IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 5 Ver. II (May. 2015), PP 38-42
www.iosrjournals.org

Synthesis and structural characterization of Sm doped Ni-Cd Nano Ferrites by Citrate-Gel Auto combustion method

Shyamsunder Goud[1], Nakiraboina Venkatesh[1], Nama Hari Kumar[2], B. Rambabu[1] T. Somaiah[3] P. Veera Somaiah[1]*, B.Ravinder Reddy
[1]*Department of chemistry, Osmania University, Hyderabad, 500007- India.*
[2]*Department of Physics, Osmania University, Hyderabad, 500007- India.*
[3]*University College of Engineering, Osmania University, Hyderabad, 500007- India.*
Corresponding author Email: vs_puppala@rediffmail .com Ph (+91)9247562742

Abstract: *Ferrite nano particles of basic composition $Ni_{0.3}$ $Cd_{0.5-x}$ Sm_x Fe_2O_4(0.0 ≤ x ≤ 0.5, X=0.1) where synthesized by citrate-gel auto combustion method have investigated. X-ray diffraction profile indicates that the samples are in single phase structure for the sample without Sm content. For the samples with Sm ions, some diffraction peaks appeared which belongs to the orthorhombic phase structure further, the XRD have been used calculated the lattice parameter, density and grain size. The particle size of the starting powder composition varied from 35nm to 46nm. The values of lattice parameter (a) decreased and X-ray density (dx) increased with the increase of Sm content. Morphology of the prepared samples by citrate-gel method was studied using scanning electron microscope (SEM). The elemental analysis of all the Ni-Cd-Sm ferrite samples with different compositions was analyzed by Energy Dispersive Spectrometer (EDS). The observed results can be explained on the basis of composition and crystal size.*

Keywords: *citrate-gel auto combustion method, X-ray diffraction, SEM, EDS.*

I. Introduction

Magnetic nano particles have received special attention over the last years. This nano particles are widely used in high density magnetic recording[1] Their low cost, high saturation magnetization high curie temperature and hysteresis loop properties make then excellent candidates for high-density recording media, absorbents, and microwave devices [2] the nano magnetic particles have special properties as compared to the bulk because of the large volume fraction that atoms occupy at the grain boundary area, which in turn is responsible for several unusual properties like spin canting, surface anisotropy, super paramagnetism (sp), dislocations etc. This makes them quite flexible to tailor the material for specific applications [3] Ferrites are extensively used in many kinds of magnetic devices such as transformers, inductors, magnetic heads, in resonance circuits for high frequency [4] The interesting physical and chemical properties of the ferrites arise from their distribute the cations among the tetrahedral (A) and octahedral (B) sites [5] Magnetic Resonance Imaging (MRI), Target drug delivery Hyperthermia for cancer treatment [6,7] high density storage devices, magnetic fuids [8,9] It was found that all rare-earth ions favor the occurrence of second phase, resulting in an increase of the electrical resistivity and bulk density. The electronic valence of the rare- earth ions is most important for compound formation. In general , rare-earth ions are most stable when they cations, where Ce and Tb are both trivalent and tetravalent while Sm, Dy are divalent and trivalent[10] owing to their large radius compared to that of Fe^{3+} ions, the lattice will be distorted, generating internal stress and increasing the lattice constant. For the composition with orthorhombic second phase, the lattice constant is slightly smaller than un substituted ferrite and will decrease with the increase of rare-earth ion radius which suggests the existence of solubility limit for rare-earth ions[11] Several methods are used for synthesizing nano sized spinel ferrites, such as co-precipitation, sol-gel, micro-emulsion, hydrothermal and reverse micelle [12-14]. Refluxing process [15], Ceramic Method [16], Hydro Thermal Method [17], Combustion Method [18], Spark Plasma Sintering [19] and ball milling method etc. In the present work we reported the results of synthesis and structural properties of Ni-Cd-Sm Ferrites by non conventional citrate gel auto combustion method.

II. Experimental

Synthesis: The composition of Ni-Cd-Sm Ferrite particles having chemical formula $Ni_{0.3}Cd_{0.5-x}Sm_x Fe_2O_4$(0.0 ≤ x ≤ 0.5,X= 0.1) where synthesized by citrate-gel auto combustion method at low temperature. Nickel Nitrate, Cadmium Nitrate, Samarium Nitrate, Ferric Nitrate, Citric acid and ammonia(All chemicals are 99% pure AR Grade SDFCL sd Fine chemical Ltd) are raw materials for the synthesis process. Calculated quantities of metal nitrates and citric acid were dissolved in minimum amount of distilled water to get clear solution. Here citric acid acts as a chelating agent and helps in the homogenous distribution of metal ions. The above mixture was

stirred to get homogenous clear solution which is heated to 80^0C using a hot plate magnetic stirrer. Then the pH of the solution is adjusted at 7 by addition of ammonia. A sol is formed. The resulting solution was evaporated to dryness heating at about 180^0C on a hot plate with continuous stirring. The gel gave a fast flameless auto combustion reaction with the evolution of large amount of gases which results a burned powder. The burned powder was grinding using Agate Mortar and pestle to get a fine ferrite powder. Finally the grinded powder was calcinated in air at 500^0C for 4 hours and cooled to room temperature.

Characterization: The structural characterization of the synthesized samples was carried out by Philips X-ray diffractometer using Cu K_α radiation of wavelength 1.5405 A^0 at room temperature by continuous scanning in the range of Bragg's angles 10^0 to 80^0 in steps of 4^0/min to investigate the phase and crystalline size. Micro structural analysis of the prepared samples was carried out by Scanning Electron Microscopy (SEM) and elemental compositional analysis for all samples was done by Energy Dispersive Spectroscopy (EDS).

III. Results and Discussion

XRD Analysis

The X-ray Diffraction pattern of all the samples was shown in fig (1) which confirms the single phase cubic spinal structure formation without any impurity peak. For The samples with Sm ions, some diffraction peaks (such as 020,110,112,113 and 301) appeared which belong to the orthorhombic phase structure this new phase was formed beside the spinel phase. the strongest reflection has come from (311) peak for every sample. The crystalline size of all samples was calculated from the Half Width at Full Maximum (HWFM) of the (311) reflection peak in the XRD pattern using Debye- Scherer's formula [20].

Scherrer Formula:

Crystalline size of the sample $D = \frac{0.94\lambda}{\beta \cos\theta}$

Where λ =wavelength of X-ray used

$\boldsymbol{\beta}$ = Full Width Half Maxima (FWHM) in radians.

θ = peak position.

Lattice parameter (a) of the sample was calculated by the formula

$$\mathbf{a = d * (h^2 + k^2 + l^2)^{1/2}}$$

Where a = Lattice Constant

(hkl) are the Miller Indices

d = inter planner spacing,

The X-ray density $dx = \frac{nM}{a^3 N}$ **[g/cm^3] [21]**

Where M = molecular weight of the sample

n = number of molecules in a unit cell of spinel lattice

a = lattice parameter and N is the Avogadro number.

The Volume of the Unit Cell V= a^3

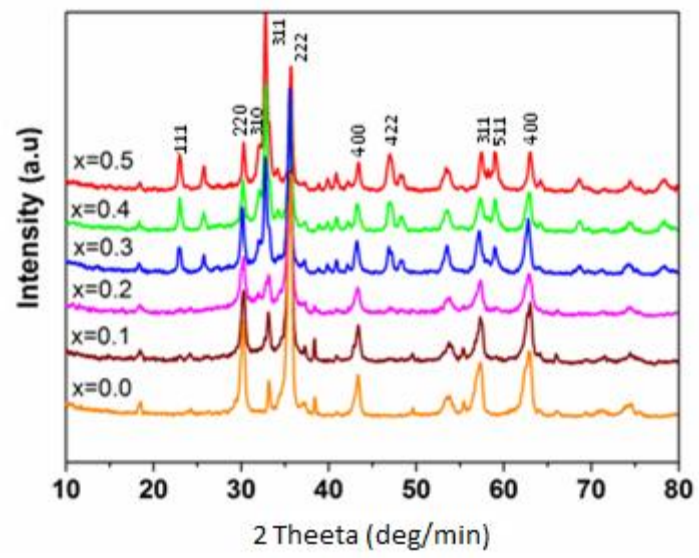

Fig (1). XRD Pattern of Sm substituted Ni Cd nano Ferrite

Values of Crystallite size, lattice parameter, X-ray density and volume of all the samples were given in the table(1).

Table(1): Crystalline size, Lattice Parameter, X-ray density & volume.

S.No	Sample	Mol. wt (gm/mol)	Crystallite size(nm)	Lattice constant (A^o)	X-ray density (gm/cc)	Volume $(A^o)^3$
1	$Ni_{0.3}Cd_{0.5}Fe_2O_4$	249.511	28.03	8.490	0.541	611.960
2	$Ni_{0.3}Cd_{0.4}Sm_{0.1}Fe_2O_4$	253.305	31.57	8.469	0.553	607.430
3	$Ni_{0.3}Cd_{0.3}Sm_{0.2}Fe_2O_4$	257.099	27.21	8.369	0.582	599.077
4	$Ni_{0.3}Cd_{0.2}Sm_{0.3}Fe_2O_4$	260.893	40.52	8.378	0.589	588.059
5	$Ni_{0.3}Cd_{0.1}Sm_{0.4}Fe_2O_4$	264.687	46.46	9.056	0.473	742.692
6	$Ni_{0.3}Sm_{0.5}Fe_2O_4$	268.481	36.17	9.058	0.479	742.938

From the table we can observe that the crystallite size of the prepared samples were in the range of 35nm to 46nm. Value of lattice constant is increasing with samarium doping (expect for sample with X = 0.2) which shows the expansion of unit cell with rare earth doping. This is expected due to Cd^{2+} ions (0.97) large ionic radius with substitution of small ionic radius of Sm^{3+} ions ($0.964A^0$). Decreases in ' a' value with Sm^{3+} concentration for sample with X = 0.2 suggests the occupancy of rare- earth ion in B – sites. The crystal size is decreasing with increases in Sm concentration, which is similar to the reported results [22, 23, 24]. X - ray density is increasing with doping which is due its dependence on molecular weight .

SEM Analysis

Micro structural analysis determines the average grain size and the type of grain growth of samples. Which influence the magnetic properties of the materials. The SEM micrographs of various $(Ni_{0.3}\ Cd_{0.5-x}\ Sm_x)\ Fe_2O_4$ samples as prepared and sintered at 400^0c are shown in Fig 4. Average grain sizes of the samples are determined from these micro graphs. The average grain sizes of the samples increases due to the substitution of Sm^{3+}.This increases in grain sizes may be attributed to the higher atomic mobility of sm. This may be due to the fact that the melting point of sm(1345.15K) is higher than that of Cd (594.05K) The grain size of the samples lies in the nano meter region have a spherical shape and narrow size distribution. SEM image revealed that with increasing in the Sm concentration, then the grain size has increased which is an evidence for the XRD analysis.

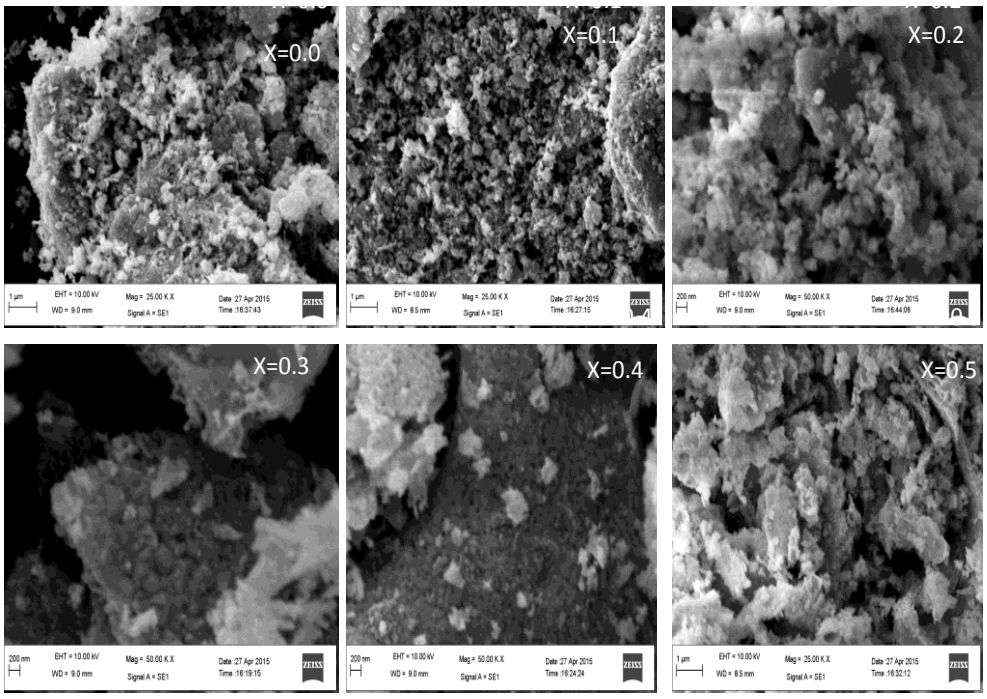

Fig (2). SEM Micro graphs of Ni Cd Sm nano ferrites

Elemental Analysis by EDS

The experimental analysis of all the Ni-Cd-Sm nano Ferrite sample with different composition was analyzed by Energy Dispersive Spectrometer (EDS) and the elemental % atomic% different Elements shown in the table 3 the EDS pattern of sample s with X= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 were shown in the fig 3 which indicates the Elemental and atomic composition in the sample. The compounds show the presence of Ni, Cd, Sm, Fe and O without precipitating cation.

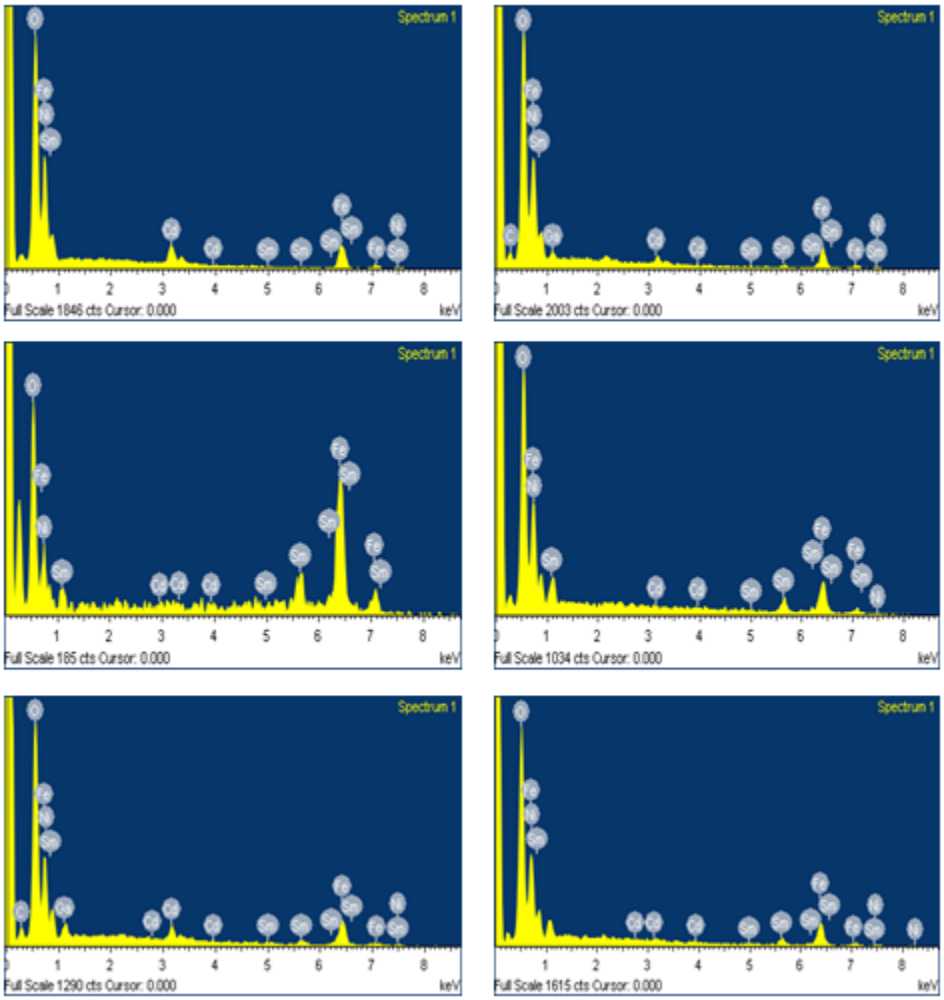

Fig (3). EDS Patron of $Ni_{0.3}$ $Cd_{0.5-x}$ Sm_x Fe_2O_4 with x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5.

Table-2. Elements of each sample composition analyzed by (%weight) obtained by EDS

S.No	Element	Ni		Cd		Sm		O		Fe	
	Ferrite Composition	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %	Element %	Atomic %
1	$Ni_{0.3}Cd_{0.5}Fe_2O_4$	9.48	5.25	8.98	2.66	0.00	0.00	27.36	58.52	54.28	33.27
2	$Ni_{0.3}Cd_{0.4}Sm_{0.1}Fe_2O_4$	9.42	5.26	5.28	1.02	6.30	4.00	26.29	56.92	52.71	32.80
3	$Ni_{0.3}Cd_{0.3}Sm_{0.2}Fe_2O_4$	9.21	7.28	5.47	3.64	12.25	6.43	25.46	56.90	47.70	31.79
4	$Ni_{0.3}Cd_{0.2}Sm_{0.3}Fe_2O_4$	7.93	5.06	0.68	0.23	20.00	4.98	25.13	55.76	46.26	33.97
5	$Ni_{0.3}Cd_{0.1}Sm_{0.4}Fe_2O_4$	0.92	0.47	1.02	0.47	62.17	21.98	19.81	62.37	16.08	14.80
6	$Ni_{0.3}Sm_{0.5}Fe_2O_4$	5.51	3.83	0.46	0.17	28.90	7.85	22.27	56.82	42.86	31.33

IV. Conclusions

Diffraction pattern of the Ni Cd Sm nano Ferrites conform the formation of single phase structure for the sample without Sm content. For the samples with Sm ions, some diffraction peaks appeared which belongs to the orthorhombic phase structure. Crystallite size of the Ni-Cd-Sm nano Ferrites was in the range of 35 nm to 46 nm which indicates the nano crystalline size. Lattice parameter increasing and experimental density of the prepared sample were decreases with composition.

References

[1]. G. Bate, magnetic recording materials since 1975, magn. magn. mater 100(1991) 413 – 423

[2]. Xiaofei Cao, Kangning Sun, chang sung, Liang Long, J: magn. magn. Mater. 321 (2009) 2896.
[3]. Vinod kumar, Anu Rana, M. S. Yadav,R.P.Pant, J.magn.magn. mater 320(2008) 1729
[4]. Sumon Kumar Nath , M. Mahabubhr Rahman , S. S. Sikder, M. A. Hakim, S.Manjura Hoghe. "Magnetization and magnetic Behavior of Ni_x Cd_x Fe_2O_4 Ferrites " VoL 3 No. January 2013
[5]. G.Blasse. Philips Research reports. Suppl. 3. 1964
[6]. D. H. Kim. S. H. Lee. K. N. Kim. K. N. Kim. I .B. Shin and Y. K. Lee "Cytotaxicity of ferrite particles by MTT and Agar Diffusion methods for Hyperthermic Application". "Journal of magnetism and magnetic materials. VoL, 293. No. 1. 2005. PP. 287-292". doi:10.1016/j.jmmm.2005.02.078
[7]. S. Somiya. S.Aldinger. N.Clussen, R. M. Uchino. K.Koumto and K.Kanenoin. "Handbook of Advanced Ciramics. VoL. 1 . processing and their Applications" Elsvier Academic press. Waltham. 2003. P.394
[8]. F. Zhang. S. Kantake. Y. Kitamoto and M. Abe."Spin spray ferrite -plated co ferrite films with High coercivit for perpendicular magnetic recoding media"IEEE Transactions on agnetics. VoL. 35. No. 5.1999. PP.2751 – 2753. Doi: 10. 1109/20. 800974
[9]. J. A. Paulsen. A. P. Ring C. C. HLO. J. E Snyder and D. C. Jiles. "Manganese – substituted Cobalt Ferrite magnetostrictive materials for magnetic stress sensor Applications". Journal of Applied Physics. VoL 97. No. 4.2005. Article ID: 044552. doi: 1. 1063.1. 1839633
[10]. B. johanson, J. Phys. Chem. Solids, 39, (1978), 467.
[11]. H. Takagi, S. Uchida, H. Eiski and S. Tanaka, J.APPL. Phys., 63, (1988),4009.
[12]. E. Veena Gopalan, K.A. Malini, S. Saravanan, D. Sakthi Kumar, Yasuhiko Yoshida, M. R. Anantharaman, Evidence of Polaron Conduction in Nano structured Manganese Ferrite, Journal of Physics D: Applied Physics 41 (2008) 185005 – 185013.
[13]. Manish Srivastava, S. Chaubey, Animesh K. Ojha Investigation o size dependent structural and magnetic behaviour of nickel ferrite nano particles prepared by Sol-gel and hydro thermal method. Materials Chemistry and Physics 118 (2009) 174 – 180
[14]. A. Dias and R. L. Moreira, Chemical Mechanical and dielectric properties after sintering of Hydro Thermal Ni-Zn Ferrites Mat Letters Vol. 39 num 1, 1999, pp 69 – 76. doi :10.1016 / S / 0167 – 5777 X (98) 00219 – 5.
[15]. S. E. Jacobo, S. Duhalde and H. R. Bertorello "Rare earth influence on the Structural and Magnetic Properties of Ni-Zn Ferrites" J of Mag and Mag materials Vol. 272 – 276 No. 3, 2004 PP 2253 – 2254.
[16]. S.D. Shenoy, P. A. Joy and M. R. Anantha raman "Effect of Mechanical Milling on the Structural, Magnetic and Di electric properties of Co-precipitated Ultra Fine Zn Ferrite, J of Magn Magn Mater Vol. 1269, No. 2, 2004, pp 217 – 226, doi : 10.1016 / S0304 – 8853 (03) 00596 – 1.
[17]. S.A. Morrison, C. L. Cahill, E. E. Carpenter, S. Calvin, R.Swaminathon, M. E. Mc Henry and V. G. Harris Magnetic and Structural properties of Ni-Zn Ferrite Nano particles synthesized by at room temperature J of Applied Physics, Vol. 95, No. 11, 2004, pp 6392 – 6395, doi 10.1063 / 1.1715132.
[18]. G.P. Lopez, S. Psilvetti, S. SE. Urreta and E. D. Caban illas, Magnetic Interaction in High Energy ball milled Ni-Zn Ferrite / SiO_2 composites "Physics B, Vol. 398, No. 2, 2007 pp 241 – 244, doi : 10, 1016 / J. Phy S.B 2007.04, 024.
[19]. Lijun Zhao, Hua Yang, Xueping Zhao.Lianxiang Yu,Yuming, Cui, Shouhua Feng, Magnetic Properties of CoFe2O4 Ferrite doped with rare earth ion. Materials letters 60 (2006) 1 – 6.
[20]. B.D. Cullity elements of XR Diffraction Addision wesely publishing reading 1959 p132.
[21]. R.C.Cumbale, P.A.Sheikah, S.S.camble and Y.D.Kolekar effect of cobalt substitution on structural magnetic and electric properties of nickel ferrites. J Of Alloys and Compound Vol478.n0 1-2,2009 pp 599-603,doi10.1016/J.Jmmm.2005.03.007
[22]. M.M. Rashed, R. Mohmed , H. EL-Shall, Magnetic properties of nano crystalline Sm- substituted $CoFe_2O_4$ Synthesized by citrate precursor method, jounal of materials processing Technology 198 (2008) 139 – 146.
[23]. Jing Jiang, Yan- Min Yang, Liang – Chao Li, Synthesis and magnetic properties of Lanthanum – substituted Lithium – Nickel Ferrites via a soft chemistry route, physica B: condenced matter 399 (2007) 105 – 108.
[24]. Zhao Lijun. Yang Hua,Yu Lianxiang, Cui Yuming,Zhao Xueping,Yan Yu, Feng Shouhua, The studies of nano crystalline $Ni_{0.7}$ $Mn_{0.3}Nd_xFe_{2-x}O_4$ Ferrites, Physics letters A 332(2004) 268- 274.