a
E4	260	66.1
	250 ^a	66.9 ^a
E5	424	54.3
	431 ^a	55.0 ^a
E6	430	63.8
	423 ^a	64.0 ^a
E7	142	55.6
	149 ^a	57.1 ^a
E8	220	69.0
	193 ^a	69.1 ^a

^a Replication.

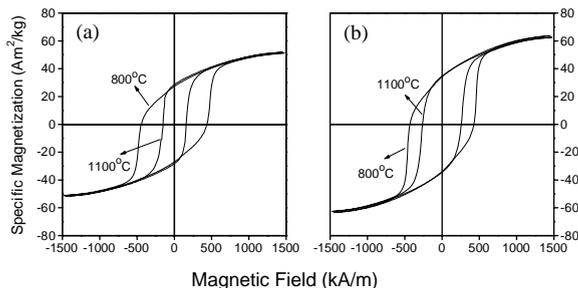


Fig. 5. Hysteresis curves of the samples calcined at 800°C and 1100°C for 1.5 h, obtained by: (a) Method 1 and (b) Method 2.

The following two equations express these results:

$$iH_c \text{ (kA/m)} = 309 + 18M - 119T - 8.0t, \quad (\text{A})$$

$$\sigma_S \text{ (Am}^2\text{/kg)} = 56.4 + 5.67M + 1.34T. \quad (\text{B})$$

For the intrinsic coercivity, iH_c , a sharp negative effect of the increase of the calcination temperature is observed. There is a positive effect in σ_S when Method 1 is changed to Method 2 (level +), as is discussed below.

Considering the samples obtained by Method 1 calcined for 1.5 h, the value of intrinsic coercivity decreases from 440 kA/m (5.5 kOe) for samples calcined at 800°C to 162 kA/m (2.04 kOe) at 1100°C. This result indicates that with the increase of the calcination temperature, a particle growth occurs, with consequent reduction of the intrinsic coercivity [9]. This result is in accordance with that previously described in literature [9,17]. The value of 440 kA/m, is higher than that found for barium ferrites obtained by the conventional ceramic method at 1200°C (173 kA/m) [18] and by micro-emulsion at 700°C (414 kA/m) [2]. However, this value is lower than that achieved for barium ferrite powders calcined at 925°C for 1.5 h, produced by coprecipitation (477 kA/m) [6].

The results also show a reduction of the coercivity with the increase of the calcination time, considering the same temperature. Eq. (A) estimates this effect in 8 kA/m, for the two investigated temperatures, that is, with the increase of calcination time from 1.5 to 4.0 h, the coercivity decreases by about 2.5%.

For the saturation magnetization σ_S , the preparation method has the sharper effect, as Eq. (B) indicates. Table 2 shows that the σ_S values of the samples obtained by Method 1 are systematically lower than those obtained by Method 2. The hematite formation in the samples produced by Method 1 reduces the volumetric fraction of barium ferrite and consequently reduces σ_S . The calcination temperature has a small effect on σ_S , about 2.4%, and the calcination time presented no significant effect. The results in Table 2 show that the highest value for σ_S was 69.1 Am²/kg (E8), that is close to the theoretical one (72 Am²/kg) [17]. Higher values for barium ferrites produced by coprecipitation have been reported elsewhere [4,6].

4. Conclusions

Coprecipitation method enabled to obtain barium ferrite at 800°C, a temperature considerably lower than the typical ceramic process. The preparation method leads to the formation of different crystalline phases and affects the magnetic properties of the obtained products, mainly the saturation magnetization σ_S . The calcination temperature has a sharp effect on the intrinsic coercivity of the barium ferrite powders, while calcination time shows a small influence.

According to the statistical analysis, the best results for the intrinsic coercivity were obtained in the following conditions: Method 2, lower calcination temperature (800°C) and time (1.5 h). For the saturation magnetization, σ_S , the highest value was found for the sample obtained by Method 2 and calcined in higher temperature.

Acknowledgements

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