Investigation of Structural and Magnetic properties of Cobalt Manganese Ferrite Nanoparticles

M. Margabandhu[1], S. Sendhilnathan[2], and G. Vijayakumar[3]

[1]Department of Physics,
Anna University Chennai: University College of Engineering-Ariyalur,
Ariyalur, Tamilnadu, India

[2]Department of Physics,
Anna University Chennai: University College of Engineering-Pattukkottai,
Pattukkottai, Thanjavur, Tamilnadu, India

[3]Department of Civil Engineering,
Anna University Chennai: University College of Engineering-Ariyalur,
Ariyalur, Tamilnadu, India

ABSTRACT: Cobalt Manganese Ferrite nanoparticles ($Co_{1-x}Mn_xFe_2O_4$ with x varying from 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) of size varying from 16nm - 73 nm were synthesized by simple co-precipitation method. The obtained samples were characterized by X-ray diffraction analysis, Fourier Transform Infrared spectroscopy, Vibrating Sample Magnetometer. The structure of the samples was determined by using X-ray diffraction Characterization. X-ray diffraction analysis shows that the synthesized samples were cubic spinel in structure. The obtained XRD result shows that the lattice constant (a_o) increased and the average crystallite size shows decrement with manganese substitution. The average crystallite size of the particles was determined by using Debye Scherrer's Formula. Fourier transform infrared spectroscopy (FTIR) in the range 4000-400 cm^{-1} was reported. The water absorption bonds and the spinel structure of crystalline cobalt manganese ferrite nanoparticles were reported. The Vibrating sample magnetometer (VSM) results revealed the magnetic properties of the synthesized samples such as Remenance, Coercivity and saturation magnetization. The VSM results reported that the remenance and Coercivity were in decrement and the Saturation Magnetization found to be decrease and increase with Manganese implementation in cobalt ferrite nanoparticles. The synthesized cobalt manganese ferrite magnetic nanoparticles could be used in ferroelectric and in magnetic recording applications.

KEYWORDS: Co-precipitation, Spinel, Magnetic nanoparticles, Remenance, Coercivity, Saturation magnetization, Morphology.

1 INTRODUCTION

Cobalt Ferrite compounds with metal combination such as manganese gives wide application in magneto elastic stress sensors due to its magnetostriction property [1]. Magnetic nanoparticles (MNPs) possessing super paramagnetic nature can be used in various applications such as targeted drug delivery, hyperthermia, human cell segregation process, correcting repaired tissues, MRI contrast enhancement of immuno assay and detoxification of biological fluids[2, 3]. The basic requirement for the biomedical applications is that the MNPs should possess high magnetization values and the particles should be smaller than 100nm. The MNPs should be nontoxic, biocompatible and should permit targeted drug delivery. These MNPs should possess suitable surface coating so that it can bind with drugs, proteins, enzymes, antibodies and nucleotides which can be allowed to an organ, tissue by using external magnetic field [2, 4]. Cobalt Ferrite MNPs is widely used in various applications such as high density magnetic recording [5, 6], ferrofluids technology [5, 7], biomedical drug

delievery [5, 8], magnetic resonance imaging [5, 9], biocompatible magnetic nanoparticles for cancer treatment [5, 10] and magneto optical devices [5, 11]. Vaidhyanathan and Sendhilnathan et.al [12] demonstrated that metal ion M^{2+} substitution in $CoFe_2O_4$ ($Co_{1-x}M_xFe_2O_4$) exhibits enhanced properties such as high chemical stability, high corrosion resistance, excellent magnetostriction and magneto optical characteristics. Hence MNP_S and the metal ion substituted cobalt ferrite MNPs possess various applications in technical and in medicine field. In the present work, an attempt was made to synthesize manganese substituted cobalt ferrite nanoparticles ($Co_{1-x}Mn_xFe_2O_4$ with x varying from 0.0, 0.2, 0.4, 0.6 0.8 and 1.0) and to study its structural and magnetic properties in detail. Magnetic nanoparticles can be synthesized through various processes such as hydrothermal method, sol-gel method, thermal decomposition, ball milling, microemulsion and coprecipitation method. Among the various methods, the coprecipitation technique is the cost effective method for the synthesis of MNPs with homogenous particle size. Hence the whole experiment was carried out with simple coprecipitation technique.

2   EXPERIMENTAL PROCEDURE

2.1   SYNTHESIS

The magnetic nano particles prepared via co-precipitation method depends on parameters such as molarity, temperature, pH of the solutions etc [12]. In this process, magnetic nanoparticles are prepared by mixing $FeCl_3$, $MnCl_2$, $CoCl_2$ mixtures in Sodium Hydroxide solution. The ratio between the mixed solutions was maintained as 2:1. The boiling solution of sodium hydroxide with the above mentioned chemical constituents were subjected to stirring process at 70 deg Celsius for one hour duration. The time period left for stirring process is enough for the transformation of metal salts into hydroxides. In few seconds the added salt solutions get transformed into metal particles. The sufficient amount of obtained fine particles at the end of stirring process will be deposited as residue. The obtained residue was washed repeatedly with double distilled water several times to remove impurities. Finally the particles are collected using magnetic segregation. The obtained nanoparticles were washed with acetone to remove other chemical agents and the residue was allowed to dry at normal temperature [12].

2.2   PARTICLE CHARACTERIZATION

X-ray powder diffractometer using Cu K$\propto$ (λ = 1.54060 Å) radiation was used to record the X-ray diffraction patterns. Complete tracing process was carried out in prescribed step size, measurement time and at normal room temperature. The average size of the obtained nanocrystalline powders was measured using Debye-Scherrer formula.

$$D_{xrd} = \frac{0.89\lambda}{\beta cos\theta}$$ (2)

D_{xrd} – Average crystalline size in nm, θ-Bragg's diffraction angle, λ - X-ray Wavelength in Å, β – is the full width half maximum [12, 13].

2.3   MAGNETIC MEASUREMENTS

Vibrating sample magnetometer (VSM) was used to calculate the important magnetic parameters such as Retentivity, Coercivity and Saturation magnetization at normal temperature with maximum magnetic field limits of 15000 (G). The obtained values revealed the basic magnetic properties of the Magnetic nanoparticles.

2.4   SPECTRAL MEASUREMENTS

Fourier transform infrared spectra were recorded for the cobalt manganese magnetic nanoparties of different molar ratio between 4000 cm^{-1}-400cm^{-1}. The obtained results pointed out the water absorption bands and metal oxide bonds respectively.

3   RESULTS AND DISCUSSION

3.1   STRUCTURAL CHARACTERIZATION

X-ray diffraction pattern was used to identify the basic crystalline parameters such as size, lattice constant and even distribution of the particles. In Table.1, the variation of average crystallite size and lattice constant with manganese substitution in cobalt manganese ferrite was clearly shown.

Table 1. Summary of Lattice constant (A°) and Average crystallite size(D_{aveXRD})(nm) of
$Co_{1-x}Mn_xFe_2O_4$ with x varying from 0.0, 0.2, 0.4, 0.6, 0.8 & 1.0

Samples	Lattice Constant (A°)	Average Crystallite size (D_{aveXRD})(nm)
$CoFe_2O_4$	8.382	31.89
$Co_{0.8}Mn_{0.2}Fe_2O_4$	8.432	26.29
$Co_{0.6}Mn_{0.4}Fe_2O_4$	8.430	22.19
$Co_{0.4}Mn_{0.6}Fe_2O_4$	8.449	17.95
$Co_{0.2}Mn_{0.8}Fe_2O_4$	8.469	15.93
$MnFe_2O_4$	8.489	8.12

All the obtained powders of different molar ratio were being with single phase cubic spinel structure. The sharp end obtained from (311) plane, represents that the samples are in single phase cubic spinel in structure [15]. The strongest peaks at various reflection planes of (511) (422) (400) (311) and (440) showed the presence of single phase cubic spinel structure [5]. The increment in latticle constant (A^0) with manganese substitution in cobalt manganese ferrite nanoparticles was due to the occupying nature of Mn^{2+} ions in the position of Co^{2+} ions [14]. The linear value increment in lattice constant is because of the larger atomic radii of Mn^{2+} ions than Co^{2+} ions.

3.2   MAGNETIC MEASUREMENTS

Vibrating sample magnetometer was used to determine the magnetic properties of the obtained samples at normal temperature. The strength of the applied magnetic field was in the range of 15000 Guass to -15000 Guass and the results were revealed in emu. The variation in magnetic parameters such as coercivity, remanance, saturation magnetization of cobalt manganese ferrite samples of different molar ratio were shown in Fig. (1a, 1b, 1c, 1d and 1e).
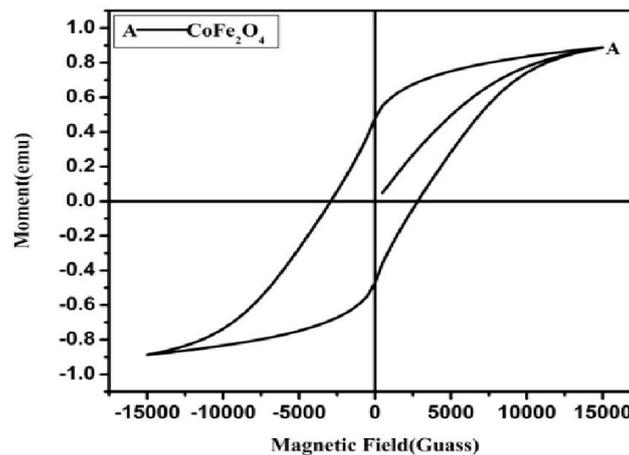
Fig 1a: Magnetization curve of $CoFe_2O_4$
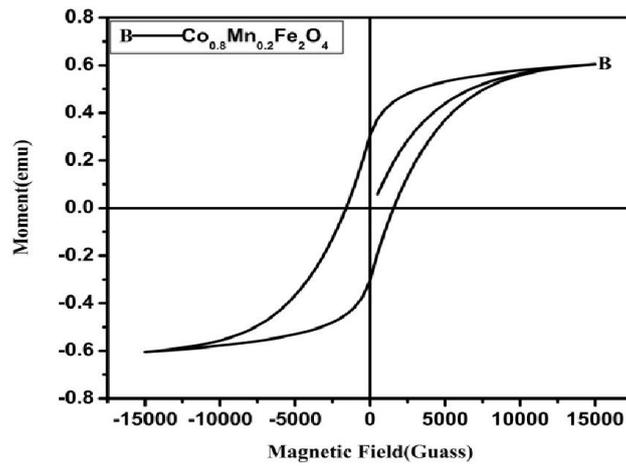
Fig 1b: Magnetization curve of $Co_{0.8}Mn_{0.2}Fe_2O_4$
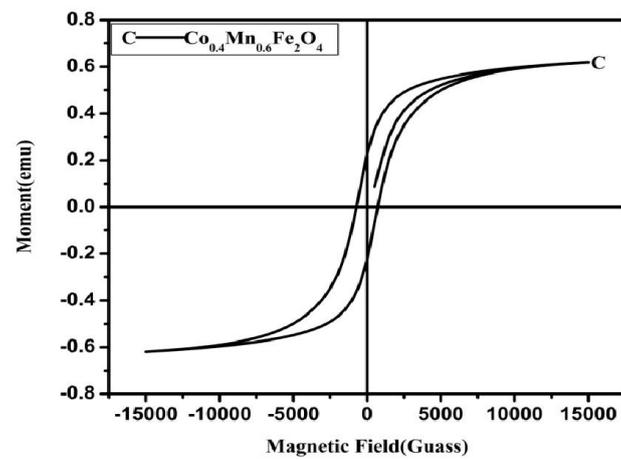
Fig 1c: Magnetization curve of $Co_{0.4}Mn_{0.6}Fe_2O_4$
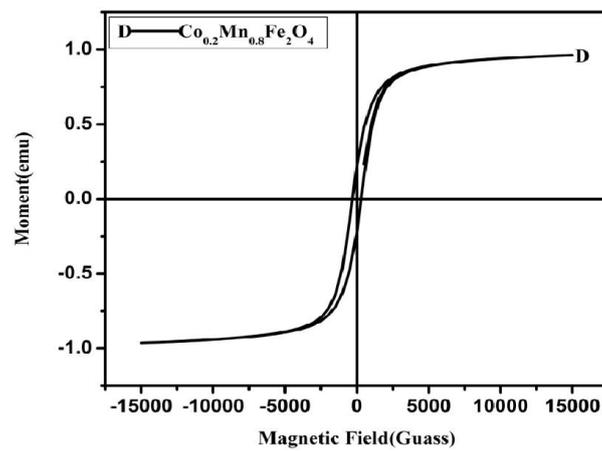
Fig 1d: Magnetization curve of $Co_{0.4}Mn_{0.6}Fe_2O_4$
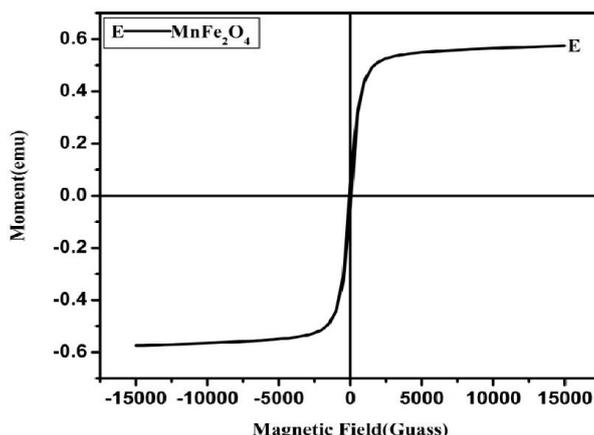
Fig 1e: Magnetization curve of $Co_{0.4}Mn_{0.6}Fe_2O_4$

Fig.1a, 1b, 1c, 1d and 1e Magnetization curves at Room temperature of Cobalt Manganese Ferrite ($Co_{1-x}Mn_xFe_2O_4$ with x varying from 0.0, 0.2, 0.4, 0.6 0.8 and 1.0) magnetic nanoparticles

The figure shows that the coercivity and remanance decreases due to manganese substitution and saturation magnetization was found to in decrement and increment with manganese implementation in cobalt ferrite nanoparticles.

Table.2 Magnetic Properties of Manganese substituted $CoFe_2O_4$ nanoparticles ($Co_{1-x}Mn_xFe_2O_4$ with x varying from 0.0, 0.2, 0.4, 0.6 0.8 and 1.0) Magnetic nanoparticles

Samples	Magnetic Parameters		
	Hc(G)	Mr(emu)	Ms(emu)
$CoFe_2O_4$	2751	0.46992	0.87992
$Co_{0.8}Mn_{0.2}Fe_2O_4$	1579.0	0.30399	0.59942
$Co_{0.4}Mn_{0.6}Fe_2O_4$	719	0.21950	0.60989
$Co_{0.2}Mn_{0.8}Fe_2O_4$	301.5	0.22199	0.95999
$MnFe_2O_4$	75.95	0.04959	0.56982

In Table.2, it can be seen that the coercivity and remanance decreases with manganese substitution in Cobalt manganese ferrite nanoparticles of different molar ratio. The saturation magnetization reduced, increased and again reduced with manganese substitution in Cobalt ferrite nanoparticles. The variations in magnetic parameters of cobalt manganese ferrite nanoparticles was due to super exchange interaction mechanism occurring between the metal ion in the A and B sub lattices. The manganese nonmagnetic ion substitution has preferentially A site occupancy results in the reduction of the exchange interaction between A and B sites [15, 16]. Changing the amount of manganese ions implementation was possible to vary magnetic parameters of the powdered samples. The implementation of Mn^{2+} in cobalt manganese ferrite nanoparticles of different molar ratio an exchange interaction between A and B sites lowered results in strengthening of B-B interaction and weakening of A-B interaction due to which the saturation magnetization decreased [12, 16]. The results revealed that the magnetic parameters such as remanance and coercivity decreases to a minimum value [12].

3.3 SPECTRAL MEASUREMENTS

Fourier transform infrared spectra (FTIR) of cobalt manganese ferrite nanoparticles of different molar ratio was shown in Fig. 2. The results were in coincidence with previously found out ftir values [17]. The vibrational bands in range 3688-3299 cm^{-1} correspond hydroxyl groups which represents hydroxyl groups. It represents that the water is being attached to the surface of iron layer and the molecules were adsorbed to the total surface [18, 19].
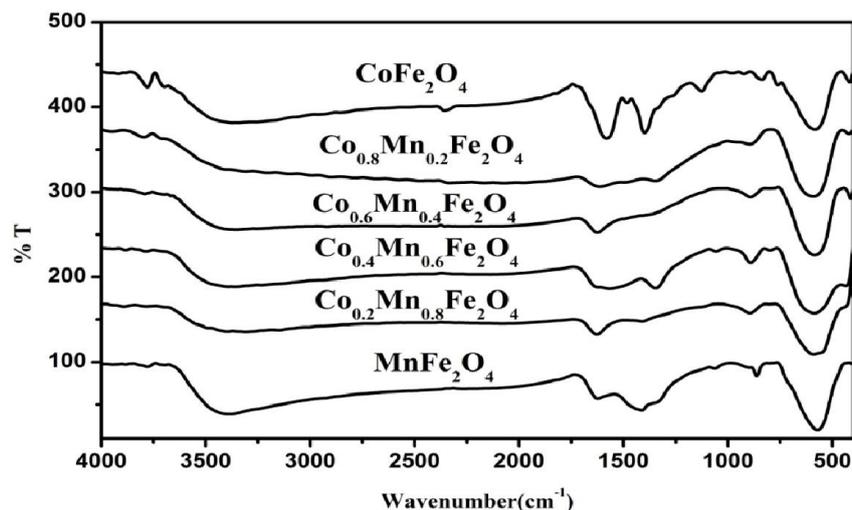
Fig.2 FTIR Spectra of Cobalt Manganese Ferrite nanoparticles

The range 1579-1619 cm^{-1}.correspond to the hydroxyl groups opted for in-plane bending vibrations [18]. The range 976-859 cm^{-1} corresponds to the out-of-plane bonds [19]. The obtained result clearly shows that the cobalt manganese ferrite nanoparticles retains the hydroxyl groups during synthesis process. The range 589-569 cm^{-1} represents the octahedral and tetrahedral structural vibrations and it confirms the existence of metal oxygen bonds in obtained nanoparticles [16][18]. The existence of tetrahedral structures was found to more than octahedral structures, it was the reason for the prevalence of short bond lengths [16]. The range in between 589-569 cm^{-1} was the evidence for the existence of metal oxygen bonds [19].

4 CONCLUSION

The co-precipitation technique for the synthesis of metal substituted magnetic nanoparticles was considered as the simplest technique and it has been confirmed. Cobalt manganese ferrite magnetic nanoparticles ($Co_{1-x}Mn_xFe_2O_4$ by varying x from 0.0 to 1.0) were synthesized and reported. Manganese substituted cobalt ferrite nanoparticles formed a cubic spinel structure which was confirmed by x ray diffraction. In xrd analysis, the lattice constant was found to increase with the increase in manganese substitution and the average crystallite size D_{avg} decreased with increase in manganese substitution. From the results of VSM, it was confirmed that the Coercivity (H_c) and Retentivity (M_r) decreases with the manganese substitution and the specific saturation magnetization (M_s) was found to be increase and decrease with manganese substitution. Hence from the above work, it was clear that the samples shows super paramagnetic behavior which was identified from the hysteresis loop. From the very small area of hysteresis loop of $MnFe_2O_4$, it was found that the sample was not to be considered as a hard magnetic material. The soft magnetic nature of $MnFe_2O_4$ possesses various usages in magnetic recording, ferromagnetic optical devices and in ferro fluid technology. The presence of –OH vibrations and Metal oxide bonds confirms the absorption of water by the surface of the samples and the Fe-O and Co-o bonds from FTIR spectra.

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