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Characterization of nanodimensional Ni-Zn ferrite prepared by mechanochemical and thermal methods

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Abstract. Nickel zinc ferrite nanoparticles, $Ni_{1-x}Zn_xFe_2O_4$ (x = 0, 0.2, 0.5, 0.8, 1.0), with dimensions below 10 nm have been prepared by combining chemical precipitation with high-energy ball milling. For comparison, their analogues obtained by thermal synthesis have also been studied. Mössbauer spectroscopy, X-ray diffraction, and magnetic measurements are used for the characterization of the obtained materials. X-ray diffraction shows that after 3h of mechanical treatment ferrites containing zinc are formed, while 6h of treatment is needed to obtain $NiFe_2O_4$. The magnetic properties of the samples exhibit a strong dependence on the phase composition, particle size and preparation method.

1. Introduction

The Ni-Zn ferrites have been extensively studied for various properties as well as for structural issues [1-4]. Zn and Ni are known to have very strong preferences for the tetrahedral and octahedral sites, respectively, making Ni–ferrite a model inverse ferrite and Zn–ferrite a model normal ferrite. The general formula of these materials is: $(Zn_xFe_{1-x})_{tetra}[Ni_{1-x}Fe_{1+x}]_{octa}O_4$. Ni-Zn ferrite is of particular interest because the magnetic properties of the nanoparticles differ markedly from those of their bulk counterpart. It is of further interest to replace a non-magnetic Zn^{2+} ion by a magnetic Ni^{2+} in Zn-ferrite to understand the difference in the properties of the system of ferrites in the limit of nano-regime. The properties of these ferrites are highly sensitive to the cation distribution which in turn depends on the method of preparation and sintering conditions. Spinel-type ferrites can be prepared by a variety of methods [4-7]. The high-energy milling as a solid-state method for synthesis of nanodimensional materials has the advantage that it can be easily operated and produce large amounts of nanostructured powders in a fairly short time. Furthermore, the highly nonequilibrium nature of the milling process allows one to prepare solids with improved and/or novel physical and chemical properties.

The purpose of the present work was to investigate the possibility of synthesizing $Ni_{1-x}Zn_xFe_2O_4$ (x = 0, 0.2, 0.5, 0.8, 1.0) nanodimensional powders by co-precipitation of the corresponding hydroxide

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carbonates followed by mechanochemical or thermal treatment. The relationship between synthesis method, phase composition and structural properties of the obtained materials was investigated.

2. Experimental

The mechanochemical synthesis (MS) of nickel-zinc ferrite powders was performed by two steps: (i) co-precipitation, and (ii) high-energy ball-milling (3h to obtain $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.2, 0.5, 0.8, 1.0) and 6h for $NiFe_2O_4$) following the procedure, described in [7]. The thermal synthesis (TS) was performed by annealing of the co-precipitation precursors at 773 K.

The phase composition and structure was determined by X-ray diffraction (XRD) using TUR M62 diffractometer with Co Kα radiation. Data interpretation was carried out using JCPDS (Joint Committee on Powder Diffraction Standards) database. Transmission ^{57}Fe Mössbauer spectra were obtained at room temperature (RT) with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode. A ^{57}Co/Cr (activity ≅ 20 mCi) source and an α-Fe foil standard were used. Experimentally obtained spectra were treated using the least squares method. The parameters of hyperfine interactions such as isomer shift (δ), quadrupole splitting (Δ) and effective internal magnetic field (B) as well as the line widths (Γ) and the relative weight (G) of the partial components of the spectra were determined. Isothermal magnetizations of the Ni-Zn ferrites were measured on a Quantum Design SQUID Magnetometer.

3. Results and discussion

The XRD patterns of the co-precipitated precursors (not shown) are characteristic of layered double hydroxides as found for Pyroaurite (PDF 25-0521) and Hydrotalcite (PDF 41-1428). After 3h of milling the diffraction lines of the spinel phases $Ni_{1-x}Zn_xFe_2O_4$ (x = 0.2, 0.5, 0.8, 1.0) are well defined, while $NiFe_2O_4$ is obtained after 6h of mechanical treatment. The diffractograms of all mechanochemically synthesized samples are composed of broadened low intensity peaks, suggesting very small particles dimensions. For all thermally treated samples $Ni_{1-x}Zn_xFe_2O_4$ ferrites are obtained. The average crystallites size (D), the degree of microstrain (e), and the lattice parameter (a) of the studied nickel-zinc ferrites are also determined from the experimental XRD profiles (Table 1) by using the Williamson-Hall analysis. A well defined effect of the crystals size decrease and increase in the crystal defects and lattice parameter is observed for the mechanochemically obtained materials (Table 1). A dependence of the lattice parameter on the preparation method and the phase composition exists.

Table 1. Crystallite size (D), microstrain (e) and lattice parameter (a) of investigated sample.

Sample	D (nm)	$e*10^3$ (a.u.)	a (Å)
$NiFe_2O_4$, TS	19.30	1.599	8.332
$Ni_{0.8}Zn_{0.2}Fe_2O_4$, TS	19.34	1.233	8.363
$Ni_{0.5}Zn_{0.5}Fe_2O_4$, TS	24.60	0.646	8.387
$Ni_{0.2}Zn_{0.8}Fe_2O_4$, TS	26.00	0.427	8.416
$ZnFe_2O_4$, TS	28.67	2.275	8.432
$NiFe_2O_4$, MS	5.32	15.945	8.381
$Ni_{0.8}Zn_{0.2}Fe_2O_4$, MS	5.32	15.974	8.396
$Ni_{0.5}Zn_{0.5}Fe_2O_4$, MS	5.83	14.268	8.403
$Ni_{0.2}Zn_{0.8}Fe_2O_4$, MS	11.24	3.700	8.422
$ZnFe_2O_4$, MS	10.16	5.398	8.444

The Mössbauer spectra of the precursors exhibits a quadrupole doublet with δ=0.34 mm/s and Δ=0.65−0.70 mm/s, indicating that the hydroxide carbonates are paramagnetic. Figure 1 shows the RT Mössbauer spectra of samples obtained after different processing routes. The corresponding parameters, listed in Table 2, are typical of Fe^{3+} ions in octahedral and tetrahedral spinel sites [1, 6, 7].
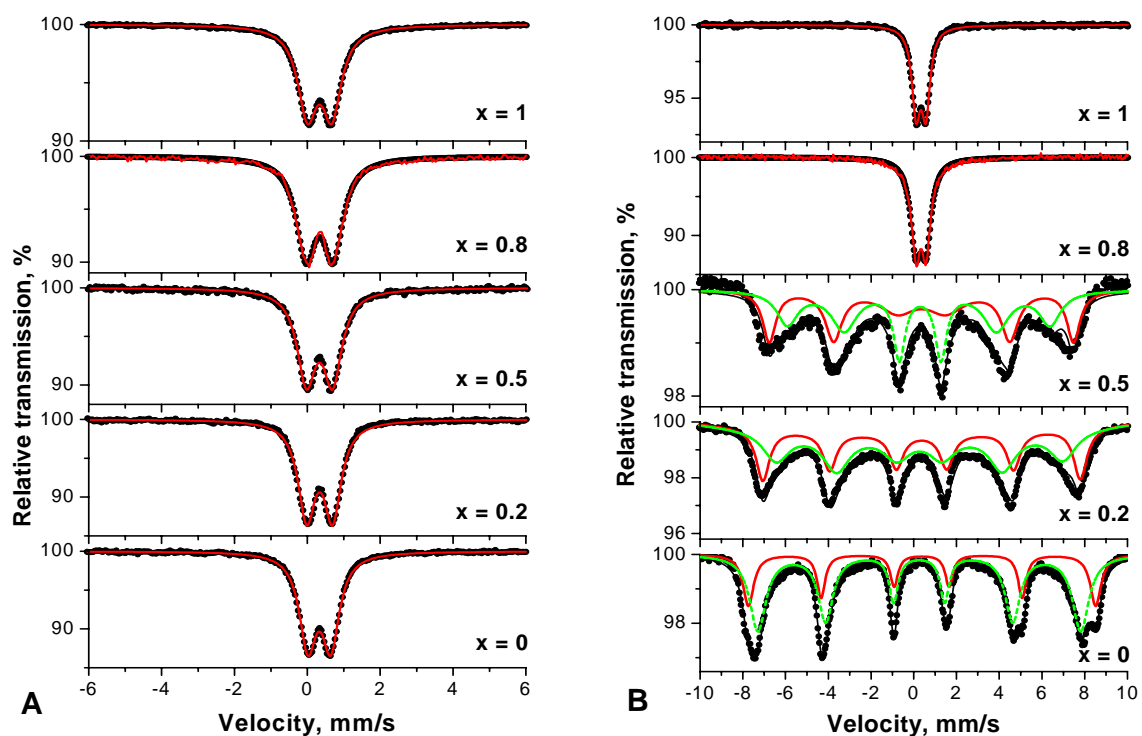
Figure 1. RT Mössbauer spectra of mechanochemically (A) and thermally (B) synthesized $Ni_{1-x}Zn_xFe_2O_4$. (—— – Fe^{3+} octa; - - - – Fe^{3+} tetra)

Table 2. Parameters of Mössbauer spectra.

Sample	Components[a]		δ (mm/s)		Δ (mm/s)		B (T)		Γ (mm/s)		G (%)	
	MS	TS	MS	TS	MS	TS	MS	TS	MS	TS	MS	TS
$ZnFe_2O_4$	Db	Db	0.34	0.34	0.70	0.46	-	-	0.64	0.48	100	100
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	Db	Db	0.34	0.34	0.77	0.49	-	-	0.66	0.59	100	100
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	Db	Sx1	0.33	0.37	0.72	0.00	-	44.3	0.62	1.00	100	47
		Sx2		0.27		0.00		38.2		1.50		53
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	Db	Sx1	0.33	0.37	0.71	0.00	-	46.2	0.57	0.75	100	42
		Sx2		0.27		0.00		41.7		1.50		58
$NiFe_2O_4$	Db	Sx1	0.33	0.37	0.63	0.00	-	50.6	0.57	0.54	100	37
		Sx2		0.27		0.00		46.9		0.78		63

[a] Db = doublet (Fe^{3+} octa); Sx1 = sextet (Fe^{3+} octa); Sx2 = sextet (Fe^{3+} tetra)

As shown in Figure 1A the spectra of all milled samples are doublets. It is well known that the magnetic characteristics of the material are strongly affected when the particle size becomes very small, due to the influence of thermal energy on the magnetic moment ordering, originating the superparamagnetic (SPM) relaxation phenomenon. Taking into account the XRD data we suppose that the doublets observed in all milled samples arise from Fe^{3+} ions in ultrafine ferrite particles exhibiting SPM behavior. This particle size effect is confirmed by the RT isothermal magnetizations where the absence of saturation in the magnetic field range explored, the "S" shape of the curves together with the lack of coercivity indicate the presence of SPM particles.

A difference in structure between the materials, depending on the preparation method is observed. The spectra of $ZnFe_2O_4$ and $Ni_{0.2}Zn_{0.8}Fe_2O_4$ formed by co-precipitation and thermal treatment show

only doublet components (Figure 1B). Comparing with mechanochemically synthesized $ZnFe_2O_4$ and $Ni_{0.2}Zn_{0.8}Fe_2O_4$ we note that the average isomer shifts show no significant variation thus indicating that the s-electron charge distribution of Fe^{3+} ions is negligibly influenced by the synthesis method. But the quadrupole splitting and the spectral line width of the Zn rich ferrite particles are larger for the MS samples (Table 2). This broadening is likely to be associated with several effects induced by milling. As the average grain size decreases, the fraction of disordered and interfacial regions increases and changes in the site distributions of Fe^{3+} and Zn^{2+} ions as well as changes in tetrahedral and octahedral bond lengths and angles probably occur. The isothermal magnetization at RT confirms the paramagnetic character of the TS zinc ferrite, while the mechanochemically obtained sample is superparamagnetic. A magnetic ordering of $ZnFe_2O_4$ is possible only if there is an inversion of cation distribution – some of the Zn^{2+} ions occupy the octahedral sites and some of the Fe^{3+} ions occupy the tetrahedral sites. Therefore the milling process induces structural transformation of the spinel with cationic redistribution into the system which induces magnetic ordering of the ferric ions leading to changes in the magnetic behavior of the materials.

On the other hand, the Mössbauer spectra of thermally synthesized $NiFe_2O_4$, $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ exhibit magnetic splitting at RT. The registered broad spectral lines are probably due to SPM relaxation and Fe^{3+} disorder with increase of Zn-content. As zinc is introduced in the system, the effective internal magnetic field B is reduced. The variation of B with zinc introduction can be explained on the basis of Yafet-Kittel type of spin arrangement [8]. With the increase in zinc concentration, the Fe^{3+} ions will have no magnetic neighbors and hence spins become uncoupled, the saturation magnetization decreases, and hence the hyperfine field decreases. Smaller values of the RT isothermal magnetizations are registered for the MS phases and could be related to local canting of magnetic ions due to the imperfect structure, and mainly to the surface effect of nanosize particles of large surface area.

4. Conclusions

In this work it has been demonstrated that the high-energy ball milling of layered nickel-zinc-iron hydroxide carbonates results in the formation of nanocrystalline Ni-Zn ferrites, where the particle size is below 10 nm. The zinc introduction facilitates the ferrite formation. The structural and magnetic properties of the samples exhibit a strong dependence on the phase composition, particle size and preparation method. This work shows that the combination of the co-precipitation method and subsequent mechanical milling is a promising technique for a relatively large scale preparation of Ni-Zn ferrite nanoparticles.

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