1 Introduction

Fine magnetic particles systems have generated an appreciative interest in last few years due to their possible applications in the emerging field of nanostructured materials technology. The properties of these nanosized particles are drastically different from those of their bulk part. This results from small grain sizes and effect of magnetic interactions between particles. Spinel ferrites are one of such promising materials that are having great potential from the industrial point of view. Various techniques, such as sol-gel method, mechanical alloying, hydrothermal route NiZn and MnZn ferrites, etc. are used to produce nanoparticles of spinel ferrites. Chemical co-precipitation is such a versatile technique to synthesize nano ferrites and has been used to produce almost all kinds of spinel ferrites like CoFe$_2$O$_4$ (Refs 8,9), NiFe$_2$O$_4$ (Ref. 10), ZnMn ferrite (Ref. 11), CoZn and MnZn ferrites etc. The magnetic properties largely depend on the particle size and their distributions as the domain structure and magnetization process are particle size dependent. If their size is quite large and consists of several domains, the magnetization in the direction of applied field will take place by domain wall displacement as well as by domain magnetization rotation. If the volume of the particles is such that these contain only single domain, the change in magnetization occurs only by rotation. If the volume is reduced further, at a particular temperature, the thermal energy becomes greater than anisotropy energy and when a field is applied, the magnetization is observed with no hysteresis, a notable phenomenon called superparamagnetism.

We have prepared nano particles Cr substituted CoZn ferrite of various crystallite sizes by varying the annealing temperature in chemical co-precipitation technique. The phase and particle size have been estimated using X-ray diffraction and EDX technique. RT and LT Mössbauer spectroscopy was also carried out to know the microscopic properties.

2 Experimental Details

Nano particles of Cr$_{0.25}$Co$_{0.25}$Zn$_{0.5}$Fe$_2$O$_4$ were synthesized by a chemical co-precipitation method. Analytical grade Fe(NO$_3$)$_3$.9H$_2$O, CoCl$_2$.6H$_2$O, anhydrous ZnCl$_2$ and CrCl$_3$.6H$_2$O (from Merck), were the starting materials. The aqueous solutions of these materials were mixed together and 30% NH$_4$OH solution was added, with continuous stirring, to form a precipitate. After complete precipitation, the mixture was stirred continuously for another two hours, maintaining a pH value of 10. Washing and filtration was repeated until the pH of the solution became neutral. The precipitate was dried and subsequently annealed at 573, 673, 773 and 873K for 24 h at each temperature to obtain the nano samples. X-ray diffractograms of samples were obtained on a Rigaku Miniflex diffractometer (30 kV, 15 mA) at room temperature. Cu Kα radiation was used.

A standard Austin drive and controller assembly was used in the constant acceleration mode for Mössbauer spectroscopy. The source used was a 5-mCi Co$^{57}$ in rhodium matrix. Velocity calibration

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was done using metallic iron foil. Ferrite sample equivalent to 10 mg/cm$^2$ of natural iron was used for the Mössbauer measurements. The Mössbauer spectra were fitted using a standard program that fits for Lorentzians.

3 Results and Discussion

The energy dispersive X-ray (EDX) spectra for the prepared sample is shown in Fig. 1. The stoichiometry of prepared ferrite is within 2% error of desired ratio. Fig. 2 shows X-ray diffraction pattern for the sample annealed at 573K. The single phase spinel structure could be produced at quite low annealing temperature with no additional impurities. The broad peaks confirm the presence of particles of very small sizes which were estimated using standard Scherrer equation, $t = \frac{0.9\lambda}{\beta\cos\theta}$ (where $t$ is the crystallite size, $\lambda$ the X-ray wavelength, and $\beta$ is the FWHM of the XRD peak at 2$\theta$), from the width of the prominent (311) reflection. Table 1 presents the average particle sizes with various annealing temperatures.

Figure 3 shows the Mössbauer spectra for the samples measured over the temperature range 25-300 K. The spectrum at 25 K shows six well-defined lines that are having large line widths as compared to their bulk counterpart. It broadens further as we increase the temperature until a central peak appears around 80 K. The hyperfine field collapses at room temperature giving the signatures of superparamagnetic relaxation phenomenon. This phenomenon may be analyzed using the expression given by Blume and Tjon$^{14,15}$ for the line shape of Mössbauer absorption spectra in the presence of a fluctuating magnetic field. However, the line broadening is due to the distribution of quadrupole shifts which is explained as follows:

When the quadrupole interaction is much weaker than the magnetic hyperfine interaction, the Mössbauer line shift quadrupole interaction can be given by:

$$E_Q = \frac{1}{8} e^2 q Q [3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos(2\phi)]$$

### Table 1 — Average particle sizes calculated using Scherrer equation

<table>
<thead>
<tr>
<th>Annealing temperature (K)</th>
<th>Average particle size (nm)</th>
</tr>
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<tbody>
<tr>
<td>573</td>
<td>5.0</td>
</tr>
<tr>
<td>673</td>
<td>773</td>
</tr>
<tr>
<td>773</td>
<td>16.0</td>
</tr>
<tr>
<td>873</td>
<td>23.0</td>
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</table>

Fig. 1 — EDX spectra for the sample Cr$_{0.25}$Co$_{0.25}$Zn$_{0.5}$Fe$_2$O$_4$ annealed at 573K

Fig. 2 — X-ray diffraction pattern for sample Cr$_{0.25}$Co$_{0.25}$Zn$_{0.5}$Fe$_2$O$_4$ annealed at 573K

Fig. 3 — (a) RT Mössbauer spectra for samples annealed at 573, 673, 773 and 873K; (b) Low temperature Mössbauer spectra for sample Cr$_{0.25}$Co$_{0.25}$Zn$_{0.5}$Fe$_2$O$_4$ annealed at 573K
where $\theta$ and $\phi$ are the polar and azimuth angles of the magnetic hyperfine field vector and the principal axes of the electric field-gradient tensor, respectively. Assuming that the maximum electric field gradient $q$ and the asymmetry parameter $\eta$ are independent of $\theta$ and $\phi$, the average value of $E_Q$ taken over all directions vanishes, i.e.,

$$<E_Q>=\frac{1}{4\pi} \int \frac{\sin \theta d\theta d\phi}{\phi} q Q (3 \cos^2 \theta \cos(2\phi)) \left( 1 + \eta \sin^2 \theta \cos 2\phi \right)$$

Thus, a vanishing quadrupole shift is observed below $T_N$ if the magnetic hyperfine field is randomly oriented with respect to the principal axis of the electric field-gradient tensor. However, the line broadening is not zero due to this random distribution, i.e.,

$$2 \Delta E_Q = 2 [(E_Q - <E_Q>)^2]^{1/2}$$

$$= 2 \left( \frac{1}{4\pi} \int \frac{\sin \theta d\theta d\phi}{\phi} q Q (3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi) \right)^{1/2}$$

$$= \frac{1}{\sqrt{5}} e q Q \frac{\phi}{\phi} + \frac{1}{3} \eta \frac{\phi}{\phi}^{1/2}$$

$$= \frac{1}{\sqrt{5}} 0.736 = 0.33 \text{ mm/s}$$

The isomer shift at room temperature was calculated out as 0.16 mm/s, with respect to natural iron, and consistent with Fe$^{3+}$.

The QS above Néel temperature $T_N$ is given by:

$$QS = \frac{1}{2} e^2 q Q \frac{\phi}{\phi} + \frac{1}{3} \eta \frac{\phi}{\phi}^{1/2}$$

The QS at 25 K has been calculated from the positions of Mössbauer absorption lines from the expression:

$$QS = \frac{1}{2} (V_6 - V_5 + V_1 - V_2)$$

where $V_i$ is the position of the $i$th absorption line in mm/s.

The calculated Mössbauer parameters are presented in Table 2. RT Mössbauer spectra$^{16}$ show the samples with small particles (around 10 nm) are superparamagnetic at RT whereas the comparatively large particles ones have coexisting superparamagnetic as well as ferromagnetic phases$^{17}$.

The blocking temperatures of these samples were determined by FC-ZFC measurements using a vibrating sample magnetometer (Table 3). Figure 4 shows a typical FC-ZFC curve for sample annealed at 673 K. It can be easily noticed that the blocking temperature of the nanoparticles decreases with decrease in crystallite size in case of cooling with applied field. The divergence of FC and ZFC curves is a characteristic feature of superparamagnetic behaviour. When a magnetic field is applied, the magnetization direction of the nanoparticles becomes easier to switch to the field direction, and less assistance is required from the thermal activation. Hence, the blocking temperature shifts to a lower value with an applied field$^{18}$.
4 Conclusions

The nano particles of $\text{Cr}_{0.25}\text{Co}_{0.25}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were prepared using chemical co-precipitation method at quite low temperatures as compared to conventional methods. The FC-ZFC measurements using vibrating sample magnetometer confirm the nature of the material to be superparamagnetic and values of blocking temperature were seen to increase with an increase in particle size. The Mössbauer spectra taken at various temperatures confirm that the samples prepared by annealing at 773K and 873K are consisted of ferrimagnetic as well as superparamagnetic particles coexisting at room temperature while for the samples annealed at 573K and 673K, the only phase present is superparamagnetic one. The low temperature Mössbauer spectrum taken well below blocking temperature shows two well resolved sextets that confirms it to be ferrimagnetic below blocking temperature.

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References