Magnetic properties and microstructure of Ba-ferrite powders prepared by ball milling

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Abstract

The magnetic properties and the phase constitution of barium ferrite powders with Fe/Ba ratios varying from 7 to 15 and heat-treated in the temperature range 1000-1200°C are reported. The results showed that heating temperature was e!ective in increasing the magnetization (M_s) of the powders for ratios> 10. For lower ratios M_s increased initially and then decreased with increasing temperature, presumably due to the formation of $BaFe_2O_4$. The coercivity (H_{ci}) presented a maximum for all the compositions and then decreased due to particle growth. In addition, the effect of the milling time on the magnetic properties and powder characteristics was investigated. It was found that 40 h of milling led to having samples with less volume fraction of second phases and that the magnetic properties were also maximized. TEM micrographs show particle sizes varying from 0.1 to 2 μm.

Introduction

Mechanical alloying via ball-milling is a technique that is being recently adapted to the preparation of barium and strontium ferrites. This simple and economical procedure is useful for the production of powders composed of very small particles [1,2], usually smaller than the single-domain size (~1 lm).

There are several studies concerning the synthesis and characterization of $Ba(Sr)Fe_{12}O_{19}$ ferrites prepared using high-energy ball milling [1,2]. It has been reported

that optimum M_s values (~70 emu/g) can be obtained by annealing as-milled Ba-ferrites samples at temperatures between 1000°C and 11003° [1]. Values of coercivity (H_{ci}) in the range 5-6 kOe have been achieved by this technique. However, for lower milling speeds, H_{ci} values higher than 5 kOe have not been obtained. High values of coercivity are related to particles significantly smaller than the single-domain size. The studies have shown that the magnetic properties are strongly linked to the powder microstructure, which is controlled by the milling and heat-treatment conditions. Some workers [2 reported that the milling time had little influence on the magnetic properties of $SrFe_{12}O_{19}$ powders after milling for periods of 2-30 h. The heattreatment temperature greatly a!ected the values of the magnetic properties, reaching maxima at &1000-1100°C.

The present study reports on the magnetic properties and microstructure of Ba-ferrites powders, prepared using ball-milling, in relation to the milling time, the Fe/Ba ratio and the heat treatment temperature.

Experimental

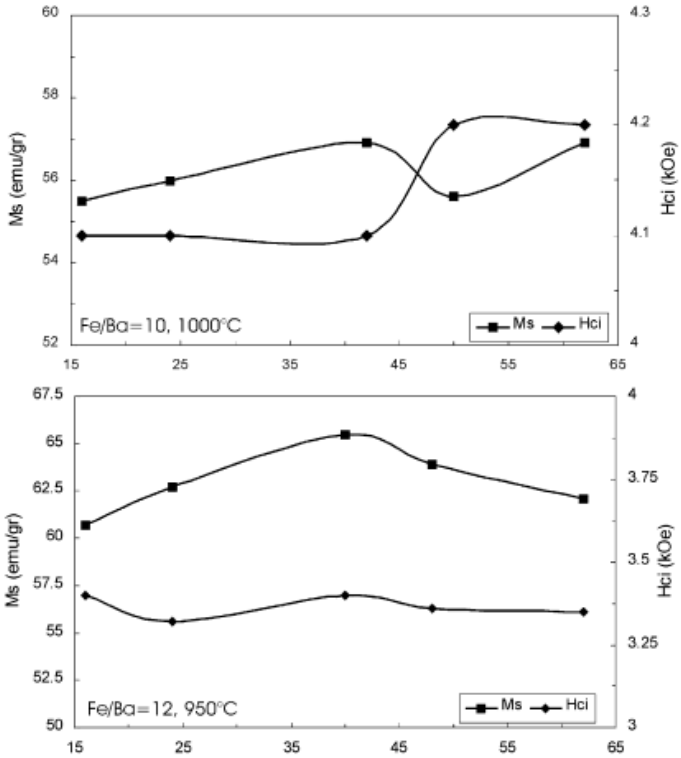
Samples with different Fe/Ba ratios (7-15) were prepared by ball-milling $BaCO_3$ and α-Fe_2O_3 of 99% purity. Mechanical alloying was performed in a ball mill rotating at 95 rpm, with a ball to powder mass ratio of 10: 1. To investigate the effect of the milling time on the magnetic properties, samples with different Fe/Ba ratios were milled from 16 to 62 h and calcined at different temperatures. The as-milled samples were heat treated for 2 h at temperatures in the range 1000-1200°C, as this temperature range has been reported as the optimum to attain the most favorable magnetic properties.

XRD analyses using Cu-Kα radiation were carried out for phase identification and qualitative analyses on some selected samples. The magnetic properties were measured using a LS-VSM with an applied field up to 1.2 T. TEM observations were also carried out to evaluate the particle size and shape.

Results and discussion

Influence of the milling time on the magnetic properties

Fig. 1 shows the magnetic properties of powders with Fe/Ba ratios of 10, 12 and 15, heat treated at 1000°C, 950°C and 1050°C, respectively, as a function of the milling time which varied from 16 to 62 h. The XRD diffractograms of the as-milled samples did not apparently show any presence of amorphous phase. However, even after 16 h milling the $BaCO_3$ reflections disappeared and the only XRD peaks observed were those corresponding to α-Fe_2O_3.



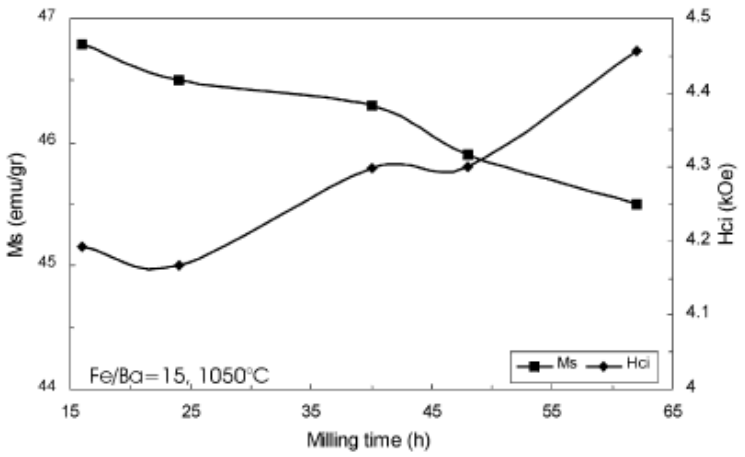


Fig. 1. Effect of the milling time on the magnetic properties of samples with different Fe/Ba ratios.

These reflections diminished in height as the milling time increased. Once the samples were annealed, only slight variations in the magnetic properties could be observed. TEM observation revealed that this parameter mainly influenced the particle size, which decreased with increasing milling time. Fig. 2 shows a TEM micrograph of a sample with Fe/Ba ratio of 15, milled for 40 h and heat treated at 1050°C, showing a particle size below 1 μm. Jin et al. [2] investigated $SrFe_{12}O_{19}$ powders milled from 0 to 30 h and heated at 1000°C, observing only a slight increase in the magnetic properties with increasing milling time.

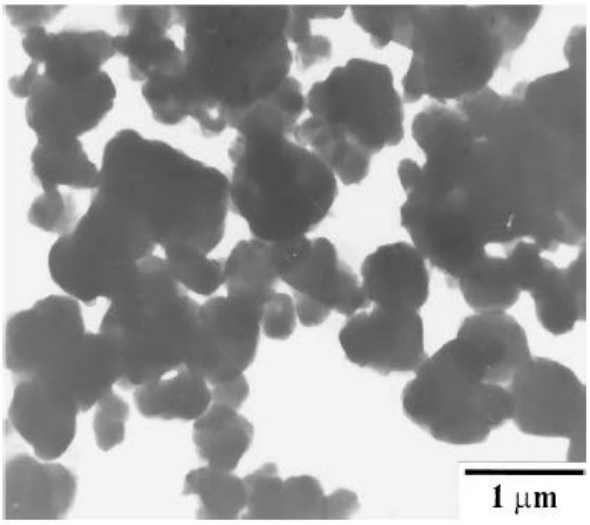


Fig. 2. TEM micrograph of a sample with Fe/Ba ratio of 15 annealed at 1050°C for 2 h.

In the present study, for $BaFe_{12}O_{19}$ samples, M_s and H_{ci} increased up to 40 h and then decreased slowly until 62 h, though variations in H_{ci} were much smaller than for M_s. However, this situation changed with the composition and the annealing temperature. For the ferrites with Fe/Ba ratios of 10 and 15, M_s and H_{ci} increased with increasing milling time up to 62 h for the former, while H_{ci} increased and M_s decreased for the latter. It might be said that M_s is more sensitive to milling time than H_{ci} . A compromise has to be reached between milling time and particle size. On one hand, increasing the milling time reduces the particle size and increases the reactivity of the powders to form pure $BaFe_{12}O_{19}$. However, on the other hand, this also brings about excessive wear of the milling media and contamination of the sample. Short milling times yields coarse particles, which become larger after annealing at high temperatures, decreasing the coercivity. Some workers reported their investigations on the influence of the milling time on the magnetic properties of pure $BaFe_{12}O_{19}$ and $BaFe_{12}O_{19}$+Fe_2O_3 mixtures [3,4]. Since the milling process creates defects or leads to amorphization of the crystal

structure, the magnetic properties deteriorated. After annealing the properties improved due to stress release and recovery from the defective structure.

Particle sizes achieved under the conditions imposed in this study were mostly below the single domain size (<1 μm). However, some authors [1] have achieved sizes much smaller (<200 nm) by using high-energy milling. It is then thought that since coercivity depends strongly on the particle size, to obtain H_{ci} values near the theoretical limit, it is necessary to reduce the particle size down to a few tens of nanometers, which is only possible by using high-energy milling.

Effect of the heat treatment temperature and composition on the magnetic properties

It is well known that the milling conditions and posterior treatment greatly affect the magnetic properties [2,5,6] of powders. Table 1 summarizes the magnetic properties of samples with different Fe/Ba ratios heated at several temperatures.

Table 1
Magnetic properties of samples with various Fe/Ba ratios annealead at different temperatures

Fe/Ba	1000°C	1050°C	1100°C	1150°C	1200°C
7	$M_s = 54.0$ $M_r = 29.3$ $H_{ci} = 3.71$	$M_s = 61.0$ $M_r = 31.5$ $H_{ci} = 3.99$	$M_s = 57.0$ $M_r = 31.0$ $H_{ci} = 3.91$	$M_s = 57.1$ $M_r = 30.1$ $H_{ci} = 3.18$	$M_s = 59.2$ $M_r = 30.1$ $H_{ci} = 3.02$
8	$M_s = 46.8$ $M_r = 25.6$ $H_{ci} = 3.70$	$M_s = 50.1$ $M_r = 27.9$ $H_{ci} = 4.07$	$M_s = 51.9$ $M_r = 28.4$ $H_{ci} = 4.00$	$M_s = 65.1$ $M_r = 35.4$ $H_{ci} = 3.30$	$M_s = 56.4$ $M_r = 30.2$ $H_{ci} = 3.95$
10	$M_s = 56.0$ $M_r = 31.3$ $H_{ci} = 3.80$	$M_s = 56.6$ $M_r = 31.9$ $H_{ci} = 3.96$	$M_s = 56.9$ $M_r = 31.6$ $H_{ci} = 4.20$	$M_s = 58.2$ $M_r = 31.3$ $H_{ci} = 3.93$	$M_s = 62.1$ $M_r = 30.7$ $H_{ci} = 2.63$
12	$M_s = 59.5$ $M_r = 31.1$ $H_{ci} = 3.30$	$M_s = 62.2$ $M_r = 36.5$ $H_{ci} = 3.95$	$M_s = 63.5$ $M_r = 33.7$ $H_{ci} = 4.03$	$M_s = 64.8$ $M_r = 36.4$ $H_{ci} = 4.10$	$M_s = 68.5$ $M_r = 38.3$ $H_{ci} = 3.85$
15	$M_s = 43.6$ $M_r = 24.4$ $H_{ci} = 4.50$	$M_s = 48.5$ $M_r = 25.6$ $H_{ci} = 4.48$	$M_s = 51.3$ $M_r = 28.1$ $H_{ci} = 4.43$	$M_s = 52.0$ $M_r = 27.0$ $H_{ci} = 4.26$	$M_s = 53.9$ $M_r = 29.0$ $H_{ci} = 3.88$

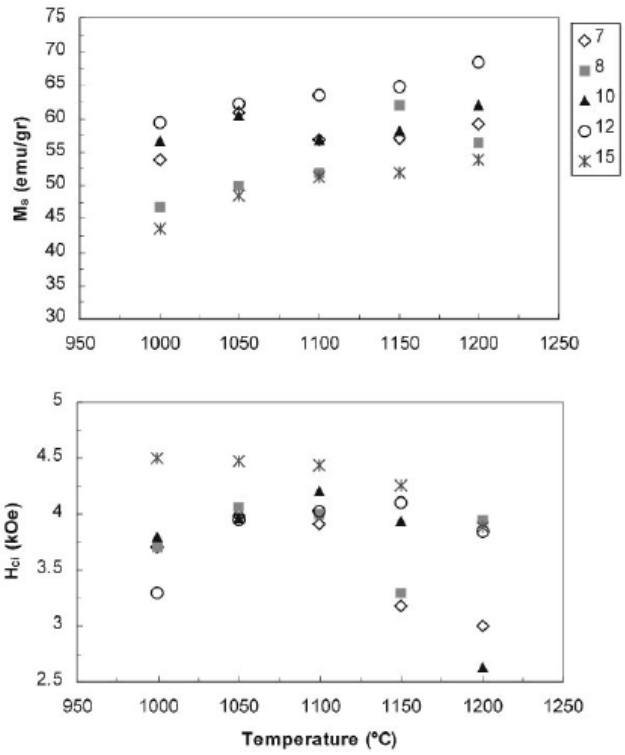


Fig. 3. Effect of the annealing temperature on the magnetic properties of samples with several Fe/Ba ratios.

Fig. 3 shows the effect of the temperature on M_s and H_{ci} for samples treated at 1000-1200°C for 2 h. These results showed that the heating temperature was effective in increasing M_s for samples with Fe/Ba>10. For lower Fe/Ba ratios M_s achieved a maximum and then decreased. H_{ci} was initially enhanced, attained a maximum and then dropped. TheM_s enhancement could directly be related to the higher amount of $BaFe_{12}O_{19}$ formed as the temperature was raised, as confirmed from the XRD patterns for the samples with Fe/Ba ratios>10. For lower Fe/Ba ratios, M_s enhancement showed a maximum due to the formation of BaFe2O4. The amount of the $BaFe_2O_4$ phase depended on the amount of free $BaCO_3$ and the annealing temperature. Fig. 4 shows XRD patterns for samples with different Fe/Ba ratios, heat-treated at various temperatures.

The behavior of H_{ci} with increasing temperature might be explained in terms of the higher amount of hard phase, causing an enhancement of the coercivity.

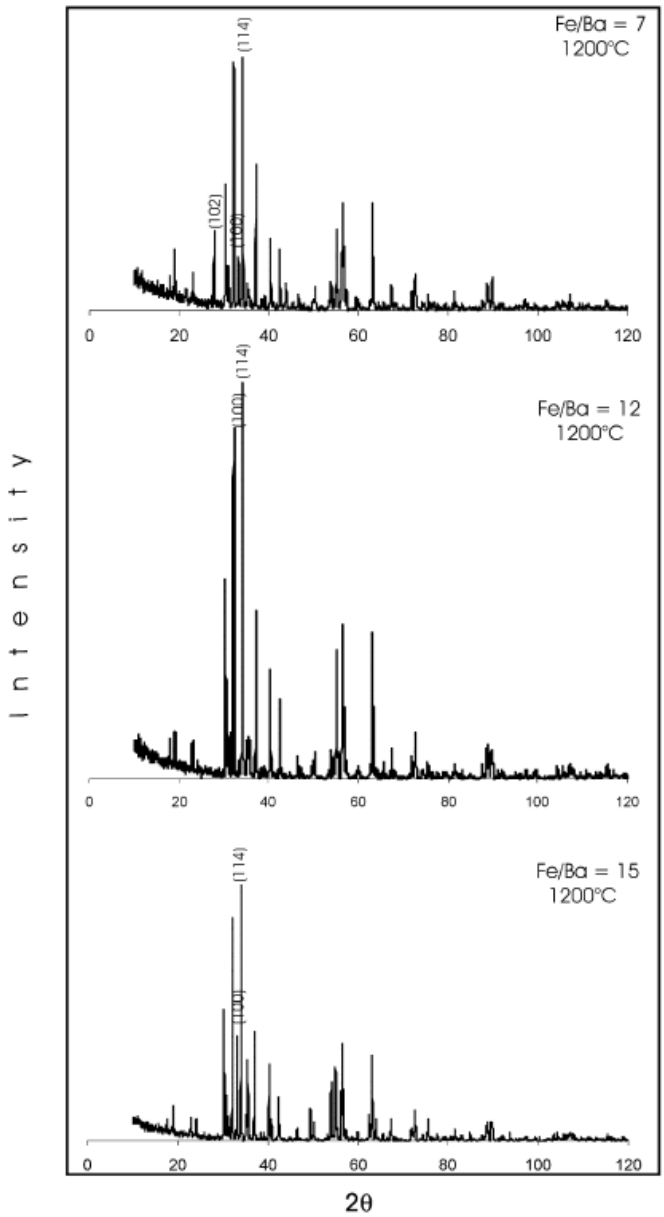


Fig. 4. XRD patterns showing the main diffraction peaks of the $BaFe_{12}O_{19}$, α-Fe_2O_3 and $BaFe_2O_4$ phases.

However, beyond a certain temperature, particle coarsening begun to affect this property negatively. Fig. 5 presents micrographs of powders heated at 1000 and 1200°C, where it is observed that high temperatures promoted particle growth and

agglomeration. Compositional variation affected greatly the magnetic properties and the powder microstructure. Excess of Ba or Fe led to the formation of $BaFe_2O_4$ and/or α-Fe_2O_3, which resulted in deterioration of the magnetization (Fig. 3).

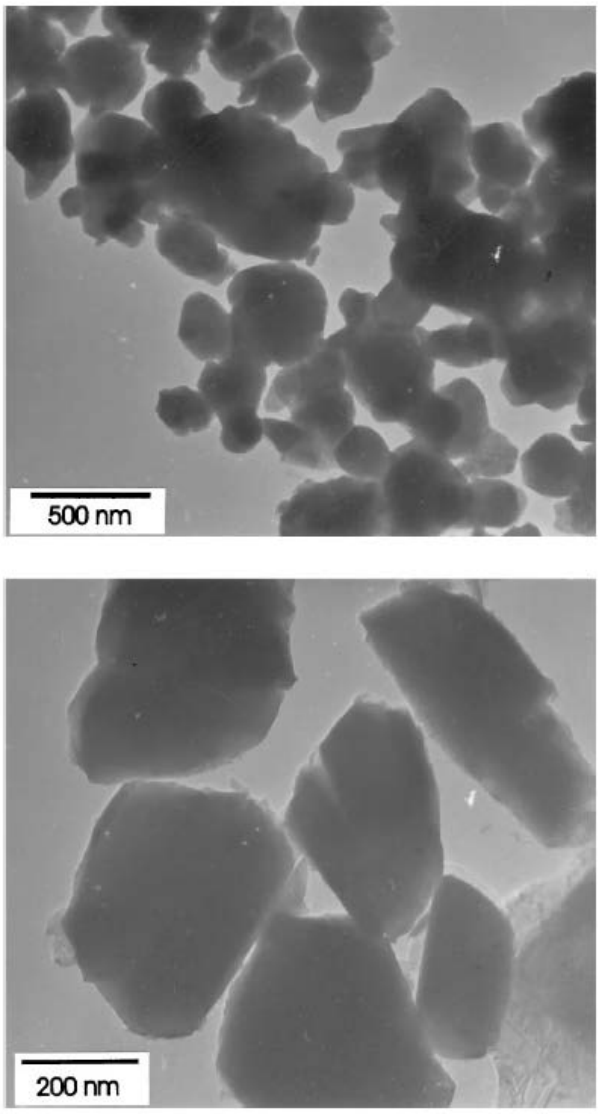


Fig. 5. Micrographs of samples with (a) Fe/Ba = 10, and (b) Fe/Ba = 7, heat-treated at 1000°C and 1200°C, respectively.

It appeared as well that the coercivity seemed to be enhanced by the presence of large amounts of α-Fe_2O_3, i.e. Fe/Ba=15. For Fe/Ba ratios from 7 to 12 H_{ci} did not

experience large variations. The highest magnetization achieved for the series of compositions studied here corresponded to the sample with Fe/Ba ratio of 12, which reached 68 emu/g. This value is comparable to those reported by other workers [1].

Table 2
Relative XRD peak intensities for (1 1 4) $BaFe_{12}O_{19}$, (1 0 0) α-Fe_2O_3 and (1 0 2) $BaFe_2O_4$ and estimated volume fractions for samples composed of two phases

Fe/Ba ratio	$I_{(1\,1\,4)}/I_{(1\,0\,0)}$	$I_{(1\,1\,4)}/_{(1\,0\,2)}$
7	32.91 (1050°C)	15.29 (1050°C)
	5.87 (1200°C)	2.19 (1200°C)
8	11.45 (1050°C)	6.52 (1050°C)
	21.96 (1200°C)	8.05 (1200°C)
10	23.76 (1000°C)	18.46 (1000°C)
	21.45 (1100°C)	11.95 (1100°C)
	27.77 (1200°C)	8.33 (1200°C)
12	6.83 (950°C)	—
	($\%M_{phase} = 87.23$)	
	8.51 (1000°C)	
	($\%M_{phase} = 89.48$)	
	19.14 (1200°C)	
	($\%M_{phase} = 95.00$)	
15	2.14 (1050°C)	—
	($\%M_{phase} = 68.00$)	
	2.46 (1200°C)	
	($\%M_{phase} = 71.00$)	
12	$T = 950$°C 7.53 (16 h)	—
	($\%M_{phase} = 88.27$)	
	7.46 (40 h) ($\%M_{phase} = 88.18$)	
	6.0 (62 h) ($\%M_{phase} = 85.71$)	
15	$T = 1100$°C 2.0 (16 h)	—
	($\%M_{phase} = 66.00$)	
	3.25 (40 h)	
	($\%M_{phase} = 76.47$)	
	2.15 (62 h)	
	($\%M_{phase} = 68.25$)	

Microstructure of powders

XRD and TEM techniques were employed to investigate the phase constitution, the particle size and morphology of the ferrite samples. To estimate qualitatively the amounts of the phases, the relative intensity of the main non-overlapping peaks were evaluated. The intensities were measured from a series of selected peaks, namely (114), (100) and (102) for $BaFe_{12}O_{19}$, α-Fe_2O3 and $BaFe_2O_4$, respectively. Table 2 summarizes these results. Similar analyses were performed for samples with Fe/Ba ratios of 12 and 15 milled for various times and are also shown in Table 2. An estimation of the volume fraction for the $BaFe_{12}O_{19}$ phase was carried out when the sample was composed of only two phases.

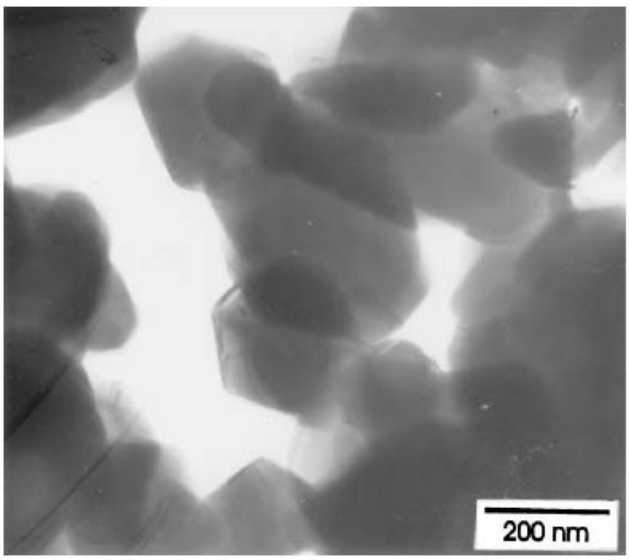


Fig. 6. TEM image of a sample with a Fe/Ba = 12, annealed at 1000°C.

It can be observed that the percentage of the hard magnetic phase increased with increasing temperature, leading to a higher M_s . On one hand, samples with Fe/Ba=7 and 8 containing relatively large amounts of $BaFe_2O_4$ showed poorer M4 than samples with Fe/Ba ratios of 10 and 12. This could be explained by the fact that the

latter compositions possessed only small amounts of α-Fe_2O_3 and/or $BaFe_2O_4$. On the other hand, samples with Fe/Ba=15 showed the lowest M_s values which might be related to the larger amounts of α-Fe_2O_3. From these results it seems that α-Fe_2O_3 is more harmful to M_s than $BaFe_2O_4$.

From the phase composition estimations of samples milled for different times at a given temperature, it seemed to be that 40 h was the most favorable milling time to obtain the largest amount of $BaFe_{12}O_{19}$. It appears sensible to study Fe/Ba ratios spanning in a narrower range, near the stoichiometric composition of the $BaFe_{12}O_{19}$ phase, as small amounts of α-Fe_2O_3 still remained after annealing at 1200°C. It has been reported that Fe/Ba ratios slightly lower than the stoichiometry lead to the production of pure $BaFe_{12}O_{19}$ with improved properties [7].

TEM images showed that particles had a wide range of sizes from ~0.1 to 2 lm with irregular shapes along with only a few hexagonal-shaped particles were observed as shown in Fig. 6.

Analyses of the hysteresis loops showed that samples consisted of single and multidomain grains. Curves for samples with large amounts of second phases manifested an anomalous behavior in the demagnetization quadrant when the samples were heat-treated at high temperatures. Figs. 7 and 8 show hysteresis loops of samples with different compositions, prepared under several conditions.

Conclusions

The magnetic properties and the microstructure of Ba-ferrite powders with different Fe/Ba ratios, prepared by ball milling and heat-treated at several temperatures were investigated. The results showed that the highest M_s values were attained for

samples with the stoichiometric composition, though slight deviations from the $BaFe_{12}O_{19}$ stoichiometry is recommendable to eliminate second phases completely. H_{ci} did not change to a great extent with this deviation for Fe/Ba ratios of 7 to 12. However, when large amounts of α-Fe_2O_3 were present (Fe/Ba=15) improvement of the coercivity was evident; a fact not well understood. When there was an excess of Ba, α-Fe_2O_3 and $BaFe_2O_4$ phases appeared in the structure, this was linked to the annealing temperature. However, α-Fe_2O_3 seemed to be more harmful to M_s than $BaFe_2O_4$. Maximum values in M_s were achieved for the samples with Fe/Ba=12 and these were comparable to those reported in the literature. Nevertheless, only moderate values of H_{ci} were attained, suggesting the need of reducing further the particle size.

Milling time was also investigated in this study, finding that 40 h milling led to the highest magnetic properties.

TEM observations revealed that the powders consisted of particles with irregular shapes having sizes in the range 0.1-1.3 μm, which was manifested in the hysteresis loops.

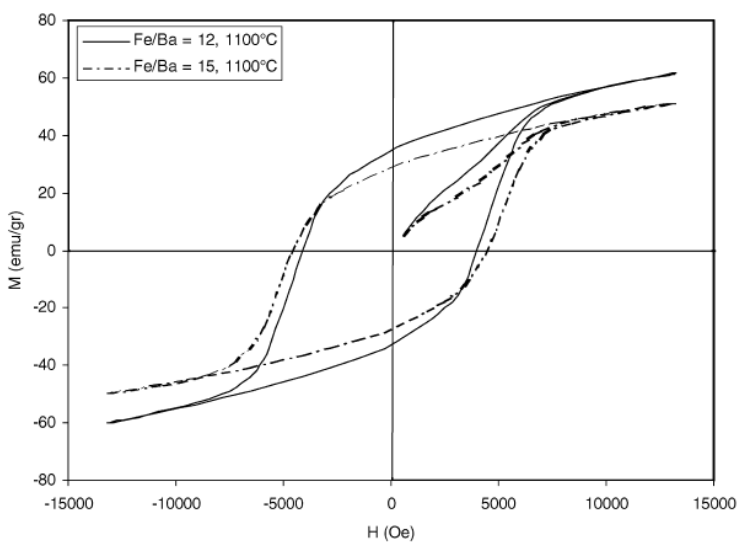


Fig. 7. Hysteresis loops for samples processed under different conditions, showing single and multidomain behavior.

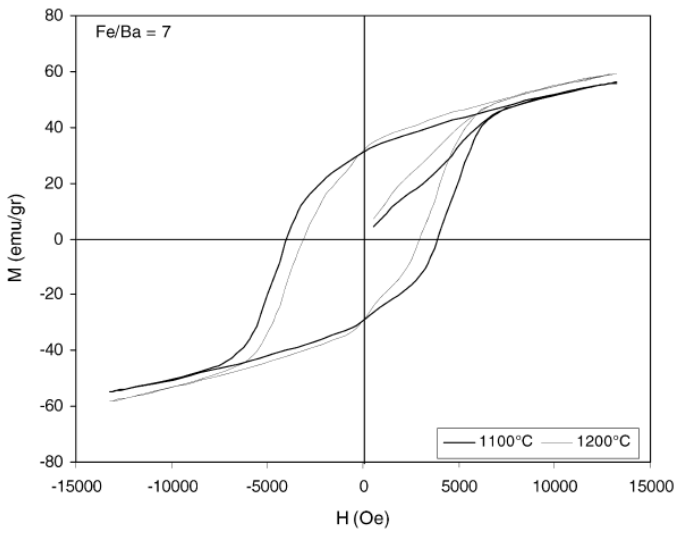


Fig. 8. Hysteresis loops for samples with a Fe/Ba ratio of 7 heat-treated at 1100°C and 1200°C, showing the effect of heating temperature on the shape of the demagnetization curve.

Acknowledgements

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