ELSEVIER

Journal of Magnetism and Magnetic Materials 203 (1999) 141–142

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

# Magnetic properties of $ZnFe_2O_4$ synthesized by ball milling

G.F. Goya*, H.R. Rechenberg

*Laboratório de Materiais Magnéticos, Instituto de Física, Universidade de São Paulo C.P. 66318, São Paulo 05315-970 SP, Brazil*

**Abstract**

We present a study of the intermediate and final phases during mechanosynthesis of $ZnFe_2O_4$. Mössbauer measurements at $T = 4.2$ K indicate creation of oxygen vacancies and local disorder at Fe sites during milling. Magnetization data show lack of saturation and irreversibility at high fields. Our data is qualitatively well described by a model of particles with a magnetic ordered core coupled to a spin-disordered surface layer. © 1999 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Spinel ferrites; Ball milling; Nanoparticles

Ball milling has been extensively used to produce ferrite nanoparticles [1] and, more recently, as a new synthesis route [2]. The magnetic properties of these nanoparticles can be notably different from the bulk material regarding ordering temperatures, coercivity and saturation magnetization [3]. In $ZnFe_2O_4$ ferrite, the ordering temperature ($T_N \approx 10$ K) of bulk samples can be raised by increasing $Fe^{3+}$ population at A sites through mechanical activation [3,4]. Spin canting and surface spin disorder have been found for many nanosized ferrite systems [5,6], although some of the mechanisms involved in these core/shell models are not yet understood.

We report X-ray diffraction (XRD), Mössbauer and magnetization measurements on the intermediate and final phases during mechanosynthesis of $ZnFe_2O_4$ spinel. The starting powder was a 1 : 1 molar mixture of $\alpha$-$Fe_2O_3$ and ZnO (99.99% purity). Samples were milled in a planetary ball mill with closed containers of hardened steel, with ball to sample mass ratio 20 : 1. Acetone was added to improve homogeneity during milling. The milling process was stopped after selected intervals of 100, 300, 400 and 623 h, to extract small amounts of sample (labeled as Z100, Z300, Z400 and Z623, respectively). X-ray diffraction measurements were performed using Cu $K_\alpha$ radiation in the $10^\circ \leqslant 2\theta \leqslant 80^\circ$ range. Mössbauer measurements were performed with a constant-acceleration spectrometer in transmission geometry between $T = 296$ and 4.2 K. Isomer shifts are given relative to that of $\alpha$-Fe at room temperature. Magnetization measurements were performed in a vibrating sample magnetometer between 4.2 and 300 K, in fields up to 9T. Hysteresis loops were taken after field cooling in a field of 80 kOe.

XRD data of samples milled from 100 to 623 h show the presence of $\alpha$-$Fe_2O_3$ and spinel phases (Fig. 1). As milling time increases, the $\alpha$-$Fe_2O_3$ peaks become less intense, and for sample Z623 an upper limit of $\approx 5\%$ hematite was roughly estimated. The mean grain size estimated for sample Z100 was $\langle d \rangle = 18(4)$ nm, which remained constant within error along the series. After annealing sample Z623 at $T = 500$ K for 1 h, the XRD pattern showed only spinel peaks, and a $\langle d \rangle = 47(3)$ nm value was obtained. Thermogravimetric data on sample Z623 (not displayed) showed continuous loss of mass up to $T = 394$ K, mainly due to desorption of the carrier liquid bound to the particles. A final loss of $\approx 4\%$ of mass at $T = 573$ K indicates the complete $ZnFe_2O_4$ crystallization, in agreement with XRD data. This temperature, considerably low if compared with a standard solid state reaction, is due to the high reaction surface of the final particles. For all milled samples, Mössbauer spectra taken at $T = 4.2$ K were fitted with three magnetic sextets, corresponding to $\alpha$-$Fe_2O_3$ and both sites of

* Corresponding author. Tel.: 55-11-818-6881; fax: 55-11-818-6984.

*E-mail address:* goya@macbeth.if.usp.br (G.F. Goya)

0304-8853/99/$ - see front matter 
PII: S0304-8853(99)00250-4

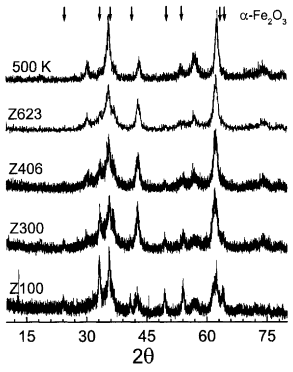


Fig. 1. X-ray diffraction patterns for samples milled different times. The topmost pattern was obtained after annealing sample Z623 at 500 K. Arrows indicate the peak positions of $\alpha$-$Fe_2O_3$ phase.

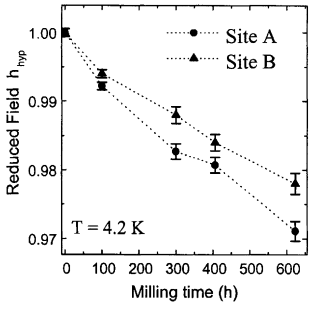


Fig. 2. Reduced hyperfine fields $h = H/H_{bulk}$ vs. milling time, corresponding to A and B sites of $ZnFe_2O_4$ spinel, at $T = 4.2$ K.

$ZnFe_2O_4$. Reduced hyperfine fields, $h = H/H_{bulk}$, of A and B sites in $ZnFe_2O_4$ as a function of milling time are shown in Fig. 2. Both fields decrease with milling time. This cannot be due to collective magnetic excitations, since at $T = 4.2$ K the system is well below its blocking temperature. Size effects are also unlikely to occur considering that $\langle d \rangle$ remains constant for all milled samples. We assign the observed change in hyperfine magnetic interactions to oxygen vacancies produced during milling, which can break superexchange paths and induce spin disorder [7]. Magnetization data taken at $T = 4.2$ K (Fig. 3) show lack of saturation which increases with milling time. For sample Z623, the irreversible behavior extends up to fields $H \approx 65$ kOe, which is notably higher than the expected for rotational reversal of the spins. As shown in the inset of Fig. 3, the zero field cooling (ZFC) and field cooling (FC) curves begin to separate below $T_B \approx 40$ K, which marks the onset of irreversible behavior. Both the high-field irreversibility and the FC/ZFC curves can be qualitatively explained assuming that particles consist of a ferrimagnetically

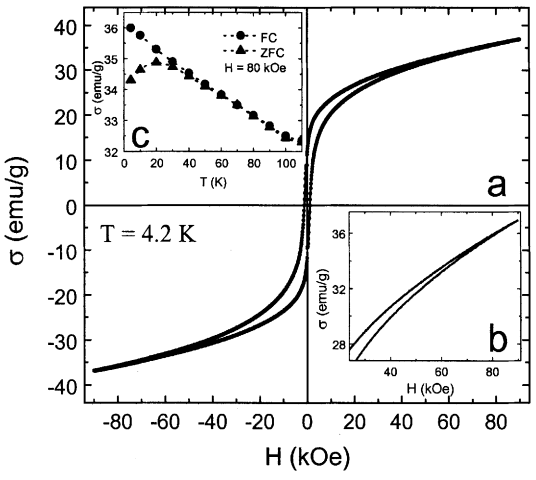


Fig. 3. Magnetization data $M(H, T)$ of Z623 sample: (a) Complete hysteresis loop after field cooling in a $H = 80$ kOe field. (b) Enlarged high-field region showing irreversible behavior. (c) Field cooled and Zero Field cooled M vs. $T$ curves.

ordered core and a spin-disordered surface layer, coupled by exchange interactions. Below $T \approx 40$ K, the spin-disordered layer is blocked in a configuration determined by the external field (for FC mode), preventing the reversal of the ordered phase and shifting the irreversible region to the observed fields of $H \approx 65$ kOe. The non-saturating magnetization curves suggest that the spin disorder at the surface may be related with spin canting produced by the milling process.

## Acknowledgements

G.F.G. acknowledges financial support from the Fundação de Amparo á Pesquisa do Estado de São Paulo (FAPESP), through a postdoctoral fellowship.

## References

[1] See the proceedings of the Seventh International Conference on Ferrites, ICF7" (Bordeaux), J. Phys. IV, 7 (1) (1997) C1-47.
[2] J. Ding, P.G. McCormick, R. Street, J. Magn. Magn. Mater 171 (1997) 309.
[3] H.H. Hamed, J.C. Ho, S.A. Oliver, R.J. Willey, G. Olivieri, G. Busca, J. Appl. Phys. 81 (1997) 1851.
[4] J. Battle, T. Clark, B.J. Evans, J. Phys. IV 7 (1997) C1-257.
[5] A.H. Morrish, K. Haneda, J. Appl. Phys. 63 (1981) 2496.
[6] R.H. Kodama, A.E. Berkowitz, E.J. McNiff, S. Foner, Mat. Sci. Forum 235–238 (1997) 643.
[7] M.P. Morales, C.J. Serna, F. Bødker, S. Mørup, J. Phys. Condens. Mater 9 (1997) 5461.