

NANOCRYSTALLINE Ni-Zn FERRITES PREPARED BY SOL-GEL METHOD

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Nanocrystalline Ni-Zn ferrites have been synthesized in silica matrix by sol-gel processing and thermal treatment at 1100 °C. Samples with weight fraction of 20 % $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ in silica matrix were obtained for $x = 0.15, 0.35, 0.50, 0.65$ and characterized by X-ray diffraction (XRD), high resolution transmission electron microscope (HRTEM), Mössbauer spectroscopy (MS) at room temperature and vibrating sample magnetometry (VSM) measurements. The cubic spinel structure is proved both by XRD and Mössbauer spectroscopy. The ferrites embedded in the matrix have nanoparticles in the range 5-13 nm. The obtained composites, display superposed superparamagnetic and ferrimagnetic behavior, as a function of Zn/Ni ratio. Both lattice constant parameter and average hyperfine fields vary with the degree of substitution of nickel ions with zinc ones.

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1. Introduction

Spinel ferrites are known to be materials extremely sensitive to the manufacturing process. Soft-ferrites crystallize in spinel structure, in which the cations can be found in tetrahedral (A) and octahedral (B) sites. Ni-Zn ferrites are materials having many technical applications, especially in high frequency fields, due to their reduced magnetic losses. The preparation of nickel zinc ferrite nanoparticles was usually realized by wet chemical methods (coprecipitation and hydrothermal oxidation) that lead to formation of ferrite particles having size between 10 to 100 nm [1-4]. The sol-gel processing was recently used for obtaining of nickel zinc nanoparticles with narrow grain size distributions. The growth of magnetic nanocrystals occurs in the nanopores of an inorganic or organic amorphous matrix. The nanopores impose an upper limit for the magnetic nanoparticles size and assure avoiding of nanoparticles agglomeration [5-9]. It was reported the obtaining of 6-78 % (vol.) $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles in silica matrix having diameters ranging from few nanometers, up to 90 nm [10-12]. Wang and Li [13] have prepared by sol-gel method, $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 1.0$), ferrite nanoparticles in PVA matrix, having a particles distribution size between 6-50 nm, and studied the influence of different degree of substitution of nickel ions by zinc ones.

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The present paper is dealing with synthesis and characterization of nanocomposites of weight fraction of 20 % $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite in silica matrix, (where x express the substitution mole fraction of Ni^{2+} by Zn^{2+} cations and takes the values: 0.15, 0.35, 0.50, 0.65) by sol-gel processing in situ followed by thermal treatment in air at 1100 °C.

2. Experimental

The used proportions were chosen to form the composites with $(\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4)_{0.20}(\text{SiO}_2)_{0.80}$ formula. The samples were synthesized using Ni, Zn and Fe nitrates as precursors, by dissolving them in water/ethanol mixture and adding tetraethoxysilane (TEOS) dropwise while stirring at room temperature for 15 minutes, in mole ratio EtOH: TEOS: H_2O = 3: 1: 10. The measured pH was situated within 1,5-2 range. The sols were allowed to gel at room temperature. After drying at 60 °C the powdered gels were subjected to thermal treatment at 1100 °C. The resulted samples denoted Z15a 1100 ($x = 0.15$), Z35a 1100 ($x = 0.35$), Z50a 1100 ($x = 0.50$) and Z65a 1100 ($x = 0.65$) were finely crushed in an agate mortar.

The crystalline phases obtained in the composites were identified by X-ray diffraction, in a Siemens D 5005 X-ray powder diffractometer, with diffracted beam monochromator, using $\text{CuK}\alpha$ radiation. The XRD pattern was recorded from 10° to 70° with a step size of 0.1° and a scanning rate of 15 s per step. High resolution transmission electron micrographs and electron diffraction pattern were obtained with a JEOL JEM-2010 FAS TEM electron microscope.

Mössbauer spectra were carried out at room temperature. Measurements were done in the transmission mode with ^{57}Co diffused into a Cr matrix as the source moving with constant acceleration. The spectrometer was calibrated using a standard Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed with the help of the NORMOS program. Vibrating sample magnetometry measurements were preformed with VSM PAR 4500 equipment at room temperature and field of 2 T.

3. Results

Fig. 1 show X-ray diffraction spectra of Z15a 1100, Z35a 1100 and Z65a 1100 samples. The X-ray diffraction patterns show well developed diffraction lines assigned to pure spinel phase, with all major peaks matching the standard pattern of $(\text{Ni,Zn})\text{Fe}_2\text{O}_4$, JCPDS 8-0234. The average crystallite size of the spinel phase has been estimated from the broadening of the (311) X-ray diffraction peak using the Scherrer equation [14] at about 7 nm for Z15a 1100. In the case of the samples having a greater content of zinc in the ferrite structure, the average diameter of the particles of spinel phase slightly increases to 9-10 nm.

Fig. 2 shows nearly uniform spherical ferrite particles having a distribution size between 5.5-12.5 nm. The ED pattern (inset) reflects that these nanoparticles are well crystallized, the d values calculated from the ring diameters correspond well to the spinel structure and are consistent with the XRD pattern. The EDX spectrum revealed that the darker particles contain both Fe and Ni.

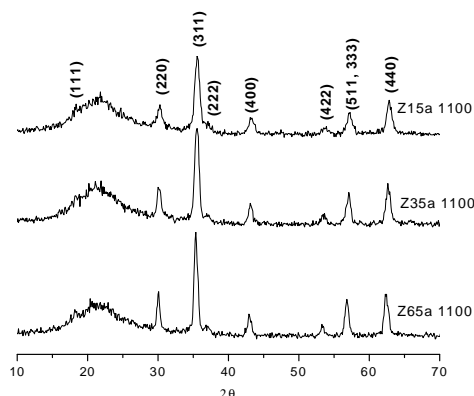


Fig. 1. X-ray diffraction patterns of Z15a 1100, Z35a 1100 and Z65a 1100 samples.

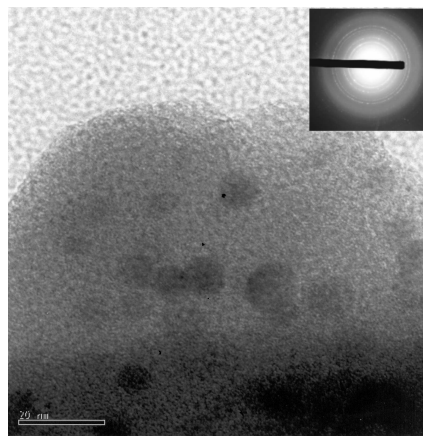


Fig. 2. TEM micrograph and ED pattern of Z15a 1100 sample.

Fig. 3 shows the Mössbauer spectra (data+fit) obtained at room temperature in the case of different specimens.

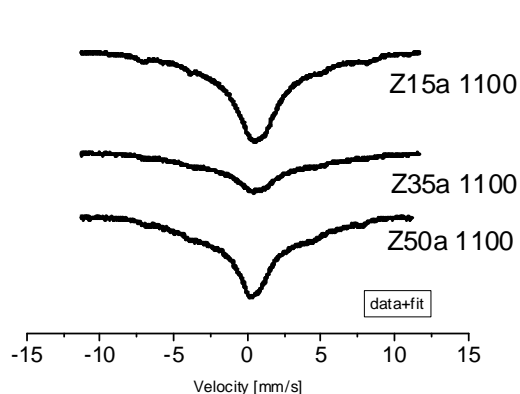


Fig. 3. Mössbauer spectra for the ferrites with zinc content ($x = 0.15, 0.35$ and 0.50).

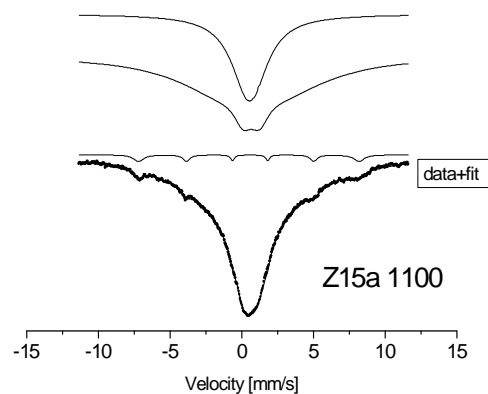


Fig. 4. Mössbauer spectrum of Z15 1100 sample.

Each spectrum was fitted by one doublet and two broad sextets, as it can be seen in the case of Z15a 1100 sample (Fig. 4). The corresponding values of isomer shift, quadrupole splitting and hyperfine field are given in the Table 1.

Table 1. Mössbauer hyperfine parameters of the ferrites with zinc content ($x = 0.15, 0.35$ and 0.50).

No. sample	No. subspectrum	Isomer shift δ [mm/s]	Quadrupole splitting ΔE_Q [mm/s]	Hyperfine field H_{bf} [T]	Relative intensity [%]
Z15a 1100	Subspectrum I	0.28	0.36	-	30
	Subspectrum II	0.27	-0.09	48.4	2.9
	Subspectrum III	0.46	0.1	21.9	67.1
Z35a 1100	Subspectrum I	0.56	1.03	-	1.7
	Subspectrum II	0.30	0.04	46.7	1.8
	Subspectrum III	0.32	0.27	21.6	96.5
Z50a 1100	Subspectrum I	0.32	0.02	-	8.2
	Subspectrum II	0.32	0.09	45.3	1.8
	Subspectrum III	0.35	-0.09	22.2	90.0

The deconvoluted Mössbauer spectra show a doublet (subspectrum I) superposed on a clear sextet (subspectrum II) having reduced intensities (2.9-1.8 %) and a subspectrum III which have very low hyperfine fields.

The magnetization curve of the Z15 1100 sample recorded at room temperature in applied magnetic fields of 2.5T is shown in Fig. 5.

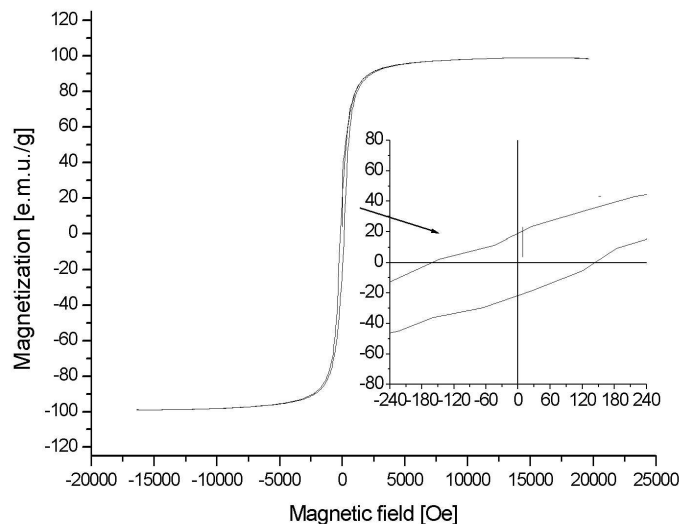


Fig. 5. Magnetization curve at room temperature, of Z15a 1100 sample.

The magnetization curve of the Z15a 1000 sample was expressed in emu/g of ferrite. Soft ferrimagnetic behavior with a coercive field of about 150 Oe is indicated by the hysteresis curve of the ferrite with lowest degree of substitution of nickel with zinc ions.

4. Discussion

Nickel-zinc ferrite nanocrystals were prepared by homogeneous dispersion in the amorphous silica matrix, as it can be seen from HRTEM micrographs (Fig. 2). The lattice parameter increases as Zn ion substitution increases (see Fig. 6). This increase of lattice parameter is due to the fact that Zn^{2+} ion has a radius of 0.88 Å which is larger than that of 0.83 Å for the Ni^{2+} ion.

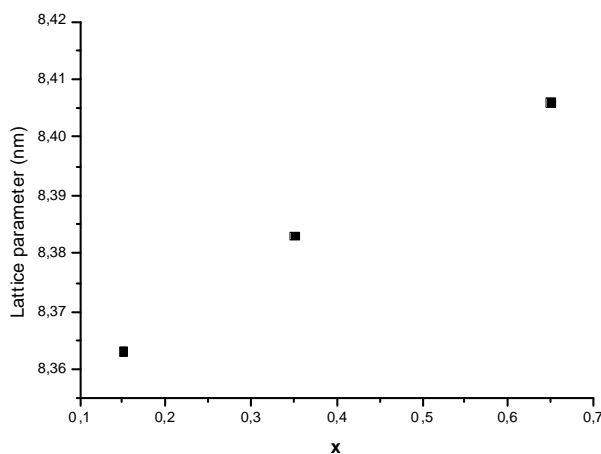


Fig. 6. Variation of lattice parameter with degree of substitution x.

The lattice constant is slightly larger than that of the bulk material, as result of small particles size and a large volume fraction of interface structure, in agreement with the results obtained by Wang [13].

Analysis of Mössbauer spectra indicates that nanoparticles both in ordered and disordered magnetic state are formed in the pores of the matrix. The subspectra I reveals the superparamagnetic character of the particles, which are present in the higher amount in the case of Z15a 1100, as a result of smaller particle sizes in the case of this sample. The subspectra II can be attributed without doubts to spinel phase in magnetic ordered state, in base of quadrupole splitting values close to zero, which is an indication of cubic symmetry. The values of isomer shift between 0.27-0.32 mm/s are consistent with iron ions in trivalent state and the hyperfine fields having values between 48.4 –45.3 T are typical for spinel ferrite. A possible interpretation of both sextets (subspectra II and subspectra III) is the presence of iron atoms in two inequivalent sites, A (tetrahedral) and B (octahedral), characteristic for spinel structure. The low hyperfine fields values for the B sites between 14.4 T and 41.0 T are reported in a similar work [10]. The content of iron (evaluated from relative area of the subspectra) in the B site (67.1-96.5 %) is much higher than those corresponding to the A sites (1.7-2.9 %). Arshed et al.[15] have investigated the dependence of magnetic behavior of octahedral sublattice on the number of tetrahedral sites occupied by Zn^{2+} ions in $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with x having values between 0 and 1. The areas corresponding to octahedral sites were larger by 30 %, which was explained if some Ni^{2+} ions also occupy the tetrahedral sites through the displacement of Fe^{3+} ions from tetrahedral sites to the octahedral sites. However, in our case the area corresponding to octahedral sites is larger by 60 %. It is very probable that a remarkable amount of ferrite has particles size corresponding to transition state between superparamagnetic and ferromagnetic state, which means we deal with particles having dimensions around the critical one corresponding to the blocking temperature. This fraction of particles could be responsible to part of the area of the broad sextets, which display unusually small hyperfine fields.

The decrease of the average hyperfine fields with the increase of zinc concentration is the result of the fact that Fe^{3+} ions will have no magnetic neighbours, spins become uncoupled, and the saturation magnetization decrease and hence the hyperfine field decreases.

The observed value of saturation magnetization of Z15a 1100 sample is about 80 emu/g and the coercive field of 150 Oe which is significantly higher, but characteristic to nanocrystalline magnetic particles [11].

5. Conclusions

The results of the experimental work could be resumed as $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4/\text{SiO}_2$ nanocomposites were prepared at a concentration of 20% weight of ferrite by sol-gel method and thermal treatment at 1100 °C. The lattice constant of the cubic structure, characteristic to spinel ferrite, increases with the Zn ion substitution degree. The Mössbauer studies indicate a decrease of average hyperfine fields with the increase of the degree of substitution of nickel with zinc. The nanocomposites present a superposed superparamagnetic and ferrimagnetic character due to a distribution of particles size in the range 5.5-12.5 nm, which include the critical one characteristic to magnetic nanoparticles in blocked state.

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