Preparation and Characterization of Cobalt Doped Mn-Zn Ferrites

M. Bhuvaneswari and S. Sendhilnathan

Abstract $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9,0.5, 0.1 and y = 0.45, 0.25, 0.05.) nanoparticles of average crystalline size of 61 nm were prepared by chemical co-precipitation method. XRD, FTIR, SEM were utilized in order to study the effect of variation in the cobalt substitution and its impact on size and associated water content. The average crystalline size (D_{aveXR}) of the particles was found to be decreased from 85 to 41 nm with the increase in cobalt concentration. Fourier transform infrared spectroscopy (FTIR) spectra of the $Co_{(1-x)}Mn_yZn_yFe_2O_4$ in the range 400–4000 cm^{-1} were reported. The spinel structure and the crystalline water adsorption of cobalt doped Mn-Zn nanoparticles were studied by using FTIR.

Keywords Ferrites • Spinel • Co-precipitation • Crystalline size

1 Introduction

Magnetic nanoparticles are of great technological importance because of their use in magnetic fluid, information storage system, medical diagnostics, and so on. Various preparation techniques have been used for the synthesis of fine particles of ferrites, which exhibit novel properties when compared to their properties in the bulk. Non-conventional methods such as co-precipitation, thermal decomposition, sol-gel and hydrothermal methods have been widely used. Ultra

M. Bhuvaneswari (✉)
Department of Physics, Mount Zion College of Engineering and Technology, Pudukkottai, India
e-mail: bhuvanjothi@gmail.com

S. Sendhilnathan
Department of Physics, Anna University of Technology,Tiruchirappalli, Pattukkottai Campus, Rajamadam, Pattukkottai, India
e-mail: sendhil29@yahoo.co.in

S. Sathiyamoorthy et al. (eds.), *Emerging Trends in Science, Engineering and Technology*, Lecture Notes in Mechanical Engineering,
DOI: 10.1007/978-81-322-1007-8_55, © Springer India 2012

fine ferrite particles can be prepared by chemical co-precipitation method. Auzans et al. [1, 2] have studied the preparation and properties of Mn-Zn ferrite nano particles, which were, used in ionic and surfacted ferrofluids with different degrees of Zn substitution prepared by co-precipitation method. Chandana Rath et al. [3] have reported the dependence on cation distribution of crystallite size, lattice parameter and magnetic properties in nano size Mn-Zn ferrite for different degrees of inversion of Zn substitution prepared by hydrothermal precipitation method.

The use of Mn-Zn ferrite for the preparation of temperature sensitive magnetic fluid by co-precipitation method has already been studied [4–6]. $Co_{0.2}Zn_{0.8}Fe_2O_4$ fine particles have been prepared by chemical co-precipitation method followed by sintering [7]. Control of crystalline size in the nanometer range by the variation of synthesis condition is always a difficult task. It becomes mandatory in the case of ferrofluid preparation using co-precipitation method. In order to prepare ferrofluid having such fine particles, specific size restriction is imposed considering the stability criteria. $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9,0.5,0.1 and y = 0.45, 0.25, 0.05.) substituted ferrites were prepared by co-precipitation method have not yet been fully studied like Mn-Zn substituted ferrites. In this paper we report preparation of $Me_{1-x}Mn_yZn_yFe_2O_4$ fine particles, where Me = Co^{2+} with x = 0.9, 0.5, 0.1. Average crystalline size 61 nm by chemical co-precipitation method and the consequent change in their lattice parameter, crystalline size and associated water content due to increase in cobalt concentration were reported.

2 Synthesis and Characterization of $Co_{(1-x)}Mn_yZn_yFe_2O_4$ of Nanoparticles

2.1 Synthesis of Cobalt Doped Mn-Zn Ferrites

The cobalt doped ferrite nanoparticles synthesized by co-precipitation depends mostly on parameters such as reaction temperature, pH of the suspension, initial molar concentration etc. [4].Ultra fine particles of $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9, 0.5, 0.1 and y = 0.45, 0.25, 0.05.) were prepared by co-precipitating aqueous solutions of $CoCl_2$, $MnCl_2$, $ZnCl_2$ and $FeCl_3$ mixtures respectively in alkaline medium. The mixed solution of $CoCl_2$, $MnCl_2$, $ZnCl_2$ and $FeCl_3$ in their respective stoichiometry (100 ml of 0.1 M $CoCl_2$, 100 ml of 0.45 M $ZnCl_2$, 100 ml of 0.45 M $MnCl_2$ and 100 ml of. 2 M $FeCl_3$ in the case of $Co_{0.1}Mn_{0.45}Zn_{0.45}Fe_2O_4$ and similarly for the other values of x) was prepared and kept at 333 K (60 °C).

This mixture was added to the boiling solution of NaOH (0.63 M dissolved in 1200 ml of distilled water) within 10 s under constant stirring. Nano ferrites are formed by conversion of metal salts into hydroxides, which take place immediately, followed by transformation of hydroxides into ferrites. The solutions were maintained at 358 K (85 °C) for 1 h. This duration was sufficient for the transformation of hydroxides into spinel ferrite (dehydration and atomic rearrangement involved in the conversion of intermediate hydroxide phase into ferrite) [4]. Sufficient amount of fine particles were collected at this stage by using magnetic separation. These particles were washed several times with distilled water followed by acetone and dried at room temperature.

2.2 XRD

The X-ray diffraction (XRD) patterns of the samples were recorded on a BRUKER-binary V2 (.RAW) powder diffractometer using Cu $K_{\alpha}(\lambda = 1.54060\ A°)$ radiation. Slow scans of the selected diffraction peaks were carried out in step mode (step size 0.02°, measurement time 5 s, measurement temperature 323 K (25 °C), standard: Si powder). The crystalline size of the nanocrystalline samples was measured using Debye- Scherrer formula,

$$D_{XRD} = \frac{0.89\lambda}{\beta\cos\theta}. \quad (1)$$

2.3 FTIR

FTIR spectra were recorded for the dried samples of $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9, 0.5, 0.1 and y = 0.45, 0.25, 0.05.) with **Nexus 670** (range 400–4000 cm^{-1}) spectrometer. The dried samples were mixed with KBr and spectra were measured according to transmittance method.

3 Results and Discussions

Generally, XRD can be used to characterize the crystallinity of nanoparticles, and it gives average diameters of all the nanoparticles. The precipitated fine particles were characterized by XRD for structural determination and estimation of crystallite size. XRD patterns were analyzed and indexed using JCPDS. All experimental peaks were matched with (JCPDS #653111) the theoretically generated one and indexed. Analysis of the diffraction pattern using powder-X software [8] confirms the formation of cubic spinel structure for all the samples. All the compositions had a spinel structure. The XRD pattern for $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9, 0.5, 0.1 and y = 0.45, 0.25, 0.05.) shown Fig. 1.

The broad XRD lines indicate that the particles are of nanosize range. The particle size was found to decrease from 85 to 41 nm with the increase in cobalt concentration. The crystallite size (D_{XRD}) was estimated by the Debye-Scherrer formula [9] using the full width at half maximum value of the respective indexed peaks. Though all the samples were prepared under identical condition, the

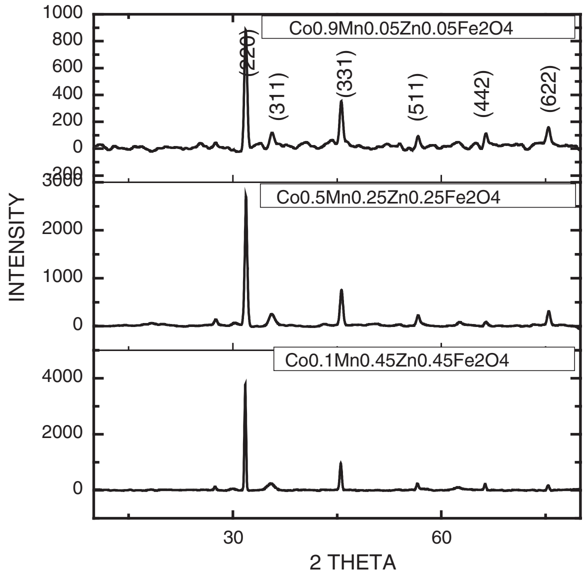


Fig. 1 X-ray diffraction pattern for Co_{1-x} Mn_y Zn_y Fe_2O_4 with x = 0.9, 0.5, 0.1 and y = 0.45, 0.25, 0.05

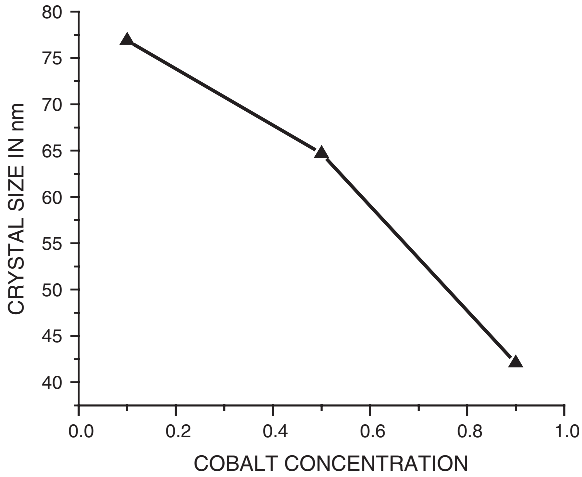
Table 1 The average crystalline size (D_{aveXR}) for $Co_{(1-x)}Mn_yZn_yFe_2O_4$

Composition	2θ	FWHM	SIZE 'D' nm	Ave. SIZE nm
$Co_{0.1}Mn_{0.45}Zn_{0.45}Fe_2O_4$	31.7	0.09	85.19	76.90
	45.5	0.12	71.08	
	56.5	0.12	74.43	
$Co_{0.5}Mn_{0.25}Zn_{0.25}Fe_2O_4$	31.9	0.14	56.81	64.69
	45.6	0.11	74.60	
	56.6	0.14	62.05	
$Co_{0.9}Mn_{0.05}Zn_{0.05}Fe_2O_4$	31.9	0.19	41.57	42.07
	45.6	0.19	43.36	
	56.6	0.21	41.27	
				61.15

crystallite size was not the same for all concentrations (Table 1). This was probably due to the preparation condition followed here, which gave rise to different rate of ferrite formation for different concentrations of cobalt, favoring the variation of crystalline size.

The variation of average crystalline size with the cobalt concentration is given in Fig. 2. Ferrofluids can be conveniently prepared by making use of particles in this size range. The average crystallite size (D_{aveXR}) for $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9,0.5,0.1 and y = 0.45,0.25,0.05.) is shown in Table 1. The particle size was confirmed by SEM data (Fig. 3).

Fig. 2 Cobalt concentration versus particle size



3.1 SEM

3.2 FTIR

From the FTIR spectra for Fe_3O_4 and for $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9,0.5,0.1 and y = 0.45, 0.25, 0.05.), the spectral similarities were observed. The main transmittance frequencies observed in the region 400–4000 cm^{-1} of the FTIR spectra for $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9, 0.5, 0.1 and y = 0.45, 0.25, 0.05.) are summarized in Table 2.

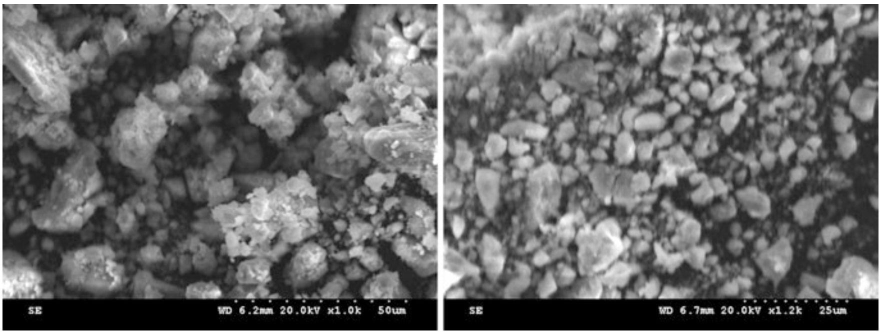


Fig. 3 SEM images of cobalt doped ferrites

Table 2 The transmittance frequencies for $Co_{(1-x)}Mn_yZn_yFe_2O_4$

	IR absorption bands cm^{-1}			
Sample	ν_1	ν_2	ν_3	ν_4
$Co_{0.1}Mn_{0.45}Zn_{0.45}Fe_2O_4$	3460.66	1640.02	988.21	584.74
$Co_{0.5}Mn_{0.25}Zn_{0.25}Fe_2O_4$	3492.59	1646.12	987.29	584.03
$Co_{0.9}Mn_{0.05}Zn_{0.05}Fe_2O_4$	3031.56	1509.94	986.49	583.66

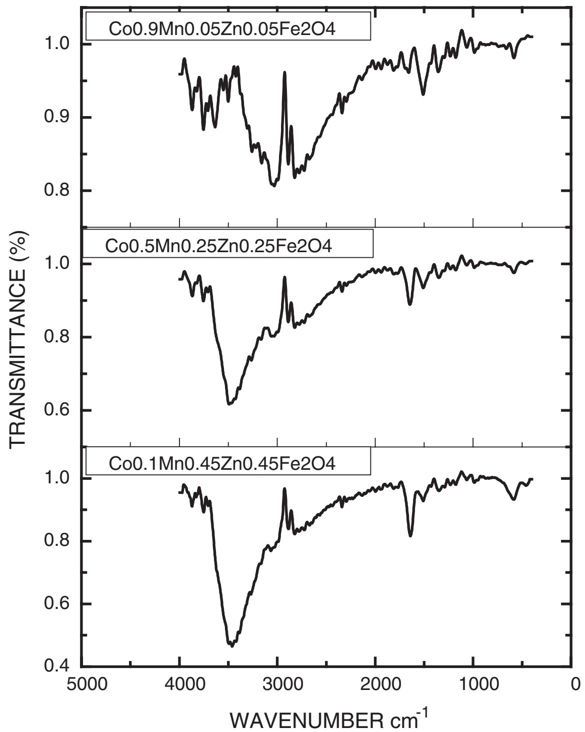


Fig. 4 FTIR spectra for $Co_{(1-x)}Mn_yZn_yFe_2O_4$ ($x = 0.9, 0.5, 0.1$ and $y = 0.45, 0.25, 0.05$)

The broad feature between 3460.66 and 3031.56 cm^{-1} is due to O–H stretch (ν_1), which corresponds to the hydroxyl groups attached by the hydrogen bonds to the iron oxide surface and the water molecules chemically adsorbed to the magnetic particle surface (associated water content) [8]. From these results, it appears that the hydroxyl groups are retained in the samples during the preparation of the uncoated $Co_{(1-x)}Mn_yZn_yFe_2O_4$. Ghose et al. [7] have reported that the presence of some hydroxyl ions are completely removed when the sample is sintered at temperatures ≥973 K. The O–H in-plane (ν_2) and out-of-plane (ν_3) bonds appear at 1640.02–1509.94 cm^{-1} and 988.21–986.49 cm^1, respectively. The spectrum of the uncoated sample $Co_{(1-x)}Mn_yZn_yFe_2O_4$ shows a strong band at ν_4 (635.57–573.51 cm^{-1}) due to Fe_3O_4 [10]. The transmittance waveband at ν_4 (584.74–583.66 cm^{-1}), which corresponds to the metal-oxygen bonds are considered as the confirmation for the ferrite formation. This is in good agreement with Zins et al. [1, 11–14] (Fig. 4).

4 Conclusion

The preparation technique of nano particles has a definite impact on the control of particle size and alteration of magnetic properties. The estimated cations from the product are in comparison with the initial substitution degree, indicating that the preparation procedure favors the formation of only ferrites. The formation of $Co_{(1-x)}Mn_yZn_yFe_2O_4$ (x = 0.9, 0.5, 0.1 and y = 0.45, 0.25, 0.05.) was confirmed by the X-ray diffraction. The average crystallite size (D_{aveXR}) decreased when the partial substitution of cobalt increased. The Cobalt doped Mn-Zn ferrite particles can be used to prepare ferro fluids with higher magnetization. FTIR was used to confirm the formation of Fe–O bonds and presence of the associated water content in the samples.

Acknowledgments One of the authors Dr. S. Sendhilnathan gratefully acknowledges DST (Ref No.SR/FTP/PS -59/2008) for the financial assistance received through the project.

References

1. Auzans E, Zins D, Blums E, Massart R (1999) Synthesis and properties of Mn-Zn Ferrite ferrofluids. J Mater Sci 34:1253
2. Auzans E, Zins D, Blums E, Massart R (1999) Magn. Gidrodinamika, Mn-Zn nanoparticles for ferrofluid preparation, Science direct 36:78
3. Chandana Rath S, Anand RP, Das KK, Sahu SD, Kulkarni SD, Date SK, Mishra NC (2002) Dependence on cation distribution of particle size, lattice parameter and magnetic properties in nanosized Mn-Zn ferrite. J Appl Phys 91(4):2211
4. Jeyadevan B, Chinnasamy CN, Shinoda K, Tohji K (2003) Mn-Zn ferrite with magnetization for temperature sensitivity magnetic fluid. J Appl Phys 93(10):8450
5. Parekh K, Upadhyay RV, Mehta RV (2000) Electron spin resonance study of temperature sensitive magnetic fluid. J Appl Phys 88(5):2799
6. Upadhyay T, Upadhyay RV, Mehta RV (1997) Characterization of a temperature sensitive magnetic fluid. Phys Rev B 55(9):5585
7. Dey S, Ghose J (2003) Synthesis, characterization and magnetic studies on nanocrystalline $Co_{0.2}Zn_{0.8}Fe2_{o4}$. Mater Res Bull 38:1653
8. Creanga D, Calugaru Gh (2005) Physical investigations of a ferro fluid based on hydrocarbons. J Magn Magn Mater 289:81
9. Dong C (1999) PowderX: Windows -95 based program for powder X-ray diffraction data processing. J Appl Crystallogr 32:838
10. Ahn Y, Choi EJ, Kim EH (2003) Superparamagnetic relaxation in cobalt ferrite nanoparticles synthesized from hydroxide carbonate precursors. Rev Adv Mater Sci 5:477
11. Ma M, Zhang Y, Yu W, Shen H-Y, Zhang H-Q, Gu N (2003) Preparation and characterization of magnetic nano particles coated by aminosilane. J Colloid and Surface A: Physicochem Eng Aspects 212:219
12. Ahmed SR, Kofinas P (2005) Magnetic properties and morphologyof block co-polymer-cobalt oxide nanoparticles. J Magn Magn Mater 288:219
13. Ishikawa T, Nakazaki H, Yasukawa A, Kandori K, Seto M (1999) Influences of Co2 +, Cu2 + and Cr3 + ions on the formation of magnetite. Corros Sci 41:1665
14. Wu N, Fu L, Su M, Aslam M, Wong KC, Dravid VP (2004) Interaction of fatty acid monolayers with cobalt nanoparticles. Nano Letters 4:383