



# Structural and magnetic study of Sm doped NiFe<sub>2</sub>O<sub>4</sub> nanoparticles

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## Abstract

NiFe<sub>2-x</sub>Sm<sub>x</sub>O<sub>4</sub> ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoferrites samples were prepared by sol–gel method. The structural properties of the samples were studied by X-ray powder diffraction, where the formation of a cubic spinel phase was confirmed. The lattice parameter and the particle size were determined by applying Rietveld refinement. A slight change in the lattice parameter was observed for Sm doped nanosamples. Whereas, the particle sizes were found to decrease with increasing Sm concentration ( $x$ ) and have the highest value (42 nm) for pure NiFe<sub>2</sub>O<sub>4</sub> nanoparticles. The magnetic properties were characterized using Mössbauer effect (ME) spectroscopy and vibrating sample magnetometer (VSM). ME spectroscopy was used to study the distribution of cations in tetrahedral (A) and octahedral [B] sites of the nanoparticles and the degrees of inversion values were obtained. The saturation magnetization, coercivity and remanent magnetization were determined using VSM measurements. These magnetic parameters vary with Sm substitution and found to be mainly affected by the change in the cations distribution and particle sizes.

## 1 Introduction

Rare earth (R) doped nano-ferrites have been investigated because of their novel physics and chemical properties. These (R) doped nano-ferrites are technologically important materials that are used to produce permanent magnets, electronic and microwave devices, magnetic fluids, spintronics, data storage, magnetic filters, transformers and magnetic switches [1–4]. The magnetic properties of these spinel ferrites are governed by the chemical composition and the method of preparation [5–7]. In the case of nickel ferrites, altering the chemical composition can be achieved by doping with different transition metals and rare earth (R) ions [5, 8].

Not only is the type of the dopant but also its amount is critical in changing the cation distribution and accordingly the physical properties of the doped Ni-ferrite. Using different synthesizing methods could yield different particle sizes, particle size distribution, morphology and cation distribution [8, 9]. There are many preparation methods of nickel ferrite nanocrystals; mechanical milling, sol–gel methods, ceramic method, microwave processing approaches and co-precipitation, microemulsions. Among these methods,

sol–gel process stands as an important method used to obtain ferrite nanoparticles with enhanced homogeneity and controlled particle size in a relatively short processing time and low reaction temperatures.

Single phase NiFe<sub>1.99</sub>R<sub>0.01</sub>O<sub>4</sub> (R = Sm, Gd, Eu, La) samples were prepared using the standard ceramic method [8]. Mössbauer effect (ME) measurements suggested that R ions substitute Fe<sup>3+</sup> ions in the octahedral B site. An increase in the coercivity and saturation magnetization was observed for all doped samples, where the highest saturation magnetization was obtained for Sm-doped Ni-ferrite sample. Then, Zn and Ga doped Ni<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>1.49</sub>Ga<sub>0.5</sub>Sm<sub>0.01</sub>O<sub>4</sub> samples were prepared using the standard ceramic method [10]. Measurements confirmed that Sm<sup>3+</sup> ions favor the B sites and support magnetism in the studied system, whereas Zn substitution clearly destabilizes the magnetic order and suppresses magnetism in the studied systems. Later, ultrasmall Zn-substituted Ni–Sm–Ga (NiFe<sub>1.99</sub>Sm<sub>0.01</sub>O<sub>4</sub> and Ni<sub>1-x</sub>Zn<sub>x</sub>Fe<sub>1.49</sub>Ga<sub>0.5</sub>Sm<sub>0.01</sub>O<sub>4</sub>) ferrites nanoparticles were synthesized using sol–gel method [9]. The particle size ranged from  $D=4-8$  nm, and hence a pronounced superparamagnetism was observed for all the prepared nanoparticles.

In this work, Sm-substituted Ni ferrites NiFe<sub>2-x</sub>Sm<sub>x</sub>O<sub>4</sub> ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) were prepared by the sol–gel technique. The influence of Sm<sup>3+</sup> doping on the structural and magnetic properties of Ni ferrite were systematically studied. The crystal structure was investigated using

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X-ray powder diffraction and Fourier transform-infrared (FTIR), whereas the cation distribution and the magnetic properties were studied using ME spectrometer and vibrating sample magnetometer (VSM).

## 2 Experimental

$\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles were synthesized using  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  [99% Merck, Germany],  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [99.9% Strem Chemicals, USA],  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  [99.9% Strem Chemicals, USA], citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) [99.7% Winlab, UK] and distilled water. The structure of the prepared samples was studied at room temperature using X-ray diffraction (XRD) (Philips X'pert multipurpose diffractometer) with  $\text{CuK}\alpha$  radiation (with  $\lambda = 1.5418 \text{ \AA}$ ). The crystal structure was refined applying Rietveld profile method using the Rex software [11]. The crystallographic parameters: lattice constant ( $a$ ), ionic radius per molecule of the tetrahedral and octahedral sites ( $r_A, r_B$ ), bond length in the two crystallographic sites ( $R_A$  and  $R_B$ ) and oxygen position parameter ( $u$ ) have been calculated. Jasco FT-IR 310 spectrophotometer were used to carry out FTIR measurements in the frequency range of  $2000\text{--}250 \text{ cm}^{-1}$ . Austin Science Mössbauer Effect Spectrometer with constant acceleration laser-interferometer-controlled drive and data acquisition system is used in a standard transmission setup with a personal Computer Analyzer (PCA II-card with 1024 channel). The radioactive source is  $^{57}\text{Co}$  embedded in Rh matrix with initial activity of 50 mCi. Metallic iron spectrum is used for the calibration of both observed velocities and hyperfine magnetic fields. The cation distributions and all (ME) parameters are calculated from the recorded Mössbauer spectra. Magnetic measurements on the synthesized nanoferrites were carried out using VSM (9600-1 LDJ, USA) with a maximum applied field of nearly 20 kG at room temperature and the saturation magnetization  $M_S$  and the coercivity  $H_C$  were determined.

## 3 Results and discussion

### 3.1 XRD measurements

The XRD patterns of  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles are shown in Fig. 1. For all samples, the observed diffraction peaks can be indexed to  $\text{NiFe}_2\text{O}_4$  with Fd-3m space group. The diffraction patterns exhibit additional impurity peaks of Ni. Using Rex software (Fig. 2), the percentage of Ni phase was calculated and ranged from 3.4% for pure Ni ferrite to < 1% for all Sm doped samples. The lattice parameter  $a_{\text{exp}}$  obtained from the Rietveld refinement of XRD measurements is summarized in Fig. 3b. On the other

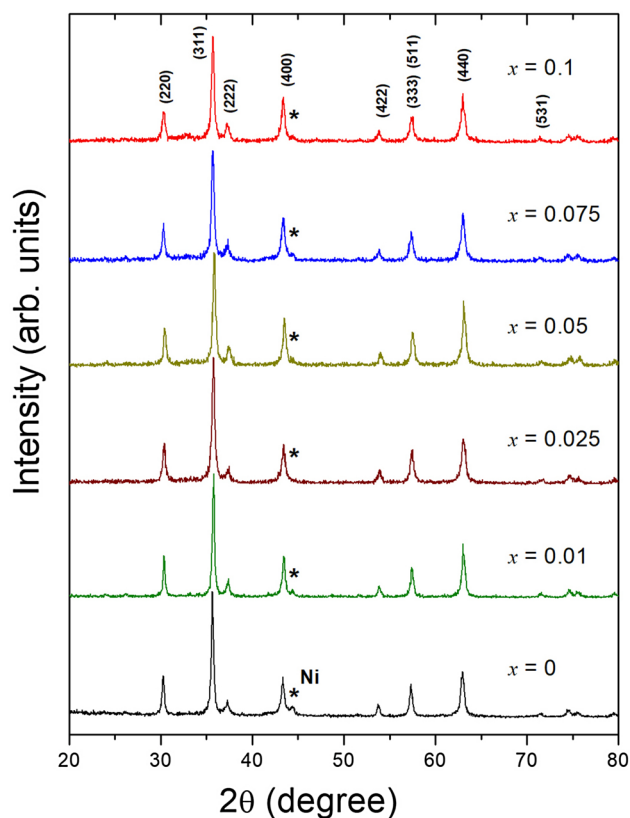


Fig. 1 XRD patterns of different  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

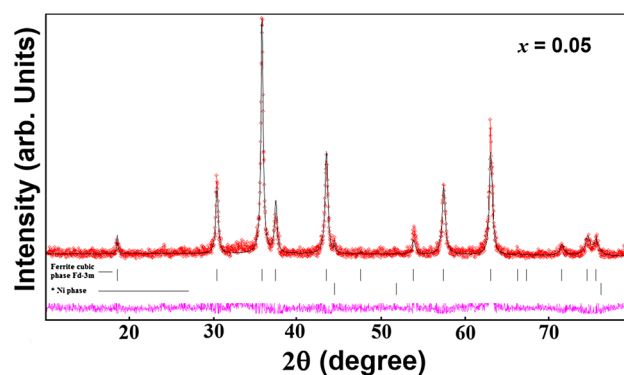
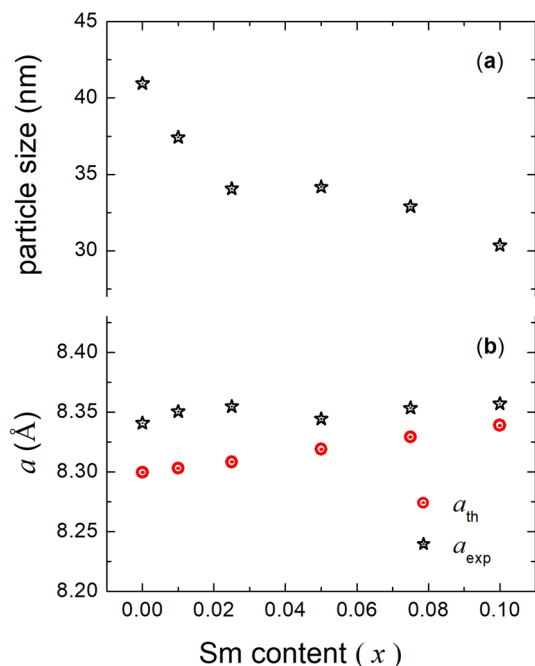


Fig. 2 Rietveld refinement profile for  $\text{NiFe}_{1.95}\text{Sm}_{0.05}\text{O}_4$  sample

hand, the lattice parameter  $a_{\text{th}}$  can be theoretically calculated using the cation distribution obtained from ME spectroscopy (Sect. 3.2). The Mean ionic radius per molecule of the A-site ( $r_A$ ) and B-site ( $r_B$ ) are given by [12]:

$$r_A = C_{\text{Fe}}r(\text{Fe}^{3+}) + C_{\text{Ni}}r(\text{Ni}^{2+}) \quad (1)$$

$$r_B = \frac{1}{2} [C_{\text{Fe}}r(\text{Fe}^{3+}) + C_{\text{Ni}}r(\text{Ni}^{2+}) + C_{\text{Sm}}r(\text{Sm}^{3+})] \quad (2)$$



**Fig. 3** **a** Variation of particle size with the substitution of Sm content. **b** Variation of the lattice parameter ( $a$ ) with Sm content  $x$ .  $a_{exp}$  is the lattice parameter obtained from the XRD measurements and  $a_{th}$  is the lattice parameter calculated according to the cation distribution obtained from the ME measurements

**Table 1** The effective ionic radii of  $r(Fe^{3+})$ ,  $r(Ni^{2+})$  and  $r(Sm^{3+})$  ions in the tetrahedral A-site and octahedral B-site [13]

Ion	Tetrahedral A-site (Å)	Octahedral B-site (Å)
$r(Fe^{3+})$	0.49	0.645
$r(Ni^{2+})$	0.55	0.69
$r(Sm^{3+})$	–	0.958

where  $r(Fe^{3+})$ ,  $r(Ni^{2+})$  and  $r(Sm^{3+})$  are the ionic radii of  $Fe^{3+}$ ,  $Ni^{2+}$  and  $Sm^{3+}$  ions given in Table 1. The concentration of  $Fe^{3+}$ ,  $Ni^{2+}$  and  $Sm^{3+}$  ions in A- and B- sites are  $C_{Fe}$ ,  $C_{Ni}$  and  $C_{Sm}$ , respectively and were taken from (ME) results. The average (A–O) and (B–O) bond lengths are  $R_A$  and  $R_B$  respectively and can be expressed as:

$$R_A = r_A + r_O \quad (3)$$

$$R_B = r_B + r_O \quad (4)$$

where  $r_O = 1.32$  Å is the radius of oxygen ion. The lattice parameter  $a_{th}$  can be obtained from:

$$a_{th} = \frac{8}{3} \left[ (r_A + r_O) + \sqrt{3}(r_B + r_O) \right] \quad (5)$$

The calculated values of  $a_{th}$ ,  $r_A$ ,  $r_B$ ,  $R_A$ ,  $R_B$  and  $u$  are illustrated in Table 2. The comparison between the calculated lattice parameter  $a_{th}$  and the experimentally obtained  $a_{exp}$  are shown in Fig. 3b. According to the ME measurements (Sect. 3.3), nano  $NiFe_2O_4$  is a partial inverse spinel, where most of the  $Ni^{2+}$  ions set on the B-site, while a small fraction (~9%) enters the A-site. By increasing  $x$ ,  $Sm^{3+}$  ions have a clear preference to enter the B-site and gradually substitute  $Fe^{3+}$  ions. This process is accompanied by the migration of the  $Ni^{2+}$  from the A-site to the B-site. The ionic radius  $r(Sm^{3+})$  is bigger than both  $r(Fe^{3+})$  and  $r(Ni^{2+})$ . This why by increasing  $x$ , both  $r_A$  and  $R_A$  slightly decrease, while  $r_B$  and  $R_B$  increase monotonically. The resultant effect is an increase in the lattice parameter. The values of the lattice parameter are very close to the values observed for the bulk Ni ferrite sample [4]. For the A-site, center of symmetry is at  $\left(\frac{3}{8}, \frac{3}{8}, \frac{3}{8}\right)$  and the ideal value of the oxygen positional parameter ( $u^{43m}$ ) is 0.375. While, the center of symmetry for the B-site is at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  and the ideal value of  $u^{3m}$  is 0.25. In this case, the arrangement of  $O^{2-}$  ions correspond exactly to a cubic closed packing. However, in the actual spinel lattice a small deformation from this ideal pattern is observed. As shown in Table 2, the values of  $u^{3m}$  and  $u^{43m}$  are higher than the ideal values, which indicate that  $O^{2-}$  ions move away from the tetrahedrally coordinated A-site cation along the  $\langle 111 \rangle$  directions due to the contraction of the tetrahedral interstices, correspondingly the octahedral B-sites become smaller [9]. Such changes in the oxygen positional parameter will affect the A–A interactions and B–B magnetic interactions.

The particle size of  $NiFe_{2-x}Sm_xO_4$  nanoparticles can be obtained from the Rietveld refinement of XRD measurements. The broad diffraction peaks observed for all the samples reflect the reduced particle size. The particle size

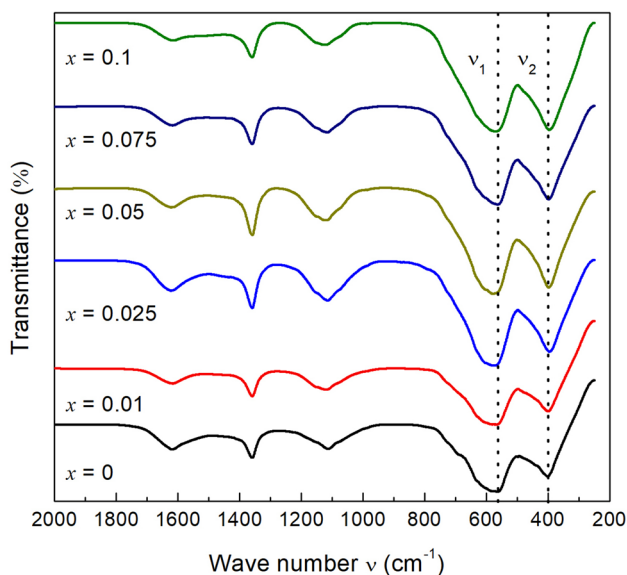
**Table 2** Experimental ( $a_{exp}$ ) and theoretical ( $a_{th}$ ) lattice constants, ionic radii of A- and B-sites ( $r_A$  and  $r_B$ ), the average bond lengths ( $R_A$  and  $R_B$ ) and the oxygen positional parameter ( $u$ ) of  $NiFe_{2-x}Sm_xO_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

$x$	$a_{exp}$ (Å)	$a_{th}$ (Å)	$r_A$ (Å)	$R_A$ (Å)	$r_B$ (Å)	$R_B$ (Å)	$u^{3m}$ (Å)	$u^{43m}$ (Å)
0	8.341	8.2997	0.4951	1.8651	0.6656	2.0356	0.271	0.396
0.01	8.351	8.3032	0.49379	1.8638	0.6676	2.0376	0.2712	0.396
0.025	8.355	8.3084	0.49178	1.8618	0.6707	2.0407	0.2704	0.395
0.05	8.344	8.3191	0.49222	1.8622	0.6745	2.0445	0.2696	0.395
0.075	8.353	8.3292	0.49169	1.8617	0.6786	2.0486	0.2698	0.395
0.1	8.357	8.339	0.49051	1.8605	0.683	2.053	0.2689	0.394

D are shown in Fig. 3, where it varies from  $\sim 42$  nm for pure Ni-ferrite to  $\sim 30$  nm for  $\text{NiFe}_{1.9}\text{Sm}_{0.1}\text{O}_4$ . Generally, by increasing the Sm content  $x$ , the particle size decreases. A similar behavior was observed for  $\text{Nd}^{3+}$  substituted nano Mg–Cd ferrites [14, 15].

### 3.2 FTIR analysis

FTIR spectra of  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoferrites are shown in Fig. 4 and the vibration frequencies of all the samples are listed in Table 3. Spinel ferrites generally are branded with two vibrational frequency bands,  $\nu_1$  around  $600\text{--}500\text{ cm}^{-1}$  which is related to the  $\text{Fe}^{3+}\text{--O}^{2-}$  and  $\text{Ni}^{2+}\text{--O}^{2-}$  complexes at the tetrahedral site (A) and vibrational frequency  $\nu_2$  around  $450\text{--}350\text{ cm}^{-1}$  which is related to the  $\text{Fe}^{3+}\text{--O}^{2-}$ ,  $\text{Sm}^{3+}\text{--O}^{2-}$  and  $\text{Ni}^{2+}\text{--O}^{2-}$  complexes at octahedral (B) site [16]. The differences in vibration frequencies between the two crystallographic A and B-sites are attributed to the differences in bond length between the two sites, where the ionic radius of A-site is smaller than B-site. In this case, the change in values of  $\nu_1$  and  $\nu_2$  with increasing Sm content reflects the change in bond lengths of  $\text{Fe}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Ni}^{2+}$  metal ions complexes present in this ferrite. As discussed before in Sect. 3.1, XRD measurements suggest a slight change in the average bond length  $R_A$ ,  $R_B$  and the lattice parameter  $a$ . Accordingly, a minor change in the vibrational frequency  $\nu_1$  and  $\nu_2$  was observed. The bands at  $1613\text{ cm}^{-1}$ ,  $1359\text{ cm}^{-1}$  and  $1115\text{ cm}^{-1}$  are attributed to; (a) the stretching vibration in the residual H–O–H modes of water molecules, (b) the symmetric stretching of the carboxyl group (COOH) and (c) the asymmetric stretching



**Fig. 4** FTIR spectra of different  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

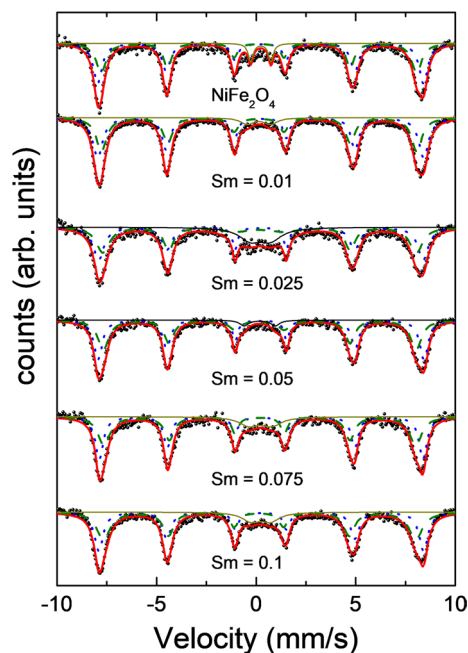
**Table 3** Tetrahedral and octahedral vibrational frequencies ( $\nu_1$  and  $\nu_2$ ) of  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

$x$	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )
0	565	397
0.01	580	400
0.025	579	396
0.05	578	397
0.075	563	398
0.1	567	396

vibration of the adsorbed  $\text{NO}_3$  produced as a residue from the nitrate group after the combustion of the samples [17].

### 3.3 ME measurements

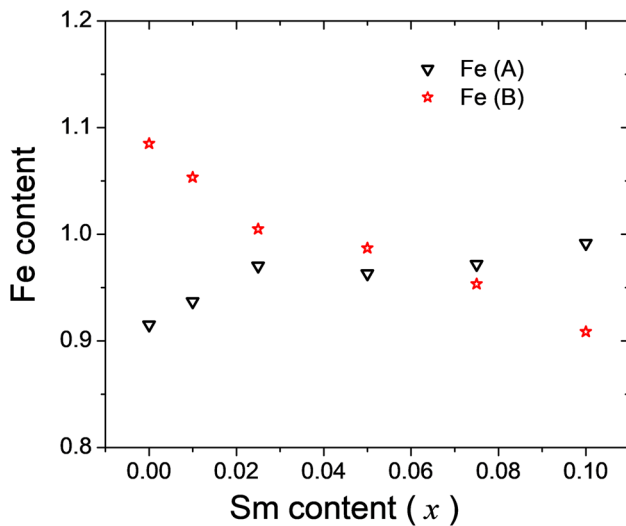
Figure 5 shows the room temperature transmission ME spectra of  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ). ME spectra spot the hyperfine interactions between the nucleus and its neighboring electrons. There are three main hyperfine interactions, one originates from the electron density at the nucleus (Isomer shift  $\delta$ ), the other from the gradient of the electric field at the nucleus (Quadrupole splitting  $\Delta E_Q$ ), and finally from the unpaired electron density at the nucleus (Hyperfine field  $H_f$ ). The spectra of all samples were fitted with two magnetic sextets and a paramagnetic doublet. All the fitting parameters are summarized in Table 4. The magnetic sextets are a direct proof of the magnetic order in the studied samples. The existence of two sextets is typical for inverse and partially inverse spinel ferrites, where they



**Fig. 5** Room temperature ME spectra of different  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

**Table 4** The isomer shift ( $\delta$ ), quadrupole splitting ( $\Delta E_Q$ ), Hyperfine field ( $H_f$ ) and the doublet linewidth  $\omega_d$  of different  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

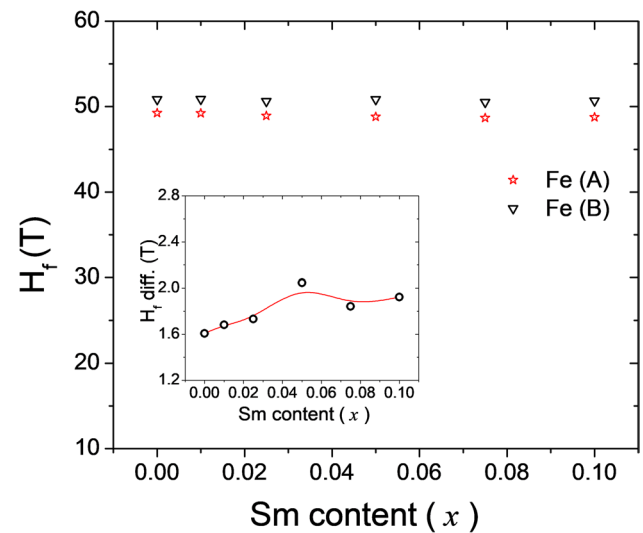
		Sample					
		0	0.01	0.025	0.05	0.075	0.1
$\delta_A$	(mm/s)	0.1402	0.1461	0.1663	0.1745	0.1817	0.151
$\delta_B$	(mm/s)	0.2199	0.2242	0.2359	0.2411	0.2467	0.2427
$\Delta E_{QA}$	(mm/s)	0.0011	0.0016	0.0051	0.0107	0.0149	0.0382
$\Delta E_{QB}$	(mm/s)	0.0019	0.0035	0.0097	0.0031	0.0072	0.0135
$H_{fA}$	(T)	49.254	49.2087	48.9165	48.8219	48.6768	48.7667
$H_{fB}$	(T)	50.8608	50.891	50.6492	50.8678	50.5192	50.6907
Doublet							
$\delta_d$	(mm/s)	0.2331	0.2172	0.2068	0.1755	0.21	0.2343
$\Delta E_{Qd}$	(mm/s)	1.0147	1.1779	1.0194	1.5628	1.1412	0.9733
$\omega_d$	(mm/s)	0.2945	0.7927	1.3403	0.521	1.1822	1.1008



**Fig. 6** Fe content calculated from ME spectra for different  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

refer to  $\text{Fe}^{3+}$  in both tetrahedral and octahedral environments. For this reason, the area of these two sextets are used for the determination of Fe amount in the A- and B-sites. The sextets attributed to the  $\text{Fe}^{3+}$  ions at the octahedral (B) have a larger isomer shift and hyperfine field [18]. As presented in Fig. 6, the  $\text{Fe}^{3+}$  amount in the B-site is slightly higher than that in the A-site, which straight forwardly refers that a portion  $\text{Ni}^{2+}$  ions set on A-site (~9%). This unusual partial inverse Ni ferrite is due to the reduced particle size [4]. For  $x=0.01$ ,  $\text{Sm}^{3+}$  ions replace  $\text{Fe}^{3+}$  in the B-site and in the same time some of the  $\text{Ni}^{2+}$  ions transfer from the A- to the B-site. By increasing the Sm content  $x$ , the behavior continues and the amount of  $\text{Fe}^{3+}$  ions in the A-site exceed that in the B-site for  $x > 0.05$ .

In addition to the two sextets components, the spectra of all samples have doublets due to the presence of nano-sized ferrite crystallites below the single domain size ( $D_{sp}$ ) with superparamagnetic behavior [4, 19]. The area of the



**Fig. 7** Mössbauer hyperfine field of different  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

doublets is ranging from (3.58–16.24%).  $\delta$  values are typical for  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral environment [4, 5]. Since, the s-electrons charge density of the  $\text{Fe}^{3+}$  ions is not influenced by crystalline size, the observed values of the isomer shift show a weak change with decreasing D. The quadrupole splitting ( $\Delta E_Q$ ) has values close to zero for both (A)- and [B]-sites.

Figure 7 presents the hyperfine field ( $H_{fA}$  and  $H_{fB}$ ) for both A- and B-sites. Generally, the hyperfine field reflects the internal magnetic field produced by the magnetic ordering on  $\text{Fe}^{3+}$  ions on both sites. This field is strongly affected by intersite A–A and B–B interactions and the inter sites A–B interactions. As the cation distribution changes due to the  $\text{Sm}^{3+}$  doping, these magnetic interactions change and consequently affect both hyperfine fields. Also, the hyperfine field is sensitive to the decreased particle size, where decreasing the particle size tends to decrease the hyperfine field [20, 21]. Figure 7 suggests that increasing  $\text{Sm}^{3+}$

concentration slightly changes  $H_{fA}$  and  $H_{fB}$ . Generally, for  $x \leq 0.1$ ,  $Sm^{3+}$  ions has a minor effect on the magnetic interactions and magnetic order. However, the changes in the cation distribution due to Sm doping is reflected in the difference between  $H_{fB}$  and  $H_{fA}$ . The difference between  $H_{fB}$  and  $H_{fA}$  increases gradually by introducing  $Sm^{3+}$  ions and it peaks at  $x=0.05$  and then decreases again for higher concentration ( $x > 0.05$ ) where the  $Fe^{3+}$  in the A-site exceeds that in the B-site. The change in the cation distribution can also be spotted in the doublets parameters. As indicated in Fig. 8, pronounced differences are observed in the behavior of  $\delta_d$ ,  $\Delta E_{Qd}$  and doublet linewidth  $\omega_d$  for  $x < 0.05$  and  $x > 0.05$ . Such behavior can be attributed to the changes in the A–B interactions due to partial transfer of the  $Fe^{3+}$  ions from the B-site to the A-site by increasing  $Sm^{3+}$  concentration.

### 3.4 Magnetic properties

Figure 9 shows the variation of magnetization as a function of the applied magnetic field for various  $NiFe_{2-x}Sm_xO_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles at 300 K. The M–H curve provides information regarding the

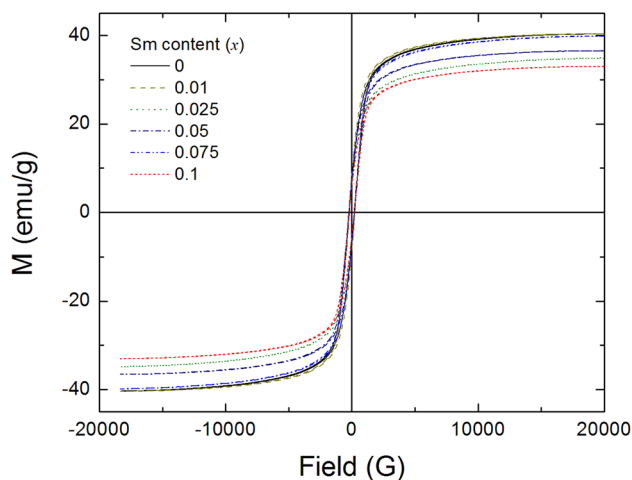
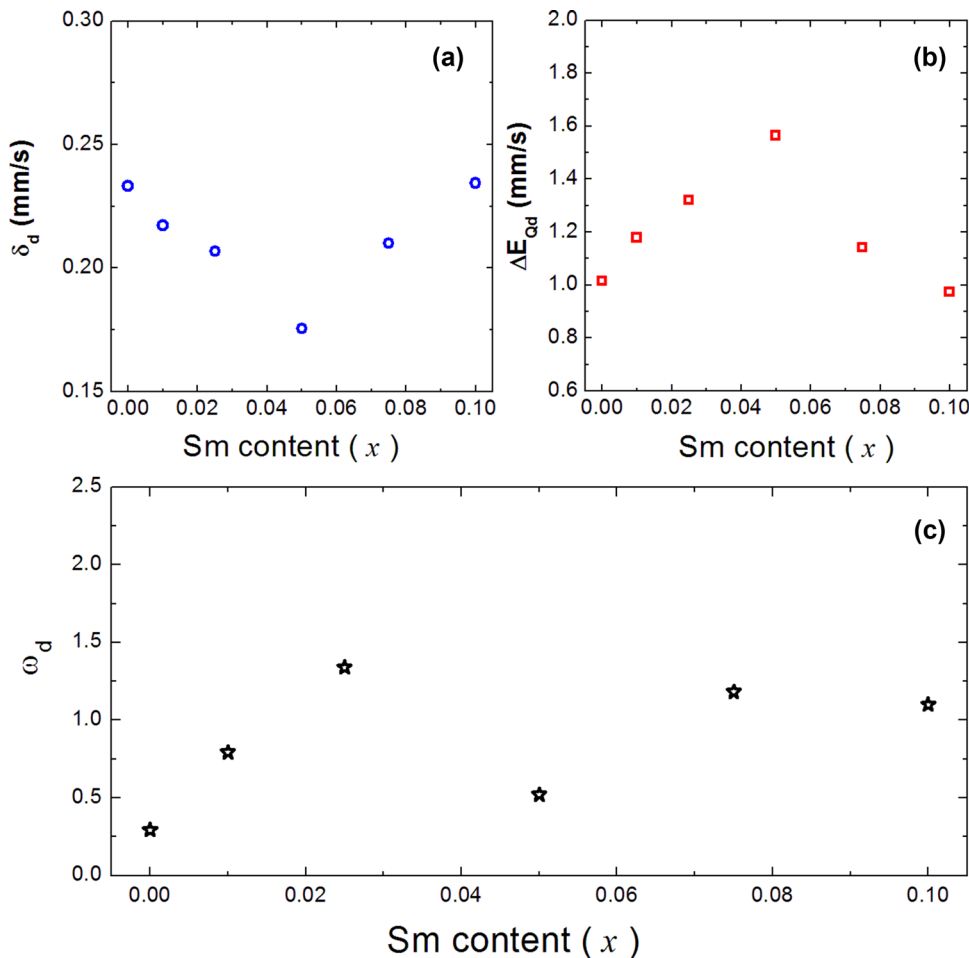


Fig. 9 VSM measurements for  $NiFe_{2-x}Sm_xO_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

magnetic parameters such as saturation magnetization ( $M_S$ ), coercivity ( $H_C$ ) and remanent magnetization ( $M_r$ ), which are summarized in Table 5. Saturation magnetization ( $M_S$ ) and

Fig. 8 For different nanoparticles **a** Isomer shift of the paramagnetic doublet. **b** Quadrapole splitting of the paramagnetic doublet. **c** Linewidth of the paramagnetic doublet



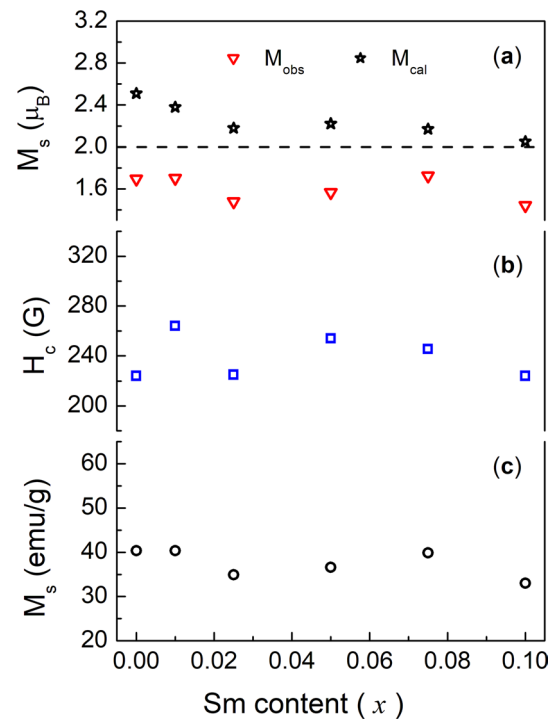
Coercivity ( $H_C$ ) are shown in Fig. 10. Generally, the magnetic properties should mainly depend on  $\text{Sm}^{3+}$  content and the cation distribution of different ions between A and B sites. However, the magnetic properties of nanoferrites also strongly depend on the particle size and the particle size distribution. The saturation magnetization ( $M_S$ ) is expected to decrease with decreasing the particle size [4]. The magnetic moment per formula unit in Bohr magneton ( $\mu_B$ ) can be calculated using the relation [8]:

$$M_{\text{obs}} = \frac{(\text{saturation magnetization}) \times (\text{molecular weight})}{5585} \quad (6)$$

The value of  $M_{\text{obs}}$  is presented in Table 4 and Fig. 10a. The magnetic properties of ferrites are mainly governed by super exchange interactions and therefore changing the cation distribution and introducing rare earth Sm would affect A–A, A–B and B–B magnetic interactions. According to Néel's theory, the magnetic moment  $M_{\text{cal}}$  is expressed as:

$$M_{\text{cal}} = M_B - M_A \quad (7)$$

The concentration of different ions in the A- and B-sites are obtained from the ME measurements and the magnetic moment of  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Sm}^{3+}$  ions are  $2 \mu_B$ ,  $5 \mu_B$  and  $5 \mu_B$ , respectively. The dashed line is the expected value for complete inverse  $\text{NiFe}_2\text{O}_4$ , which is exact  $2 \mu_B$ . For all the samples,  $M_{\text{cal}}$  values are significantly higher than the observed values.  $M_S$  value depends on the ions magnetic moments, and the distance and angle between two adjacent magnetic ions. The larger ionic radii of  $\text{Sm}^{3+}$  ions compared to  $\text{Fe}^{3+}$  ions causes changes in the lattice parameter, bond lengths, bond angles and oxygen positional parameter, which would lead to the variation of the magnetic interactions. Moreover, the change in the cation distribution will also affect the magnetic interactions. Finally, the reduced particle size of the prepared nanoparticles decreases  $M_S$  values [3, 22, 23]. The coercivity of the ferrites nanoparticles depends on internal micro stress



**Fig. 10** a Comparison between observed magnetic moment obtained from VSM measurements ( $M_{\text{obs}}$ ) and calculated magnetic moments according to Néel's theory ( $M_{\text{cal}}$ ). b Coercivity ( $H_C$ ) and c Saturation magnetization ( $M_S$ ) for  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

due to distortion of lattice, different electronic configuration of the ions and particle size.  $\text{Sm}^{3+}$  ions concentration would logically affect  $H_C$  since  $\text{Sm}^{3+}$  4f electrons have a strong spin–orbit coupling [22]. The change in coercivity with  $\text{Sm}^{3+}$  ions concentration can be attributed to the decrease in particle size and the changes in the cation distribution. The squareness  $R^2 = M_R/M_S$  for all the studied samples is ranging from 0.235–0.314. Since the squareness is smaller than 0.5,  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  nanoparticles would have uniaxial anisotropy which arises due to surface effect [23, 24].

**Table 5** Saturation magnetization ( $M_S$ ), Coercivity ( $H_C$ ), Remanent magnetization ( $M_r$ ), Squareness ration ( $R^2$ ), observed magnetic moment ( $M_{\text{obs}}$ ) and calculated magnetic moments according to Néel's

theory ( $M_{\text{cal}}$ ) for  $\text{NiFe}_{2-x}\text{Sm}_x\text{O}_4$  ( $x=0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanoparticles

$x$	$M_S$ (emu/g)	$H_C$ (G)	$M_r$	$R^2$	$M_{\text{obs}}$ ( $\mu_B$ )	$M_{\text{cal}}$ ( $\mu_B$ )
0	40.372	224.07	9.49	0.235	1.69425	2.51
0.01	40.37	264.07	12.7	0.314	1.70099	2.38
0.025	34.901	225.09	8.35	0.239	1.47942	2.18
0.05	36.589	254.1	10.56	0.289	1.56645	2.22
0.075	39.898	245.58	10.73	0.269	1.72499	2.17
0.1	33.035	224.01	7.93	0.24	1.44225	2.05

## 4 Conclusion

NiFe<sub>2-x</sub>Sm<sub>x</sub>O<sub>4</sub> ( $x = 0.0, 0.01, 0.025, 0.05, 0.075, 0.1$ ) nanocrystalline ferrites were synthesized by sol–gel technique. The structural parameters; lattice parameter ( $a$ ), bond lengths and oxygen positional parameter ( $u$ ) were calculated from the X-ray powder diffraction measurements. These structure parameters vary systemically with the substitution of Sm<sup>3+</sup> ions. ME spectroscopy was utilized to study the magnetic properties and determine the cation distribution. For all the samples, ME spectra contain two magnetic sextets and a paramagnetic doublet, which suggest the coexistence of the magnetic order for large particle sizes and superparamagnetic behavior for small particle sizes below  $D_{sp}$ . The saturation magnetization ( $M_s$ ), coercivity ( $H_c$ ) and remanent magnetization ( $M_r$ ) were determined from the VSM measurements. The squareness ratio suggests that all the studied nanoparticles have uniaxial anisotropy. The observed magnetic moment values ( $M_{obs}$ ) for all samples are significantly lower than the calculated magnetic moments according to Néel's theory ( $M_{cal}$ ). These reduced values of  $M_{obs}$  can be attributed to the reduced particle sizes of the prepared nanoferrites.

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