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Structural and magnetic properties of $NiFe_2O_4$–SnO_2 nanocomposite

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Abstract

The structural and magnetic properties of the $NiFe_2O_4$–SnO_2 composite, obtained by ball-milling during different times, were investigated by X-ray diffraction, small-angle X-ray scattering, Mössbauer spectroscopy and vibrating sample magnetometry. The results showed the reduction of the crystalline particle size and modification in the nature of the system interfaces as a consequence of the mechanical treatment. Specimens with smaller particles displayed strong superparamagnetism. Large variation of the hysteresis loops for the different milling times was observed.

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Granular solids formed by magnetic nanoparticles dispersed in an insulating matrix show considerable changes in the magnetic properties when compared with their equivalent pure, bulk materials [1–5]. In this work, we have investigated the structural and magnetic properties of a composite obtained by the dispersion of Ni ferrite particles in a nonmagnetic tin oxide matrix (ferrite–SnO_2).

The composite, with 30% volume concentration of ferrite, $(NiFe_2O_4)_{0.3}$–$(SnO_2)_{0.7}$, was obtained by mechanical alloying. The Ni ferrite powders were prepared by the coprecipitation method, as described in Ref. [6]. After annealing at 700°C for 2 h, the ferrite and high-purity SnO_2 (Merck) powders were mixed and milled in a Spex 800 ball-milling equipment. The ball mass to powder mass ratio was 1:4, and the milling times (t_m) were 1.25, 2.5, 5 and 10 h.

The structural evolution of the samples after mechanical treatment was followed by X-ray diffraction analysis (XRD). This data allowed the determination of the average particle size $\langle D \rangle$ using Scherrer's formula. Small-angle X-ray scattering (SAXS) experiments were performed in order to obtain information on the nanostructure of the system, using synchrotron radiation at the SAXS beamline of the National Synchrotron Light Laboratory (Campinas) [7]. The SAXS data were collected in transmission geometry, with incident wavelength $\lambda = 1.757$ Å, at a sample-detector distance equal to 839 mm, allowing the measurements of the scattered radiation in the range of the scattering vector q from 0.01 to 0.33 $Å^{-1}$ (where $q = (4\pi/\lambda)\sin(\theta)$, θ being half of the scattering angle). The SAXS curves were interpreted on the basis of the fractal theory for a two-phase system. When smooth interfaces are present, the asymptotic dependence of the SAXS intensity at larger q values can be described by Porod's law, $I(q) = (K_p/q^4) + I_b$, where K_P is the Porod constant and I_b is related to the background contribution to the intensity originated in the electron density fluctuations in the individual phases [8]. Deviations of the intensity from the q^{-4} power law can be observed. Values of the

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exponent between 3 and 4 may be explained in terms of the fractal nature of the two components interface according to the Bale–Schmidt formula, $I(q) \propto q^{Ds-6}$, where D_s is the surface fractal dimension [9]. Transmission ^{57}Fe and ^{119}Sn Mössbauer spectra (MS) have been collected at different t_m. Hyperfine parameters were obtained from the analysis of the MS data. Magnetic properties were determined by vibrating sample magnetometry (VSM) at 20 and 100 K.

For the samples of $(NiFe_2O_4)_{0.3}$–$(SnO_2)_{0.7}$, the two phases are initially identified in the X-ray diffractograms. The effects of mechanical alloying are evidenced by the increasing line broadening, which is attributed to smaller particle size. The average diameter of the Ni ferrite particles is reduced from 360 Å to 132 Å after 5 h milling time (Table 1). This phase becomes practically undetectable in the granular material after $t_m = 10$ h.

Fig. 1 shows $\log I(q)$ vs. $\log q$ plots for all the samples. A power law behavior extended for one decade (0.02 to 0.2 Å^{-1}) is observed. Results of the fittings are shown in Table 1. The sample that was not milled (poor physical mixture) resulted in a curve that follows the q^{-4} scaling law, typical of smooth and nonfractal interfaces. For milled samples, D_s goes from 2.05 to 2.52, indicating that changes related to the nature of the nanoparticles interface are taking place during the milling process.

Fig. 2 shows ^{57}Fe and ^{119}Sn Mössbauer spectra at 20 K for the samples after different t_m. ^{57}Fe spectra of the samples milled until 2.5 h were fitted using two magnetic sextets, corresponding to Fe^{3+} ions in tetrahedral (Fe_A), and octahedral (Fe_B) sites, and a weak central doublet (less than 5% intensity) attributed to a fraction of superparamagnetic particles. The Mössbauer parameters obtained for the sextets were $IS_A = 0.38(1)$ mm/s and $IS_B = 0.48(1)$ mm/s (relative to α-Fe), $\Delta Q \sim 0$ mm/s for both sites and B_{HF} varying from 50.5(3) to 49.9(3) T for Fe_A and from 54.8(3) to 51.0(3) T for Fe_B, as the t_m increases. After 5 h milling, strong broadening of the magnetic sextets is observed, and can be attributed to a superparamagnetic relaxation, in agreement with the magnetization data described below.

^{119}Sn MS at 20 K indicated that for $t_m \leqslant 2.5$ h the hyperfine parameters obtained are $IS = 0.03(1)$ mm/s (relative to $Ca^{119}SnO_3$) and $\Delta Q = 0.45(1)$ mm/s, characteristic of SnO_2 phase. After 5 h milling, a variation on ΔQ was observed and, after 10 h milling, line broadening is evident, indicating that tin ions are alloyed with the ferrimagnetic phase. This lead us to fit the spectrum using a doublet referring to SnO_2 (35% intensity) and a distribution of B_{HF} due to the magnetic phase.

VSM measurements presented large variation of the hysteresis loop for different t_m. Magnetization, under 10 kOe, varies from 9 to 4.5 emu/g as $\langle D \rangle$ reduced from 360 Å to less than 130 Å. The changes in magnetization can be caused by the presence of superparamagnetic relaxation and/or noncolinearity of the magnetic moments at the surface of the particles. The coercivity (H_c) vs. average particle size presents a maximum of 1830 Oe at 20 K, and 1270 Oe at 100 K for samples with $\langle D \rangle$ around 150 Å, while the as-prepared composite and pure bulk Ni ferrite present Hc values near 400 Oe and less than 50 Oe, respectively.

In summary, we have shown the effects of ball milling on the size of the crystalline nanograins of $(NiFe_2O_4)_{0.3}$–$(SnO_2)_{0.7}$ as evidenced by XRD. The evolution of the interface regions in the ball milled material is attributed to changes in the fractal nature of the grain boundaries, related to the fractal dimension obtained by SAXS. MS

Table 1
Ferrite average particle size $\langle D \rangle$ and surface fractal dimension (D_S) for Ni ferrite–SnO_2 samples

t_m (h)	0	1.25	2.5	5	10
$\langle D \rangle$ (Å)	360	200	152	132	—
$D_S(\pm 0.006)$	*n*-fractal	2.050	2.030	2.201	2.521

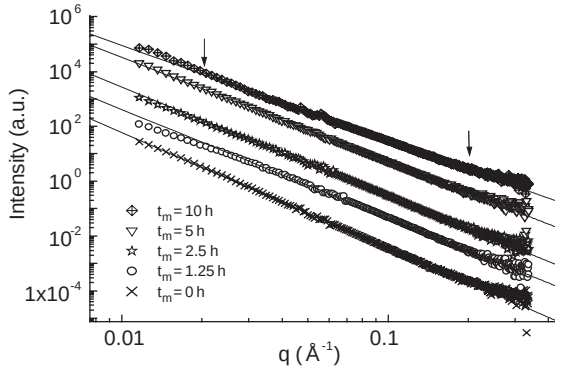

Fig. 1. Scattering from the Ni ferrite–SnO_2 samples for several milling times. The arrows indicate the fitting range of q used to determine D_s.

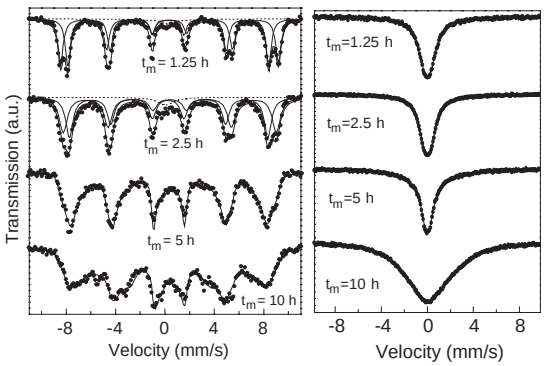

Fig. 2. ^{57}Fe (left) and ^{119}Sn (right) MS obtained at 20 K for Ni ferrite–SnO_2 samples after different milling times.

and VSM have shown superparamagnetic relaxation of smaller particles and a large variation of the magnetic hysteresis loops for the different milling times.

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