Magnetic properties of magnesium–cobalt ferrites synthesized by co-precipitation method

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Abstract. The alternating current (a.c.) low field susceptibility vs temperature, magnetization and ^{57}Fe Mössbauer effect measurements are reported for the spinel solid solution series $Mg_xCo_{1-x}Fe_2O_4$ synthesized by a wet-chemical method before and after high temperature annealing. The observed features for the wet samples, such as the coexistence of paramagnetic doublet and magnetic sextets in Mössbauer spectra and lower saturation magnetization values confirm small particle ferrite behaviour. Especially, Mössbauer spectra of wet samples reveal the presence of superparamagnetic particles which exist simultaneously with ferrimagnetic regions in the materials well supported by a.c. susceptibility data. The high temperature annealing changes the wet-prepared ferrites into the ordered magnetic structure of ceramic ferrites.

Keywords. Ferrites; co-precipitation; collinear spins; superparamagnetic clusters.

1. Introduction

As wet chemically prepared ferrites normally consist of fine particles, exhibit unusual magnetic properties. It has motivated us to synthesize the mixed spinel solid solution series $Mg_xCo_{1-x}Fe_2O_4$ ($x = 0.1$ to 0.9) consisting of two partially inverted spinel ferrites $MgFe_2O_4$ and $CoFe_2O_4$ having different degrees of inversion strongly dependent on the preparation conditions (Sawatzky *et al* 1962; De Grave *et al* 1979), by co-precipitation technique (wet chemical method) at lower temperature (55°C) and also to examine the effect of non-magnetic Mg^{2+} substitution for Co^{2+} in $CoFe_2O_4$ on the magnetic and structural properties. Since no attempt has been made to prepare this system so far, no measurements have been reported on the same. The spinel oxide materials synthesized by two different methods exhibit differences in their magnetic properties (Borriesci *et al* 1978; Petrera *et al* 1982), has generated a considerable interest in the comparative study of magnetic and structural properties of spinel ferrites such as $MgFe_2O_4$ (Kulkarni and Joshi 1986), $CuFe_2O_4$ (Pandya *et al* 1990) and $Zn_xCo_{1-x}Fe_2O_4$ (Pandya *et al* 1991).

In this paper we report X-ray diffraction, magnetization, a.c. susceptibility and ^{57}Fe Mössbauer effect measurements on the mixed spinel solid solution series $Mg_xCo_{1-x}Fe_2O_4$ synthesized by wet chemical method. For the sake of a comparative study, we annealed the wet samples of $Mg_xCo_{1-x}Fe_2O_4$ at 1100°C and their magnetic properties were studied as well.

2. Experimental

The Mg–Co ferrites with variable composition ($x = 0.1$ to 0.9) were prepared by air oxidation of an aqueous suspension containing Co^{2+}, Mg^{2+} and Fe^{2+} cations in

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proper proportions. The starting solutions were prepared by mixing 50 ml of aqueous solutions of $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 7H_2O$ in stoichiometric proportions. A 2 M solution of NaOH was prepared as a precipitant. The starting solution was added into the precipitant because the solubility product constants for the hydroxides of the cation are exceeded and sequential precipitation of the hydroxides can be avoided. The suspension (pH = 11·25) containing dark green intermediate precipitates was formed. Then the suspension was heated and kept at 55°C temperature, while oxygen gas was bubbled uniformly into the suspension to stir it and to promote oxidation reaction, until all the intermediate precipitates changed into the dark brownish precipitates of the spinel ferrite. The samples were filtered, washed and dried at 150°C under vacuum.

The wet samples of Mg–Co ferrites were annealed in air at 1100°C for 24 h. The weight loss for each specimen was obtained by weighing it before and after high temperature annealing. After high temperature annealing the wet samples exhibited weight loss (around 20%) because of the removal of water and the hydroxyl ions even after the drying process.

The X-ray powder patterns were recorded using FeK_α radiation on a Philips diffractometer. The saturation magnetization of each sample was measured using high field hysteresis loop technique (Radhakrishnamurthy et al 1978). The low field a.c. susceptibility measurements on powdered samples were carried out in the temperature range 77 K–800 K using double coil set-up (Radhakrishnamurthy and Likhite 1970) operating at a frequency of 263 Hz and in the RMS field of 39·8 Am^{-1}. It is quite possible that the nature of the sample will be continuously changing when the sample temperature increases beyond 150°C (i.e. preparation temperature) but our main objectives in this work were to determine Curie temperatures of the samples and to see the collective response of particles of various sizes at different temperatures. Mössbauer spectrometer of electromechanical type was used, in the constant acceleration mode, to obtain the spectra of the samples at room temperature and 77 K, in the transmission mode. A 10 mCi: ^{57}Co source in rhodium matrix was used where the absorber thickness was ideally thin.

3. Results and discussion

X-ray powder diffraction patterns showed that all the samples were single phase spinels. A representative XRD pattern indicating (hkl) values of each peak for wet and AW samples of $x = 0·5$ is shown in figure 1. The diffraction lines were slightly broad for wet samples due to particle size effect, whereas they were sharp for the annealed-wet (AW) samples. No impurity phase was observed. This indicates that the high temperature annealing of wet samples has increased the crystalline size up to the order of that in a ceramic ferrite. The average particle size estimated from full width at half maximum of the (400) X-ray diffraction line is 300 Å. The wet-samples are characterized by slightly smaller values of lattice constant than that of the annealed-wet samples. The lattice constant gradually decreases on increasing Mg content obeying Vegard's law (Whinfreg et al 1960).

The saturation magnetization for each sample was obtained from field dependence of magnetization data recorded at 300 K on high field hysteresis loop tracer. The value of saturation magnetization per formula unit (n_B) in Bohr magneton, for wet and annealed-wet samples were calculated and the variation of n_B as a function of Mg concentration (x) is depicted in figure 2a, which shows the decreasing n_B with increasing x.
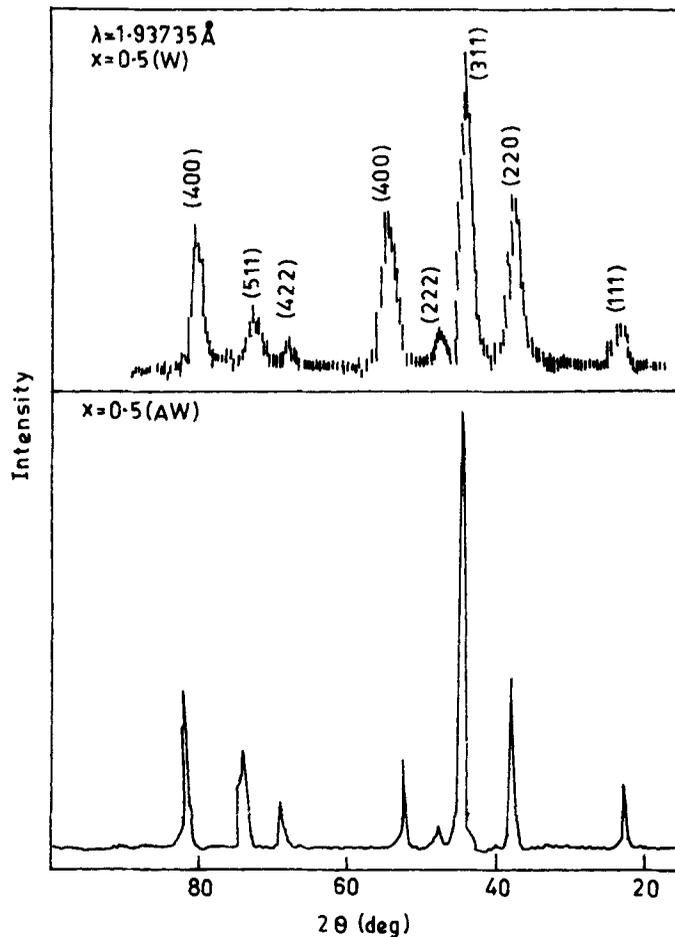
Figure 1. X-ray diffractogram of $x = 0.5$ sample.

The smaller n_B values of wet-samples compared with AW samples (figure 2a) is due to the presence of water and hydroxyl ions which decreases per gram magnetization for wet-samples. This can also arise from the stronger covalency effects (Burriesci 1978) and spin transfer mechanism at smaller cationic site dimension for wet-samples.

The thermal variation of low field a.c. susceptibility curves $(\chi - T)$ depicted in figure 3 for typical wet and AW samples of $Mg_xCo_{1-x}Fe_2O_4$ exhibit differences in the shape of the $\chi - T$ curves. If the temperature of a fine accicular single domain (SD) particle is increased it may so happen that the thermal energy may become comparable to the effective magnetic anisotropy when the magnetization direction spontaneously fluctuates between the easy axes of the grain. In such a state, a particle is said to be exhibiting superparamagnetism (SP). The specific temperature at which the SD to SP transition for a particle or cluster of volume V takes place is known as the blocking temperature, T_b, and the relation governing this is given by

$$VJ_sH_c = 2kT_b,$$

where J_s is the saturation intensity, H_c the coercive force of the material and k the Boltzman constant. For single domain particles H_c is large whereas it tends to zero for SP particles
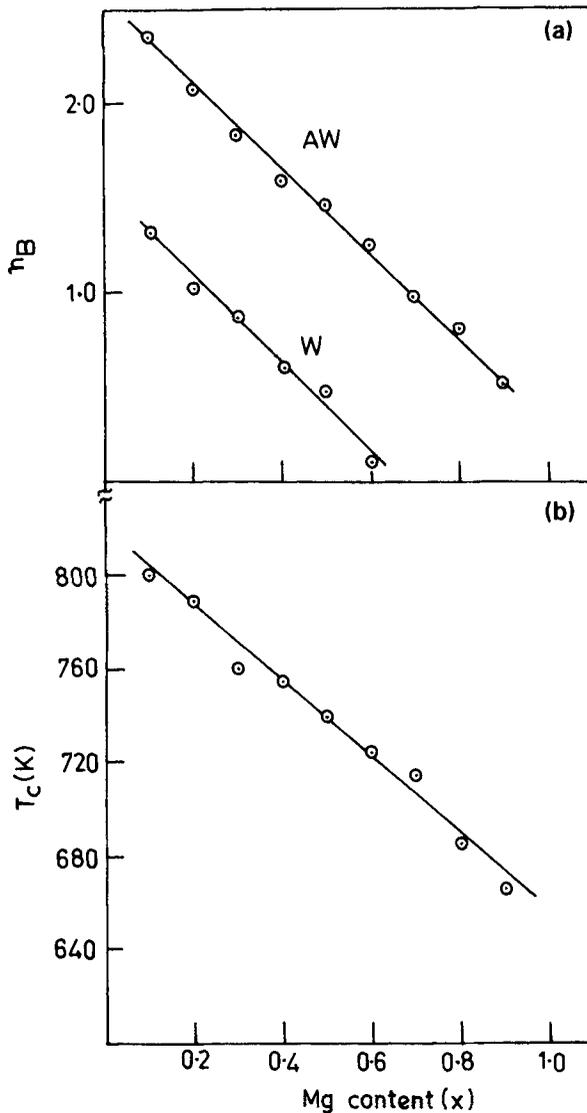
Figure 2. **a.** Variation of n_B with Mg-content (x) and **b.** T_c vs x for AW samples.

(Bean 1955). Thus, susceptibility which is inversely proportional to H_c is large for SP of the same material and hence there is peak in $\chi \rightarrow T$ curve at T_b. A broad maximum observed in $\chi - T$ curves of wet samples ($x = 0.2$, 0.4, figure 3) may be due to the response of single domain (SD) particles of various sizes as they undergo SD to SP (superparamagnetic) transition (Bean 1955). A sharp peak observed near Curie temperature (T_c) for AW samples (figure 3) is due to the SD to SP transition or competing anisotropies of the particles indicating more uniform particle size in AW samples compared to W-samples. The T_c determined through high temperature susceptibility measurements of AW samples are shown in figure 2b. The linear decrease in T_c as a function of x is due to the substitution of non-magnetic Mg^{2+} ions in the $CoFe_2O_4$.

Typical room temperature (300 K) Mössbauer spectra for wet and AW samples of $Mg_xCo_{1-x}Fe_2O_4$ system are shown in figures 4 and 5. The Mössbauer spectra of wet
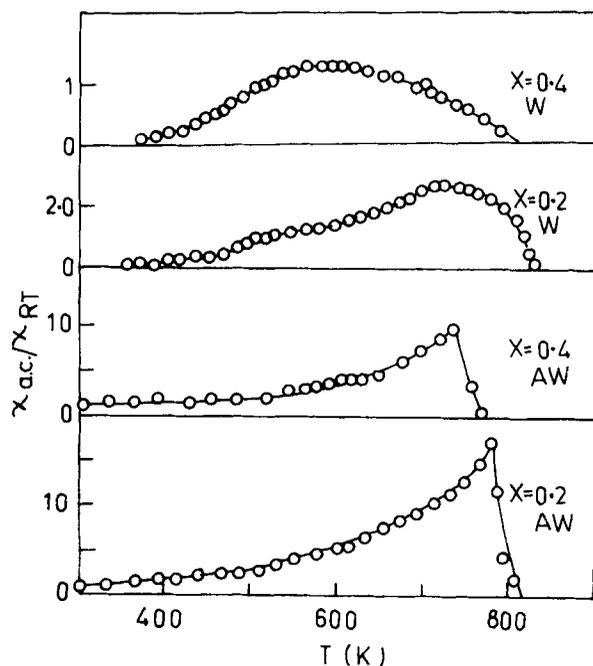
Figure 3. Thermal variation of ac susceptibility for wet (W) and annealed-wet (AW) samples.

samples (figure 4) are characterized by the simultaneous presence of a central paramagnetic doublet and a magnetically split component. The intensity of the central paramagnetic doublet increases with respect to the magnetic sextet on increasing Mg concentration. The appearance of the central paramagnetic doublet in the Mössbauer spectra agrees with their lower values of n_B compared to the AW samples (figure 2a) and can be attributed to the presence of superparamagnetic particle induced by the fine particle size effects. The spectra at 300 K for the wet samples with $0.3 < x < 0.9$ exhibit very similar quadrupole doublets indicative of the absence of magnetic hyperfine interaction (long range ordering). This observation leads to the conclusion that in the Mg^{2+} substituted wet-samples the particles have a very fine size or more probably this ferrimagnetic fine particles are separated magnetically from the matrix since the region is surrounded by non-magnetic Mg^{2+} ions. Thus, the Mössbauer spectra of wet-samples reveal the existence of SP clusters or paramagnetic centres (Ishikawa 1964). This indicates that ferrimagnetic wet samples $(x \geqslant 0.3)$ are superparamagnetic at 300 K, their blocking temperature being lower than the room temperature. The solid lines through the data points in figures 4 and 5 are the results of computer fits of spectra obtained assuming equal line widths for A and B sites.

The Mössbauer spectra of the AW-samples (figure 5) with $0.1 \leqslant x \leqslant 0.9$ exhibit normal Zeeman split sextets, one due to the Fe^{3+} ions at the tetrahedral (A) site and the other due to the Fe^{3+} ions at the octahedral (B) site. No features characteristic of ionic spin relaxation were observed. As both ferrites $MgFe_2O_4$ $(x = 1.0)$ and $CoFe_2O_4$ $(x = 0.0)$, have partially inverted cation distribution, the A–B super-transferred exchange interaction dominates for all the samples of $Mg_xCo_{1-x}Fe_2O_4$ system. The $Fe^{3+}(B)/Fe^{3+}(A)$ area ratio for $x = 0.0$ to 1.0 remains nearly constant (≈ 1.13) indicating that the average value of hyperfine field varies between the two end member values. Mössbauer parameters of wet
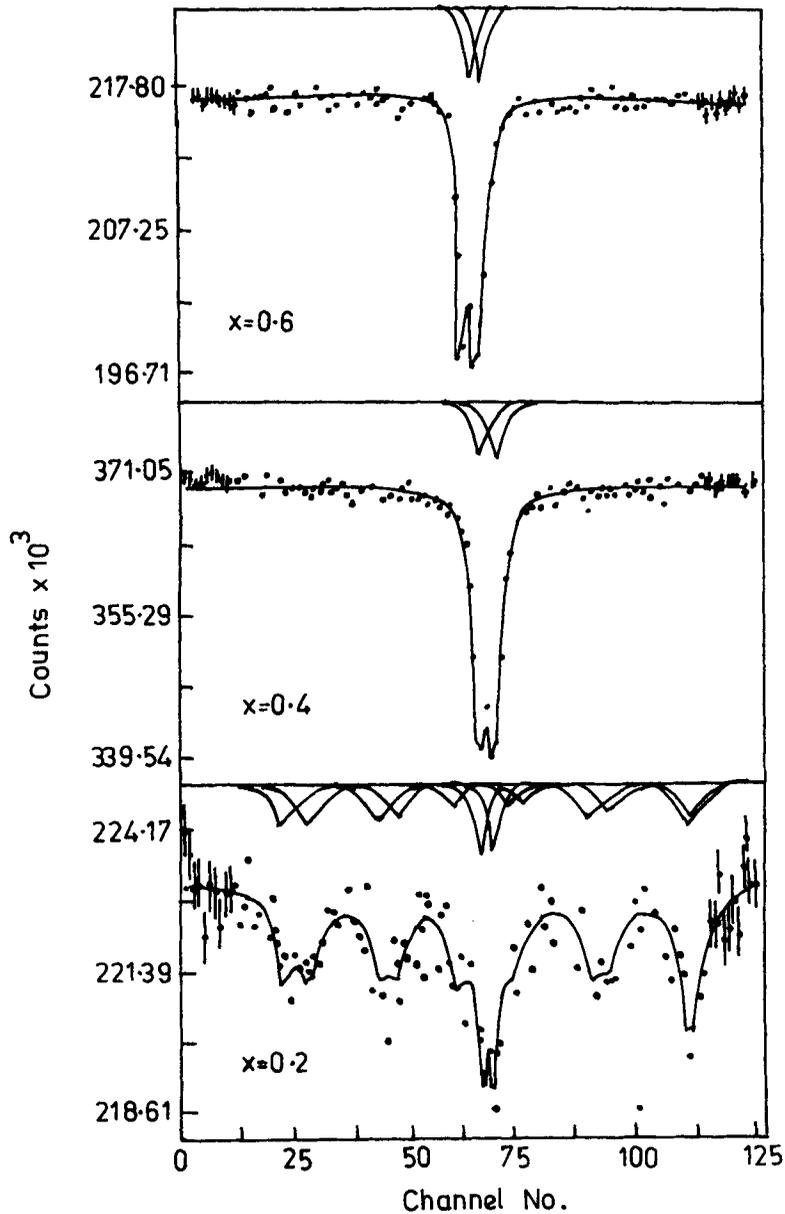
Figure 4. Room temperature Mössbauer spectra for wet samples ($x = 0.2$, 0.4 and 0.6).

samples are quite different from those of the AW samples compare very well with the reported values on the ceramically prepared ones (Kulkarni and Joshi 1986; Pandya *et al* 1990).

Typical Mössbauer spectra of wet-samples at 77 K are also shown in figure 6. It is clear that the central paramagnetic doublet observed at 300 K for $x = 0.1$ and 0.2 disappears at 77 K and completely transforms into the ordered magnetic structure due to the predominance of long-range magnetic interactions at 77 K over short-range localized paramagnetic interactions. Wet samples at $x = 0.4$ to 0.6 display clear paramagnetic doublet at 300 K but
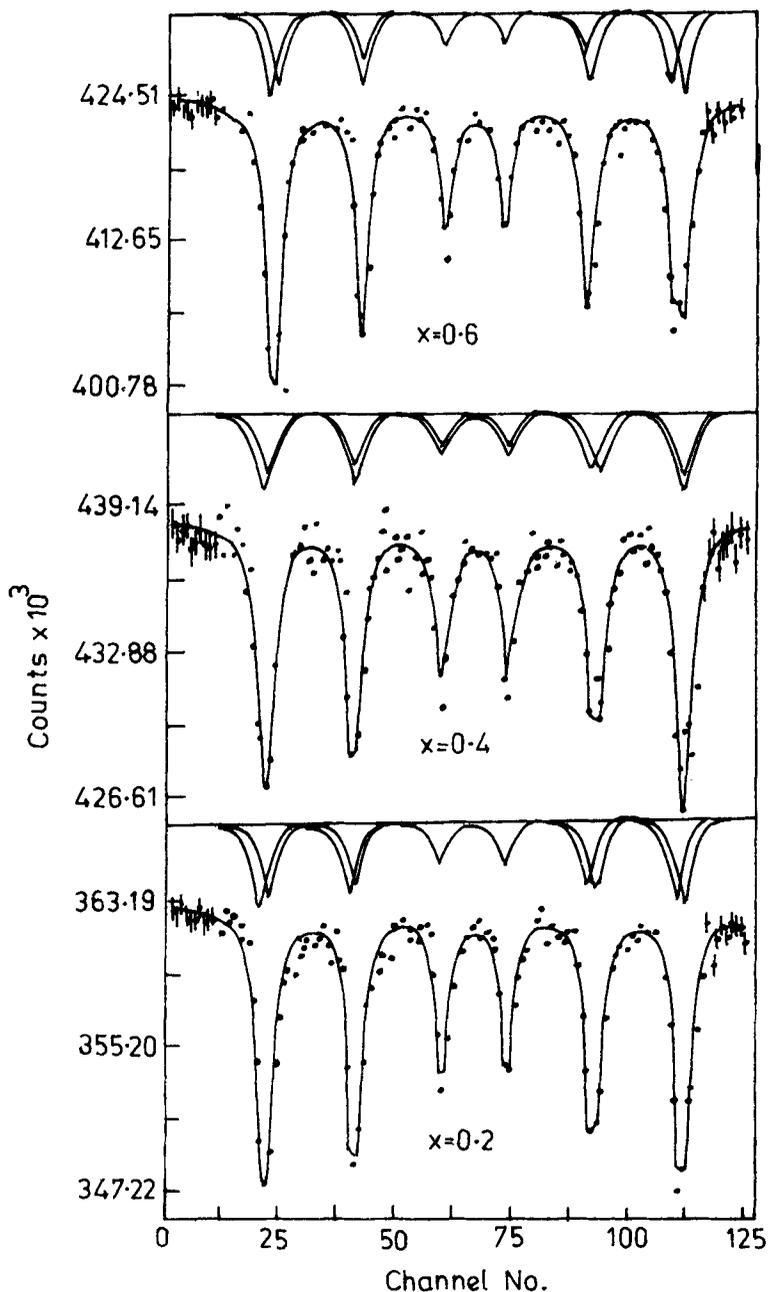
Figure 5. Mössbauer spectra of AW samples ($x = 0.2$, 0.4 and 0.6 at 300 K).

they show simultaneous presence of a central paramagnetic doublet superimposed on broad magnetic sextet at 77 K indicating the partial transformation to an ordered magnetic structure. The samples with $x > 0.7$ exhibit paramagnetic doublets, displaying superparamagnetic behaviour as their blocking temperature being lower than 77 K.

The observed differences in the structural and magnetic properties of wet and annealed wet samples are attributed to the fine particle size effect and non-magnetic Mg^{2+}
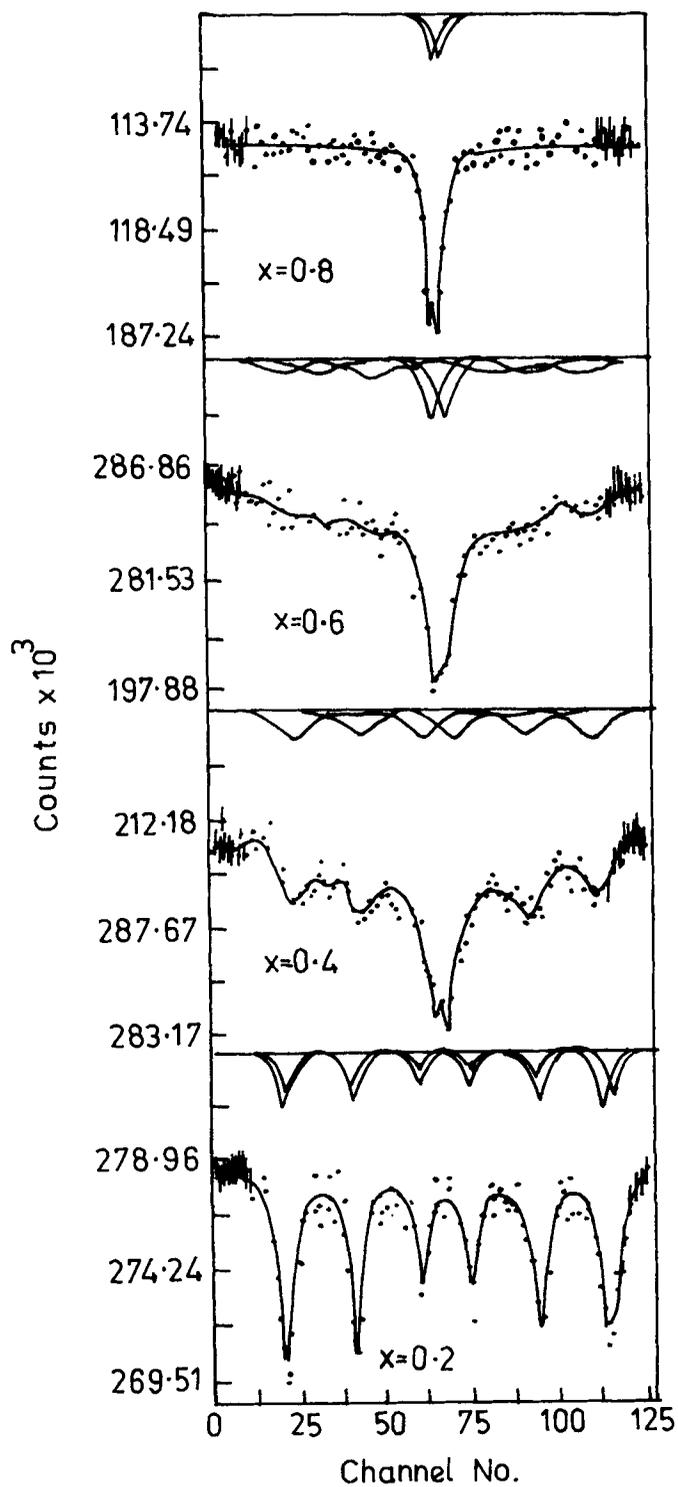
Figure 6. Mössbauer spectra of wet samples at 77 K for $x = 0.2$, 0.4, 0.6 and 0.8.

substitution for Co^{2+}. The high temperature annealing changes the wet prepared ferrites into the ordered magnetic structure of ceramic ferrite.

4. Conclusion

Fine particles play an important role in controlling the magnetic properties or the ferrites has been shown by the present study. We have established that the wet chemically prepared mixed spinel series $Mg_xCo_{1-x}Fe_2O_4$ contain fine particles of the order of 300 Å which give rise to the unusual magnetic properties to the system like superparamagnetism leading to the suppression of long range magnetic ordering and quenching of magnetic moments at 300 K in spite of having Curie temperature > 650 K in annealed wet state. The high temperature annealing of the wet prepared ferrites transforms them into the ordered magnetic structure of ceramic ferrites having long-range ferri-magnetic ordering.

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