

COBALT DOPED NICKEL ZINC FERRITE NANOPARTICLES – XRD ANALYSES AN INSIGHT

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ABSTRACT

Properties of Ferrites strongly depend on the chemical composition and the microstructure. Cobalt doped nickel zinc ferrite ($\text{Ni}_{0.6-x}\text{Zn}_{0.4}\text{Co}_x\text{Fe}_2\text{O}_4$) (NZCF) (where $x= 0, 0.011$) is prepared by simple Sol-Gel technique and annealed at 700°C . The formation of inverse spinel ferrite is confirmed by XRD diffraction pattern. The crystallite size of prepared samples is calculated in nm range by XRD diffraction pattern, using Scherer formula. The influence of Co doping on the structural properties of Ni Zn ferrite is observed by calculating various parameters.

1. INTRODUCTION

Ferrites represent an important category of materials, which are largely used, due to their numerous practical applications, such as magnetic devices in electronic, optical and microwave installations [1]. Spinel ferrites, with common formula of MFe_2O_4 (M is various divalent or trivalent metals cations) have been extensively used in various components for applications in the high-frequency range due to their high electrical resistivity, high permeability, and chemical stability. The unit cell of spinel ferrites is composed of 32 oxygen atoms in cubic closed-packed arrangement distributed in tetrahedral (A) and octahedral sites (B). Chemical and structural properties of spinel ferrite nanocrystals are affected by their compositions and synthesis methods and corresponding electric and magnetic properties depends on cation substitutions. Doping of ferrite nanocrystals with various metals, such as chromium, copper, manganese, cobalt and zinc are usually used to improve their electric or magnetic properties [2-4]. Substituted Ni-Zn ferrites have wide applications in radio frequency (RF) electronic devices due to the high initial permeability in combination with huge resistivity [5]. Ni-Zn ferrites with their ease preparation and versatility for use in wide ranging application are very attractive materials from the commercial point of view. Ni-Zn ferrites with high permeability and high frequency are widely used in the telecommunications, electronics and information technology, surface-mount technology and various sensors. Properties of ferrites are dependent upon several factors such as composition, method of preparation, doping of different cations and substitution, sintering temperature and time, sintered density, grain size and their distribution [6-7]. Ferrites are materials of relatively low cost which are applicable to several kinds of sensors to probe, such as current [8], magnetic field [9], mechanical stresses [10], gas concentrations [11-12], and temperature [13]. Ferrite temperature sensors for biological applications have been developed, which can monitor human body temperature and also have biochemical applications [14-16]. Ferrites are important materials both from application point of view as well as theoretical point of view. One of the reasons of being ferrites are interesting due to it's their high resistivity. The resistivity of ferrites varies from 10^2 to 10^{10} ohm-cm, which is about 15 orders of magnitude higher than that of iron [17]. This outstanding property of ferrites makes them highly demandable for high frequency applications. Other reasons which make Ferrites to be the most important are their applicability at higher frequency, lower price, greater heat resistance and higher corrosion resistance. Along with the technological advances in a variety of areas, the

demand for soft magnetic materials increases day by day. Among the soft magnetic materials, polycrystalline ferrites have received special attention due to their good magnetic properties and high electrical resistivity over a wide range of frequencies; starting from a few hundred Hz to several GHz. Spinel type ferrites are commonly used in many electronic and magnetic devices due to their high magnetic permeability and low magnetic losses [18-19] and also used in electrode materials for high temperature applications because of their high thermodynamic stability, electrical resistivity and electrolytic activity [20-21]. Moreover, these low cost materials are easy to synthesize and offer the advantages of greater shape formability than their metal and amorphous magnetic counterparts. Almost every item of electronic equipment produced today contains some ferrimagnetic spinel ferrite materials. Loudspeakers, motors, deflection yokes, electromagnetic interference suppressors, radar absorbers, antenna rods, proximity sensors, humidity sensors, memory devices, recording heads, broadband transformers, filters, inductors, etc. are frequently based on ferrites. In this paper we report Cobalt doped Nickel zinc Ferrite nanoparticles were synthesized by simplest sol gel technique and various parameters such as crystallite size, d-spacing, lattice constant, strain, dislocation density and packing fraction of un-doped Nickel Zinc Ferrite and Cobalt doped Nickel Zinc Ferrite calculated by XRD diffraction pattern.

2. EXPERIMENTAL

Stoichiometric amount of Ni (II) nitrate hydrate, Zn (II) nitrate hydrate, Co (II) nitrate hydrate and Fe (III) nitrate hydrate were dissolve in distilled water, having compositions $Ni_{0.6-x}Zn_{0.4}Co_xFe_2O_4$ (NZCF) (where $x=0, 0.011$) under magnetic stirring for 30 min, followed by addition of citric acid monohydrate to make final solution molar ratio between nitrates to citric acid is 1:3. Adjust the pH=7 in the above solution and heat it at $75^{\circ}C$ with continue stirring to form viscous gel. Dried the gel at $110^{\circ}C$ for 24 hour to form the powder and annealed at $700^{\circ}C$ for six hour. Finally Ni Zn ferrite and Co doped Ni Zn ferrite nanoparticles have prepared.

3. RESULTS AND DISCUSSION

The synthesized samples were characterized by Philips PW-1730 X-ray diffractometer using Cu-K α radiation ($\lambda = 1.546 \text{ \AA}$) source. The X-ray diffraction patterns of both prepared samples ($Ni_{0.6-x}$

$x\text{Zn}_{0.4}\text{Co}_x\text{Fe}_2\text{O}_4$ (NZCF) (where $x = 0, 0.011$) were taken with X-ray diffractometer using Cu-K α radiation, which are shown in Figure 1 and Figure 2.

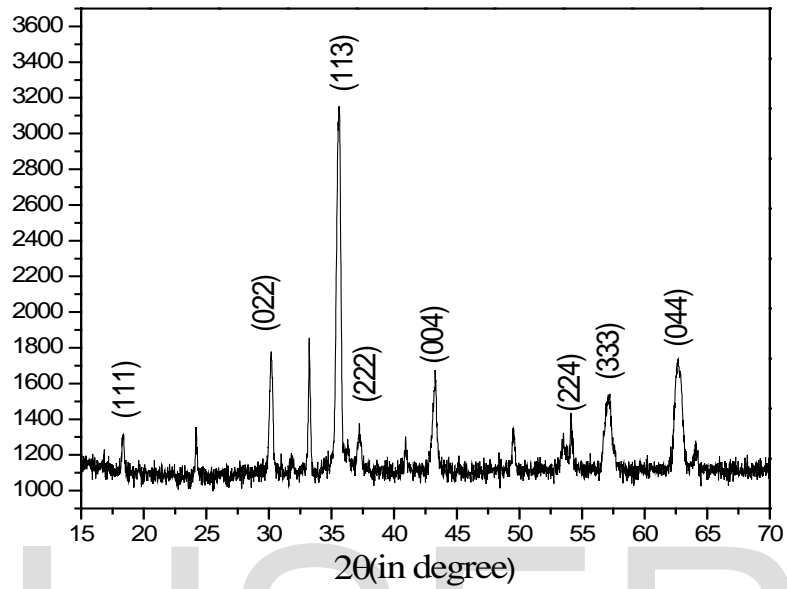


Figure 1: XRD Spectra of Ni Zn Ferrite

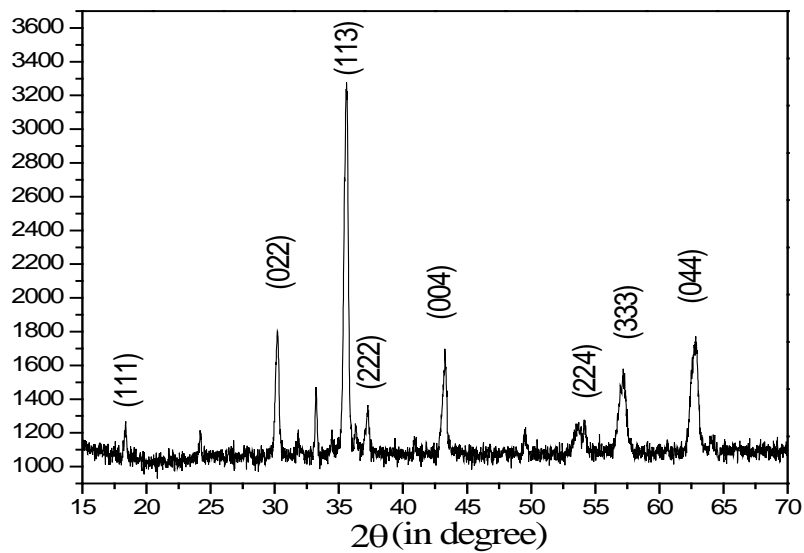


Figure 2: XRD Spectra of Co doped Ni Zn Ferrite

The crystallite size of NZCF (at $x=0, 0.011$) nanoparticles were calculated from most prominent peak (113) of XRD using the Scherer formula [22].

$$D = k \lambda / \beta \cos \theta_{\beta}$$

Where D is the crystallite size, $\lambda = 1.546 \text{ \AA}$ is the wavelength of incident X-ray, θ_{β} is the diffraction angle and β is the full width at half maximum (FWHM).

The d-spacing is calculated by using Bragg's equation [23].

$$2d \sin \theta = n \lambda$$

The lattice constant (A) for cubic crystal system was calculated using equation [24].

$$A = d (h^2 + k^2 + l^2)^{1/2}$$

where hkl are the Miller indices of the diffraction peak and d is the inter plane (113) spacing.

where n is the order of diffraction, λ is the wavelength of the incident X-rays, d is the distance between planes parallel to the axis of the incident beam and θ is the angle of incidence relative to the planes in crystal.

The strain (ϵ) has been calculated by using the relation

$$\epsilon = 1/d^2$$

Also using the size of the crystallites (D), the dislocation density (δ), has been calculated

Using [25].

$$\delta = 15\epsilon/aD$$

To explain the variation in the strain and dislocation density, we calculate the packing factor (p) which is given by [26].

$$p = D/d$$

All the parameters which are calculated by XRD diffraction pattern are shown in the table below.

Sample	2 θ (degree)	D(nm)	d(Å)	A(Å)	ϵ	δ	p
NZCF At x=0	18.430	23	4.8083	8.3282	0.0432	0.0003387	47.8339
	30.125		2.9629	8.3806	0.1139	0.0008863	77.6242
	35.585		2.5198	8.3574	0.1574	0.0012289	91.2743
	37.277		2.4092	8.3460	0.1722	0.0013461	95.4637
	43.293		2.0874	8.3496	0.2295	0.0017925	110.1846
	54.121		1.6925	8.2918	0.3490	0.0027455	135.8885
	57.215		1.6081	8.3562	0.3866	0.0030177	143.0202
	62.715		1.4796	8.3704	0.4567	0.0035585	155.4370
NZCF At x=0.011	18.411	24	4.8132	8.3367	0.04316	0.0003376	49.8626
	30.230		2.9529	8.3521	0.1146	0.0008954	81.2749
	35.595		2.5189	8.3545	0.1575	0.0012299	95.2687
	37.237		2.4117	8.3546	0.1719	0.0013420	99.5112
	43.280		2.0880	8.3520	0.2293	0.0017910	114.9424
	54.180		1.6908	8.2834	0.3497	0.0027538	141.9395
	57.188		1.6088	8.3598	0.3863	0.0030138	149.1739
	62.860		1.4766	8.3530	0.4586	0.0035807	162.5318

In spinel ferrite, oxygen form fcc structure which contains two type of interstitial sites tetrahedral and octahedral sites (64 tetrahedral and 32 octahedral sites). One eight of the tetrahedral sites and one half of the octahedral sites are occupied by the cations (divalent and trivalent cations). When tetrahedral sites are occupied by the divalent cations and octahedral sites are occupied by trivalent cations, this type of distribution is known as normal spinel. While as half of the octahedral sites and tetrahedral sites occupied by trivalent cations and remaining half octahedral sites occupied by divalent cations, this type of distribution is known as inverse spinel. Nickel-zinc ferrite has inverse spinel cubic structure. There are 8 tetrahedral sites occupied by Zn^{2+} ions and 16 octahedral sites occupied by Ni^{2+} and Fe^{3+} ions in unit cell. By doping of Cobalt in Nickel Zinc ferrite, the Ni^{2+} (ionic radius=0.74 Å) ions has replaced by Co^{2+} (ionic radii=0.82 Å) ions in octahedral sites, due to larger ionic radius of Co^{2+} (ionic radii=0.82 Å) as compare to Ni^{2+} (ionic radii=0.78 Å). It has been revealed from XRD peaks that crystallite size increases from 23 nm to 24 nm. Other parameters such as d-spacing, lattice constant, strain, dislocation density and packing fraction also vary with the enlargement of lattice.

4. CONCLSIONS

$Ni_{0.6-x}Zn_{0.4}Co_xFe_2O_4$ (at $x=0$) and $Ni_{0.6-x}Zn_{0.4}Co_xFe_2O_4$ ($x=0.011$) were successfully synthesized by Sol-Gel technique. The XRD studies prove the formation of nanocrystalline materials. Crystallite size of $Ni_{0.6-x}Zn_{0.4}Co_xFe_2O_4$ (at $x=0$) and $Ni_{0.6-x}Zn_{0.4}Co_xFe_2O_4$ ($x=0.011$) were found to be 23 nm and 24 nm respectively, calculated by most prominent peak (113) of XRD diffraction pattern. The variation of structure parameters such as d-spacing, lattice constant, strain, dislocation density and packing fraction has to be done by Co doping, which have calculated by XRD peaks.

REFERENCES:

1. Anil Kumar PS, Shrotri JJ, Deshpande CE, Date SK. "Systematic study of magnetic parameters of NiZn ferrites synthesized by soft chemical approaches" *Journal of Applied Physics*, **81**(8), 4788–4790 (1997)
2. S. Gubbala, H. Nathani, K. Koizol, R.D.K. Misra, "Magnetic properties of nanocrystalline Ni-Zn, Zn-Mn, Ni-Mn ferrites synthesized by reverse micelle technique", *J. Phys. B*, **348**, 317–328 (2004)
3. S.A. Saafan, T.M. Meaz, E.H. El-Ghazzawy, M.K. El Nimr, M.M. Ayad, M. Bakr, "A.C. and D.C. conductivity of NiZn ferrite nanoparticles in wet and dry conditions", *J. Magn. Mater.*, **322**, 2369–2374 (2010)
4. S. Singhal, K. Chandra, "Cation distribution and magnetic properties in chromium-substituted nickel ferrites prepared using aerosol route", *J. Solid. State. Chem.*, **180**, 296–300 (2007)
5. Rezlescu E, Sachelarie L, Popa PD, Rezlescu N. "Effect of substitution of divalent ions on the electrical and magnetic properties of Ni-Zn-Me ferrites" *IEEE Trans Magn.*; **36**:3962–3967 (2000)
6. B. Parvatheeswara Rao, P. S. V. Rao and K. H. Rao, *J. Phys. IV France* **7**, CI-241 (1997)
7. A. Goldman, *Handbook of Modern Ferromagnetic Materials*, (Springer Science + Business Media, New York, (1999)
8. Brito, V. L. O., A. C. C. Migliano, L. V. Lemos, and F. C. L. Melo, "Ceramic processing route and characterization of a Ni-Zn ferrite for application in a pulsed-current monitor," *Progress In Electromagnetics Research, PIER* **91**, 303–318 (2009)
9. Sedlar, M., V. Matejec, and I. Paulicka "Optical fibre magnetic field sensors using ceramic magnetostrictive jackets," *Sens. Act. A*, **84**, 297–302 (2000)
10. Bienkowski, A. and R. Szewczyk, "The possibility of utilizing the high permeability magnetic materials in construction of magnetoelastic stress and force sensors," *Sens. Act. A*, **113**, 270–276 (2004)
11. Zhang, G., C. Li, F. Cheng, and J. Chen, "ZnFe₂O₄ tubes: Synthesis and application to gas sensors with high sensitivity and low-energy consumption," *Sens. Act. B*, **120**, 403–410, (2007)

12. Arshak, K. and I. Gaidan, "Development of a novel gas sensor based on oxide thick films," *Mat. Sci. Eng. B*, **118**, No. 1–3, 44–49 (2005)
13. Shin, H.-S., "Ferrite device for sensing temperature," U.S. Patent No. **5**, 775, 810 (1998)
14. Kim, Y. H., S. Hashi, K. Ishiyama, K. I. Arai, and M. Inoue, "Remote temperature sensing system using reverberated magnetic flux," *IEEE Trans. Magn.*, **36**, No. 5, 3643–3645, (2000)
15. Osada, H., K. Seki, H. Matsuki, S. Kikuchi, and K. Murakami, "Temperature-sensitive magnetic thin-film for micro sensor," *IEEE Trans. Magn.*, **31**, No. 6, 3164–3166 (1995)
16. Osada, H., S. Chiba, H. Oka, H. Hatafuku, N. Tayama, and K. Seki, "Non-contact magnetic temperature sensor for biochemical applications," *J. Magn. Magn. Mater.*, **272–276**, 1761–1762 (2004)
17. L. G. Van Uitert, *J. Chem. Phys.*, **24** , 306 (1956)
18. T. Suzuki, T. Tanaka, and K. Ikemizu, *J. Magn. Magn. Mater.*, **235** , 159 (2001)
19. T. Giannakopoulou, L. Kompotiatis, A. Kontogeorgakos, G. Kordas, *J. Magn. Magn. Mater.*, **246** , 360 (2002)
20. E. Olsen, and J. Thonstad, *J. Appl. Electrochem.* **29** , 293 (1999)
21. C. O. Augustin, D. Prabhakaran, and L.K. Srinivasan, *J. Mater. Sci. Lett.* **12** , 383 (1993)
22. George M, Nair SS, John AM, Joy PA, Anantharaman MR, *J Phys D Appl Phys* **39**:900 (2006)
23. Iqbal MJ, Siddiquah MR, *J Magn Magn Mater* **320**:845 (2008)
24. M. Saleem, L. Fang, H.B. Ruan, F. Wu, Q.L. Huang, C.L. Xu, and C.Y. Kong, "Effect of zinc acetate concentration on the structural and optical properties of ZnO thin films deposited by Sol-Gel method", *Int. J. Phys. Sci.*, **7**, 2971 (2012)
25. S. Prabahar, and M. Dhanam, CdS thin films from two different chemical baths-structural and optical analysis, *J. Cryst. Growth*, **285**, No.1-2, 41 (2005)
26. T. Kavetsky, O. Shpotyuk, M. Popescu, A. Lorinczi, and F. Sava, "FSDP-related correlations in chalcogenide glasses", *J. Optoelectron. Adv. Mater.*, **9**, No.10, 3079 (2007)