Structural and Mössbauer studies of Mn$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrites prepared by high energy ball milling and glycolthermal methods

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Abstract. We have investigated the properties of three Mn$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrites synthesized directly from high purity metal oxides (Sample A) and from MnFe$_2$O$_4$ and CoFe$_2$O$_4$ ferrites (Sample B) by mechanical milling and by glycolthermal process (Sample C). XRD results show essentially single phase spinel structure. Sample C is the best sample followed by Sample B based on the presence of minor impurity peaks near $2\theta \approx 38^\circ$ and 52$^\circ$. More impurity peaks appear to grow after annealing above 400 $^\circ$C. Samples A and B have been found to have similar Fe-57 Mössbauer spectra before and after annealing at 1050 $^\circ$C. The spectrum for each sample changes significantly after annealing. This is attributed to changes of both grain sizes and impurity phases with thermal annealing. At least two sextets and two doublets are used to fit the Mössbauer spectra.

1. Introduction
Cobalt ferrites (CoFe$_2$O$_4$) are important materials for high density magnetic and magneto-optic recording media [1, 2]. Mn doped cobalt ferrites exhibit high magnetostriction, good mechanical properties and have low eddy current losses making them suitable in high frequency applications [3]. It has been observed that a pure and uniform form of a Co$_{0.9}$Mn$_{0.1}$Fe$_2$O$_4$ compound appears difficult to obtain by high temperature synthesis [3]. We have therefore prepared related compounds with higher Mn content by different synthesis routes and at lower synthesis temperature in order to investigate their single phase formation, thermal stability and magnetic properties. We have made Mn$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ by high energy ball milling metal oxides, single phase MnFe$_2$O$_4$ and CoFe$_2$O$_4$ ferrites and by glycolthermal reaction from metal chlorides.

2. Experimental details
Mn$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ compounds were produced from high purity metal oxides (Sample A) and from a mixture of single phase MnFe$_2$O$_4$ and CoFe$_2$O$_4$ ferrites (Sample B) by mechanical milling for at least 60 hours using a Retch planetary ball mill (type: PM 400) operated at 300 rev/min. The ball to sample mass ratio used was 20:1 under air atmosphere. The preparation procedure from single phase ferrites is similar to the work on MnZn ferrite [4, 5]. To test the consistency of the two synthesis routes, bulk densities of compacted pellets of samples annealed at 1050 $^\circ$C were measured. The densities were found to be 3.89 $\pm$ 0.01 g/cm$^3$ for sample A and 3.87 $\pm$ 0.01 g/cm$^3$ for sample B. The x- ray density can be calculated from XRD measurements using the equation $\rho_x = 8M/N_Aa^3$ where is $M$ the...
molar mass, \( N_A = 6.022 \times 10^{23} \) mol\(^{-1}\) and \( a \) is the lattice parameter. For samples A and B the x-ray densities we found to be 5.18±0.02 g/cm\(^3\) and 5.23 ± 0.02 g/cm\(^3\) respectively. In the glycolthermal method (Sample C) metal chlorides and ammonium nitrate were used as starting materials. Stochiometric amounts of chlorides were mixed in deionised water to obtain Mn\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\). The solutions were thoroughly mixed using a magnetic stirrer for about 20 minutes. Ammonium nitrate solution was then slowly added to the chloride mixture under rapid stirring until a pH ≈ 9. The precipitate was then washed several times by deionized water until all the chloride ions were removed as confirmed by using a standard solution of AgNO\(_3\). During the washing process, the precipitate was filtered using Whatman glass microfibre filters (GF/F). The clean wet precursor was thereafter dispersed in 300 ml of ethylene glycol under rapid stirring. The precursor was then placed in a 500 ml glass lining in a stainless steel pressure vessel (watlow series model PARR 4843). The pressure vessel was heated to 200 °C and the pressure gradually rose to 140 psi. These conditions were held for 6 hours. The cooled products were filtered and washed by deionized water and finally by ethanol. The recovered synthesized powders were dried under an infra red lamp and homogenized using agate mortar and pestle. The products were characterized by x-ray diffraction (XRD). The XRD patterns of the samples were obtained using CoK\(_\alpha\) radiation (\( \lambda = 1.7903 \) Å) of the Phillips diffractometer (type: PW1710). The Mössbauer spectra were recorded using a conventional constant acceleration Mössbauer spectrometer with a \(^{57}\)Co source sealed in a Rh matrix.

3. Results and discussion

Figure 1 shows the XRD spectra for the three samples. All the major peaks are characterized by the basic single phase spinel structure. Some small impurity peaks are observed at \( 2\theta \approx 38^\circ \) and 52° which are more significant for Sample A, and least for Sample C. The impurity peaks have been attributed to an intermediate hematite \( \alpha\)-Fe\(_2\)O\(_3\) phase [6].

![Figure 1. XRD spectra for Samples A, B (annealed at 200 °C) and C (synthesized at 200 °C).](image-url)

The variation of XRD spectra with annealing temperature for samples milled for 60 hours are shown in figure 2. All samples were annealed in air at each temperature for about 6 hours. No significant changes to the XRD spectra are observed until after an annealing temperature of about 400 °C. Above this temperature significant changes to the spectra are observed as more impurity peaks grow. The narrowing of the peaks is an indication of increasing particle size. The particle sizes were estimated using the Scherrer equation: \( D = 0.9\lambda / (\beta \cos \theta) \) where \( \beta \) is the full width at half maximum of the 311 XRD peak [3, 7, 8]. After milling for 60 hours the grain sizes for samples A and B were found to be 7.23±0.03 nm and 7.58±0.03 nm respectively. Similar values were obtained for Mn\(_{0.1}\)Zn\(_{0.9}\)Fe\(_2\)O\(_4\) prepared by hydrothermal process [9]. The grain size for Sample C was found to be
15.12±0.09 nm. Hence nanosized samples have successfully been produced through the three synthesis routes employed.

In figure 3 we show the Mössbauer spectra for samples A, B and C. The spectra for milled samples A and B are similar and were successfully fitted by three sextets and two doublets. The sextets represent the fractions of ordered Fe ions in tetrahedral (A) and octahedral (B) sites. In Table 1 we show results of the Mössbauer spectra analysis. The third sextet may be attributed to small Fe clusters induced by milling [10]. The doublets represent Fe ions in paramagnetic states. A broad central
Table 1. Isomer shifts (IS), hyperfine fields (H), line widths (LW) and site fractions (f) at A and B sites for raw samples (A, B and C) and annealed samples (A-400 °C, B- 200 °C and B- 400 °C).

| Sample | IS_A (mm/s) | IS_B (mm/s) | H_A (kOe) | H_B (kOe) | H_3rd (kOe) | LW_A (mm/s) | LW_B (mm/s) | f_A (%) | f_B (%) |
|--------|-------------|-------------|-----------|-----------|-------------|-------------|-------------|--------|--------|
| A      | +0.36       | +0.32       | 434       | 480       | 271         | 0.46        | 0.46        | 38     | 20     |
| A-400°C| +0.30       | +0.34       | 482       | 488       | 283         | 0.38        | 0.60        | 52     | 30     |
| B      | +0.33       | +0.37       | 412       | 449       | 317         | 0.44        | 0.50        | 13     | 47     |
| B-200°C| +0.33       | +0.40       | 453       | 481       | 433         | 0.38        | 0.73        | 54     | 32     |
| B-400°C| +0.31       | +0.43       | 488       | 458       | 389         | 0.40        | 0.71        | 56     | 34     |
| C      | +0.32       | +0.37       | 481       | 449       | -           | 0.29        | 0.48        | 53     | 43     |

doublet is observed in unannealed samples, which disappears drastically with increased sintering temperature.

The reduction of doublet with increasing annealing temperature appears to be related to single phase formation. The spectra for samples annealed at 400 °C are comparable with those of similar compounds prepared by sol-gel method [1]. There is no evidence of a broad doublet in the spectra for Sample C. This also compares well with insignificant hematite phase as indicated by XRD results for sample C. The criterion used to assign sextets and doublets at A and B sites was based on the fitted results of isomer shifts, which are expected to be lower due to cubic symmetry on sites A [10]. The Mössbauer parameters deduced from the Mössbauer spectra are also shown in Table 1. The values of isomer shifts, hyperfine fields and line widths are similar to those previously reported for similar compounds [11, 12].

4. Conclusions

We have successfully made Mn_{0.5}Co_{0.5}Fe_{2}O_{4} nanoparticles by high energy ball milling and by glycolthermal process. A predominant single phase spinel structure is obtained below 400 °C. The Mn substituted cobalt ferrites appear to be unstable at temperatures higher than about 400 °C when significant increases in extra impurity peaks are observed. High temperature synthesis seems to be unsuitable for this compound. Significant changes in the Mössbauer spectra with increase in sintering temperature should be attributed to both increased grain sizes and extra impurity phases at high temperatures. The sample prepared by glycolthermal method appears to be of higher quality than milled samples. Better samples are also obtained from MnFe_{2}O_{4} and CoFe_{2}O_{4} than from metal oxides.

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