Characterization of coprecipited Ba-hexaferrites with addition of SiO_2

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Preliminary results about the effect on magnetic, electrical and structural properties of the M-type ferrite $BaFe_{12}O_{19}$, due to the addition of SiO_2, prepared by the chemical coprecipitation method are reported. Several firing temperatures were used in order to investigate the admixture of SiO_2 in the samples. The ferrites were systematically examined using scanning electron microscopy (SEM), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). Experimental data of electrical conductivity were obtained by ac measurements.

Keywords: Hexaferrites; chemical coprecipitation

Se presentan resultados preliminares sobre los efectos en las propiedades estructurales, eléctricas y magnéticas de ferritas tipo M de bario, debidos a la adición de SiO_2. Las ferritas fueron preparadas usando el método de coprecipitación química. Se usaron varias temperaturas de sinterización para investigar el efecto del SiO_2 sobre las muestras. Las ferritas se examinaron por medio de un microscopio electrónico de barrido (SEM), difracción de rayos X (XRD) y magnetometría de muestra vibrante (VMS). Usando mediciones de ac se obtuvo la conductividad eléctrica.

Descriptores: Hexaferritas; coprecipitación química

PACS: 75.50.G; 75.60.E; 72.20.Pa

1. Introduction

M-type hexaferrites have been widely used in motors and loudspeakers as well as in microwave devices and in magnetic bubble memories. Also they have received much attention due to their potential application as high density magnetic storage media [1]. It is well known that the preparation process of these kind of compounds influences their structural and magnetic properties [2, 3], as well as the addition of oxides [4] and the substitution of some iron atoms by other ions [5]. Therefore, it is important to know the relationship that exists between preparation procedures, structural characteristics and magnetic properties. Magnetic and structural characteristics can be modified adding oxides into the raw materials [4]. It has been found that the admixture of SiO_2 reduces the grain size and at the same time the coercivity is increased [6].

The aim of this paper is to present preliminary results about the effect of the admixture of SiO_2 on the structural, electrical and magnetic properties of coprecipited M-type Ba hexaferrites. Magnetic characterization was performed in order to evaluate the magnetic properties such as coercivity (iHc), saturation (σ_s) and remanent magnetization (σ_r), and orientation ratio (σ_r/σ_s). In order to observe the electrical response from grains and grain boundaries, results of the electrical characterization are presented. Electrical characterization was performed using the impedance spectroscopy method [7]. These results are complemented with studies of scanning electron microscopy and X-ray diffractograms.

2. Experimental procedure

The chemical coprecipitation method was used to prepare Ba-hexaferrite powder [2]. A solution of $FeCl_3 6H_2O$ and

$BaCl_2 2H_2O$ in water was poured into a $NaOH/Na_2CO_3$ alkaline solution. The resultant powder was separated into four parts and 1% of SiO_2 in weight was added to each one. These mixtures were intimately mixed and polyvinyl alcohol was used as binding medium. Samples of different sizes were pressed as discs by applying a pressure of 3.5 Ton/cm^2. Thermal treatment of the obtained samples was performed at 950°C, 1040°C, 1130°C and 1220°C, respectively to each set of samples during 1 hour. This procedure was carried out in normal atmosphere.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of samples with 1% SiO_2 fired at 1220°C. The same pattern is obtained for samples without oxide and with other concentrations. The lattice parameters obtained are: $a = 0.589$ nm, $b = 0.589$ nm, and $c = 2.323$ nm. These parameters agree with those previously reported for pure Ba-ferrite. The surface morphology

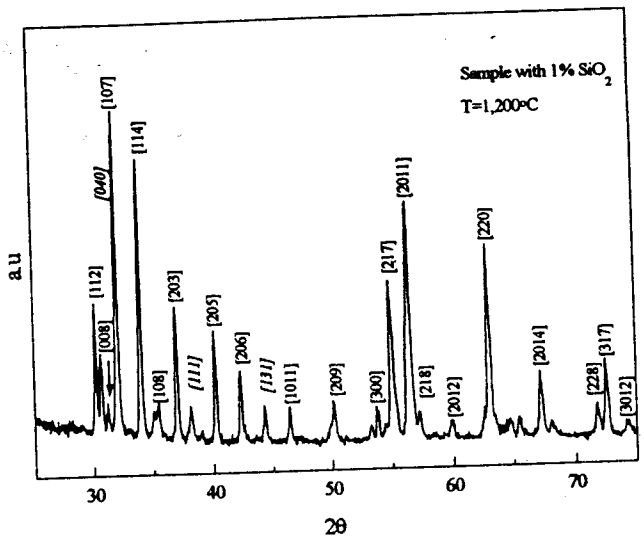

FIGURE 1. X-ray spectrum of samples with 1% SiO_2 in weigth, fired at 1220°C. Italic indexes correspond to NaOH.

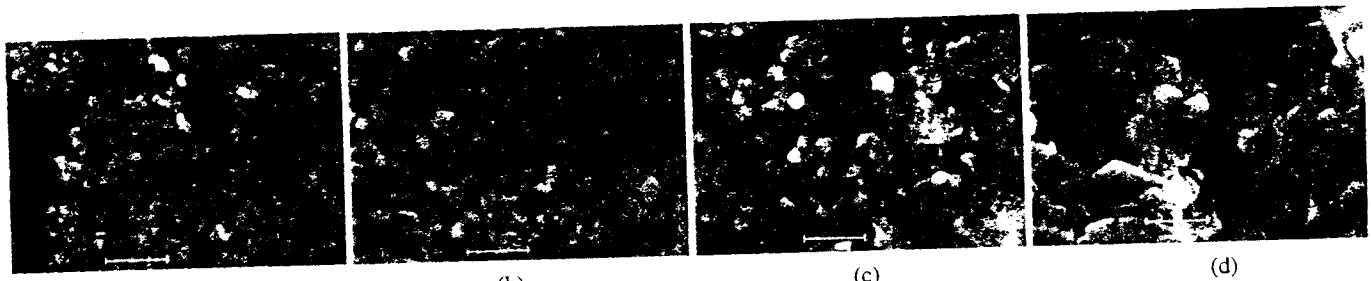

FIGURE 2. SEM micrographs of samples with 1% SiO_2 in weight, fired at (a) 950°C, (b) 1040°C, (c) 1130°C, and (d) 1220°C. The mark corresponds to 1 μm.

of samples with 1% SiO_2, fired at different temperatures is presented in Fig. 2. From electron scanning micrographs it is possible to measure the average grain sizes (see Table I). At high temperatures a larger grain size is obtained. It is important to observe that samples sintered at 1220°C exhibit two different grain sizes (Fig. 2). One size ranges from 8 μm to 22 μm and the other one from 0.40 μm to 0.50 μm. Figure 3 shows the magnetization saturation and coercitive field of the samples with thermal treatment at different temperatures. As can be seen, the higher the firing temperature the lower the coercivity (*iHc*). Low values of coercivity have been already observed in samples with large grain size [6]. For $T = 1220$°C the small value of the coercivity is probably due to the coexistence of very different grain sizes (Table I). From SEM analysis it is observed that samples sintered at 1220°C showed no diffusion of SiO_2 into the grains.

Results of electrical characterization are also presented. Figure 4 shows Arrhenius plots of electrical conductivity *versus* temperature for ferrite samples fired at 1220°C without dopant, and samples with 1% of SiO_2. The activation energy is 0.68 eV for the pure sample, whereas for the other one is

TABLE I. Effect of firing temperature on the magnetic parameters of coprecipited Ba-ferrite with addition of 1% in weight of SiO_2.

T_s(°C)	Av. grain size (μm)	σ_s (emu/g)	σ_r (emu/g)	σ_r/σ_s	*iHc* (kOe)
950	0.20	54.71	30.56	0.5585	5750
1040	0.22	59.09	32.67	0.5528	5350
1130	0.45	59.07	32.62	0.5522	4300
1220	0.475/15.0	63.17	22.30	0.3530	1100

0.46 eV; that means that the presence of SiO_2 promotes the electrical conduction. Plots of Fig. 5 show the usual behavior of isothermal conductivity as a function of frequency for samples without SiO_2 dopant. As shown, at low temperatures ($T < 100$°C) and low frequencies, the conductivity exhibits only an ac component. At higher temperatures ($T > 339$°C) the dc conductivity dominates. For constant frequency, plots of conductivity against $1000/T$ are presented in Fig. 6. Conductivity values remain almost constant for the whole fre-

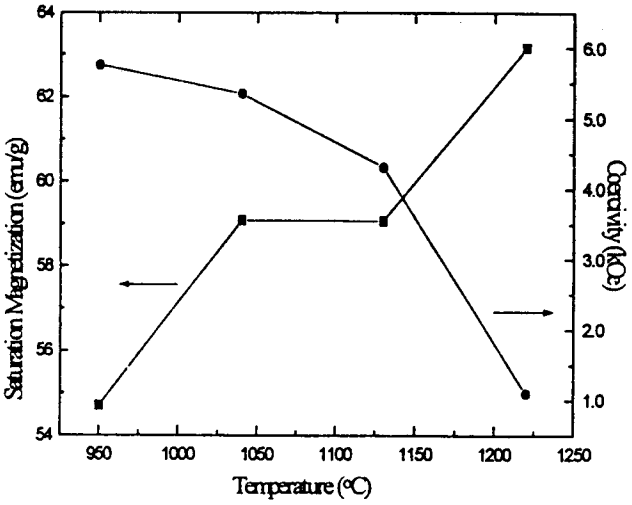

FIGURE 3. Saturation and coercivity of samples with 1% SiO_2 in weight with thermal treatment at different temperatures.

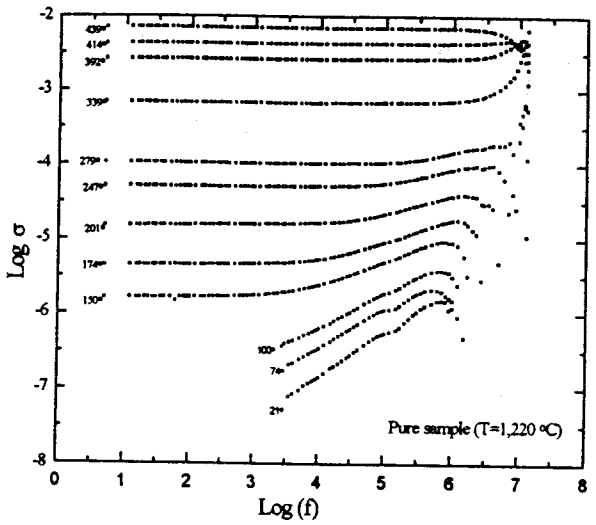

FIGURE 5. Isothermal conductivity as a function of frequency for samples without admixture.

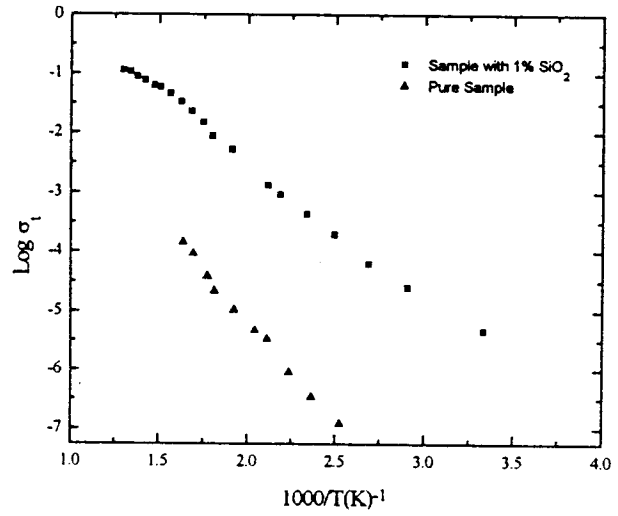

FIGURE 4. Arrhenius plots of electrical conductivity *versus* temperature for ferrite samples without dopant and with 1% of SiO_2, fired at 1220°C.

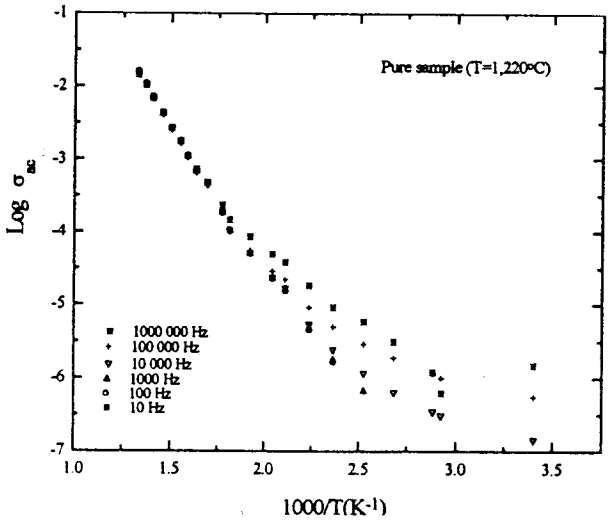

FIGURE 6. Conductivity *versus* $1000/T$ at fixed frequencies.

quency range; at higher temperatures it is possible to find the component corresponding to the activation energy for the dc conductivity (0.85 eV). At low temperatures conductivity values are dispersed and ac conductivity can be found (Table II).

TABLE II. Activation energy for samples fired at 1220°C with 1% SiO_2 for different frequencies.

f	E_{ac}(eV) Pure samples	E_{ac}(eV) Samples with 1% SiO_2
10^{-2}	0.66	0.40
10^{-1}	0.65	0.39
10^{0}	0.62	0.26
10^{1}	0.42	0.20
10^{2}	0.36	
10^{3}	0.35	

4. Conclusions

Barium M-type ferrites were synthesized using the chemical coprecipitation method. Using this method small grain size ($< 1\,\mu$m) is achieved when a relative low firing temperature (925°C) is applied. Moreover it has been found that the addition of SiO_2 inhibits the grain growth. Samples fired at 1220°C present the coexistence of both very large and very small grains. This fact is directly related with obtaining small coercivity values. Furthermore, the addition of silicon oxide was not relevant to limit the grain growth as the sintering temperature increases above 1220°C. The minimum firing temperature to observe SiO_2 diffusion into the grains, and its consequences on the magnetic and electrical properties, is not

available at this time. Finally it is worth to mention that relevant information about the influence of SiO_2 on grain boundaries, to promote electrical conductivity, may be obtained by using impedance spectroscopy, a powerful technique used to characterize electrical properties of a wide variety of materials. Electrical and magnetic measurements of samples with other oxide concentrations and firing temperatures are under study.

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