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Magnetic and Mössbauer spectral studies of nano crystalline cobalt substituted magnesium ferrites ($Mg_xCo_{1-x}Fe_2O_4$)

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Abstract Nano size $Mg_xCo_{1-x}Fe_2O_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) ferrites have been prepared using sol gel method and characterized using i.r., TEM, XRD, magnetic and Mössbauer spectral studies. The particle size of as obtained samples was found to be ~6 nm, which increases up to ~80 nm after annealing at 1,000°C. The saturation magnetization decreases from 80.0–27.5 emu/g on increasing the Mg^{2+} ions after annealing at 1,000°C due to the diamagnetic behaviour of the Mg^{2+} ions. Room temperature (RT) Mössbauer spectra (MS) of as obtained samples exhibit a broad doublet, suggesting super paramagnetic nature of the sample. However, annealed samples exhibited a broad sextet, resolved into two sextets, corresponding to tetrahedrally and octahedrally coordinated Fe cations.

Keywords Saturation magnetization · Mössbauer spectra · Nano particles · Powder X-ray diffraction

1 Introduction

Magnesium ferrite plays an important role in ferrites technology as an end member of the ferrites, particularly for high-frequency applications [1, 2]. Kawade et al. [3] suggested that the lattice parameter, X-ray density and the distance between magnetic ions in both octahedral and tetrahedral decreases with Cr in $MgCr_xFe_{2-x}O_4$. Berchmans et al. [4] synthesized $Ni_{1-x}Mg_xFe_2O_4$ using citrate gel process and suggested that Mg^{2+} ions causes appreciable changes in the structural and electrical

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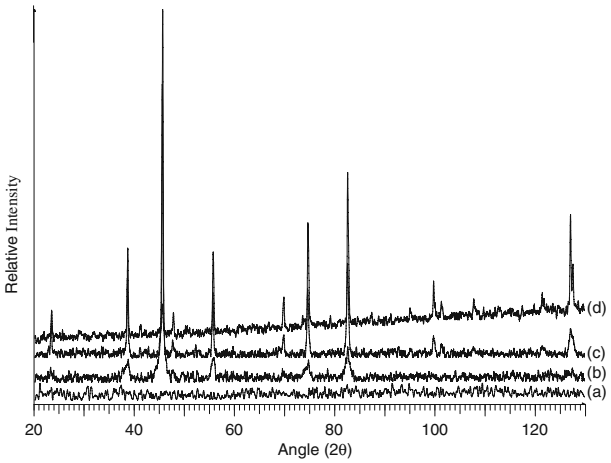

Fig. 1 X-ray diffraction pattern of $Mg_{0.8}Co_{0.2}Fe_2O_4$ (**a**) as obtained and after annealing at (**b**) 400°C, (**c**) 600°C and (**d**) 1,000°C

properties of the ferrites. In the present study, the influence of addition of Co in $MgFe_2O_4$ ferrite system has been investigated.

2 Experimental

2.1 Preparation of ferrites

Nanoparticles of cobalt substituted magnesium ferrites $Mg_xCo_{1-x}Fe_2O_4$ (where $x =$ 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared using sol–gel. In this method the desired proportion of cobalt, magnesium and iron nitrates were separately dissolved in minimum amount of water according to the formula After heating the solutions at 80–90°C all the solutions were mixed. After some stirring, citric acid and ethylene glycol were added to the nitrates solution and stirrer until the gel was formed. After that gel was heated to self-ignition and then samples were annealed at different temperatures.

2.2 Physical measurements

The X-ray diffraction studies were carried on X-ray diffractometer (Bruker AXS, D8 Advance) with FeKα radiation. The magnetic measurements were made on a vibrating sample magnetometer (VSM) (155, PAR). Mössbauer spectra were recorded using a constant acceleration transducer driven Mössbauer spectrometer using 25 mCi ^{57}Co (Rh) source.

3 Results and discussion

Elemental analytical data for Mg, Co and Fe were obtained by EPMA. About 2 mm thick pellet was prepared, fixed on the sample holder and coated with the carbon to make them conducting. The results were found to be consistent.

Table 1 Lattice parameters and magnetic data of the ferrites after annealing at 1,000°C

Ferrites composition	Lattice parameter a (Å)	Volume (Å^3)	Saturation mag. (emu/g)	Coercivity (G)	Remanent magnetization (emu/g)
$MgFe_2O_4$	8.3687	586.10	27.6	100	5.8
$Mg_{0.8}Co_{0.2}Fe_2O_4$	8.3742	587.26	44.4	165	10.5
$Mg_{0.6}Co_{0.4}Fe_2O_4$	8.3802	588.52	51.2	250	16.9
$Mg_{0.4}Co_{0.6}Fe_2O_4$	8.3865	589.85	57.6	395	20.6
$Mg_{0.2}Co_{0.8}Fe_2O_4$	8.3923	591.08	65.3	510	24.0
$CoFe_2O_4$	8.3950	591.65	80.2	650	28.5

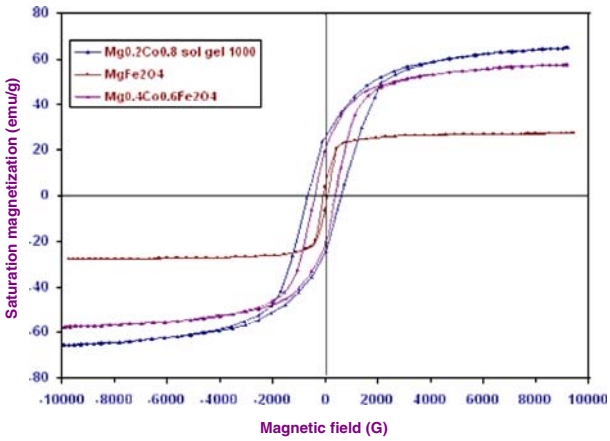

Fig. 2 Typical Hysterisis loops of some samples after annealing at 1,000°C

FTIR spectra of all the ferrites for as prepared and annealed at 400°C were recorded using KBr pellets in the range of 500 to 4,000 cm^{-1}. The frequency band near 555–565 cm^{-1} is assigned to tetrahedral clusters and confirms the presence of M–O stretching band in ferrites as suggested by Pradeep and Chandrasekaran [5]. The TEM micrograph of the as obtained samples shows well separated particles of size ~6 nm as described in our earlier paper [6, 7]. The micrographs for the annealed samples at 1,000°C show that the particle size increases with annealing temperature.

The X-ray diffractographs of the as obtained samples confirms the amorphous nature of the sample. Peaks start appearing and lines become sharp as the annealing temperature increases, which can be attributed to the grain growth at higher temperatures. The crystallite size was calculated using Sherrer formula. It has been seen that it increases from ~20 to ~80 nm as the annealing temperatures are raised from 400 to 1,000°C. Figure 1 represents the diffraction patterns for $Mg_{0.8}Co_{0.2}Fe_2O_4$ as obtained and after annealing at different temperatures. The lattice parameters were calculated using Powley as well as Le Bail refinement methods from the annealed samples are listed in Table 1. All the samples were found to be face centered cubic with Fd-3m space group. Lattice parameter 'a' was found to increases with cobalt concentration in view of the fact that ionic radius of Mg^{2+} is lower than that of cobalt ions [8].

Hysteresis loops were recorded for all the as obtained and annealed samples. Typical loops for some samples annealed at 1,000°C are shown in Fig. 2. The as obtained sample exhibits no hysteresis, which may be attributed to superparamagnetic

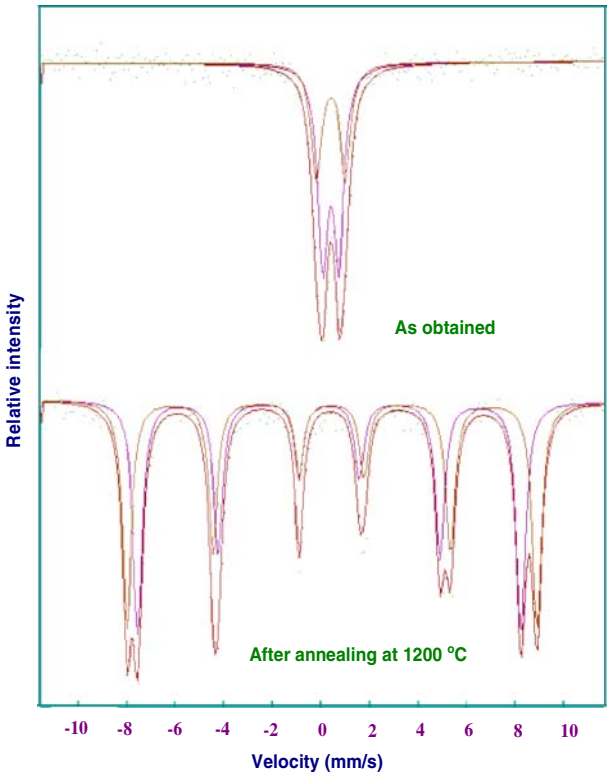

Fig. 3 Typical Mössbauer spectra of $Mg_{0.6}Co_{0.4}Fe_2O_4$

relaxation inconformity with the XRD result. The saturation magnetization for all the ferrites after annealing at 1,000°C are listed in Table 1 indicates that saturation magnetization decreases with the increase of Mg^{2+} ions. This may be attributed to the weakening of exchange interactions due to non-magnetic Mg^{2+} ions. From the Table 1 it is clear that the coercivity decreases with the magnesium concentration. This may be attributed to the decrease in anisotropy field which in its turn decreases the domain wall energy [9]. Decrease of remanent magnetization with the Mg^{2+} ions may be due to the lesser exchange interactions [10].

Figure 3 shows the typical Mössbauer spectra of $Mg_{0.6}Co_{0.4}Fe_2O_4$. The presence of broad doublet in the as obtained sample indicates the superparamagnetic nature of the sample. This broad doublet was fitted with the two sets of the doublets corresponding to the surface and internal region of the particles as described in our earlier paper [6, 7]. The Mössbauer data after the least square fitting are given in Table 2. From the data it can be seen that ΔE_Q in the surface region (0.78–0.99 mms^{-1}) is much larger than the ΔE_Q in the internal region (0.35–0.56 mms^{-1}). This can be attributed to the existence of a broader distribution of interatomic spacing and partly disordering in the surface region of the ultrafine particle [11].

The RT Mössbauer spectra after annealing at 1,000°C for all the samples exhibit two normal zeeman split sextets due to the A and B-site Fe^{3+}, which indicates ferrimagnetic behaviour of the samples. A typical Mössbauer spectrum of $Mg_{0.6}Co_{0.4}Fe_2O_4$ is given in Fig. 3. It is evident that there is a monotonic decrease

Table 2 Mössbauer parameters of the cobalt substituted magnesium ferrites as obtained and after annealing at 1000°C

Ferrite composition	As obtained				Annealed Sample			
	Internal region		Surface region		Octahedral		Tetrahedral	
	δ(Fe) (mms^{-1})	ΔE_Q(mms^{-1})	δ(Fe) (mms^{-1})	ΔE_Q(mms^{-1})	δ(Fe) (mms^{-1})	H_{eff}(kOe)	δ(Fe) (mms^{-1})	H_{eff}(kOe)
$MgFe_2O_4$	0.44	0.35	0.44	0.78	0.45	495	0.38	472
$Mg_{0.8}Co_{0.2}Fe_2O_4$	0.45	0.38	0.42	0.82	0.47	502	0.41	485
$Mg_{0.6}Co_{0.4}Fe_2O_4$	0.45	0.43	0.44	0.87	0.42	498	0.40	480
$Mg_{0.4}Co_{0.6}Fe_2O_4$	0.46	0.49	0.43	0.91	0.44	514	0.42	476
$Mg_{0.2}Co_{0.8}Fe_2O_4$	0.44	0.51	0.44	0.96	0.46	502	0.40	496
$CoFe_2O_4$	0.46	0.56	0.45	0.99	0.48	516	0.40	490

in the internal hyperfine field values with increasing magnesium substitution. This happens; because the replacement of cobalt by magnesium influences the internal hyperfine field of the nearest Fe^{3+} sites through super transferred hyperfine fields [12].

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