

Low Temperature Synthesis of Zn Doped Cobalt Ferrite Nanoparticles

Swati Tapdiya¹, A.K.Shrivastava²Research Scholar, School of Studies in Physics, Jiwaji University, Gwalior, M.P., India¹Professor, School of Studies in Physics, Jiwaji University, Gwalior, M.P., India²

ABSTRACT: Zinc substituted cobalt ferrite nanoparticles ($\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, with $x = 0.0, 0.1, 0.2$ and 0.3) were prepared via chemical co precipitation method. The effect of zinc concentration on saturation magnetization and lattice parameter were investigated. The particle sizes of the as obtained samples were found to be 22 to 38 nm. The frequency bands near 598 cm^{-1} and 421 cm^{-1} are assigned to the tetrahedral and octahedral clusters which confirm the presence of M-O stretching band in ferrites. The unit cell parameter 'a' increases linearly with increasing concentration of zinc due to larger ionic radii of Zn^{2+} ion. It was found that this substitution allows tunable changes in the magnetic properties of cobalt ferrite. Saturation magnetization increases as Zn substitution, thus tunable changes in magnetic properties of cobalt ferrite are possible. Source of such behavior could be the variation of exchange interaction between the tetrahedral and the octahedral sites.

KEYWORDS: Nano Particles, Saturation Magnetization, Coercivity, X-Ray Diffraction.

I. INTRODUCTION

Nanocrystalline ferrite materials are currently the subject of great interest because of its wide application in fundamental and applied research due to their thermal stability, mechanical hardness, large coercive field, high magnetostriction coefficient and anisotropy constant. They are attractive because of their wide range of applications from medicine (e.g. MRI contrast agents, DNA isolation, magnetically activated drug delivery) to electronics (e.g.: magnetostrictive and gas sensors, optoelectronics, microwave frequency devices, storage media) [1]. An interesting example is that of CoFe_2O_4 which has got some peculiar properties like high saturation magnetization (Ms), high coercivity (Hc) and large anisotropy [2]. Further the substitution of Co^{2+} in this ferrite with Zn^{2+} , Ni^{2+} and Mn^{2+} allows some tunable changes in its properties. CoFe_2O_4 has inverse spinel structure with Co^{2+} ions in octahedral sites and Fe^{3+} ions equally distributed between tetrahedral and octahedral sites whereas ZnFe_2O_4 has a normal spinel structure with Zn^{2+} ions in tetrahedral and Fe^{3+} in octahedral sites [3]. Therefore, Zn-substitution in CoFe_2O_4 may have some distorted spinel structures depending upon the concentration of the precursor solutions.

Arulmurugan et al. [4] suggested that substitution of Co^{2+} with Zn^{2+} lead to improved magnetic properties of nanocrystalline ferrites. They also observed a decreasing behaviour of saturation magnetization and the particle size of the Co-Zn substituted ferrite nanoparticles with increasing Zn concentration. Dey and Ghose[5] prepared $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ by co-precipitation method and found decrease in magnetization with increasing particle size. Anshu et al. [6] reported that saturation magnetization decreases with zinc concentration in cobalt zinc ferrites prepared by metallo-organic Decomposition technique. Hassadee et.al [7] reported decrease in the magnetization and the coercivity of Co-Zn ferrite with increasing zinc content due to the magnetic behavior and the anisotropic nature of cobalt Gul et.al [8] investigated magnetic and electrical properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ varying x from (0.0 to 0.6). A decrease in Curie temperature with an increasing Zinc doping concentration was observed. Temperature dependent dc resistivity measurements indicated semiconductor nature in Co-Zn ferrites. Veverka et.al [9] studied $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ around $x=0.6$ because of potential applications of the composition in the magnetic fluid hyperthermia. They reported that the cationic distribution in ferrite is more complex and the distribution is random in nature.

The present work deals with the synthesis of nano particles of zinc substituted cobalt ferrite ($\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, with $x = 0.1, 0.2$ and 0.3) via chemical co precipitation method and characterized using infrared spectroscopy (FTIR), X-ray

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diffractometer (XRD) and magnetic measurements (VSM). This work is an attempt to investigate the magnetic properties of zinc substituted cobalt ferrites.

II. SYNTHESIS AND CHARACTERIZATION

Experimental

The $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (with $x = 0.1, 0.2$ and 0.3) sample was synthesized using Cobalt Nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Zn Nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and Ferric Nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] as precursors, by dissolving them in distill water in the required mole proportion. The clear solution was co-precipitated with a 1 molar NaOH solution using magnetic stirrer, pH of the solutions maintained at 10-11. The solution thus obtained kept at CBD apparatus 3 hours at $80\text{-}90^\circ\text{C}$. Samples at this stage are referred 'as prepared'. The precipitate was filtered and then washed several times with distilled water until the pH of the filtered water became 7 (i.e., neutral). The filtrate was then dried at 100°C overnight. All the samples further annealed at 900°C .

Physical Measurements

Zinc doped Cobalt ferrite $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.1, 0.2, 0.3$) samples were subjected to XRD analysis with Bruker D8 Advance X-ray diffraction unit (Cu- $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$)) to explore the structural properties. The scanning electron microscope was used to examine the particle morphology using a LEO 435 VP scanning electron microscope (SEM) along with the energy dispersive X-ray analysis (EDX). The magnetic properties of the samples were investigated using vibrating sample magnetometer (VSM) Lakeshore VSM 7410. To confirm presence of functional group FTIR has been done.

III. EXPERIMENTAL RESULTS

The XRD patterns of samples prepared is given in Fig.1 confirms the formation of single phase cubic spinel structure with no other impurity seen. The result reveals a cubic structure, as the diffraction peaks compared with the JCPDS file (JCPDS card No. 89-4836). The peaks could be indexed as (220), (311), (400), (422), (511) and (440), which are characteristics of a cubic spinel structure. The intensity of the main diffraction peak at the plane (311) was considered as a measure of its degree of crystallinity. The average crystallite size (D) of all the samples was calculated by using the Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

D found to be in the range 22-38 nm. The lattice constant "a" obeys Vegard's law, indicating thereby its increasing trend with Zn content. The lattice constant increases from 8.36 \AA to 8.40 \AA with increasing x. This suggests the strong occupancy of Zn^{2+} ion on tetrahedral (A) site and Co^{2+} ion on the octahedral (B) site [10]. The X-ray density of all prepared nanoparticles was calculated using the relation:

$$d_x = \frac{8M}{Na^3}$$

Where M is molecular weight, N the Avogadro number and 'a' is the lattice parameter. As density is inversely proportional to the lattice constant; it decreases as the lattice constant increases Zn substitution.

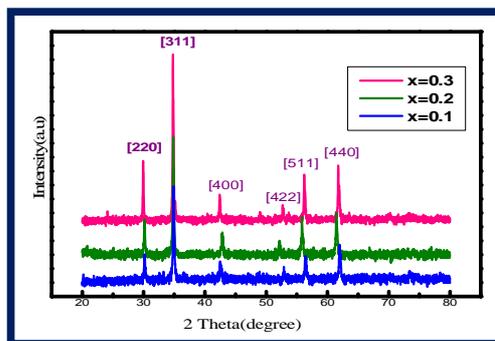


Fig. 1 XRD spectra of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (for $x=0.1, 0.2, 0.3$) nano particles annealed at 900°C

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Typical magnetic hysteresis loops for $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites where $x = 0.1, 0.2$ and 0.3 are shown in Fig. 2. It is clear that the saturation magnetization (M_s) increases with increasing Zn content. The increase in saturation magnetization may be due to the substitution of nonmagnetic Zn ion (d^{10}) for Co into the magnetic ferrite lattice. Zn^{2+} has a stronger preference for the tetrahedral site (A site), while Co^{2+} ions (for which Zn is substituted) are located on octahedral site (B site) of AB_2O_4 spinel ferrite. Thus, Zn displaces Fe^{3+} from A to B site. As the magnetic spin of neighboring A and B sites are antiferromagnetically coupled (due to the super exchange interaction in ferrite lattice), the net result is an increase in magnetic moment on B sub-lattice, as well as the increase of the net magnetic moment of the crystal [11], while the value of H_c decreases with increasing Zn-content. According to the Stoner-Wohlfarth theory, the coercivity (H_c) of a single domain particle is $H_c = 2K/M_s$, where K is the magneto crystalline anisotropy constant and M_s is the saturation magnetization of the particles. The increase of Zn content results in complete crystallization, hence the value of K decreases, while M_s increases with increasing the particle size. Variation of lattice parameter and saturation magnetization with increasing Zn content is shown in Fig.3.

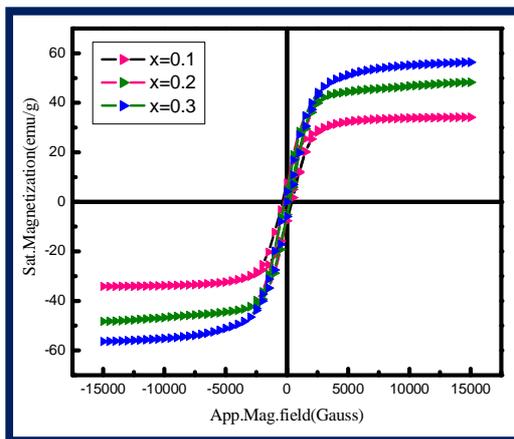


Fig. 2 The magnetic hysteresis curves of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite systems annealed at 900°C

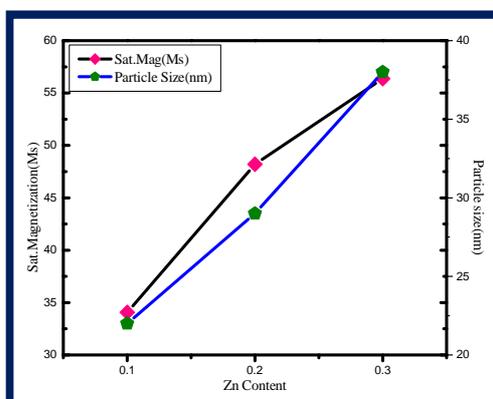


Fig. 3 Variation of saturation mag.(M_s) and particle size of Zn doped cobalt ferrite nanoparticles with increasing Zn content

Fourier transform infrared spectra (FT-IR) were recorded in the range 4000 to 400 cm^{-1} . The FT-IR spectra for the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $x = 0.10; 0.20;$ and $0.30;$ annealed at 1173K are shown in Fig. 4. (A) and [B] spinel structure of the samples is confirmed from the band in the region $400\text{-}600\text{ cm}^{-1}$. Stretching and bending of bonds at tetrahedral and octahedral sites are noticed. The broad peak observed at $\sim 3144\text{ cm}^{-1}$ is attributed to the stretching vibration of surface

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Vol. 5, Issue 5, May 2016

hydroxyls absorbed on surface and O–H groups in absorbed water, which indicates the adsorbed moisture. The peaks at $\sim 1383\text{ cm}^{-1}$ are assigned to H–O–H bending vibration in water molecular or OH deformation vibration due to surface hydroxyls [12].

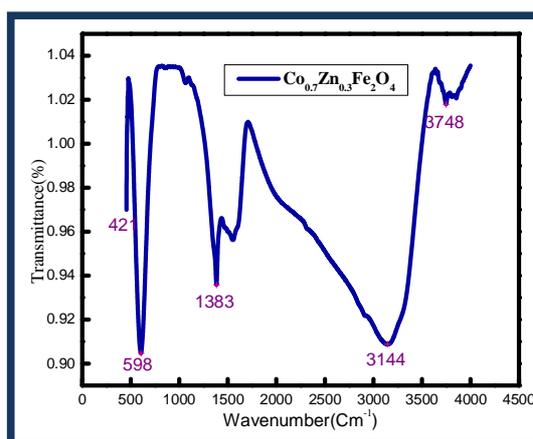


Fig. 4 FT-IR spectra of $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ nano particles

IV. CONCLUSION

Low temperature synthesis of zinc doped cobalt ferrite nanoparticles ($\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for $x=0.1,0.2,0.3$) have been using chemical co precipitation method. To confirm cubic structure XRD have been done which confirms the samples are cubic with increasing particles size with Zn content. FT-IR confirms the presence of tetrahedral and octahedral stretching and bending modes of ferrite. Hysteresis analysis shows the variation of magnetic parameter with increasing Zn content.

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