



## CONVENIENT SYNTHESIS OF NI-ZN FERRITES FROM METAL CHLORIDES

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### Abstract

Due to unique magnetic, electrical and optical properties nanocrystalline materials are getting more technological importance day by day. In recent years, Ni-Zn ferrite nano composites have gained much interest due to applications in magnetic resonance imaging, high density magnetic recording and ferrofluids technology. Ni-Zn ferrite nanoparticles were made by chemical co-precipitation technique. Aqueous solutions of metal chlorides were coprecipitated with sodium hydroxide (NaOH) by using different concentrations of Ni and Zn. The NaOH solution was added very slowly to attain 12 pH value and the dark brown precipitates. These precipitates were kept in a pre-heated water bath at 85 °C for about 90 min. The precipitates were washed several times till neutral pH and dried at 75°C for 4h. The dried samples were ground to fine powder and calcined at 700°C for 2h. X-ray diffraction (XRD) technique was applied to characterize the nanoparticles. The determination of the particle size was done using Scherrer's formula which ranged from 22.67 to 26.29 nm. The co-precipitation method proved to be economical and convenient way to prepare Ni-Zn ferrite nano particles.

**Keywords:** Co-Precipitation; Metal Chlorides; Ni-Zn ferrite; X-ray Diffraction

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## 1. Introduction

Nanocrystalline Ni-Zn ferrites have gained much interest due to high electrical resistivity and high permeability in RF frequency region hence widely used as high frequency ferrites [1].

Ni-Zn ferrites possess properties like low coercivity, high saturation magnetization, low dielectric losses, mechanical hardness and chemical stability [2], therefore suitable for various high frequency usages in transformer cores, inductor coils, microwave absorbers and antennas etc [3]. Spinel Ni-Zn ferrites have been developed into a wide range of applications in magnetic resonance imaging, high density magnetic recording, biochemical drug delivery and ferrofluids technology [4,5]. Ferrites are usually synthesized by conventional ceramic method [6], however, this method is not much suitable to fabricate nanocrystalline ferrites because chemical inhomogeneity occurs which results in coarsening of grains [7]. Several wet chemical method had been developed for ferrite synthesis like co-precipitation [4,5], sol-gel [8], hydrothermal [9] and combustion method [10] etc. Chemical co-precipitation appears more convenient for the fabrication of nano powders due to its homogeneity and better control over particle size and as well as other properties of the materials with nano scale microstructure [11]. In the present work nanocrystalline  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  (where  $x = 0.15, 0.3, 0.45, 0.6, 0.75$  and  $0.9$ ) were prepared using co-precipitation method and the effect of different chemical composition on the crystallinity of final product have been investigated.

## 2. Materials and Methods

The materials used were  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Merck),  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  (Merck),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Merck) and NaOH (Merck). The chemicals were purchased from market and were used as such. Appropriate amounts of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 50 ml of distilled water. NaOH solution was prepared in 100 ml. The three solutions were mixed thoroughly and stirred for 30 min at room temperature and NaOH solution was started to add drop wise in the mixture solution with constant stirring. This process was completed in 90 min for each sample. There were six samples labeled as S1, S2, S3, S4, S5 and S6 listed in table 1

**Table 1:** Quantities of Chemicals used for sample preparation.

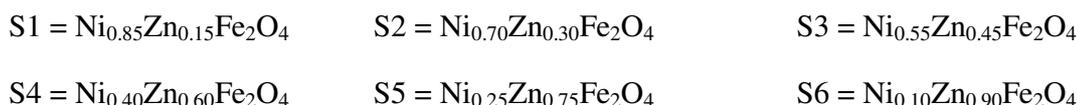
Sample No.	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (g/50ml)	$\text{Zn/Cl}_2$ (g/50ml)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (g/50ml)	NaOH (g/100ml)
S1	1.011	0.103	2.70	4.0
S2	0.833	0.205	2.70	4.0
S3	0.654	0.308	2.70	4.0
S4	0.476	0.411	2.70	4.0
S5	0.297	0.513	2.70	4.0
S6	0.119	0.616	2.70	4.0

After completion of co-precipitation the resulting mixture containing dark brown precipitates was kept in a pre heated water bath at 85 °C for about 90 min to digest and cooled to room temperature. The precipitates were filtered, washed to pH 7.0 and dried in an oven at 75 °C for 4h. The dried samples were grounded to fine powder in a pastel and mortar. The pestle and mortar was washed with acetone before each grinding[12]. The powdered samples were subjected to sintering at 700 ° C for 2 h in a muffle furnace.

The samples were subjected to XRD analysis with X-ray diffractometer (Rig. a Ku Rotaflex D/max) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was used with a glass sample holder having a cavity (10x10x1 mm<sup>3</sup>). The diffractometer was controlled with data scan software and scan parameters were set as step size 0.05, scan rate 1.2 degree per minute and  $2\theta$  range is (10 - 90°). XRD patterns are given in figure 1. The magnetization of particles was tested with the help of permanent magnet.

### 3. Results and Discussion

Nanoparticles of NiZnFe<sub>2</sub>O<sub>4</sub> were made by chemical co-precipitation. NaOH was used as precipitating agent. All the samples subjected to sintering at 700°C for about 2 hours. The detail of the samples is as under ;



The XRD results were compared with standard patterns and it can be seen from the figure 1. that typical crystal structure was obtained after calcination at 700°C for 2 h for all the samples.

The peaks present in XRD pattern were matched with JCPDS cards (00-008-0234, 00-052-0277,

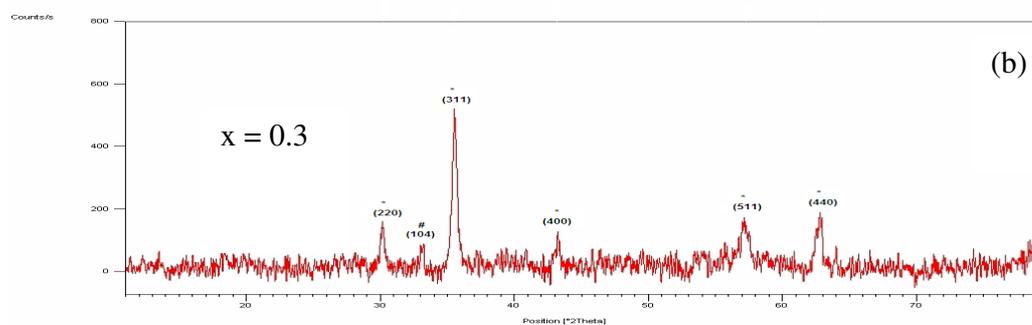
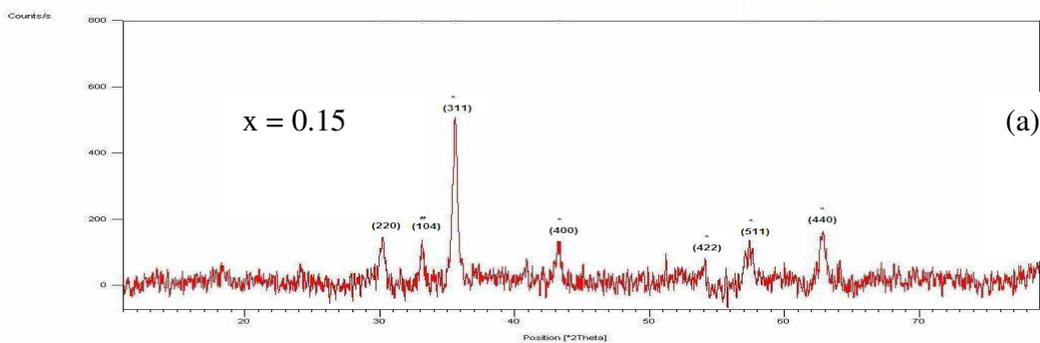
00-052-0278). It was observed in Fig. 1(a-f) that the peaks present at the  $2\theta$  angle of (30.1845°), (35.5873°), (43.2299°), (57.3565°) and (62.7777°) with miller indices (220), (311), (400), (511) and (440) respectively. The observed phases were crystalline and attributed to calcination of different types of precursors and show that for the samples that were calcined (Fig. 1(a-f)), diffraction peaks that corresponded to (220), (311), (400), (422), (511) and (440) diffraction planes of Ni-Zn ferrite were seen. [7]. It should be noticed that, for all the calcined samples attained from the precursors, made with Zn<sup>2+</sup> content ranging from 0.15-0.9, peaks corresponding to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as an impurity phase were also there and are marked as (a-f) in Fig. 1.

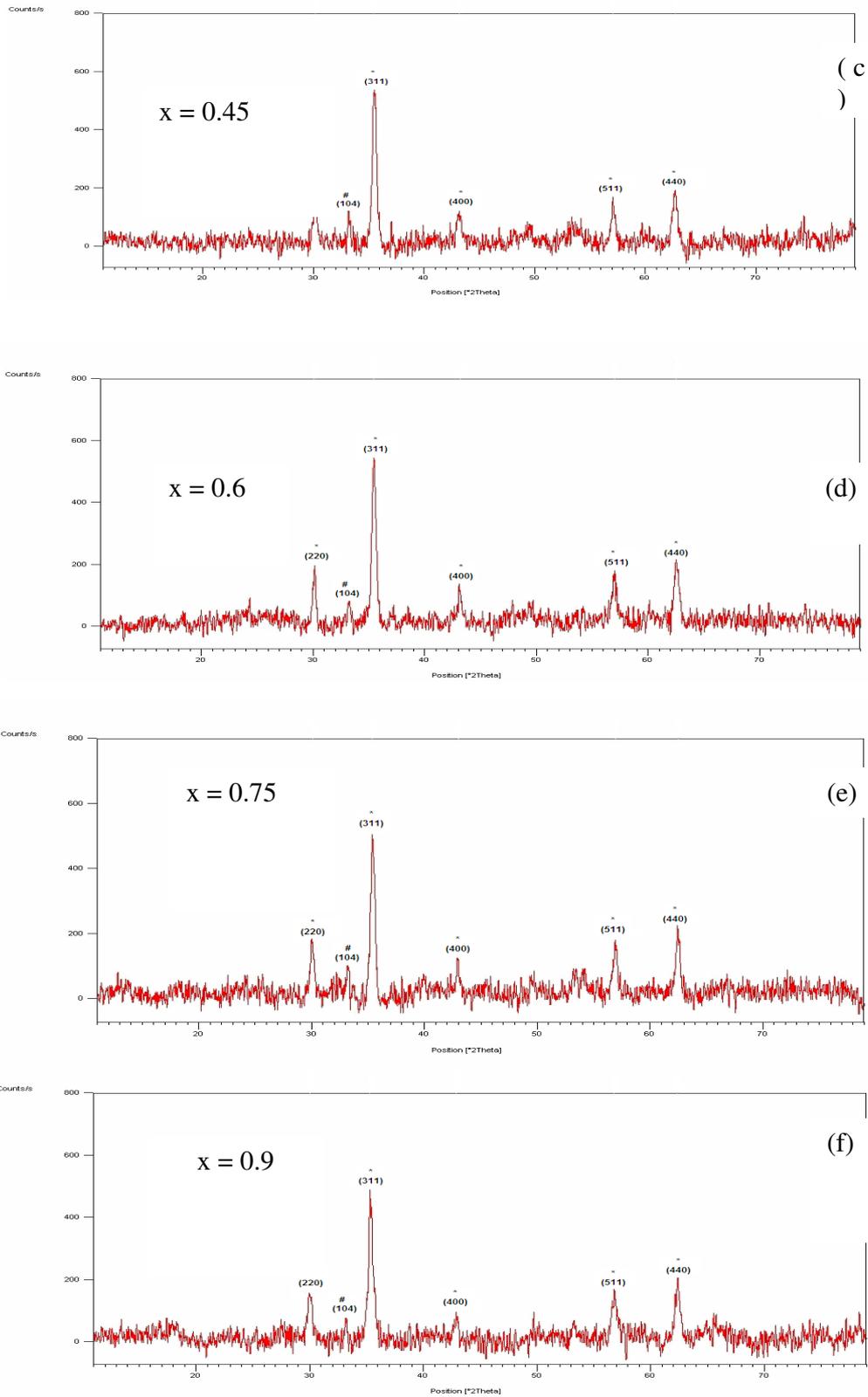
It is clear from the Fig. 1 that S1 has a peak at  $2\theta = 33.14$  which is due to the rapid addition of NaOH, however it was controlled in the remaining samples. The calculated values of crystalline size, Lattice constant, Volume of the unit cell, X-ray density, molecular weight and diameter of particles are given in Table 2.

**Table 2.** Size of crystals, Lattice constant, Volume of the unit cell, X-ray density, molecular weight and diameter of particles of all the samples.

Sample No.	Size of crystals (nm)	Lattice constant	Volume ( $\text{\AA}^3$ )	X-ray density ( $\text{g/cm}^3$ )	Molecular weight	Particle diameter ( $\text{\AA}$ )
S1	22.67	8.36	585.4	5.26	235.40	11.83
S2	22.98	8.37	586.7	5.31	236.41	11.84
S3	23.13	8.38	589.2	5.33	237.40	11.85
S4	23.80	8.39	590.9	5.35	238.42	11.86
S5	26.64	8.40	594.0	5.36	239.43	11.89
S6	26.30	8.42	597.73	5.38	240.41	11.91

It is clear from the Table 2. that average particle size is increased with the increase of  $\text{Zn}^{+2}$  concentration and concentration of  $\text{Ni}^{+2}$  is decreased [13]. This defines the particle size growth and better crystalline behavior at higher Zn concentration. The particle size ranged between 22.67 to 26.30 nm. For all the samples, the values of lattice constant were found to be in close agreement with published results of ferrite [14]. Volume of unit cell increased from 585.41 to 597.73  $\text{\AA}^3$  as the Zn concentration increased. This is because the Zn has greater atomic volume than Ni. The X-ray density, lattice constant, molecular weight and particle diameter (Table 2) increased as the Zn concentration increased which is in agreement with the previous study [15]. XRD analysis confirmed the cubic spinel structure [16].





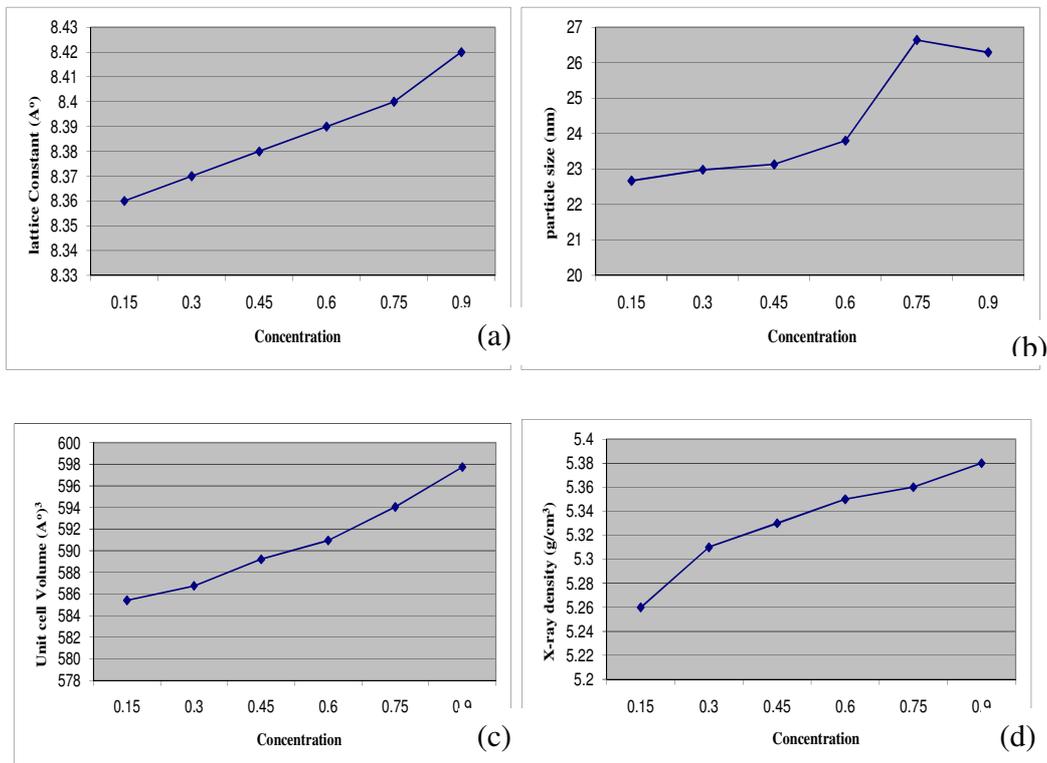
**Fig. 1:** XRD patterns of  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  calcined at  $700^\circ\text{C}$  for 2 h.

The same peaks of spinel Ni-Zn ferrite were observed in all other XRD patterns but the  $2\theta$  value varied slightly, which shows the occupying of  $Zn^{2+}$  in A sites. For cubic crystals, lattice parameter (a) can be determined by the formula  $a = \lambda / 2 \sin \theta \sqrt{h^2 + k^2 + l^2}$  where  $\theta$  is the diffraction angle and the h, k, l are the indices of crystallographic plane and  $\lambda$  is wavelength of the  $CuK_{\alpha}$  radiation. In this case lattice constant was calculated with the  $\theta$  value of (311) peak and variation with respect to  $Zn^{2+}$  concentration is illustrated in fig. 2(a).

The observation reveals an increase in the value of lattice constant from 8.36 to 8.42 Å with the increase in the  $Zn^{2+}$  concentration. This could be attributed to migration of  $Fe^{3+}$  ions from site A to B. However as the  $Zn^{2+}$  ion is larger (0.82 Å) as compared to  $Fe^{3+}$  ions (0.67 Å), makes the A sites and cause lattice distortion and the increase of A [11].

The average particle size has been calculated using the width of the prominent (311) reflection with the Scherrer's formula,  $t = 0.9 / \beta \cos \theta$  where  $\beta$  is FWHM of peaks and t is the crystallite size. The size of the crystallites is ~ 22.67nm for the sample with x= 0.15 and ~ 26.29nm for sample with x= 0.9 (fig. 2b).

Fig. 2(c) shows the variation in unit cell volume as a function of  $Zn^{2+}$  concentration. It had been observed that with excessive  $Zn^{2+}$  ion as unit cell volume depends on lattice parameter (a). Similarly variation in X-ray density (as a function of concentration) of  $Zn^{2+}$  has been shown in fig. 2(d).



**Fig. 2:** Variation of lattice constant, particle size, unit cell volume and X-ray density of Ni-Zn spinel ferrite samples with different Zn contents.

#### 4. Conclusion

Keeping in view the wide range of applications Ni-Zn ferrites with different concentration of  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_3$  ( $x=0.15$  to  $0.9$ ) were made using chemical co-precipitation technique. Average particle size was observed in the range of  $\sim 23\text{nm}$  to  $\sim 26\text{nm}$ . Co-precipitation is simple and economical method because starting materials are not very expensive as well as method does not need complicated operation involving complex equipments. Different multicomponent ferrite powders can be synthesized using this scheme.

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