Short Communication

Synthesis and Structural Studies of Nickel Doped Cobalt Ferrite Thin Films

Bhavana Singh[1,*], Nitu Katariya[2], V. Ganesan[3] and S. B. Shrivastava[4]

[1]Department of Applied Physics, Jabalpur Engineering College, Jabalpur, M. P., India.
[2]Shri Vaishnav Vidyapeeth Vishwavidyalaya, Indore, M. P., India.
[3]UGC-DAE, Consortium for scientific research, Indore, M. P., India.
[4]School of Studies in Physics, Vikram University, Ujjain, M. P., India.

(*) Corresponding author: bhavanassp@gmail.com
(Received: 18 February 2019 and Accepted: 14 November 2019)

Abstract
The growth and structural study of Nickel doped Cobalt ferrite thin films on glass substrate using spray pyrolysis technique have been done. The structural studies confirmed the growth of polycrystalline film having cubic structure with Fd3m space group. The x ray density was found to increase with Ni concentration, where as the reduction, in crystalline size, was found in XRD measurements. The AFM studies also showed the grain size and roughness of the films decrease with increase in Ni concentration.
Keywords: *Ferrite; Spray Pyrolysis; XRD; AFM.*

1. INRODUCTION

In recent years there has been a great interest in the investigation of the transition metal ferrites as they exhibit unique chemical, structural, magnetic and mechanical properties. Ferrites are potential candidates for the next generation of electronics due to their high chemical stability and tunable magnetic properties [1]. Ferrites in nanosize have wide application in designing a large variety of integrated circuits, reading–writing heads [2], sensors [3], catalysts [4] and magnetic recording media [5]. Considerable research is being directed towards using these nanomaterials as magnetic resonance imaging (MRI), contrasting agent in drug delivery systems and in environmental remediation [6]. Cobalt ferrite is a well-known hard magnetic material with relatively high coercivity and saturation magnetization while nickel ferrite is a soft material with low coercivity and saturation magnetization. Many of these (soft and hard magnetic) material make them very promising candidates for various electronic (recording technology) and biomedical applications. The formation of nano-crystalline spinel ferrites plays an important role in determining the physical properties in nano and sub nano level. The physical and the chemical properties are highly influenced by the preparation route, particle size and also by doped material.

In order to improve the properties, investigation of alternative non-conventional method to obtain ferrites in the form of nanostructured powder and thin films is the subject of current interest. Thus, in the present work our emphasis has been to obtain the Nickel doped Cobalt Ferrite thin films by spray pyrolysis technique (SPT). The work has been done to understand the effect of concentration of dopant on the structural and morphological properties of nano-ferrite samples. The characterization of the prepared samples has done by using x-ray diffraction and atomic force microscopy measurements.

2. SAMPLE PREPARATION

The nano-crystalline thin films of $Co_{(1-x)}Ni_{(x)}Fe_2O_4$ (x = 0, 0.2, 0.4, 0.8, 1.0) has been prepared by using spray pyrolysis technique. The cobalt chloride, iron chloride and nickel chloride has been used as precursors required for preparing thin films. The aqueous solution containing 0.1M $CoCl_2$ and 0.1M $FeCl_3$ and 0.1M $NiCl_2$ with required composition was used as precursor solution. The films are deposited on the microscopic glass substrates, which were chemically and ultrasonically cleaned. During the course of the spray the atomization of the solution in the fine droplets is affected by spray nozzle with the help of dry air as carrier gas. The distance between nozzle and substrate is found to be 28 cm with flow rate of 10 ml/min. The optimum substrate temperature for getting homogenous and well adherent films has been found 450^0C. The prepared samples were annealed at 500^0C for three hours in the presence of atmospheric air.

All the samples are analyzed for their structural properties by X-ray diffraction (XRD) patterns using (Rigku RINT 2000) diffractrometer and using CuKα (λ=1.5418A^o) radiation. Surface morphological studies were done by Atomic Force Microscope (AFM) (Digital instruments Nanoscopes E and IV, with Si_3N_4 100μ cantilever, 0.58 N/m force constant) measurements in contact mode.

3. RESULTS AND DISCUSSION

The X-ray diffractrographs of $Co_{(1-x)}Ni_xFe_2O_4$ (x = 0, 0.2, 0.4, 0.8, 1.0) for different samples are reported. The XRD pattern reveals the polycrystalline nature of the samples. The peak appearing at 2θ values for cobalt ferrite thin films are (JCPDS Card-22-1086) 18.3^0, 30.00^0, 35.46^0, 37.08^0, 42.98^0, 57.04^0 and 62.68^0 may be assigned for x-ray scattering from the (111), (220), (311), (222), (400), (511) and (440) phase of the spinel crystal lattice respectively. Whereas the peak appearing at 2θ values for Nickel ferrite thin films are (JCPDS Card-74-2081) 18.26^0, 30.14^0, 35.66^0, 40.74^0, 43.22^0, 53.98^0, 57.44^0 and 62.90^0 may be assigned for x-ray scattering from the (111), (220), (311) ,(400), (511) and (440) phase of the spinel crystal lattice respectively. All the samples were found to be cubic structure with Fd3m space group. The most intense peak for the cobalt ferrite sample (x=0) was found at 2θ=35.46. Upon increasing the Ni concentration the most intense peak was found to shift towards higher values of 2θ, i.e. for (x=1) $NiFe_2O_4$ sample 2θ=35.66, i.e. the small shift towards the higher 2θ values on increasing the Ni concentration is observed.

The lattice parameter ‘a’ was found to decrease with Ni concentration. This may be due to the smaller ionic radius of Ni^{+2} (0.69A^o) compared to Co^{+2} (0.74 A^o) [7], the replacement of Co by Ni ions leads to a decrease of the lattice parameter and lattice volume with the decrease in crystallite size. The similar results were shown by Velhal et al. [10]. Calculated values of lattice parameter of Co-ferrite and Ni-ferrite samples are listed in table 1, which are in close agreement with standard data 8·3919 Å and 8.3379 Å respectively.

The average crystallite size was calculated from line broadening of XRD pattern using Scherrer formula for most intense peak [8].

$$D = 0.9\,\lambda / (\beta \cos\theta), \quad (1)$$

where λ is the X-ray wavelength, θ is Bragg diffraction angle and β is the difference between the full width at half maximum. It was observed that the crystallite size decreases with the increase in Nickel concentration. The lattice constant and cell volume of $Co_{1-x}Ni_xFe_2O_4$ nanoparticles has been determined from equation (2) and (3):

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (2)$$

$$V = a^3 \quad (3)$$

The X-ray density d_x was calculated by using the formula,

$$d_x = 8M/Na^3, \quad (4)$$

where M, N and a are Molecular weight, Avogadro number and lattice parameter respectively [9]. The values so obtained for crystallite size, X-ray density are given in table 1.

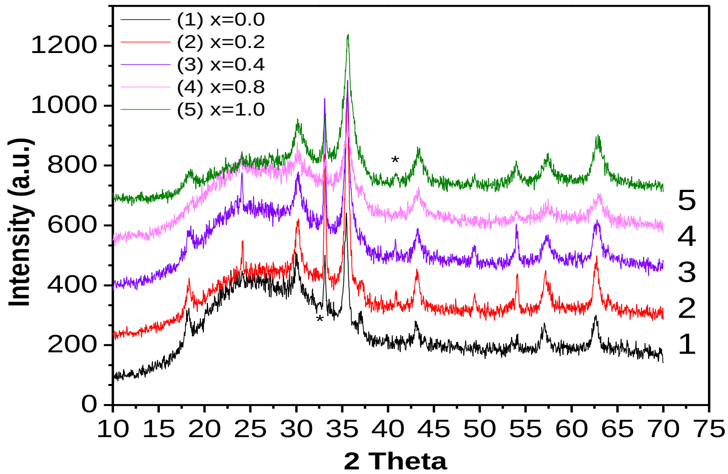


Figure 1*. The XRD measurements for Ni doped Cobalt ferrite thin films.*

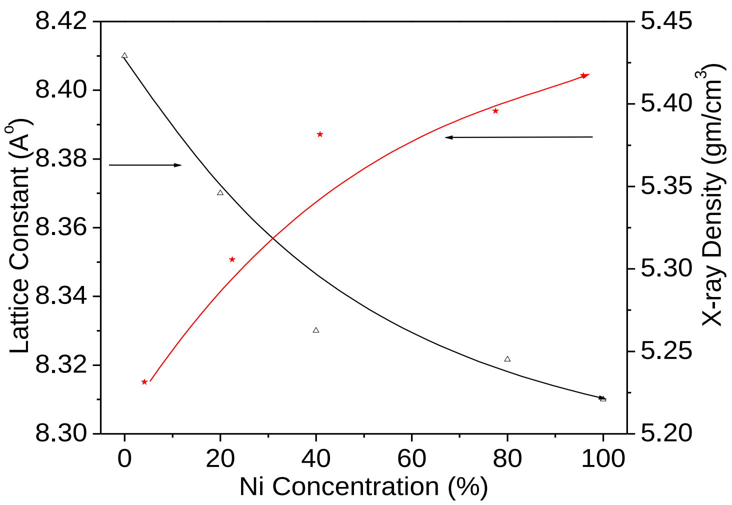


Figure 2*. Change in lattice constant and X-ray density with Ni concentration.*

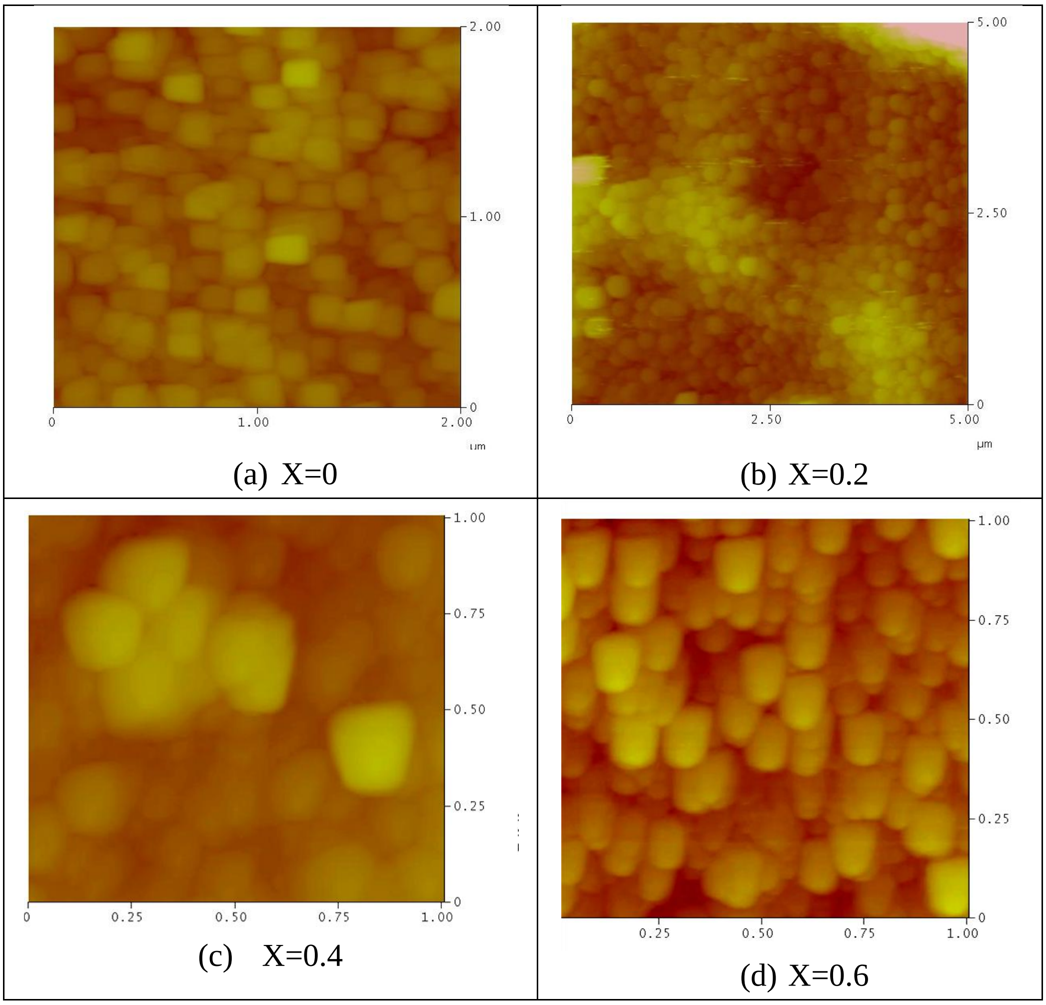
The X-density increases linearly with Ni concentration, as it depends upon the lattice parameter. As the lattice constant decreases with the increase in Ni concentration, a corresponding increase in X-ray density is expected. The bulk densities calculated for Co-ferrite is 5.26g/cm^3 and for Ni-Ferrite is 5.32g/cm^3. This calculated bulk density and experimental X-ray density fallows the same pattern. The Figure 2 is plotted for change in lattice constant and X-ray density with Ni concentration.

Atomic force microscopy is an excellent tool to study surface topography and texture of diverse surfaces of thin films. The versatility of this technique allows thorough observations and evaluations of the textural and morphological characteristics of the films. It provides high-resolution images of the surfaces. Figure 3 (a-f) shows the micrograph corresponding to cobalt ferrite film with different Ni concentration. The grain sizes and roughness calculated from these images are given in Table 1.

***Table 1**. Variation of lattice constant, cell volume, X-ray density, crystallite size, grain size and roughness for $Co_{(1x)}Ni_xFe_2O_4$ sample.*

Nickel composition (x)	Lattice constant (A^o)	Cell Volume (A^{o3})	X-ray Density (gm/cm^3)	Crystallite size (nm)	AFM grain size (nm)	Roughness (nm)
x=0.0	8.410	594.82	5.23	66.86	339	10.89
x=0.2	8.371	586.61	5.31	63.88	310	9.16
x=0.4	8.325	577.01	5.38	62.7	179	6.29
x=0.6	-	-	-	-	160	5.26
x=0.8	8.322	576.26	5.40	59.2	153	4.90
x=1.0	8.315	574.79	5.42	31.73	294	8.52

It was found that on increasing Ni concentration the grain size decreases. This is in good agreement with the XRD results. For pure (x=1) Nickel ferrite film the grain size is high, this may be due to agglomeration of particles. The roughness is also found to decrease with increase in Ni concentration.



(a) X=0

(b) X=0.2

(c) X=0.4

(d) X=0.6

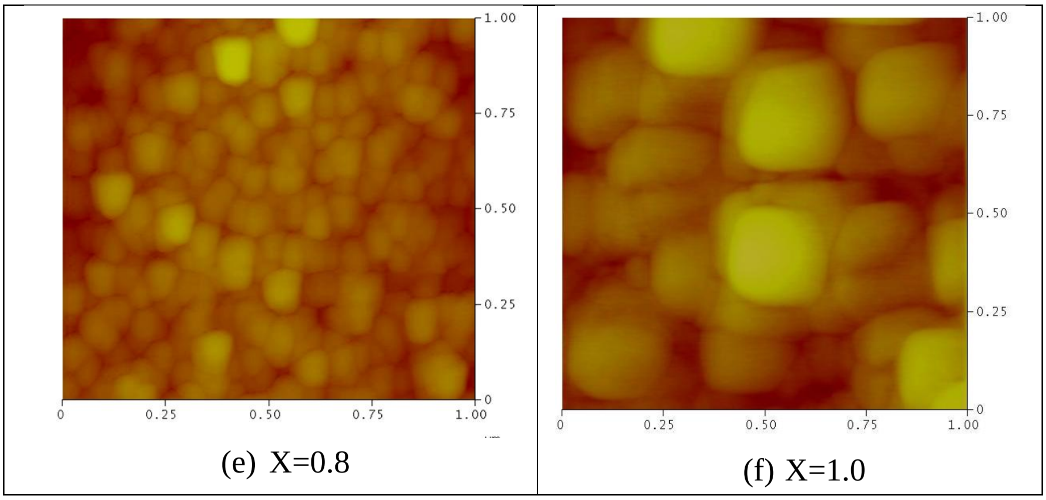


Figure 3 (a-f). *The AFM images for the Ni doped Cobalt ferrite thin films with different Ni (x) Concentration.*

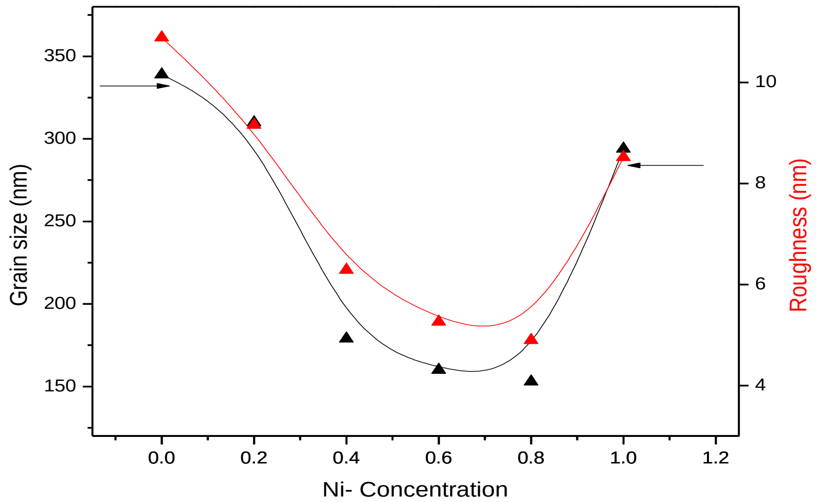


Figure 4*. The variation in grain size and roughness vs Ni concentration.*

CONCLUSION

In summary, the Cobalt ferrite thin films doped with Nickel are synthesized by using spray pyrolysis technique on glass substrates. The polycrystalline nature of film is confirmed by XRD measurements. All samples have cubic structure with Fd3m space group. The lattice parameter and crystallite size are found to decrease with the increase in Ni concentration. This may be due to the smaller ionic radius of Ni^{+2} compared to Co^{+2}. The AFM studies show that the both grain size and roughness decreases with Ni doping.

ACKNOWLEDGEMENT

The author at Jabalpur would like to thank Centre Director and staff of UGC-DAE CSR, Indore, center for the carrying out measurement like, XRD and AFM, and Dr. S.K Tiwary, (Department of Applied Physics, JEC, JBP) for encouragement and fruitful discussion.

REFERENCES

1. Caruntu, G, Dumitru, I, Bush, G. G., Caruntu, D., O'Connor, Charles J., (2005). “Magnetic characterization of nanocrystalline nickel ferrite films processed by a spin-spraying method.” *J. Phys. D: Appl. Phys*., 38: 811-815.
2. Alivisatos, A. P., (1996). “Semiconductor Clusters, Nanocrystals, and Quantum Dots”. *Science*, 271: 933-937.
3. Perkin, S. S. S., More M., Roche, K. P., (1990), “Oscillations in exchange coupling and magnetoresistance in metallic superlattice structures: Co/Ru, Co/Cr, and Fe/Cr.”*Phys. Rev. Lett*., 64: 2304.
4. Manova, E., Tsoncheva, T., Estournes, Cl., Paneva, D., Tenchev, K., Mitov L. Petrov L., (2006). “Nanosized iron and iron–cobalt spinel oxides as catalysts for methanol decomposition”. *Appl. Catal. A: General*, 300(2): 170-180.
5. Skomski R., (2003). “Nanomagnetics”, *J. Phys.: Condens. Matter*, 15: R841–R896.
6. Babita Baruwati, Rohit K. Rana, Sunkara V. Manorama, (2007) “Further insights in the conductivity behavior of nanocrystalline NiFe2O4”.*Journal of Applied Physics*,101, 014302.
7. Sonal Singhal, Singh, J., Barthwal, S. K., Chandra, K., (2005) “Preparation and characterization of nanosize nickel-substituted cobalt ferrites ($Co_{1-x}Ni_xFe_2O_4$)” *Journal of Solid State Chemistry, 178: 3183-3189.*
8. Amer M. A, Meaz T., Yehia M., Attalah S. S., Fakhry F., (2015) “Characterization, structural and magnetic properties of the as-prepared Mg-substituted Cu-nanoferrites”. *Alloys Compd*., 633: 448–455.
9. Bhavana Godbole, Nitu Badera, S. B. Shrivastava, Deepti Jain, L. S. Sharath Chandra and V. Ganesan, (2013). “Synthesis, Structural, Electrical and Magnetic Studies of Ni- Ferrite Nanoparticles,” *Physics Procedia, 49: 58-66.*
10. Ninad B., Velhal, Narayan D., Patil, Abhijeet R., Shelke, Nishad G., Deshpande, Vijaya R., Puri, Structural, (2015). “Dielectric and magnetic properties of nickel substituted cobalt ferrite nanoparticles: Effect of nickel concentration”, *AIP Advances*, 5: 097166.