

Mössbauer Study of Nickel-Substituted Cobalt Ferrites

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Nanosize nickel-substituted cobalt ferrites were prepared using the technology sol-gel with participation of auto-combustion (SGA) and characterized by EDX and Mössbauer spectroscopy. Mössbauer spectrum of CoFe_2O_4 powder at room temperature exhibited broad sextet and doublet, suggesting superparamagnetic nature of the sample. The substituted samples showed only broad sextet, which is resolved into two sub-sextets, corresponding to tetrahedrally and octahedrally coordinated Fe cations. Cation distribution calculated using XRD and Mössbauer data indicates a decrease in $\text{Fe}^{3+}[\text{B}]/\text{Fe}^{3+}(\text{A})$ ratio with increasing nickel concentration.

Keywords: Ferrite, Nanoparticles, Mössbauer spectra, Energy dispersive X-ray spectroscopy.

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1. INTRODUCTION

The development of new nanomaterials that are simultaneously economically viable and have tunable physical properties has become one of the most important researches. Among the various ferrite materials, cobalt ferrites CoFe_2O_4 are of paramount importance due to their excellent chemical stability, good mechanical hardness, high coercivity, moderate saturation magnetization, a positive anisotropy constant, and a high magnetostriction [1]. These are the most widely used magnetic materials in high frequency applications [2].

The structure of inverse spinel allows the incorporation of different metallic ions, which can considerably influence the magnetic and electrical properties. Interesting magnetic properties originate mainly from the magnetic interactions between cations that are situated in the tetrahedral (A) and the octahedral [B] sites. The substitution affects the distribution of the Fe^{3+} ions in the A and B sites, thereby, changing the structure of cobalt ferrites from inverse spinel to mixed spinel, resulting in a corresponding change in the magnetic properties [3].

The properties of the ferrites are found to be strongly dependent on the method of preparation, reaction conditions, composition of ferrites and the cation distribution. Various preparation techniques like sol-gel method, co-precipitation method, ball milling, micro emulsion processing, etc. have been developed in order to obtain substituted cobalt ferrites with tunable physical properties. By using different types of cations, the cation distribution of the ferrites may undergo a change leading to the development of materials with new properties. Therefore, the knowledge of the cation distribution plays an important role in the development of new materials which may be useful in the industry.

The properties Ni-Co ferrites make them very promising candidates for a variety of applications in

biomedical technologies [4, 5]. From the application point of view, the magnetic character of the nanoparticles depends crucially on size, shape, purity and magnetic stability of these nanoparticles. These particles should be single domain, of pure phase, suitable coercivity, moderate magnetization and stable blocking effects. In biomedical applications, the nanoparticles are used as drug carriers to the areas of the body where conventional drug delivery systems may not work [6]. For this purpose the nanoparticles used should be magnetically in superparamagnetic unblocked state with relatively low blocking temperature and coercivity.

Therefore, the aim of present paper is study the impact of Ni^{2+} ions substitution on chemical composition and magnetic properties of CoFe_2O_4 prepared by the SGA technology [7].

2. EXPERIMENTS

The ferrites with the general formula $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) have been prepared by SGA technique. The X-ray diffraction (XRD) patterns were recorded at room temperature using $\text{CuK}\alpha$ radiation. The scanning was done in the 2θ range from 15° to 60° . After completing the process auto-combustion was obtained one phase of ferrite powders which corresponded to the cubic structure of spinel space group $Fd3m$. The average size of coherent scattering regions of powders was in the range 39 – 62 nm [8].

Mössbauer absorption spectra of Ni-Co powders were obtained at room temperature on a spectrometer MS-1104Em. As a source of γ -quanta, ^{57}Co with an activity of 100 mCi in a chromic matrix was used. Gamma quanta were registered by means of a scintillation counter with a NaI crystal as a sensitive element. The resolution of experimental Mössbauer spectra into components was carried out by applying the universal program UnivemMS-7; namely, the

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spectra were approximated by sums of analytical functions describing separate components in the experimental spectrum. Isomeric shifts were calibrated with respect to metallic α -Fe.

The atomic weight composition (%) of the constituent elements in the as-prepared samples was carried out by energy dispersive X-ray spectroscopy (EDX) performed on the EXPERT 3L atomic composition analyzer.

3. RESULTS AND DISCUSSION

3.1 Mössbauer Spectroscopy

The typical Mössbauer spectrum of obtained powder of CoFe_2O_4 is shown in Fig. 1(a) which indicates a doublet and two sextets attributed to tetrahedral and octahedral site. The doublet can be attributed to the part of the sample in paramagnetic or superparamagnetic state. The sextets belonging to A and B sites have been assigned on the basis of the values of hyperfine magnetic field (H_{hf}) at the nucleus and isomer shift (I_s). The typical Mössbauer spectra of substituted samples are shown in Fig. 1(b-d). All Ni-Co ferrite samples exhibit well resolved and magnetically normal Zeeman split sextets with asymmetric lines attributed to the presence of iron ions at both tetrahedral and octahedral sites which indicates the ferrimagnetic nature of the synthesized materials with mixed spinel structure.

However, a slight broadness in Zeeman lines is observed as evident from Fig. 1. The broadening of lines could be attributed to slight changes in the magnetic environment surrounding Fe^{3+} ions in the same sub lattice; such changes in environment of Fe^{3+} ions would

lead to a change in the magnetic field and consequently results in some appreciable broadening of the Zeeman lines [9]. In addition, the changes in the magnetic environment would affect isomer shift values I_s slightly, displacing the sextets with respect to one another and cause general broadening of these lines.

A summary of the various hyperfine interaction parameters is presented in Table 1 and obtained results are in close agreement with the studies reported earlier for spinel ferrites [10, 11]. The isomer shift results from the electrostatic interaction between the charge distribution of the nucleus and s-electrons with finite probability being found in the region of the nucleus. Data of the Table 1 show that the isomer shift (A) and [B] values have random trend, indicating that s-electron charge distribution of Fe^{3+} is not much influenced by Ni^{2+} substitution. In general, most of the ferrites have higher values of hyperfine magnetic field and isomer shift correspond to B-site sextet and the lower values of the same correspond to A-site sextet. However, in studied ferrites higher values of hyperfine magnetic field (509-516 kOe) and isomer shift (0.35-0.40 mm/s) correspond to A-site sextet and the lower values of H_{hf} (489-492 kOe) and I_s (0.25-0.28 mm/s) correspond to B-site sextet. The same behavior of the above parameters was recorded by the author Singhal et al [12] in the Ni-Co ferrites prepared using aerosol route. The obtained values of the isomer shift for the A and B sites are consistent with the high spin state of Fe^{3+} ions in the spinel environment and the values of the hyperfine fields are typical for the CoFe_2O_4 spinel structure. There is no significant change observed in the hyperfine field of all the compositions.

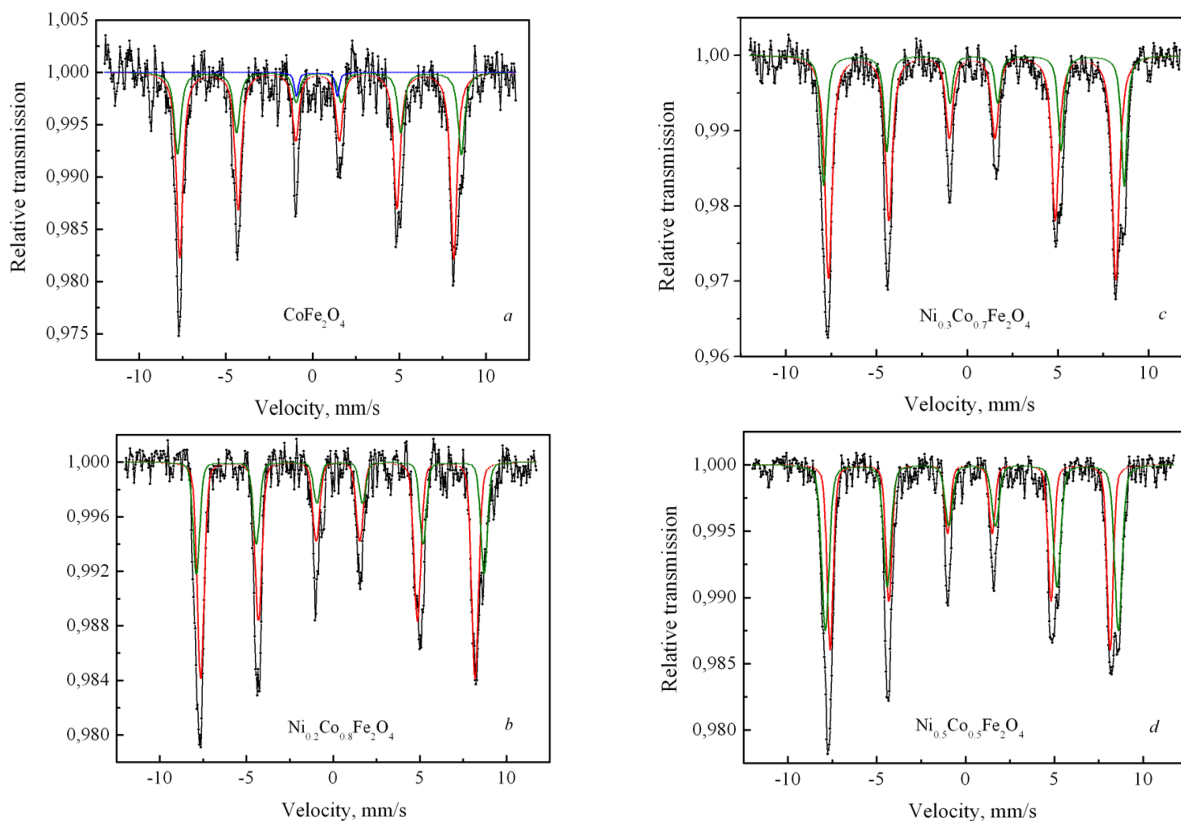
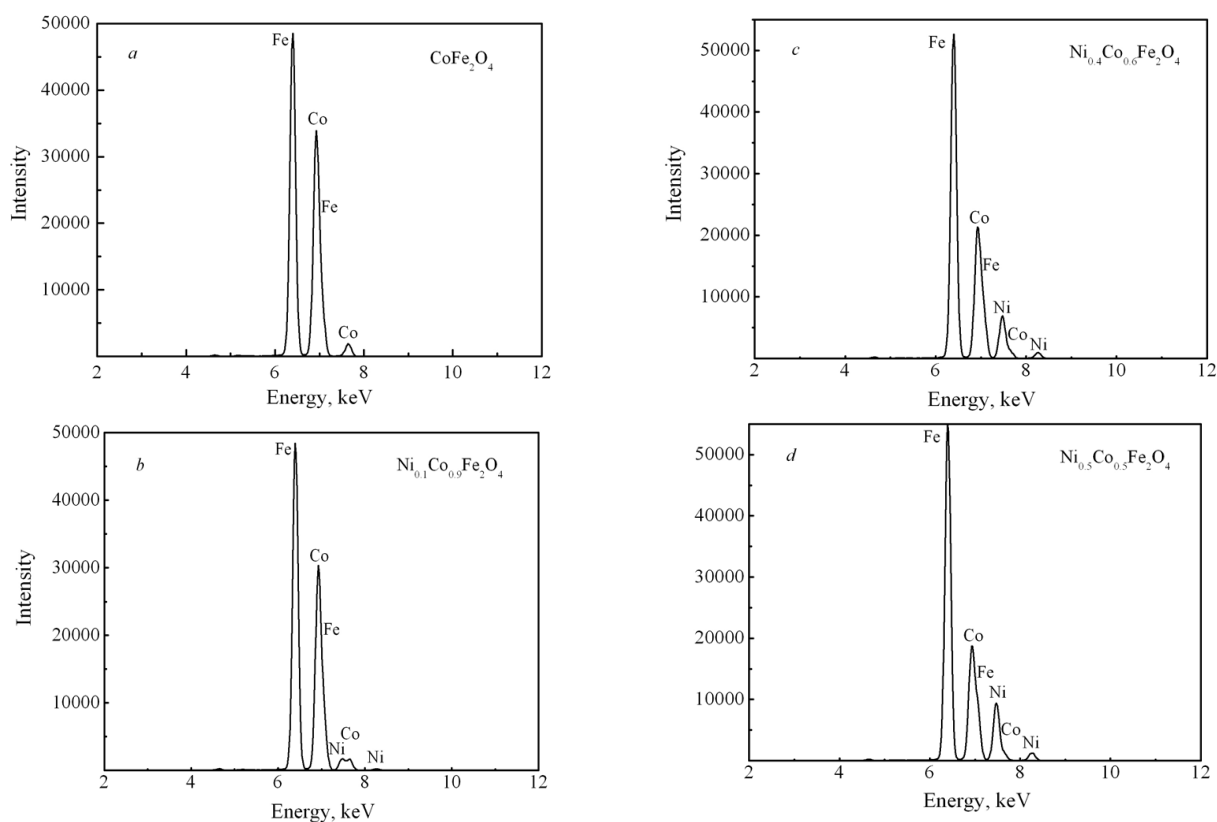


Fig. 1 – Mössbauer spectra of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$

Table 1 – Mössbauer hyperfine parameters at 300 K of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$

x	Sub-spectra	I_s , mm/s	Q_s , mm/s	G , mm/s	H_{hf} , kOe	A , %	Cation distribution	$\delta_{\text{Möss}}$	$\delta_{\text{X-ray}}$
0.0	Sextet [B]	0.27	-0.05	0.45	491	69	$(\text{Co}_{0.41}\text{Fe}_{0.59})[\text{Co}_{0.59}\text{Fe}_{1.41}]\text{O}_4$	2.38	2.39
	Sextet (A)	0.38	0.04	0.45	509	29			
	Doublet	0.25	2.37	0.27		2			
0.1	Sextet [B]	0.26	-0.01	0.42	490	69	$(\text{Co}_{0.38}\text{Fe}_{0.62})[\text{Ni}_{0.10}\text{Co}_{0.52}\text{Fe}_{1.38}]\text{O}_4$	2.22	2.18
	Sextet (A)	0.36	0.00	0.50	510	31			
0.2	Sextet [B]	0.28	0.00	0.48	492	67	$(\text{Co}_{0.34}\text{Fe}_{0.66})[\text{Ni}_{0.20}\text{Co}_{0.46}\text{Fe}_{1.34}]\text{O}_4$	2.03	2.03
	Sextet (A)	0.40	0.03	0.46	516	33			
0.3	Sextet [B]	0.27	0.00	0.48	492	65	$(\text{Co}_{0.30}\text{Fe}_{0.70})[\text{Ni}_{0.30}\text{Co}_{0.40}\text{Fe}_{1.30}]\text{O}_4$	1.86	1.82
	Sextet (A)	0.37	0.00	0.37	515	35			
0.4	Sextet [B]	0.27	0.01	0.44	491	62	$(\text{Co}_{0.24}\text{Fe}_{0.76})[\text{Ni}_{0.40}\text{Co}_{0.36}\text{Fe}_{1.24}]\text{O}_4$	1.63	1.67
	Sextet (A)	0.35	-0.07	0.38	514	38			
0.5	Sextet [B]	0.25	0.01	0.41	489	59	$(\text{Co}_{0.18}\text{Fe}_{0.82})[\text{Ni}_{0.50}\text{Co}_{0.32}\text{Fe}_{1.18}]\text{O}_4$	1.44	1.53
	Sextet (A)	0.37	-0.01	0.50	512	41			

**Fig. 2** – EDX spectra of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ samples

The values of quadrupole splitting Q_s (refer Table 1) for hyperfine spectra of all the samples have found to be negligibly small and can be attributed to the fact that overall cubic symmetry is not much altered between Fe^{3+} ions and their surroundings by substitution with Ni ions in cobalt ferrite. The relative area (A , %) under the resonance curve of the sub-spectra deduced from the measurements is helpful to conceive the Co, Ni and Fe site occupancy in sub-lattice sites. The relative peak-area of B-site decreases with the incorporation of Ni. Therefore the ratio decreases from 2.38 to 1.44 on increasing the nickel concentration.

$$\delta = \frac{\text{Fe}^{3+}[\text{B}]}{\text{Fe}^{3+}[\text{A}]} \quad (1)$$

The CoFe_2O_4 nanoparticles are well-known to have only partially inverse spinel structure, represented as $(\text{Co}_y\text{Fe}_{1-y})[\text{Co}_{1-y}\text{Fe}_{1+y}]\text{O}_4$. This so-called degree of inversion depends on temperature and method of preparation. For sample $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ the overlapped sextets do not allow to compute the degree of inversion with an high accuracy, therefore the parameter δ calculated by the data of the Mössbauer spectroscopy (1.44) somewhat lower than δ obtained by X-ray analysis (1.53).

The slight decrease in the degree of inversion is observed with increasing concentration of Ni^{2+} ions that

Table 2 – Atomic weight composition of the constituent elements of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ferrites

x	Element	Theoretical		Experimental	
		Wt, %	At, %	Wt, %	At, %
0.0	O	27.28	57.14	29.71	60.04
	Fe	47.60	28.57	45.95	26.61
	Co	25.12	14.29	24.34	13.35
0.1	O	27.28	57.14	29.69	60.01
	Fe	47.61	28.57	45.92	26.60
	Co	22.61	12.86	21.76	11.94
	Ni	2.50	1.43	2.63	1.45
0.2	O	27.28	57.14	29.70	60.03
	Fe	47.61	28.57	45.50	26.35
	Co	20.10	11.43	19.42	10.66
	Ni	5.01	2.86	5.38	2.96
0.3	O	27.29	57.14	29.69	60.01
	Fe	47.62	28.57	45.30	26.24
	Co	17.59	10.00	17.00	9.33
	Ni	7.50	4.29	8.01	4.42
0.4	O	27.29	57.14	29.70	60.03
	Fe	47.62	28.57	44.95	26.03
	Co	15.08	8.57	14.54	7.98
	Ni	10.01	5.72	10.81	5.96
0.5	O	27.29	57.14	29.72	60.06
	Fe	47.63	28.57	44.37	25.69
	Co	12.57	7.15	11.97	6.57
	Ni	12.51	7.14	13.94	7.68

is in good agreement with published results by other authors [12]. This tendency can be well-explained by the higher stabilization energy of the Ni^{2+} ions in the octahedral sites than of Co^{2+} ions [13]. The cation distribution was also calculated using the intensity ratio of the two sextets, also given in Table 1. The cation distribution [8] obtained from the X-ray intensity data agrees fairly well with the cation distribution estimated from Mössbauer data.

3.2 EDX Spectroscopy

In order to confirm the chemical composition and stoichiometric proportion of the samples, an EDX spectroscopy study was carried out. The EDX analysis for the $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ferrite powders is shown in Fig. 2. It is found that for CoFe_2O_4 the content is 24.34 wt % and 13.35 at %. As it was expected, the Co^{2+} concentration is the highest for $x = 0$ (un-doped). As the Ni^{2+} substitution increases, the percentage of Co^{2+} decreases. As shown by EDX analysis the contents of the metals in the resulting spinel ferrites are close to the theoretical values. It is showed that the theoretically expected stoichiometric molar amounts of various elements of the samples are compared with the values obtained by the EDX analysis (Table 2). The elements of each sample Ni-Co nanoferrites were obtained by EDX spectroscopy in the paper [14].

4. CONCLUSION

The $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ferrites were synthesized by the SGA-technology at low temperature. The effect of Ni substitution on the chemical composition and magnetic properties of CoFe_2O_4 were studied. The Mössbauer spectra at room temperature of all samples showed two well-resolved magnetic patterns corresponding to the tetrahedral A-sites and octahedral B-sites. For CoFe_2O_4 the Mössbauer spectrum indicates a doublet which can be attributed to the minor part of the sample in paramagnetic or superparamagnetic state. The magnetic hyperfine fields and the site occupancy of Fe ions are used to calculate the hyperfine magnetic field flux as a function of the Ni concentration. The cation distributions that are estimated from the area under resonance curve of each site fairly well with the cation distributions obtained from the X-ray intensity data agrees. All the samples possess partially inverse spinel structure.

Further, there is a very little change in the value of isomer shift for all the samples. This implies that the s-electron density is not much altered by the increase of Ni contents. The value of quadrupole splitting for all the investigated samples is negligibly small which shows that the overall symmetry of Fe^{3+} surroundings is not disturbed with the doping of Ni contents in the nickel ferrite matrix.

Мессбауерівські дослідження Ні-заміщених феритів кобальту

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Нанорозмірні Ni-Co ферити одержано за технологією золь-гель за участі автогоріння (ЗГА) і досліджено за допомогою енергодисперсійної X-променевої та мессбауерівської спектроскопії. Мессбауерівський спектр порошку CoFe_2O_4 при кімнатній температурі містить широкий секстет і дублет, що свідчить про суперпарамагнітну природу зразка. Спектри заміщених зразків містять тільки широкий секстет, який складається з двох підсекстетів, що відповідають тетраedrально та октаedrально координованим катіонам Fe. Розподіл катіонів, розрахований за даними X-променевої дифракції та мессбауерівської спектроскопії, свідчить про зменшення відношення $\text{Fe}^{3+[\text{B}]/\text{Fe}^{3+[\text{A}]}$ з підвищенням концентрації нікелю.

Ключові слова: Ферит, Наночастинки, Мессбауерівські спектри, Енергодисперсійна X-променева спектроскопія.

Мессбауэровские исследования Ni-замещенных ферритов кобальта

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Наноразмерные Ni-Co ферриты получено по технологии золь-гель с участием автогорения (ЗГА) и исследовано с помощью энергодисперсионной X-лучевой и мессбауэровской спектроскопии. Мессбауэровский спектр порошка CoFe_2O_4 при комнатной температуре содержит широкий секстет и дублет, что свидетельствует о суперпарамагнитной природе образца. Спектры замещенных образцов содержат только широкий секстет, который состоит из двух подсекстетов, что отвечают тетраedrально и октаedrально координированным катионам Fe. Распределение катионов, рассчитанное по данным X-лучевой дифракции и мессбауэровской спектроскопии, свидетельствует об уменьшении отношения $\text{Fe}^{3+[\text{B}]/\text{Fe}^{3+[\text{A}]}$ с увеличением концентрации никеля.

Ключевые слова: Феррит, Наночастицы, Мессбауэровские спектры, Энергодисперсионная X-лучевая спектроскопия.

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