June 2010 *ISSN : 0974 - 7494* *Volume 4 Issue 1*

Nano Science and Nano Technology

An Indian Journal

Trade Science Inc.

Short Communication

NSNTAIJ, 4(1), 2010 [24-26]

Size distribution of magnesioferrite nanoparticles synthesized by coprecipitation

R.S.de Biasi[1]*, D.C.S.Rodrigues[1], L.H.G.Cardoso[1], J.B.Campos[2]

[1]Secao de Engenharia Mecanica e de Materiais, Instituto Militar de Engenharia, Pr. Gen. Tibúrcio 80 SE/4, Urca, 22290-270 Rio de Janeiro, RJ, (BRAZIL)

[2]Divisao de Processamento e Caracterização de Materiais, Instituto Nacional de Tecnologia, Av. Venezuela 82, Saúde, 20081-312 Rio de Janeiro, RJ, (BRAZIL)

E-mail : rsbiasi@ime.eb.br; doracristina@uol.com.br; lh.cardoso@yahoo.com.br; josebran@int.gov.br

Received: 3rd February, 2010 ; Accepted: 13th February, 2010

ABSTRACT

Due to special properties such as superparamagnetism, magnetic nanoparticles have important technological, environmental and medical applications. In this work, nanoparticles of magnesioferrite ($MgFe_2O_4$) were prepared by coprecipitation from chloride solutions of iron and magnesium. Compared with traditional procedures, this method has the advantages of low cost, simplicity and the use of moderate annealing temperatures. The properties of the nanoparticles were investigated using X-ray diffraction to determine the average size of the crystallographic domains and Mössbauer spectroscopy to find the particle size distribution. The results showed that the coprecipitation method yields magnesioferrite nanoparticles with a fairly narrow size distribution.

KEYWORDS

Nanoparticles;
Mössbauer spectroscopy;
Magnesioferrite.

INTRODUCTION

Nanosized ferrites display physical and chemical properties which may be quite different from those of their bulk counterparts. Magnesioferrite ($MgFe_2O_4$) is one of the most interesting of these new magnetic materials, because, due to its small magnetocrystalline anisotropy, superparamagnetic properties are still present at relatively low temperatures and/or high magnetic fields. The purpose of this work was to investigate the average particle size and particle size distribution of $MgFe_2O_4$ nanoparticles synthesized by coprecipitation[1], a fast, simple and relatively inexpensive technique. The average particle size was determined by X-ray diffraction, while the particle size distribution was obtained by measuring at several temperatures the relative intensities of the Mössbauer spectra due to superparamagnetic particles and to ferrimagnetic particles, a method that has been applied successfully[2] to another nanosized ferrite, $CoFe_2O_4$.

EXPERIMENTAL

Sample preparation

Analytical grade $FeCl_3.6H_2O$ and $MgCl_2.6H_2O$ were dissolved in deionized water to obtain the starting solution. This solution was added to a 6 M NaOH solution under vigorous agitation and treated for 2 h at

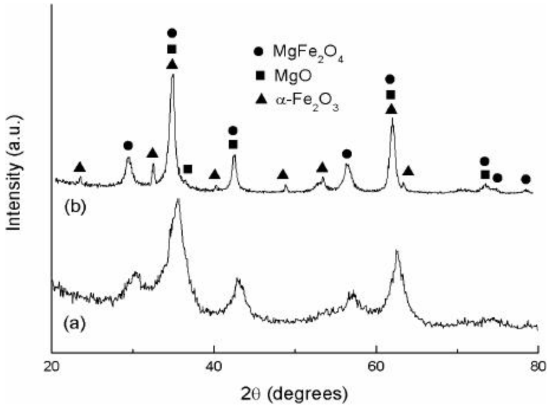

Figure 1 : X-ray diffraction patterns of samples annealed at (a) 500°C and (b) 700°C

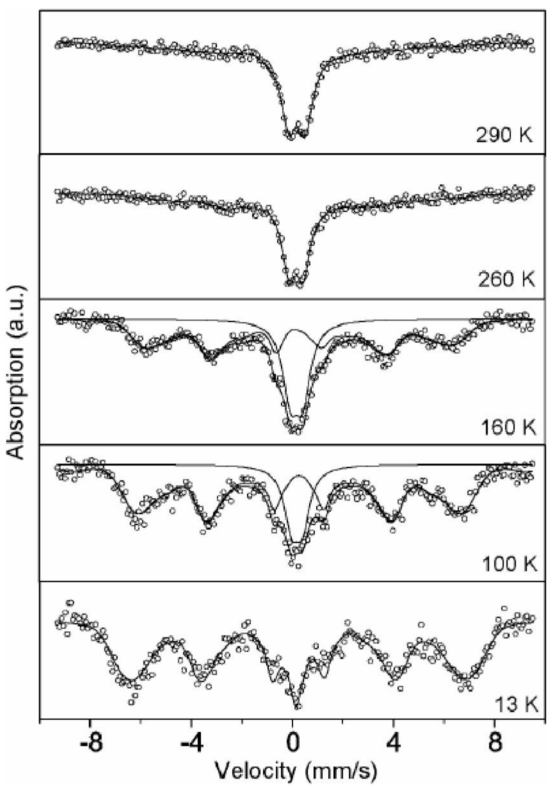

Figure 2 : Mössbauer spectra of a sample annealed at 500°C

100°C. The resulting precipitate was filtered, washed with distilled water and annealed in a muffle furnace for 1 h at four different temperatures (200, 300, 500 and 700°C).

Measurements

X-ray diffraction patterns were obtained using an XPert Pro Panalitical diffractometer with Co Kα radiation (λ = 1.5418 A°). The average particle size was calculated from line broadening using the TOPAS application[3], academic edition.

Mössbauer spectra were recorded at several

TABLE 1 : Phase composition of samples annealed at four different temperatures

T_a (°C)	Composition	Particle size (nm)
200	76% γ-Fe_2O_3	2.2
	24% MgO	1.4
300	79 % γ-Fe_2O_3	2.3
	21% MgO	1.5
500	100% $MgFe_2O_4$	3.7
700	80% $MgFe_2O_4$	10
	12% MgO	31
	8% α-Fe_2O_3	43

temperatures between 13 K and room temperature in a homemade instrument using a source of 57Co(Rh) with an activity of about 50 mCi.

RESULTS AND DISCUSSION

TABLE 1 shows the phase compositions and average particle sizes, as determined from the X-ray spectra, for samples annealed at four different temperatures. The X-ray spectra of samples annealed at 500 and 700°C are shown in figure 1.

The Mössbauer spectra of a sample annealed at 500°C are shown in figure 2 for several different measurement temperatures. While at room temperature there is a doublet due to superparamagnetic relaxation, at lower temperatures one sees a sextet which is characteristic of bulk magnesioferrite[1].

By taking the ratio of the area under the doublet to the area under the sextet, it is possible to estimate the volume fraction of unblocked particles for each measurement temperature. The result is shown in figure 3, where the dots are the experimental points and the line is a fit to a cumulative log-normal function:

$$f(T) = C_1 + C_2 \mathrm{erf}\left(\frac{\ln T - \mu}{\delta\sqrt{2}}\right) \quad (2)$$

where T is the absolute temperature, erf(T) is the error function, C_1 and C_2 are constants and μ and δ are adjustable parameters. The best fit was obtained with $C_1 = 0.55$, $C_2 = 0.44$, $\mu = 5.00$ and $\delta = 0.32$.

The distribution of unblocking temperatures of the system is given by[4,5]

$$P(T) = C\left(\frac{1}{T}\right)^{1/3} \frac{df(T)}{dT} \quad (3)$$

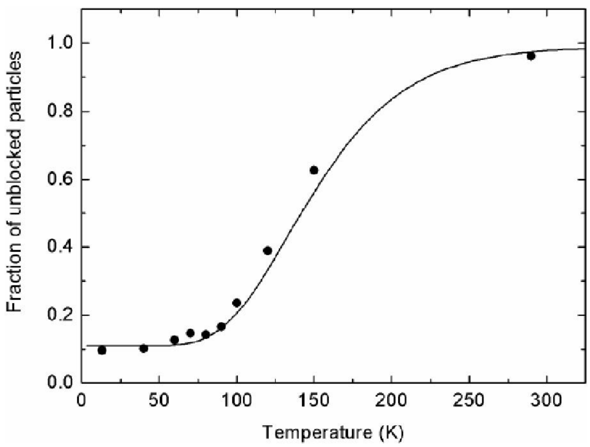

Figure 3 : Temperature dependence of the volume fraction of unblocked particles in a sample annealed at 500°C, calculated from the Mössbauer spectra. The dots are experimental points; the line is a fit to a cumulative log-normal function (see text)

where C is a normalization constant.

The temperature dependence of Eq. 3 can be converted to a dependence on particle diameter (thus yielding the particle size distribution) using the relation[4,5]

$$D(T) = \langle D \rangle \left(\frac{T}{\langle T_c \rangle} \right)^{1/3} \quad (4)$$

where D is the particle diameter, $\langle D \rangle$ is the average particle diameter, as estimated from the X-ray results, and $\langle T_c \rangle$ is the average blocking temperature, given by

$$\langle T_c \rangle = \frac{\int_0^\infty TP(T)dT}{\int_0^\infty P(T)dT} \quad (5)$$

The result is shown in figure 4, which is a log-normal distribution with average diameter $\langle D \rangle = 3.7$ nm, most probable diameter $D_m = 3.6$ nm and full width at half maximum $\Delta D = 1.0$ nm.

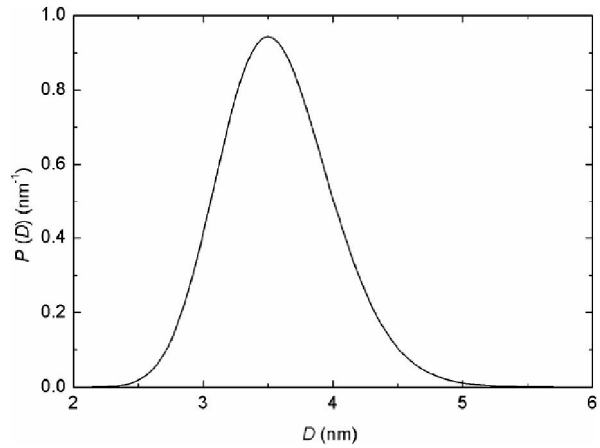

Figure 4 : Particle size distribution of a sample annealed at 500°C

CONCLUSIONS

The coprecipitation technique has been used to prepare $MgFe_2O_4$ nanoparticles, which were annealed at four different temperatures. X-ray diffraction patterns show that sample composition and particle size are influenced by the annealing temperature. Mössbauer spectra exhibit superparamagnetic behavior, confirming that the particles are in the nanometric range. Analysis of the temperature dependence of the Mössbauer spectra of annealed samples yields the particle size distribution. The results suggest that the coprecipitation technique can be used to synthesize magnesioferrite nanoparticles with a fairly uniform size distribution.

ACKNOWLEDGEMENT

The authors thank Prof. Dalber Ruben Sanchez Candela and Prof. João Batista Marimon da Cunha for their help with the Mössbauer measurements.

REFERENCES

[1] Q.Chen, A.J.Rondinone, B.C.Chakoumakos, Z.J.Zhang; J.Magn.Magn.Mater., **194**, 1 **(1999)**.
[2] R.S.de Biasi, A.B.S.Figueiredo, A.A.R.Fernandes, C.Larica; Solid State Commun., **144**, 15 **(2007)**.
[3] http://www.bruker-axs.de/topas.html.
[4] R.S.de Biasi, W.S.D.Folly; Physica, B, **321**, 117 **(2002)**.
[5] R.S.de Biasi, E.C.Gondim; Solid State Commun., **138**, 271 **(2006)**.