INFLUENCE OF Cr^{3+} ION ON MAGNETIC PROPERTIES OF NICKEL NANO FERRITES

[1]R.Sridhar, [2]D.Ravinder, [3]K. Vijaya Kumar
[1]Department of BS&H ,[2]Department of Physics,[3]Department of Physics
[1]Vignan Institute of Technology & Science, Yadadri-Bhuvanagiri,, India. [2]Osmania University, Hyderabad, India,
[3]JNTUH College of Engineering Sultanpur, Pulkal (M),Madak, Telangana State, India.

Abstract: Nanocrystalline Cr ion doped nickel ferrite system having the compositional formula $NiCr_XFe_{2-X}O_4$ (Where X = 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) were synthesized by Citrate-Gel auto combustion method and characterization was investigated by X-ray diffraction (XRD), FT-IR and vibrating sample magnetiometer (VSM). X-ray analysis revealed that the obtained powder samples are single phase cubic spine structure and average crystallite size was in the range 8.55-10.36nm. The X- ray density and bulk density were calculated. FTIR shows two absorption bonds which illustrate the tetrahedral and octahedral sites. The magnetic properties of prepared samples were characterized with using VSM at room temperature in the applied field of ±6KOe. The attained M-H loops are illustrate the prepared nano ferrites are become soft magnetic materials. Magnetic parameters such as saturation magnetization and magnetic moment were measured and discussed with Cr^{3+} ion concentration. The Curie temperature is measured from Loria-Sinha method. The observed results can be explained on the basis of composition.

***Keywords*: Ni-Cr nano ferrites, Citrate-Gel auto combustion method, XRD, FTIR, magnetic properties.**

I. INTRODUCTION

Among all the magnetic materials, ferrites are the important non-conductive ferromagnetic ceramic compounds which as composing of iron oxides (Fe_2O_3 or Fe_3O_4) and metal oxides (MO). These are show the magnetic and electrical transport properties with large number of application in various fields [1-2]. The ferrite composition is MFe_2O_4, where M is divalent metal ion and Fe is trivalent ion. Many physicists are focusing on the study of properties of nanostructured materials due to the nanostructured systems form a bridge between single molecule and bulk system and their increasing applications in several technological and scientific fields [3-4]. The nanostructure material shows evidence of novel properties over those exhibited by bulk material of same composition [5].

In the current years researchers are focus on synthesis and characterization of new class of soft nano size magnetic materials, which possess both large initial permeability and saturation magnetization [6-7]. In the field of science and technology nano size materials are important because same composition of different nano size particles can exhibit the changes in properties. When the size of the particle reduced into nano scale, the properties are change and may be useful for various applications [8].

In nanoscience and nanotechnology, a number of considers such as preparation method, preparative conditions and dopent are affected on ferrite properties. Structural parameters and magnetic properties of the material improved through changing microstructure, controlling the chemical composition and size [9-10]. Hence many researchers are paying attention on the preparation of nano size magnetic material with high purity, ultra-fine size, good dispersion and remarkable magnetism. In the previous period,

The Ceramic method [11] is commonly used to obtain nano particles, but they have disadvantages like high sintering temperature, time period is more and stoichiometry change with divalent volatilization results [12]. Hence, in recent years the wet chemical methods such as Sol-gel, Co-precipitation, hydrothermal, spray dying and Citrate-gel technique are used for preparation of nano scale materials because, easy preparation, require low temperature, less cost.

Among the ferrites, Ni ferrite and substituted nickel ferrites have extensive analysis due to having high frequency function of magnetic materials [13]. These materials scientifically interest because of its promising and interesting applications in microwave devices, colour imaging, magnetic refrigerators and high density recording devices [14]. Particularly trivalent such as Al^{+3}, Cr^{+3} are substituted in it, as for its fascinating effect on electromagnetic properties of nickel ferrite. In view of immense importance of nickel nano ferrite applications and their considerable changes in their properties by doping with trivalent ion decided to prepare chromium dopent nickel nano size ferrite with chemical formula $NiCr_XFe_{2-X}O_4$ (X=0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) with using Citrate gel auto combustion technique, which has not been reported earlier and to study their structural and magnetic properties in systematic manner.

II. EXPERIMENTAL PROCEDURE

The molar quantity of AR grade of metal nitrates such as Nickel Nitrate, Chromium Nitrate, Ferric Nitrate, Citric acid and Ammonia as raw materials. Calculated quantities of metal nitrates by sensitive digital balance and they were dissolved in deionized double distilled water and then mixed together in a beaker. Aqueous solution of calculated quantity of citric acid was added in 1:3 molar ratio of nitrate to citric acid as chelating agent to this nitrate mixture. This mixture was thoroughly stirred using magnetic stirrer to get a homogeneous solution. Ammonia solution was added to this nitrate-citrate mixture to adjust the p^H to 7. The mixed solution was then heated at about 80^0C with uniform stirring on a hot plate to obtain a highly viscous gel denoted as citrate precursor. The resultant gel was further heated on the hot plate maintained at a temperature of 180^0C to 200^0C. Finally, water molecules were removed from the mixture, the viscous gel then began frothing. The gel gave a fast flameless auto combustion reaction with the evolution of large amounts of gaseous products. It started in the hottest zones of the beaker and propagated from the bottom to the top, like the eruption of a Volcano. The reaction was completed in a minute, giving rise to dark grey voluminous product with a structure similar to a branched tree. Finally the as-burnt ferrite powders were grained by using Agate Mortar and Pestle then calcined in a muffle furnace at a temperature at 700^0C for 5hr. the calcined ferrite powders were again grained by using Agate Mortar and Pestle to obtain a better crystallization and homogeneous cation distribution in the spinel. By adopting this procedure, mixed Ni-Cr nano ferrites are prepared.

The structural characterization was determined by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.15405 nm) source between the Bragg angles 20^{O} to 80^{O} in steps of 0.04^{O}/Sec. The prepared samples crystallite sizes were measured from broadening peak (311), using the Scherer's equation [15].

$$D_{hkl} = \frac{0.91\lambda}{\beta Cos\theta} - - - - - (1)$$

X-ray density (d_x) measured with the following relation

$$d_x = \frac{8M}{Na^3}\left(\frac{g}{cm^3}\right) - - - - - - (2)$$

The bulk density d_m was determined using formula

$$d_m = \frac{m}{\pi r^2 h} - - - - - - - - - - (3)$$

Porosity (P) of the ferrite was determined using formula

$$p = 1 - \frac{d_m}{d_x} - - - - - - - - - - (4)$$

The absorption spectra of prepared Ni-Cr nano ferrite powders were recorded at room temperature by Fourier Transform Infrared Spectroscopy (Spectrum 100, Perkin Elmer, USA) in the range of 400-4000cm^{-1} with a resolution of 1cm^{-1} using KBr pellet method.

The magnetic properties were carryout from obtained M-H loops at room temperature by using VSM (GMW Magnet System, model 3473). From M-H loops saturation magnetization (M_S) directly extracted and the magnetic moment (μ_B) calculated with the following relation [16].

$$\mu_B = \frac{M_W \; X \; M_S}{5585} - - - - - - - - - - (5)$$

Where M_W – Composition molecular weight
M_S - Saturation magnetization

The Curie temperature calculated from Loria-Sinha method (gravity method).

III. RESULTS AND DISCUSSION

3.1 X-rd analysis

Figure 1 illustrates the X-RD pattern of mixed Ni-Cr nano ferrite system, it shows the crystalline phases were identified with standard data PDF# 862267 for Nickel ferrites ($NiFe_2O_4$) from the ICDD data. In XRD pattern the highest reflection comes from (311) peak that shows spinel structure and all samples represents formation of cubic spinel structure in single phase without other noticeable additional impurity phases for chromium substituted nickel nano ferrite [17]. The prepared samples crystallite size is in the nanometer scale between 8.55nm-10.36nm. To my knowledge small size mixed Ni-Cr nano ferrites samples are possible only with the Citrate-gel auto combustion method no other method has resulted the such a small size nano ferrites.

Figure 2 shows increases the X-ray density from 5.326gram/cc to 5.368gram/cc and the bulk density decreases from 5.218gram/cc to 4.813gram/cc with increases Cr^{3+} ion concentration in Ni nano ferrite. It may be because of larger atomic weight and density of Fe (55.847gm/mole, 7.874gm/cm^3) compare with atomic weight density of Cr (51.996gm/mole, 7.14gm/cm^3). The X-ray density is more than the apparent density due to the existence of pores which depends on the preparation state. Similar behavior observed for the Cr substitution nano ferrite system with others [18-19].

Figure 3 illustrate the two prominent absorption bands represent the spinel ferrites in single phase and the results are reported in **table 1**. The high frequency band (ν_1) lies in the range of 591to 607 cm^{-1} corresponds to Fe^{+3}-O^{-2} vibrations in tetrahedral (A site) and low frequency band (ν_2) lies in the range 472 to 492 cm^{-1} corresponds to M^{+2}-O^{-2} vibrations in octahedral sites (B site) [20]. The difference between A site and B site is due to the change in bond length of Fe^{+3}-O^{-2} at the octahedral and tetrahedral sites [21]. The bands around 3400cm^{-1}, 2400 cm^{-1} and 1600cm^{-1} are the contribution of the stretching vibration of free and absorbed water, indicated the removal of the -OH, -CO and -NO groups. Similar result observe by others [22].

3.2 Magnetic Properties

The obtained hysteresis loops are illustrated in **figure 4.** It shows the loop area is very narrow therefore the samples present soft ferrite nature with less saturation magnetization Hence these materials are desirable for transformers [23].

3.3 Composition dependence magnetic parameters

It is observed that the Ni-Cr nano ferrites have less saturation magnetization due to the grain size is small. From **table 2** the saturation magnetization (M_s) value has decreased from 4.49emu/gr to 2.97emu/gr and the magnetic moment values are decreases from 0.188μ_B to 0.122μ_B with increases Cr^{3+} ion concentrations in Ni nano ferrite as evidence in **figure 5** and **figure 6**. It is explained based on the non-collinear spin arrangement [24-25]. The B–O–B coupling interactions at the B sublattice become stronger than that of A–O–B coupling between magnetic ions at the A and B sublattice due to the presence of a small canting of the B site moment with respect to the direction of the A site moment. The B–O–B coupling leads to the random existence of the small canted structure at the B site and forms triangular configuration in the ferrite system. As a result, the magnetic moments of the Fe ions at the B site are shifted from the collinear parallel to nonparallel arrangements. Therefore, the saturated magnetization is being decreased corresponding to the magnetic moment which is also decreased. The decrease in saturation magnetization and magnetic moment is credited to greater tenancy of Cr^{3+} at B sites, therefore the materials are getting changed into soft ferrite materials. Similar report was observed in Cr substituted Co–Zn nano ferrites by S. Bhukal et al [26] and Al substituted Co–Zn nano ferrites by Sonal Singhal et al [27].

It was found Curie temperature decrease from 775.39 Kelvin to 635.34 Kelvin on increasing the Cr^{3+} concentration. When the replacement of Fe^{3+} ion with Cr^{3+} ions increases, the magnetization decreases in B-sublattice without disturbing the A-sublattice, this leads to a decrease in the A-B interactions (Fe^{3+}-O^{2-}-Fe^{3+}) which results in decreases of Curie temperature. Similar behavior was observed in the trivalent substitution in nano ferrite system investigated by other researchers [28-29].

IV. CONCLUSION

The Citrate-gel auto combustion technique is to be a convenient and versatile for obtaining homogeneous nanostructured mixed Ni-Cr ferrites. X-ray diffraction confirms the formation of single phased cubic spinel structure without any impurity peak. X-ray density increases and bulk density decreases with increase in Cr substitution in the mixed Ni-Cr nano ferrite system. It shows the densification of the material. FTIR absorption spectra revealed the presence of two significant absorption bands υ_1 and υ_2 around 600 cm^{-1} and 400 cm^{-1}. This confirms the formation of single phase spinel structure with two sub-lattices tetrahedral (A) site and octahedral (B) site. The obtained hysteresis loops of Ni-Cr nano ferrites illustrate soft magnetic materials with less loop area and small saturation magnetization, hence these materials are may be desirable for transformers to minimize the energy dissipation. Saturation magnetization, magnetic moment is decreases with increase Cr^{3+} ion concentrations in Ni nano ferrite. Curie temperature (Tc) decreases with increase in Cu^{2+} concentration in Ni nano ferrites.

V. ACKNOWLEDGEMENTS

The authors are grateful to Head, Department of Physics, Osmania University, Hyderabad for provided the facility to synthesis of samples. One of the author (RS) is grateful to Dr. G. Durga Sukumar Principal, Vignan Institute of Technology & Science, Yadadri-Bhuvanagiri (Nalgonda) and the authors (KVK) is grateful to Dr. K. Eshwara Prasad, Principal JNTUH College of Engineering, Sultanpur, Pulkal (M), Madak

REFERENCE

[1] M.K. Nazemi, S. Sheibani, F. Rashchi, V.M. Gonzalez-DelaCruz, A. Caballero, Adv. Powder Technol. 23 (2012) 833–838.
[2] M.M. Rashad, R.M. Mohamed, M.A. Ibrahim, L.F.M. Ismail, E.A. Abdel Aal, Adv. Powder Technol. 23 (2012) 315–323.
[3] Awschalom. D. D., Vincenzo. D. P., Phys. Today, 48 (1995) 43.
[4] Chen. Q., Zhang. Z., Journal of Appl. Phys. Lett. 73 (1998) 3156.
[5] G.A. Ozin, Adv. Mater. 4 (1992) 612.
[6] Yoshizawa Y. Oguma S and Yamauchi K, Journal of Appl. Phys. 64 (1988) 6044.
[7] Iwanable H, Lu B, McHenry, ME, and Laughlim, De, Journal of Appl. Phys. 85 B (1999) 4424.
[8] N. M. Deraz, A. Alarifi, Int. J. Electrochem. Sci., 7 (2012) 5534.
[9] X. Sui, M. Scherge, M. H. Kryder, J. E. Snyder and N. C. Koon J. Magn. Magn. Mater. 155 (1996) 132.
[10] J. kloubek, J. Colloid Interface Sci. 163 (1994) 10.
[11] Y. M. Abbas, S.A.Mansour, M.H.Ibrahim, Shehab.E.Ali, Journal of Magn. Magn. Mater. 324 (2012) 2781.
[12] E. E. Sileo, R. Rotelo and S. E. Jacobo, Journal of Physics B, 320, 1-4, (2002), 257-260.
[13] A.K.M. Akther Hossain, S.T. Mahmud, M. Seki, T. Kawai, H. Tabata, Journal of Magn. Magn. Mater. 312 (2007) 210–219.
[14] K. Maaz, S. Karim, A. Mashiatullah, J. Liu, M.D. Hou, Y.M. Sun, J.L. Duan, H.J. Yao, Phys. B: Conden. Matter 404 (2009) 3947.
[15] B.D. Cullity, Elements of X-ray Diffraction, 2nd ed, Addison-Wesley, London (1978) 102.
[16] M. A. Gabal, Y. M. Al Angari and S. S. Al-Juaid, Journal of Alloys and Compounds, 492 1-2 (2010) 411-415.
[17] Devan, R.S., Kolekar, Y.D., Chougule, B.K.: J. Phys., Condens. Matter 18, (2006) 9809–9821
[18] Muhammed Javed Iqbal, Mah Rukh Siddiquah, J. Alloys Comp. 453 (2008) 513.
[19] M.A. Gabal , W.A. Bayoumy, A. Saeed, Y.M. Al Angari Journal of Molecular Structure 1097 (2015) 45–51
[20] R. D. Waldron, Phys. Rev. 99, **1955**, 1727.
[21] A.K. Ghatage, S.C. Choudhari, S.A. Patil, *J. Mater. Sci. Lett.* 15, 1548, **1996**..
[22] A.S. Elkady, S.I. Hussein, M.M. Rashad, *J. Magn. Magn. Mater*. 385, **2015**, 70.
[23] S.A. Mazen and A.M. Abdel-Daiem, Mater. Chem. Physics, 130 (2011) 847.
[24] F. Li, H. Wang, L. Wang, J. Wang, J. Magn. Magn. Mater. 309 (2007) 295.
[25] Y. Koseoglu, H. Kavas, J. Nanosci. Nanotechnol. 8 (2008) 584.
[26] Santosh Bhukal, Tsering Namgyal, S. Mor, S. Bansal, Sonal Singhal, Journal of Molecular Structure 1012 (2012) 162–167
[27] Sonal Singhal, Rimi Sharma, Tsering Namgyal, Sheenu Jauhar, Santosh Bhukal, Ceramics International 38 (2012) 2773–2778
[28] Mohd. Hashim, S.S. Meena, R.K. Kotnala, Sagar E. Shirsath, Aashis S. Roy, Journal of Alloys and Compounds, 602 (2014) 150-156,
[29] M. Raghasudha, D. Ravinder, P. Veerasomaiah Journal of Alloys and Compounds, Volume 604 (2014) 276-280

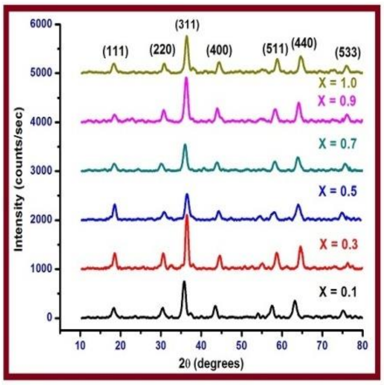

Figure 1: X-ray diffraction pattren of mixed $NiCr_XFe_{2-X}O_4$ nano ferrites

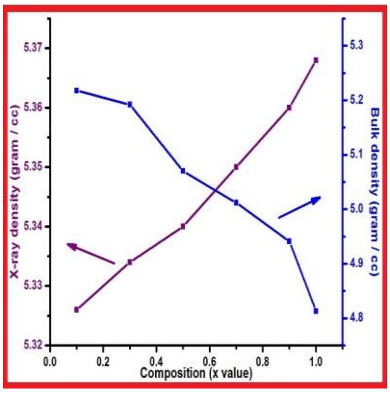

Figure 2: X-ray density and bulk density variation with Cr concentration

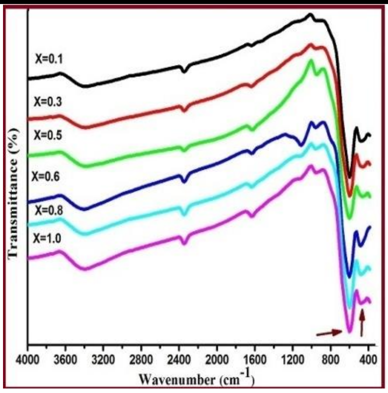

Figure 3: FTIR pattern of Ni Cr nano ferrite

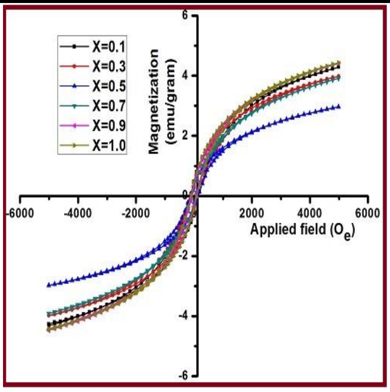

Figure 4(a-f): Magnetic hysteresis loops of Ni Cr nano ferrite

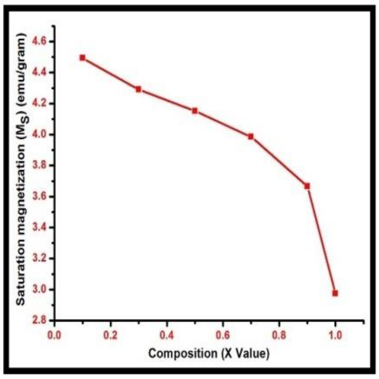

Figure 5: Variation of saturation magnetization with Cr concentration

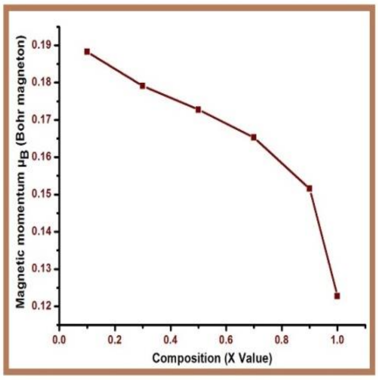

Figure 6: Variation of magnetic moment with Cr concentration

Table - 1: Structural parameters of mixed $NiCr_XFe_{2-X}O_4$ nano ferrites

Sl.No.	Composition	Molecular weight (M)(gr)	Crystallite size (nm)	X-ray density (gram/cc)	Bulk Density (gram/cc)	Absorption band	
						ν_1 (cm^{-1})	ν_2 (cm^{-2})
1	$NiCr_{0.1}Fe_{1.9}O_4$	233.945	8.96	5.326	5.218	599.96	485.35
2	$NiCr_{0.3}Fe_{1.7}O_4$	233.175	10.36	5.334	5.192	607.03	477.05
3	$NiCr_{0.5}Fe_{1.5}O_4$	232.340	7.95	5.34	5.07	602.45	479.69
4	$NiCr_{0.7}Fe_{1.3}O_4$	231.635	8.55	5.35	5.012	591.43	481.11
5	$NiCr_{0.9}Fe_{1.1}O_4$	230.865	8.84	5.36	4.941	594.86	492.42
6	$NiCrFeO_4$	230.480	9.26	5.368	4.813	597.13	472.62

Table - 2: Magnetic parameters of mixed Ni-Cr nano ferrites

Sl.No.	Composition	Saturation magnetization (M_S) (emu/gr)	Magnetic moment (Bohr magneton)	Curie Temperature
1	$NiCr_{0.1}Fe_{1.9}O_4$	4.49	0.18823	808
2	$NiCr_{0.3}Fe_{1.7}O_4$	4.29	0.17911	736
3	$NiCr_{0.5}Fe_{1.5}O_4$	4.15	0.17273	726
4	$NiCr_{0.7}Fe_{1.3}O_4$	3.99	0.16529	686
5	$NiCr_{0.9}Fe_{1.1}O_4$	3.67	0.15154	674
6	$NiCrFeO_4$	2.97	0.12272	668