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Magnetic study of some nanoferrite materials

ABSTRACT

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The Mössbauer spectra of nanoferrite materials such as $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$ have been reported and the above materials were prepared by sol-gel combustion method using metal nitrates as source material and Polyvinyl alcohol (PVA) as agglomeration reducing agent. As the structural, thermal and magnetic properties (VSM) of the above ferrites have been published already, hence, the present paper reports the Mössbauer studies of the nanoferrites. Based on the observed values of hyperfine parameter such as Isomer shift (IS), Quadrupole splitting (QS) and hyperfine field values, the distribution of ion and structure of the ferrites has been reported.

Keywords: *Nanoferrites; Isomer shift; Quadrupole shift; Spinel structure.*

INTRODUCTION

In recent years, the nanomagnetic materials have gained remarkable scientific interest owing to their interesting properties and a variety of applications [1]. The high coercivity of these magnetic nanoparticles make them interesting for applications in the fields of high-density magnetic media, recording color imaging, ferrofluids, high frequency devices and magnetic refrigeration [2] and [3]. The interesting and useful magnetic properties of spinel ferrites are governed by the choice of the cations along with Fe^{2+} and Fe^{3+} ions and their distribution between tetrahedral (A) and octahedral (B) sites of the spinel lattice. Finite size effect on the structural and magnetic properties of sol-gel synthesized NiFe_2O_4 particle was reported by George et al [4]. Chander et al [5] reported the magnetic behaviour of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles prepared using two different routes. Earlier [6, 7], we have reported the results on structural, thermal and magnetic properties of the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$. In this paper, the Mössbauer studies of some ferrite materials such as $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$ have been discussed.

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EXPERIMENTAL

All ferrites samples were synthesized using commercially available constituent nitrates. Analytical grade Lithium nitrate (99% Sigma Aldrich, India), cobalt nitrate (99% Sigma Aldrich, India), ferric nitrate (99% Sigma Aldrich, India) and citric acid (99% Sigma Aldrich, India) have been used as source materials for the preparation of ferrite nanoparticles. The ferrite nanomaterials were prepared by sol-gel combustion method [6]. Analytical grade nickel nitrate, cobalt nitrate, ferric nitrate and citric acid have been used as source materials for the preparation of ferrite nanoparticles. Here distilled water is used as a solvent. The pH of the sol was maintained in between 8 and 9. The prepared samples were labeled as: Nickel Manganese ferrites are NMF1, NMF2 and NMF4 at 300, 500 and 900°C respectively, Cobalt Manganese ferrites are CMF1, CMF2 and CMF4 at 300, 500 and 900°C respectively and also Nickel Cobalt ferrites are NCF1, NCF2, NCF3 and NCF4 at 300, 500, 700 and 900°C respectively.

Characterization

The prepared nanomaterials were characterized by Mössbauer spectroscopy studies and Mössbauer spectra recorded using a conventional Mössbauer spectrometer (MS-500) of the electromechanical type, with 30 mCi⁵⁷Co as a source in an Rh matrix at room temperature.

RESULTS AND DISCUSSION

The Mössbauer spectra of nanoferrites such as $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$ were recorded at room temperature are shown in Figure 1, Figure 2 and Figure 3. The dots in figure represents the experimental data and the continuous line through the data points is the least-squares fitting of the data by using the computer code developed by Bent et al [7].

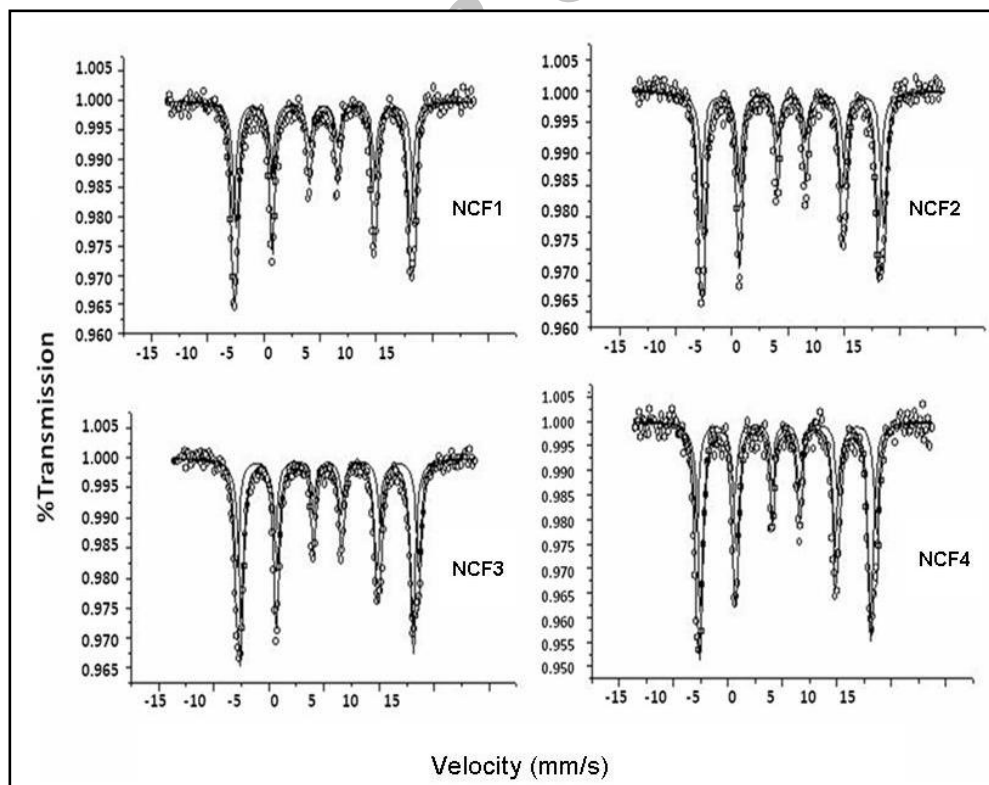


Fig .1. Mössbauer Spectra of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$ nanoparticles at 300 °C(NCF1), 500 °C(NCF2), 700 °C(NCF3) and 900 °C(NCF4)

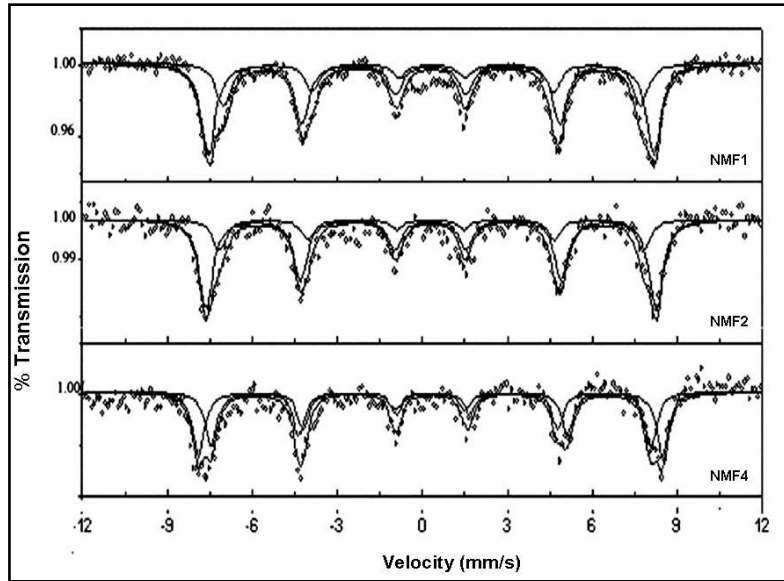


Fig.2. Mössbauer spectra of $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles at 300°C(NMF1),500°C(NMF2), and 900°C(NMF4)

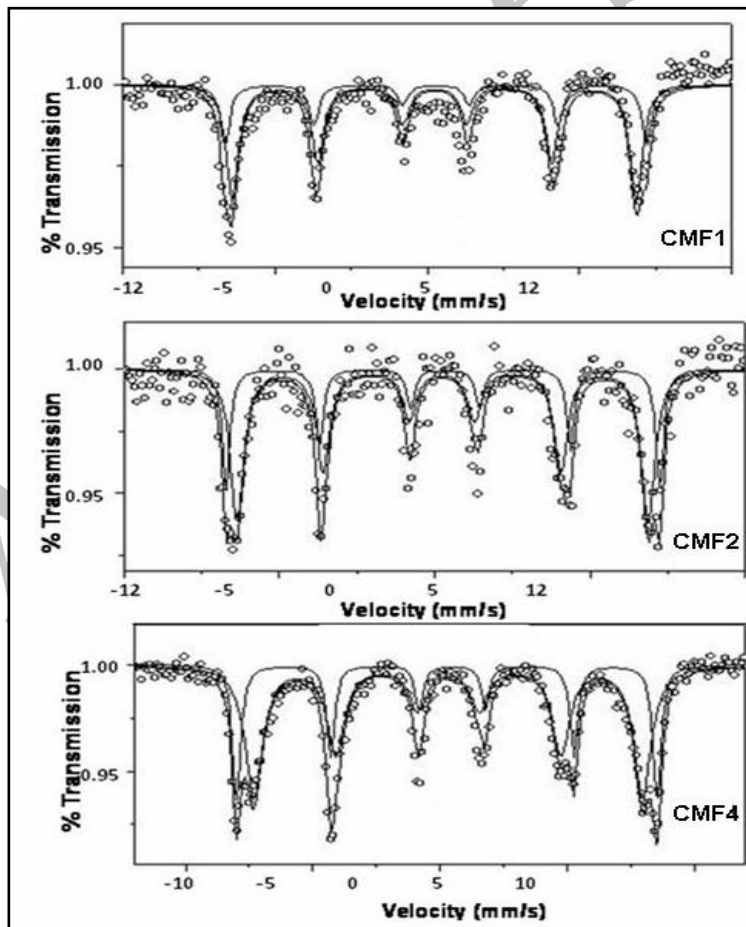


Fig.3. Mossbauer Spectra of $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at 300°C (CMF1), 500°C (CMF2) and 900°C (CMF4)

The parameters such as quadrupole splitting, hyperfine field and isomer shift obtained from Mössbauer spectra are given in Table 1. The observed results indicate that the quadrupole splitting of the system is very small. Therefore, there is no distribution of A and B sites. The first order quadrupole splitting are averaged to zero, which is one of the characteristics of the spinel ferrites. From the Mössbauer spectra of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$ nanoparticles, the average values of the hyperfine field (BHF) for the sample NMF₁ are 48.74 and 45.65 Tesla, for the sample NMF₂ are 49.445 and 46.44 Tesla, and similarly for the sample NMF₄ are 50.77 and 48.09 Tesla. Further, the observed chemical isomer shift values are almost the same as those of Mn ferrites [8]. The values of quadrupole splitting for all samples have been found to be negligibly small indicating the presence of cubic point symmetry at both sites [9]. The Mössbauer spectra of three samples of $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles with the grain sizes

of 20 nm, 32 nm and 62 nm for the corresponding temperatures such as 300°C, 500°C and 900°C have been fitted with the three sextets corresponding to the Fe^{3+} ions in octahedral and tetrahedral sites and in the grain boundaries. Since the sextets are highly overlapping with each other, the relative intensities of the sub-spectra obtained from the fitting may not be correct.

From the observed parameters of $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles from Mössbauer spectra, the quadrupole splitting (QS) of this system are very close to zero. Therefore, there is no distortion of A and B sites for each of the Mn-substituted samples. The Isomer Shift (IS) values of A-site and B-site are almost constant. These facts show that despite the substitutions of Mn cations, there are no changes in covalency between metal ions and oxygen anions. Since the values of IS are included in 3+ valence state of Fe cation, it is concluded that Fe^{3+} cation exists only in $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ system [10].

Table 1. Hyperfine parameters from Mössbauer spectra of $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$

Sample code	Isomer Shift(mm/s)	Q. Splitting (mm/s)	BHF (Tesla)	% Area
NMF1	0.321±0.006	0.012±0.011	48.74±0.05	67.77
	0.371±0.012	-0.009±0.025	45.65±0.113	32.23
NMF2	0.318±0.009	0.010±0.018	49.25±0.104	74.20
	0.322±0.030	0.014±0.057	46.44±0.299	25.80
NMF4	0.348±0.010	0.093±0.020	50.77±0.072	54.43
	0.309±0.013	0.024±0.029	48.09±0.102	45.57
NCF1	0.33 ±0.005	0.007±0.012	50.04±0.06	48.15
	0.286±0.005	0.023±0.011	47.91±0.144	51.85
NCF2	0.352±0.004	-0.02±0.007	50.90±0.06	47.8
	0.285±0.020	0.0007±0.07	48.2±0.05	52.2
NCF3	0.350±0.005	-0.03±0.009	51.3±0.036	40.4
	0.276±0.008	0.007±0.017	48.3±0.25	59.6
NCF4	0.354±0.009	0.006±0.018	51.31±0.08	37.08
	0.285±0.005	-0.01±0.011	48.41±0.06	62.92
2CMF1	0.45 ±0.060	-0.014±0.024	51.36±0.11	29.2
	0.572±0.028	-0.027±0.012	49.18±0.11	70.8
2CMF2	0.355±0.049	-0.086±0.020	51.87±0.10	31.3
	0.618±0.045	0.025±0.024	49.20±0.13	68.7
2CMF4	0.369±0.015	-0.219±0.009	51.18±0.027	31.8
	0.821±0.023	-0.012±0.010	47.32±0.058	68.2

Mössbauer spectra of the $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$ nanoparticles were calcinated at different temperatures (300°C, 500°C, 700°C and 900°C) are fitted with six-line subpatterns that are assigned to A-ions in tetrahedral sites and B-ions in octahedral sites of a spinel crystal structure [12]. A well resolved six line pattern of the sample with particles sizes (18 nm, 22 nm, 48 nm and 65 nm) are mainly attributed to the ferrimagnetic behavior. The change of magnetic property with the variation of particle size for the ferrite powder can be explained in terms of calcination temperature. Table 1 illustrates that the isomer shift (δ) values of A-sites is less than that of B-sites. This conclusion has been proved earlier by many reports [12], [13], [14] and [15]. The values of quadrupole splitting indicate the degree of deviation from cubic symmetry. The absolute values will be increased with decreasing particle sizes, and the asymmetrical electric fields surrounding the Mössbauer nucleus will be strengthened along with the decreasing particle sizes. Because the particles are small, the crystallization will be incomplete. The value of B-site is larger than that of A-site. This may due to the improved magnetic properties with the increase of crystallite size [16]. From the percentage of the absorption area of the Mössbauer spectra, we can decide about the cation distribution. The fraction of Fe ions at the tetrahedral A and octahedral B sites were determined using the area of Mössbauer spectra. For stoichiometric ferrite, it is easy to estimate the cation distribution, but it becomes rather difficult for mixed ferrites, since they contain mixtures of more than one cation other than iron.

CONCLUSION

In this paper, the Mössbauer studies of sol-gel prepared nanoferrites such as $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$ were reported. From the observed data, the values of quadrupole splitting (QS) of this system are almost zero. Therefore, there is no distortion of A and B sites for each of the Mn-substituted samples. The Isomer Shift (IS) values of A-site and B-site are almost constant. These facts show that despite the substitutions of Mn cations, there are no changes in covalency between metal ions and oxygen anions. Since the values of IS are included in 3+ valence state of Fe cation, it is

concluded that Fe^{3+} cation exists only in $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ system. On the other hand, the magnetic property of the ferrite has been controlled by modifying the heat treatment. The site occupancy of the Fe^{3+} ions have been confirmed by Mössbauer studies and hyperfine splitting confirm the spinel structure of prepared nanoferrites.

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