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A study of nanocrystalline NiZn-ferrite–SiO_2 synthesized by sol–gel

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Abstract

We have investigated the structural and magnetic properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles embedded in SiO_2 fabricated by a sol–gel processing. The obtained $(Ni_{0.5}Zn_{0.5}Fe_2O_4)_x(SiO_2)_{100-x}$ ($6 \leqslant x \leqslant 78\%$) samples were characterized by X-ray diffraction, Mössbauer spectroscopy (MS) and vibrating sample magnetometry. The results showed the formation of stoichiometric NiZn-ferrite in the SiO_2 matrix, for $x < 41\%$. Samples with higher ferrite fraction have small amounts of Fe_2O_3. MS revealed the superparamagnetism of the ferrite nanoparticles at room temperature. The combination of different ferrite content and annealing temperatures allowed the obtention of samples with saturation magnetization ranging from 1.3 to 68 emu/g and coercivity from 0 to 123 Oe, value two orders of magnitude higher than those presented by bulk $Ni_{0.5}Zn_{0.5}Fe_2O_4$. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Nickel–zinc ferrites; Sol–gel; Magnetic properties

The interest in granular magnetic solids consisting of magnetic ultra-fine or nanosized particles embedded in an immiscible insulating or metallic matrix has grown considerably in recent years due to new magnetic properties presented by these peculiar structures [1]. Different systems such as Fe [2,3], Fe_2O_3 [4], Ni [5], NiZn-ferrite [6] dispersed in insulating matrices like silica have been fabricated by sputter deposition, ball milling, evaporation and chemical methods. These materials presented considerable changes in the magnetic properties when compared with their equivalent pure, bulk materials. In a granular magnetic solid, two main parameters determine the magnetic properties of the composite material: the average diameter of the particles and the volumetric fraction of the magnetic phase.

In this work, we have investigated the correlation between the structural and magnetic properties of stoichiometric NiZn-ferrite embedded in a silica matrix, for different ferrite contents and heat treatments. NiZn-ferrite–SiO_2 powders were obtained by a sol–gel processing. The sol was prepared dissolving Fe, Ni and Zn nitrates in deionized water and, adding $Si(OC_2H_5)_4$ (tetraethylortosilicate) and drops of nitric acid, maintaining the stirring for

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30 min. The used molar proportions were chosen to form the granular composite $(Ni_{0.5}Zn_{0.5}Fe_2O_4)_x (SiO_2)_{100-x}$, where $6\% \leqslant x \leqslant 78\%$ represents the nominal volumetric fraction of ferrimagnetic NiZn-ferrite in the silica matrix. The gellation of the sol occurred during the drying at 60°C, for about 20 h. The obtained gel was annealed at 800, 1000 and 1100°C, for 2 h, under ordinary atmosphere.

For the prepared samples, phase analyses were done by X-ray diffraction using Cu K_α radiation. The hyperfine properties were investigated by Mössbauer spectroscopy at room temperature by using a $^{57}Co(Rh)$ source. Magnetization measurements were obtained by vibrating sample magnetometry (VSM) at room temperature.

Fig. 1 shows the XRD patterns of the NiZn-ferrite–SiO_2 samples annealed at 800°C, for $6\% \leqslant x \leqslant 78\%$. The evolution of crystallinity of the stoichiometric NiZn-ferrite-phase with increasing ferrite content can be seen. For $x = 6\%$ the material has an amorphous character and for $12\% \leqslant x \leqslant 34\%$ the ferrite, $Ni_{0.5}Zn_{0.5}Fe_2O_4$, is the observed Fe-phase. Starting from $x \geqslant 41\%$, occurs the formation of small amount of Fe_2O_3, as indicated by the diffraction peak at $2\theta = 33.5°$. Similar results were obtained for the samples annealed at 1000 and 1100°C. The increase of the temperature results in higher crystallization without changes in the obtained Fe-phases. The average diameter (D) of the ferrite nanoparticles was calculated from the broadening of the (3 1 1) XRD-peaks. The obtained values for different ferrite contents and annealing temperatures are shown in Table 1.

Mössbauer spectra of samples with $6\% \leqslant x \leqslant 78\%$, annealed at 800°C for 2 h are shown in Fig. 2. Samples with $x \leqslant 16\%$ (Fig. 3a and Fig. 3b) present strong superparamagnetic behavior due to their small particle sizes and volumetric fraction and these spectra were fitted to a broad doublet. By increasing the ferrite volumetric fraction the superparamagnetic behavior decreases, basically due to the growth of the particles diameter and of the

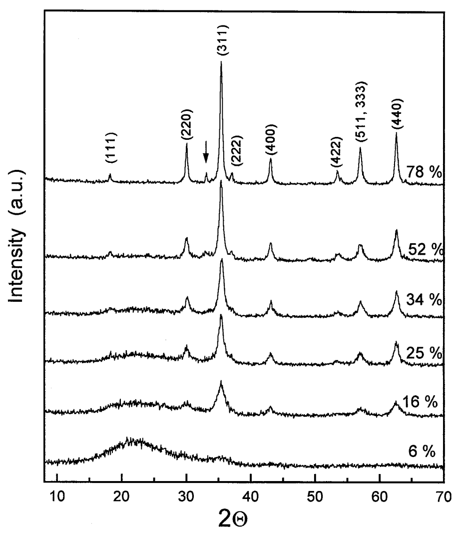

Fig. 1. XRD patterns of the samples with different NiZn-ferrite content, after annealing at 800°C for 2 h. The NiZn-ferrite peaks are identified and the arrow indicates a Fe_2O_3 peak.

Table 1
Average diameter (± 3 nm) of the ferrite particles in the NiZn-ferrite–SiO_2 samples, as determined by XRD, for different ferrite fraction (x) and annealing temperature (T)

T (°C)	x (%)								
	6	12	16	25	34	41	52	63	78
800	<6	8	9	18	19	23	27	32	40
1000	<9	30	40	46	42	54	56	64	70
1100	15	36	55	60	62	79	85	87	92

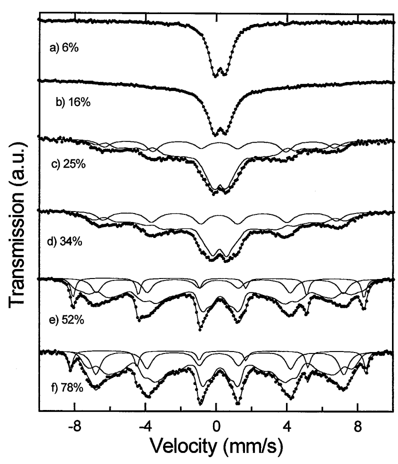

Fig. 2. Mössbauer spectra at room temperature of samples with different NiZn-ferrite volumetric fraction, after annealing at 800°C, for 2 h.

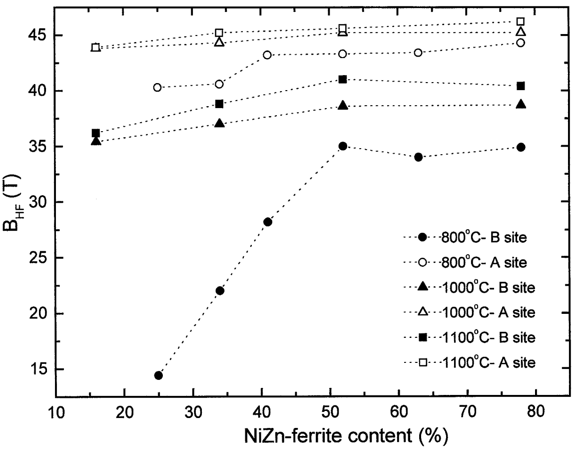

Fig. 3. Evolution of the average magnetic hyperfine field of the Fe atoms in the tetrahedral (A) and octahedral (B) sites of the NiZn-ferrite for different ferrite contents and different annealing temperatures.

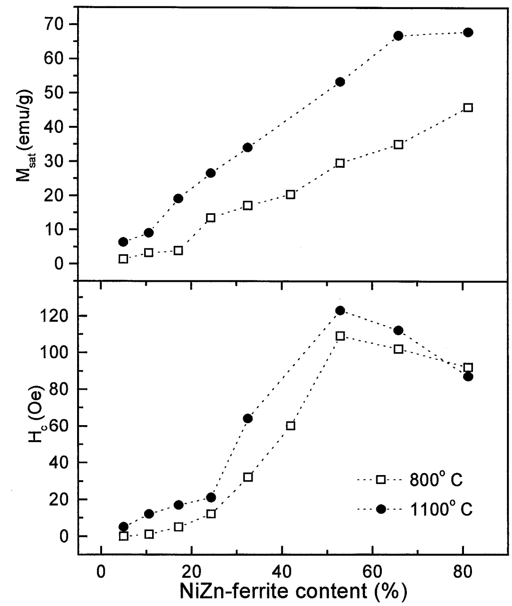

Fig. 4. Saturation magnetization and coercivity versus NiZn-ferrite content for the samples annealed at 800 and 1100°C.

interaction between the ferrimagnetic ferrite particles. Starting from $x = 25\%$ the spectra were fitted to a broad sextet with linewidth between 0.6 and 0.8 mm/s, corresponding to Fe^{3+} at the tetrahedral (A) sites, plus a hyperfine field (B_{HF}) distribution referring to Fe^{3+} atoms at the octahedral (B) sites due to the presence of different magnetic neighbors affecting the Fe atoms distinctly at these sites [7,8]. Average B_{HF} values at room temperature obtained for the A and B sites against the ferrite content are plotted in Fig. 3. Contrary to the A site, the B site shows strong decrease of the B_{HF} below 52% ferrite, in agreement with the different relaxation behavior expected for Fe atoms in the NiZn-ferrite [9].

Magnetic properties of all samples were measured at room temperature by VSM. Large variation of the hysteresis loops are obtained with the variation of the ferrite content and annealing temperature. Fig. 4 shows the saturation magnetization (M_{sat}) and coercivity (H_c) against the NiZn-ferrite content for the samples annealed at 800 and 1100°C. M_{sat} increases with the ferrite content, as expected, since this parameter depends on the total mass of the material. Changes in M_{sat} have been observed in samples with the same ferrite content and annealed at different temperatures. These changes can be caused by the presence of superparamagnetic relaxation and/or noncolinearity of the magnetic moments at the surface of the nanoparticles, resulting in a decrease of M_{sat} for small particles. The coercivity maximum observed around 52% of ferrite can be explained by the appearance of a continuous network of magnetic particles at this ferrite concentration. Above this critical volumetric fraction the material presents bulk-like behavior. Below the percolation limit the system behaves as monodomain particles and H_c decreases with D. The values of coercivity observed here are 50% higher than those measured for powders of pure stoichiometric NiZn-ferrite nanoparticles [10] and near two order of magnitude higher than bulk NiZn-ferrite [6].

Nanostructured NiZn-ferrite–SiO_2 was successfully synthesized by the sol–gel method followed by annealing at temperatures between 800 and 1100°C. Samples with NiZn-ferrite particles with average diameters ranging from few nanometers up to 90 nm were obtained. The results of Mössbauer measurements at room temperature show that the ferrite nanoparticles exhibit superparamagnetic behavior even after heat treatments at 1100°C for

2 h. The coercivity and saturation magnetization were determined as a function of the ferrite content and average particle diameters.

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