Mössbauer effect studies and X-ray diffraction analysis of cobalt ferrite prepared in powder form by thermal decomposition method

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Abstract. Cobalt ferrite ($Co_xFe_{3-x}O_4$) is prepared in powder form by thermal decomposition of iron and cobalt salts and is analysed by X-ray diffraction and Mössbauer spectroscopic techniques. The variation of Mössbauer parameters, lattice parameters and crystallite size of the products formed with variation in the composition of Fe and Co ratios are studied. The studies confirm the formation of nano-size cobalt ferrite particles with defect structure and it is found to be maximum for the Fe : Co = 60 : 40 ratio of the initial precursor oxides.

Keywords. Cobalt ferrite; thermal decomposition; Mössbauer effect; X-ray diffraction.

1. Introduction

The variation of different physical properties with method of preparation (Vanderberghe *et al* 1980; Souad *et al* 2001) has made ferrite a most demanding and technologically important material (Martha 2000). Special interest on cobalt ferrite is due to their typical changes in magnetic (Warren *et al* 1999) and electrical properties with changes in the concentration of divalent metal ions (Kwang *et al* 2000) or by the substitution of the divalent ions by other metallic ions (Rajendran 2001; Abdeen *et al* 2002).

Fine powders of nano-sized inverse spinel type cobalt ferrite particles with defect structure have been prepared by isothermal decomposition of homogeneous mixture of hydrated nitrates of iron and cobalt with varying Fe : Co ratio. This particular method reduced the duration of preparation by avoiding sintering for long periods.

The variation of Mössbauer parameters, viz. isomer shift 'd', quadrupole splitting 'Δ' and hyperfine field 'H_f' with the increase of cobalt concentration have been studied. The site occupancy ratio and the number of defects present have also been calculated using Mössbauer spectra. By making use of X-ray diffraction (XRD) patterns, the lattice parameter and crystallite size of the cobalt ferrite particles are calculated and studied with the variation of Fe : Co ratio.

2. Experimental

Mixed oxides (solid solutions) of Fe : Co = 95 : 5 to Fe : Co = 5 : 95 in steps of 5 at.% of Co were prepared by thermal decomposition of the mixture of respective nitrates in the required stoichiometric ratios at 400°C in air for 4 h using crucible-type furnace (Thipperudraiah 2001).The criterion in choosing 4 h of heating at 400°C in preparing mixed Fe : Co oxides was based on the dynamic thermogravimetric studies on iron and cobalt nitrates (Drakshayani 1987). These homogeneously mixed oxides of iron and cobalt were further heated at 950°C (Randhawa 2000) in air for 4 h inside a muffle furnace and then cooled to room temperature. Different oxide phases of iron and cobalt have been identified, as shown in table 1, and characterized by X-ray diffraction analysis using Cr-K$_a$ radiation.

Table 1. Phases identified by XRD.

Sample ratio	Identified phases		
	a-Fe$_2$O$_3$	(CoFe)$_3$O$_4$	Co$_3$O$_4$
100 : 0	√	x	x
95 : 5	√	x	x
90 : 10	√	√	x
80 : 20	√	√	x
75 : 25	√	√	x
70 : 30	√	√	x
60 : 40	√	√	x
50 : 50	√	√	√
40 : 60	√	√	√
35 : 65	√	√	√
25 : 75	√	√	√
20 : 80	√	√	√
10 : 90	√	x	√
5 : 95	x	x	√
1 : 99	x	x	√
0 : 100	x	x	√

√, for presence of the phase; x, for absence of the phase.

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The Mössbauer spectrum of each sample with different Fe : Co ratios has been recorded with a ^{57}Co(Rh) source in constant acceleration mode to identify and confirm (see table 2) the magnetic phase of the spinel cobalt ferrite. The recorded Mössbauer data were computer fitted by the versatile program NMOSFIT. The fitted Mössbauer spectra and X-ray diffractograms of each sample are displayed in figures 1 and 2, respectively. The calculated values of Mössbauer parameters are tabulated in table 3 and that of lattice parameters, crystallite size, etc from XRD are shown in table 4.

3. Results and discussion

Both the Mössbauer and XRD patterns of initial samples rich in iron content gave only a-Fe_2O_3 phase. Similarly, the final samples rich in cobalt content gave only the Co_3O_4 phase, i.e. only the oxide phase of the major con-

tent of the sample present in the mixed oxides (Note that Co_3O_4 phase cannot be detected by Mössbauer technique). The intermediate samples with Fe : Co ratio varying from Fe : Co = 80 : 20 to Fe : Co = 20 : 80 have indicated cobalt ferrite phase also in addition to other oxide phases of iron and cobalt. Typical individual peaks were obtained for each phase by XRD patterns. Mössbauer spectra of these intermediate samples indicate a combination of phases as could be ascertained from a considerable increase in the line width and some 'kinks' observed on each peak, i.e. each Mössbauer spectrum is a combination of two or three sextets. Using NMOSFIT program this could be resolved into the individual sextets of each phase. For the cobalt ferrite phase Mössbauer spectra gave two sets of sextets due to Fe^{3+} ions occupying tetrahedral (A) site and octahedral (B) site of the inverse spinel structure. Those kinks observed in Mössbauer spectra of the intermediate samples are a clear indication of this. The hyperfine fields calculated using

Table 2. Phases identified by Mössbauer spectra.

		Identified phases			
			(CoFe)$_3$O$_4$		
Sample ratio	a-Fe$_2$O$_3$	A-site	Central	B-site	Co$_3$O$_4$
100 : 0	√	x		x	x
95 : 5	√	x	√	x	x
90 : 10	√	√	x	√	x
80 : 20	√	√	x	√	x
75 : 25	√	√	x	√	x
70 : 30	√	√	x	√	x
60 : 40	x	√	x	√	x
50 : 50	x	√	x	√	x
40 : 60	x	√	x	√	x
35 : 65	x	√	x	√	x
25 : 75	x	√	√	√	x
20 : 80	x	√	√	√	x
10 : 90	x	x	√	x	x
5 : 95	x	x	√	x	x
1 : 99	x	x	√	x	x
0 : 100	x	x	x	x	x

√, for presence of the phase; x, for absence of the phase.

Table 3. Mössbauer parameters of (CoFe)$_3$O$_4$ phase.

Sample ratio	Isomer shift 'd' (± 0·0547 mm/s)		Quadrupole splitting Δ (± 0·0547 mm/s)		Hyperfine field, H_f (± 3 KOe)		Site occupancy ratio S_A/S_B = V ± 0·3	No. of defects, Z (± 0·03)
	A-site	B-site	A-site	B-site	A-site	B-site		
80 : 20	0·362	0·366	0·147	0·240	503·0	483·5	2·49	0·200
70 : 30	0·419	0·442	0·208	0·346	487·0	457·9	2·60	0·204
60 : 40	0·351	0·272	0·268	0·281	501·8	475·5	0·845	0·069
50 : 50	0·351	0·386	0·186	0·278	483·5	457·2	0·604	0·024
40 : 60	0·287	0·262	0·341	0·256	463·6	443·5	1·156	0·110
25 : 75	0·296	0·270	0·225	0·159	478·9	448·2	1·143	0·110

the final parameter obtained on curve fitting confirmed that these sextets are formed due to the A and B sub-lattice sites. The calculated values of lattice parameter and the crystallite size by using XRD also coincide very well with their standard values. They are in agreement with the results obtained by Drakshayani (1994) on the effects of dopants on ferrite oxides.

Table 3 shows that the isomer shift 'd' for both A and B sites of cobalt ferrite phase has a constant value of 0·35 mm/s. The quadrupole splitting 'Δ' also shows the values 0·27 mm/s and 0·28 mm/s for A and B sites, respectively. The hyperfine field, H_f, due to both A and B sites of these ferrite phase shows a gradual decrease with increase of cobalt concentration and the field values of the sample Fe : Co = 60 : 40 coincides very well with the standard values. This is an indication that this proportion (Fe : Co = 60 : 40) is perhaps more appropriate ratio for ferrite formation. The slight variations are due to the presence of the defect structure.

The XRD measurements given in table 4 show that the lattice parameter almost had a constant value of 7·8 Å for
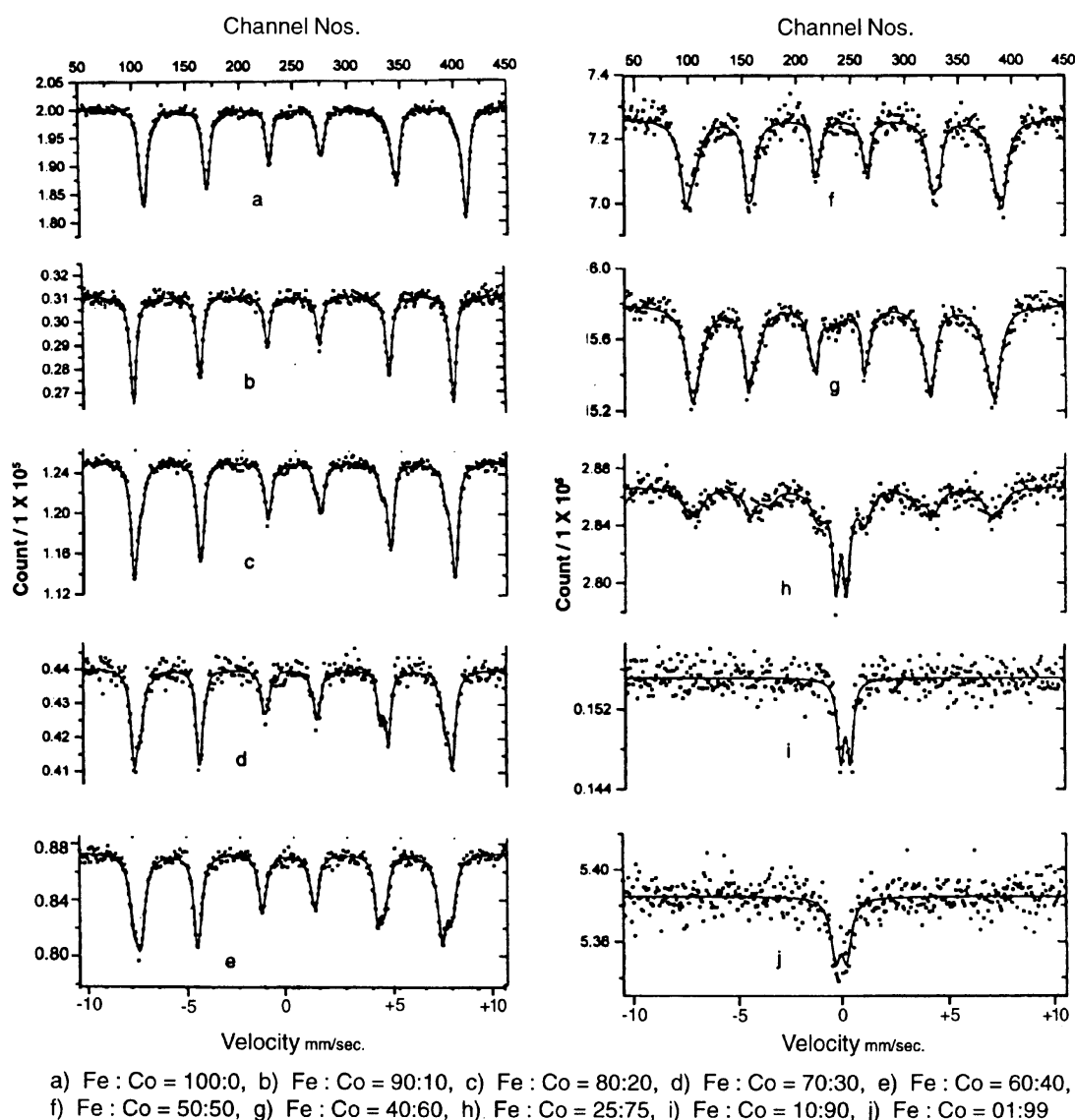
Table 4. Lattice parameter and crystallite size of $(CoFe)_3O_4$.

Sample ratio	Crystallite size $\pm$ 20 (Å)	Lattice parameter a (Å)	Unit cell volume, V (Å^3)
80 : 20	424·5	7·819	477·0
70 : 30	545·1	7·805	475·5
60 : 40	548·0	7·818	477·8
50 : 50	350·9	7·794	473·5
40 : 60	351·2	7·770	469·1
25 : 75	139·1	7·698	456·2

a) Fe : Co = 100:0, b) Fe : Co = 90:10, c) Fe : Co = 80:20, d) Fe : Co = 70:30, e) Fe : Co = 60:40,
f) Fe : Co = 50:50, g) Fe : Co = 40:60, h) Fe : Co = 25:75, i) Fe : Co = 10:90, j) Fe : Co = 01:99

Figure 1. Mössbauer spectra of different Fe–Co ratios.

a) Fe:Co = 100:0, b) Fe:Co = 90:10, c) Fe:Co = 80:20, d) Fe:Co = 70:30, e) Fe:Co = 60:40,   f) Fe:Co = 50:50,
g) Fe:Co = 40:60, h) Fe:Co = 25:75, i) Fe:Co = 10:90, j) Fe:Co = 0:100
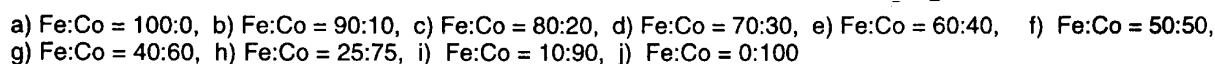
Figure 2.   X-ray diffractograms of different Fe–Co ratios.

all these samples which gave ferrite phase. The crystallite size and unit cell volume of these ferrite samples have their maximum values of 548 Å and 477·8 Å³, respectively at this particular sample ratio Fe : Co = 60 : 40. This also implies that the ferrite formation is maximum at this ratio.

Table 5 is prepared using XRD patterns to study the variation of intensity of first three intense peaks with *hkl* values 311, 440, 220, respectively with increase of cobalt concentration in the sample. This intensity variation is graphically represented in figures 3–5. These three graphs clearly indicate that the intensity of each peak attains the maximum value only at the particular sample ratio given by Fe : Co = 60 : 40.

The intensity variation study on Mössbauer spectra of these ferrite samples are shown in table 6. Here the intensity variation of the spectra due to A and B sub lattice sites of ferrite phase are separately found with the cobalt concentration. This intensity variations are graphically represented in figure 6 and it implies that the intensity of ferrite phase attains its maximum value at a cobalt concentration of 40% (circled region), i.e. Fe : Co = 60 : 40 for both A and B sites. This undoubtedly indicates the suitability of the sample ratio Fe : Co = 60 : 40 for the ferrite formation.

4. Conclusions

With this particular method of preparation we have been able to produce nano-size cobalt ferrite particles (with defect structure) in powder form. By eliminating sintering we could reduce the duration of preparation also. The growth and decay of the cobalt ferrite particles of inverse spinel type with variation of the Fe : Co ratio are clearly
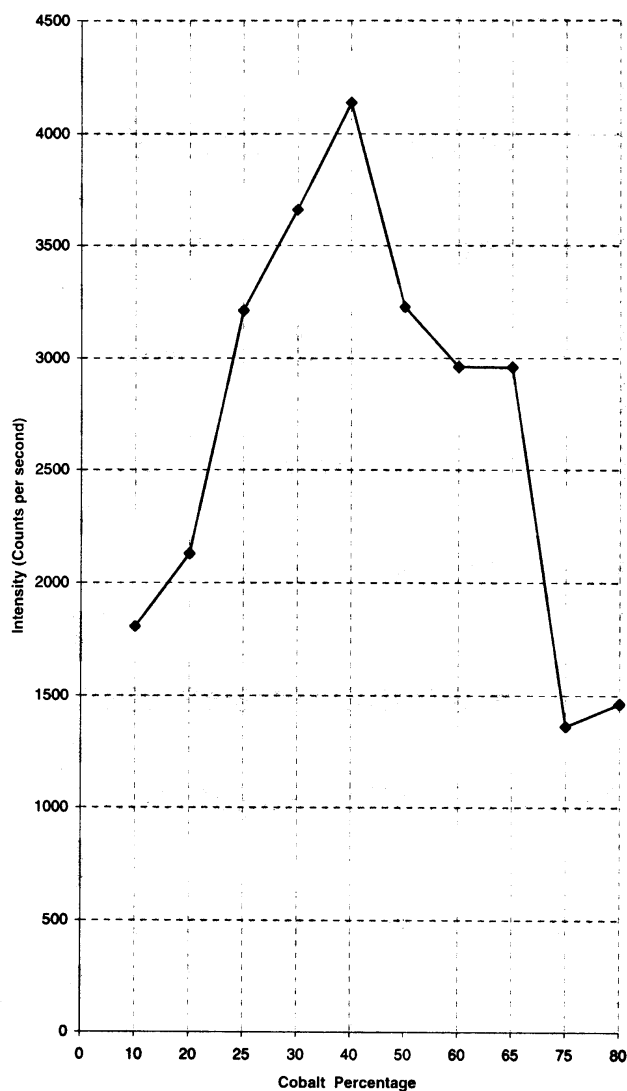

Figure 3. Intensity variation of 1st intense peak (*hkl* = 311) of ferrite phase with cobalt concentration in XRD.
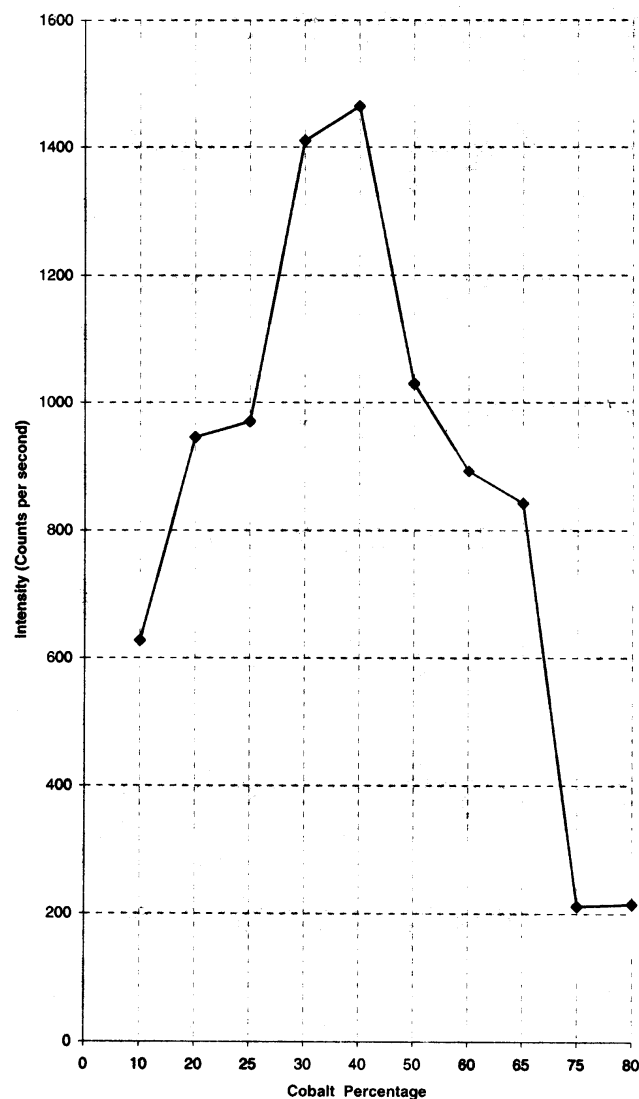
Figure 4. Intensity variation of 2nd intense peak (*hkl* = 440) of ferrite phase with cobalt concentration in XRD.
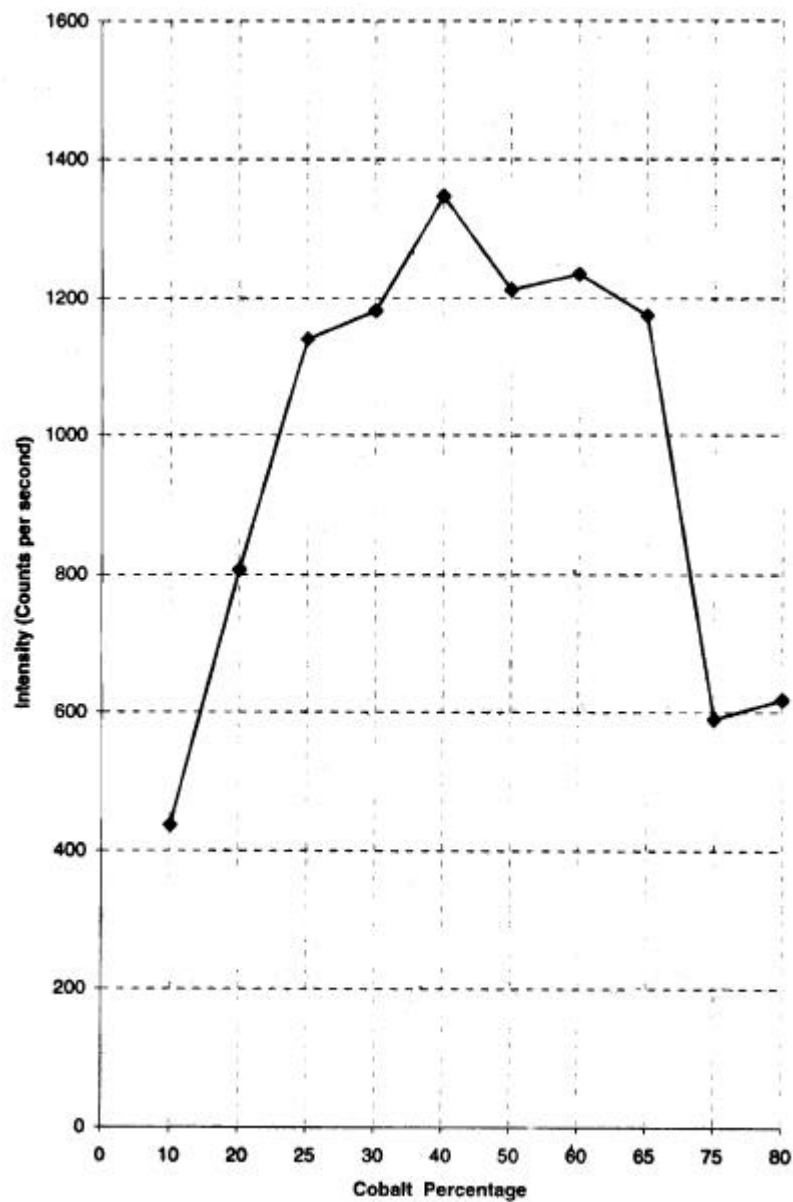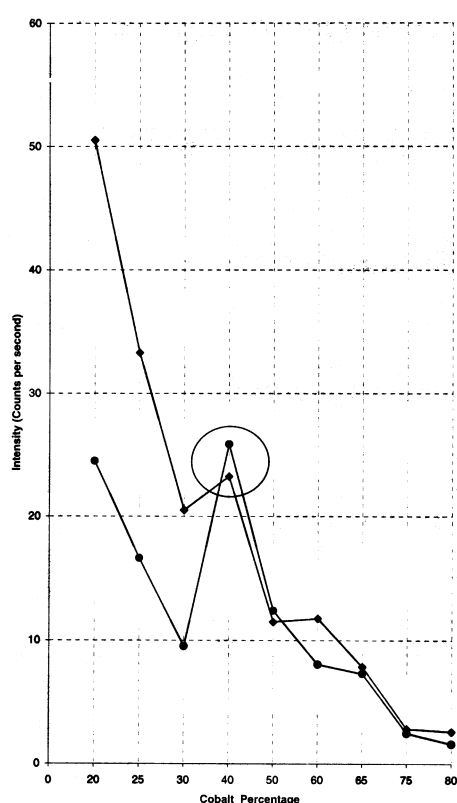
Figure 5. Intensity variation of 3rd intense peak (*hkl* = 220) of ferrite phase with cobalt concentration in XRD.

Table 5. Intensity variation of $(CoFe)_3O_4$ phase in XRD with cobalt concentration.

Sample ratio	1st intense peak *hkl* (311) (cps)	2nd intense peak *hkl* (440) (cps)	3rd intense peak *hkl* (220) (cps)
90 : 10	1807	628	437
80 : 20	2127	945	807
75 : 25	3212	970	1140
70 : 30	3662	1410	1182
60 : 40	4138	1465	1347
50 : 50	3228	1030	1212
40 : 60	2962	892	1235
35 : 65	2960	842	1175
25 : 75	1362	212	590
20 : 80	1463	215	618

Table 6. Intensity variation of $(CoFe)_3O_4$ phase with cobalt concentration in Mössbauer spectra.

Sample ratio	Intensity of $(CoFe)_3O_4$ phase (%)	
	A-site	B-site
80 : 20	50·5	24·5
75 : 25	33·27	16·67
70 : 30	20·5	9·53
60 : 40	23·23	25·87
50 : 50	11·52	12·43
40 : 60	11·8	8·04
35 : 65	7·82	7·26
25 : 75	2·824	247
20 : 80	2·58	1·595

Figure 6. Intensity variation in Mössbauer spectra due to A & B sites of spinel ferrite phase with cobalt concentration.

understood from the variations in the Mössbauer and XRD patterns. The cobalt ferrite formation is found to be maximum at the sample ratio Fe : Co = 60 : 40 from both Mössbauer and XRD analysis and this ratio can be considered as the most suitable one for the cobalt ferrite preparation by this method.

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