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Effect of Synthesis Techniques on the Structural Properties of Cobalt doped Zinc Nano-Ferrites

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***Abstract*:- Cobalt doped Zinc ($Co_xZn_{1-x}Fe_2O_4$) nano ferrites for x=0, 0.1, 0.4 has been synthesized both by Microwave hydrothermal and Chemical co-precipitation techniques to witness the effect of two different synthesis techniques on the structural properties of cobalt doped zinc nano-ferrites. All the samples with hydrothermal method were calcined at 700^{0}C for 4 hours with the application of 2.54GHz microwaves for 10 minutes whereas; samples with chemical co-precipitation method were annealed at 700°C for 6 hours. The geometry of the crystals was studied by X-Ray Diffraction analysis (XRD) and the structural properties including particle size and lattice parameter were calculated from XRD data. The average crystallite size was calculated using Debye-Scherer formula which lies in the range of 5.41nm to 3.25nm by hydrothermal technique and 6.23nm to 5.58nm by co-precipitation method. Lattice parameter of the samples sintered by both hydrothermal and co-precipitate methods are first increases from x=0 to x=0.1 and then a decreasing trend is observed with increased concentration of the cobalt due to the transfer of Co^{2+} ions from octahedral to tetrahedral sites. The morphological study has been carried out using Scanning electron microscopy (SEM) to investigate the effect of Co dopant on the structural properties of $ZnFe_2O_4$ nanoparticles using both the techniques.**

Key words: Microwave Hydrothermal, Chemical Co-precipitate method, Structural study, Cobalt Zinc Ferrites

I. INTRODUCTION

Nano technology is introduced for the reduced size and single phase particle, helping to design the efficient devices at higher frequency and low cost. The Nano ferrites synthesis sturdily depends upon preparation technique because incongruous technique strongly affects the crystal structure, physical and chemical properties and even the applications [1]. For a long time, researchers have been searching for a material synthesis method with easy procedures,
outstanding performance, and low cost [2–3]. The synthesis methods of inorganic powder materials includes many methods [4], in which the solid phase method results in a high yield and is easy to realize for large-scale industrial production. However, because of the limitations of the equipment and the process itself, it is difficult to control the particle size, purity, and morphology of powder using the solid phase method [5]. The liquid phase method mainly includes the precipitation [6], hydrothermal [7], and sol-gel methods [8]. The advantages of the liquid phase method are convenient operation, simple synthesis process, and controllable particle size. Cobalt Zinc ferrites have attracted the attention of the researchers because of their first-class chemical stability, mechanical consistency, high electromagnetic properties. These properties of ferrites made them to be used in the electronic devices [9, 10].
In this paper a comparative study is carried out to monitor the effect of two different synthesis techniques on the structural properties of cobalt doped zinc nano-ferrites. For this purpose Microwave hydrothermal and chemical co-precipitation techniques are considered due to their high purity, small and homogeneous nano particle size, energy saving, minimal heat exposure of the reactants, low temperature and low cost synthesis techniques, range and short time sample preparation.

II. EXPERIMENTAL TECHNIQUES

Ferrite nanoparticles $Co_xZn_{1-x}Fe_2O_4$ (x= 0, 0.1, 0.4) were prepared by chemical co-precipitation and hydrothermal process respectively. In order to attain the desired compositions, stoichiometric amount of $Fe(NO_3)_3$. $9H_2O$, $Zn(NO_3)_2$.$6H_2O$ and $Co(NO_3)_2$ ·$6H_2O$ were dissolved in distilled water with constant stirring. Neutralization was carried out with NaOH solution by adding it drop wise to obtain light brown precipitates. 2.45 GHz microwaves were employed for 10 minutes in case of hydrothermal method and mixture was cooled and transformed into the flask for autoclave at 121^{0}C for 1hour. Whereas, the reaction temperature was kept at 90^{o}C in co-precipitate method until the precipitates settled down. Using both techniques the PH was maintained and samples were centrifuged at 3600rpm for 5 minutes, were dried at 200^{0}C for dehydration. The dried powder was mixed consistently with an uncontaminated agate mortar and pestle and annealing was done at 700^{o}C for 6 h. The samples were allowed to cool slowly at room temperature for fine grinding.

III. RESULTS AND DISCUSSIONS

X-ray diffraction technique is used for the structural analysis of all the acquired samples using CuKα radiations with wavelength λ=1.5418Å. The 2θ range was adjusted between 20^o to 100^o with the step size of 0.05^o.
The X-Ray Diffraction pattern of the prepared samples are shown in the Fig. 1(a) and Fig. 1 (b) for x=0, 0.1, 0.4, for hydrothermal and co-precipitate methods respectively. The figures showed a sharp peak pattern with no extra reflection peaks in the diffraction pattern which confirms the structure of the synthesized material. The persistence of major lattice planes in the given XRD pattern confirms the configuration of the crystals with spinel cubic structure having space group Fd-3m. The peaks were indexed with JCPDS Cards (#22-1086) and (#89-1012) and COD (Card

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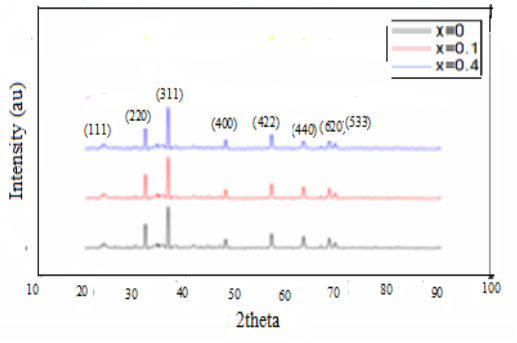
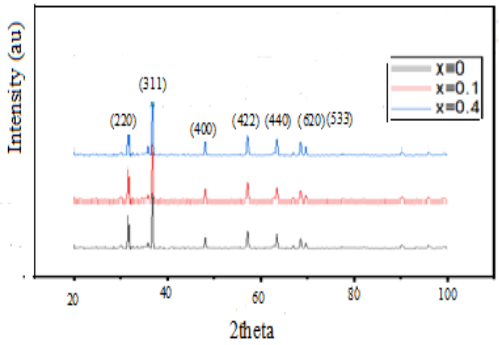
no. 9006894). The prominent peak of the sample shifts towards the higher theta values due to the difference in the radii of the Cobalt (0.78Aº) and Zinc (0.82Aº) ions [11].



(a) Hydrothermal Method



(b) Co-precipitate Method

Fig. 1: X-Ray Diffraction pattern of $Co_xZn_{1-x}Fe_2O_4$ at x=0, 0.1, 0.4

A. Variation of Particle size with Composition

In XRD spectrum width of the highest peak (311) is used to calculate average particle size by using Scherer's formula [10];

$$D=0.9/\beta\cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ (i)}$$

The particle size of the samples with increase in concentration of Co doping from x=0 to 0.4 in $Co_xZn_{1-x}Fe_2O_4$ obtained both by hydrothermal and co precipitate methods. The particle size varies between 3.25 nm to 5.41nm acquire by hydrothermal technique whereas, particle size for the same composition of Co doping using co-precipitate method lies in the range of 6.23nm to 5.58nm as shown in Fig2 and mentioned in Table1.

Table 1: Comparative Analysis of Hydrothermal and Co-precipitates method

Con x	Hydrothermal Method				Co precipitation Method			
	Peak Position 2θ degrees)	d-spacing (Å)	Lattice parameter (Å)	Crystal size (nm)	Peak Position 2θ (degree)	d-spacing (Å)	Lattice parameter (Å)	Crystal size (nm)
0	36.38	2.467	8.182	4.49	36.4	2.465	8.176	5.58
0.1	36.36	2.467	8.185	5.41	36.04	2.489	8.255	6.23
0.4	36.24	2.455	8.157	3.25	36.38	2.466	8.180	6.06

In both the cases, crystalline size first increases at x = 0.1 because the distribution of dopant changes with increasing concentration of Co till it reached to equilibrium and then for further increase in Co concentrations it decreases, as the distribution of dopant becomes regular at higher values and cobalt ions (0.78Å) replaced with zinc ions (0.82Å). Moreover, the reduced and precise particle size by hydrothermal method is obtained by changing the controlling parameters such as applying the microwaves for 10 minutes instead of reported in literature [7, 11] and for co-precipitate method is due to sintering temperature and time of sintering [6].

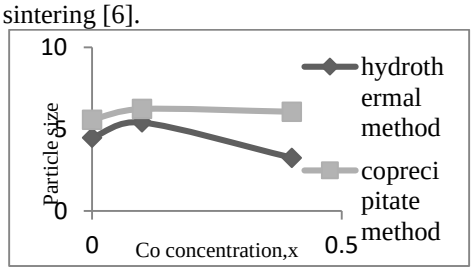


Fig. 2: Variation of particle size with composition

B. Variation of Composition with Lattice parameter

Lattice parameter, is calculated by using the formula;

$$a= d\sqrt{h^2+k^2+l^2} \quad \ldots\ldots\ldots\ldots \text{ (ii)}$$

The dependence of the lattice parameter "a" on the cobalt concentration is shown in Fig.3 for hydrothermal and co-precipitate methods respectively, which shows a mixed behavior with the increase in cobalt content in the prepared nano-ferrites due to disorder in crystal because of the large ionic radius of Co^{2+} (0.78Aº) compared to that of Fe^{3+} (0.645 A^0) and ionic radius of Zn^{2+} (0.82Aº) than that of Co^{2+} (0.78Aº) [12].

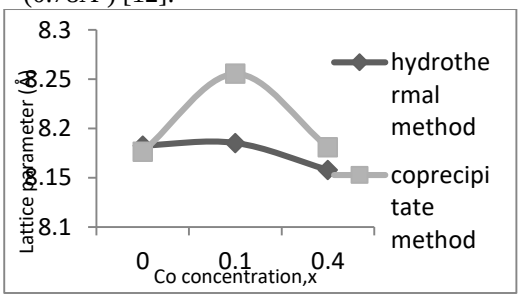


Fig. 3: Variation of lattice parameter with composition

C. Variation of d-spacing with the Composition

The variation of the cobalt content with the inter-planer distance (d-spacing) is mentioned in Table 1. It is clear from the data that first d-spacing increases from x=0 to x=1 and then decreases by further increase in Co concentration, both by hydrothermal and co-precipitate methods which is attributed with the lattice strain produced by the cobalt ions.

From the XRD results, it is being proved that the prepared nano-ferrites of cobalt doped zinc ferrites have mixed spinel structure which means that octahedral sites would be accommodated by $Co^{2+}$and Fe^{3+} and the tetrahedral sites by Zn^{2+}. When Zn ions get substituted at tetrahedral site with that of Fe^{3+} the Fe^{3+}moves on the octahedral site and get attached with Co ions [11, 12]. The replacement of the cobalt ions with zinc ions reduces the ionic radii which causes a decrease in the d-spacing.

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D. Scanning Electron Microscopy (SEM) Studies

Surface morphology of the synthesized nano-particles obtained by both the methods has been identified by using Scanning Electron Microscope (SEM). It is evident from SEM micrographs, as shown in Fig. 4 that the grains present in the samples by hydrothermal method are more evenly distributed with few voids and pores due to release of large number of gaseous products [13] whereas, the nano-particles prepared by co-precipitate method are agglomerated and less uniform.

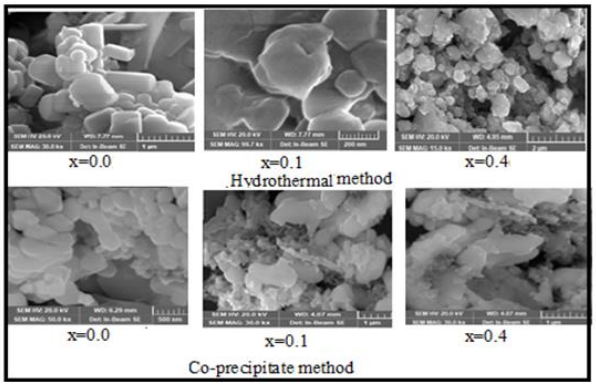

Fig.5 SEM Micrograph for x= 0.0, 0.1, 0.4

IV. CONCLUSIONS

Cobalt doped Zinc nano-ferrites ($Co_xZn_{1-x}Fe_2O_4$) were synthesized by using both microwave hydrothermal and chemical co-precipitation methods to observe the influence of two different synthesis techniques on the structural properties of Cobalt doped Zinc nano-ferrites using the precursors such as nitrates of cobalt, zinc and iron with 99.9% purity.

The formation of spinel structure was confirmed by X-ray diffraction analysis with 2θ ranging from 20^0 to 100^0. The average crystallite size was calculated by Debye-Scherer formula indicate that the size of the particles are sensitive to the method of preparation which lies in the range of 5.41nm to 3.25nm and 6.23nm to 5.58nm by hydrothermal and co-precipitation methods respectively. The lattice parameter and d spacing of the samples sintered by both the techniques shows mixed behavior due to the replacement of ions and lattice strain produced by the cobalt ions. The SEM images show that Co doped zinc nano particles are in agreement with XRD results.

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