

# The Structural and Magnetic Properties of NiFe<sub>2</sub>O<sub>4</sub> Ferrite Nano- Crystalline Prepared by Sol -gel Auto –Combustion Technique

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**ABSTRACT:** The synthesis and annealing temperature effect on the structural and magnetic properties of NiFe<sub>2</sub>O<sub>4</sub> ferrite powder was synthesized via sol-gel auto combustion method and then the dry gel powder was annealed at 600 °C for 3hrs. Investigation of magnetic and structural properties was carried out using magnetic measurements (Digital hysteresis loop tracer) and X-ray diffraction (XRD) technique. XRD confirms the formation of nanocrystalline cubic spinel ferrites with average Scherrer's grain diameter ( $D$ ) = 32.1 nm for dry gel samples and 35.0 nm for annealed samples. XRD of the studied specimens also reveals the formation of a secondary phase of  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> in both the cases (annealed and dry gel samples).  $\rho_{xrd}$  increases from 5365.4 to 5382.8 Kg/m<sup>3</sup> for the annealed samples which is ascribable to the fact of decrease in the volume of the unit cell overtakes the decrease in mass of the unit cell. Variation of hopping length for A-site ( $L_A$ ) and B-site ( $L_B$ ) is similar to that of the variation of lattice parameter. Increased in the value of  $H_c$  is observed in case of annealed samples which can be ascribed to the grain growth.

**KEYWORDS:** Ferrites, XRD, Magnetic properties.

## I. INTRODUCTION

The most important developments in the field of ferrimagnetism during last 50 years are undoubtedly the progress in metal oxides for high frequency applications. Ferrites are generally denoted by the chemical formula MO.Fe<sub>2</sub>O<sub>3</sub> where M is a divalent metal ion such as Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup> or Cd<sup>2+</sup>. The word ferrite first used at the beginning of 20<sup>th</sup> century, is derived from Latin word "ferrum" means iron [1]. The interest in nanostructured ferrite, a huge class of metal oxides, is driven by unusual physical properties of highly confined systems with reduced dimensionality than their bulk counter parts as well as by their promising applications in an impressive range. For example, millimeter wave integrated circuitry, power handling, soft and hard (*permanent*) magnets, and magnetic recording [2], electromagnetic wave absorbers, information storage systems, high-efficiency photo catalysts, and medical diagnostics [3].

Synthesis of spinel ferrite nanomaterials has attracted a great deal of attraction over the past several years due to their functional electrical and magnetic properties. These types of ferrites are widely used in the field of magnetic drug delivery, magnetic information storage device, ferrofluids, sensors, catalysis, etc. [4]. Nickel ferrite is one of the versatile and technologically important soft ferrite materials because of its typical ferromagnetic properties, low conductivity and thus lower eddy current losses, high electrochemical stability, catalytic behavior, abundance in nature, etc. Among spinel (NiFe<sub>2</sub>O<sub>4</sub>), ferrites the inverse type is most interesting due to its high magneto-crystalline anisotropy and, high saturation magnetization. Nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) exhibits ferrimagnetic properties combined with relatively low electrical properties, and it displays low eddy current loss in alternating current applications. Ferrites show high electrical resistivity, permeability, mechanical strength and permittivity compared to other materials they exhibit very low losses when magnetized in high frequency field [5]. Most of the ferrites "grow" in spinel, garnet or magnetoplumbite crystal structure. The crystal structure and the atomic configuration of these determine their intrinsic magnetic, chemical and mechanical properties.

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## II. EXPERIMENTAL TECHNIQUES

### A. SYNTHESIS

Nickel ( $\text{NiFe}_2\text{O}_4$ ) ferrite in powder form was prepared using sol-gel auto combustion method. For synthesizing Nickel Nitrate –  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Ferric Nitrate –  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and Citric acid -  $\text{C}_6\text{H}_8\text{O}_7$  were mixed in stoichmetric ratio with citric acid as fuel. Metal salt to fuel ratio was taken as 1:1. Citric acid primarily acts as a chelating agent for metal ions of varying ionic sizes, which helps in preventing their selective precipitation to maintain compositional homogeneity among the constituents. Afterwards it also serves as a fuel in the combustion reaction. De-ionized water was used to dissolve all the precursors and pH was maintained at 7, by adding ammonia solution [6]. Then the solution was heated at  $120^\circ\text{C}$  in air till the loose powder was formed, called as 'dry gel or as-burnt powder'. The dry gel was then annealed at  $600^\circ\text{C}$  for 3hr.

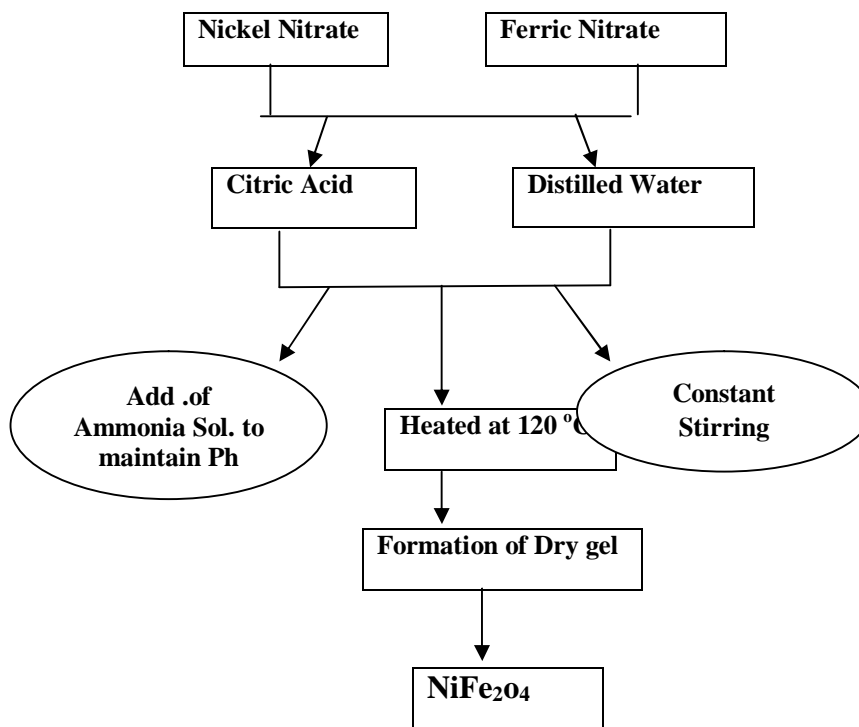


Fig.1. Schematic diagram of the synthesis of  $\text{NiFe}_2\text{O}_4$  by sol-gel auto- combustion method .

### B. CHARACTERIZATION

XRD measurements were carried out at room temperature using a Bruker D8 Advance diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.540562 \text{ \AA}$ ).

XRD patterns were analyzed to obtain the lattice parameter (a), using the expression:

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (1)$$

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Where 'a' - lattice parameter, 'd' - inter-planer spacing and (h, k, l) - miller indices.

Obtained lattice parameter (a) was used to calculate the X- ray density of the sample using the following relation:

$$\rho_{XRD} = (8M_w / Na^3) \quad (2)$$

Where  $\rho_{XRD}$  X - ray density,  $M_w$  - Molecular weight,  $N$  - Avagadro's Number and  $a$  -lattice parameter.

Average grain diameter  $D$  is obtained by integral width of the (311) line by using Scherrer's formula:

$$D = (0.9\lambda / \beta \cos\theta) \quad (3)$$

Where  $\lambda$  – wavelength of the x- ray used,  $\beta$  –line width,  $\theta$ - peak position (in  $2\theta$  scale).The hopping length between the magnetic ion ( the distance between the magnetic ion ) in the tetrahedral [A] site and in the octahedral [B] site are calculated form the following relations [7].

$$L_A = a \sqrt{3}/4 \quad (4)$$

$$L_B = a \sqrt{2}/4 \quad (5)$$

Where,  $L_A$  is hopping length for tetrahedral site and  $L_B$  is hopping length for octahedral site and  $a$  is the lattice parameter.

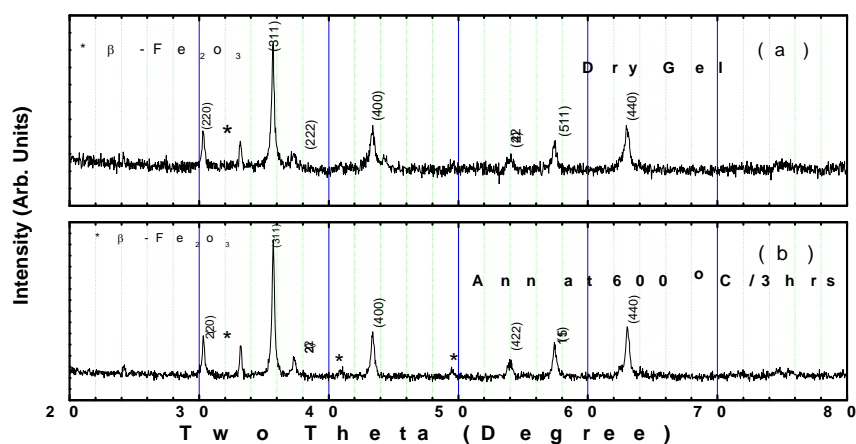
Room temperature hysteresis loops of the synthesized samples were measured at 50 Hz by conventional induction technique by applying maximum field –  $H_{max} \approx \pm 120000$  A/m (1508 Oe). Loops were analyzed by a Matlab<sup>®</sup> based program [8] to obtain coercivity ( $H_c$ ). Saturation magnetization ( $M_s$ ) values were obtained by plotting magnetization against inverse of magnetic field (1/H) and, extrapolating the data to 1/H = 0.

Anisotropy constant ( $K_1$ ) was calculated by:  $K_1 = [H_c \times M_s] / 0.96$  (6) where  $H_c$  – coercivity in Oe. and  $M_s$  – saturation magnetization in emu/cc.

## III. RESULTS AND DISCUSSION

### A. STRUCTURAL STUDIES

The XRD pattern of the as burnt and annealed (at 600 °C for 3hrs) NiFe<sub>2</sub>O<sub>4</sub> powder synthesized by the sol–gel auto combustion technique are shown in fig. 2. They exhibit typical reflections of (220), (311), (222), (400), (422), (511), and (400) planes indicating the cubic spinel structure of nickel ferrite. XRD patterns confirm the formation of spinel phase in the studied samples (JCPDS 86-2267). All the characteristic peaks of NiFe<sub>2</sub>O<sub>4</sub> are present in the diffraction pattern in both the cases. Presence of secondary phase-  $\beta$  Fe<sub>2</sub>O<sub>3</sub> (JCPDS 85-0599 and 76-1821) [9] was also detected with the help of XRD patterns in both the annealed and as burnt powders. Table.1 shows the calculated values of the lattice Parameter ( $a$ ), average Scherrer's grain diameter ( $D$ ), x-ray density ( $\rho_{xrd}$ ), hopping length for tetrahedral and octahedral site for dry gel and annealed samples. The decrease in lattice constant in the case of annealed sample indicates that lattice contracts disturbing the symmetry of lattice. The average Scherrer's grain diameter increased



**Fig.2.** XRD Pattern (a) of Dry Gel and (b) annealed (600 °C for 3hrs.) NiFe<sub>2</sub>O<sub>4</sub>.

From 32.15 to 35.05 nm, as the sample is annealed at 600 °C for 3hrs, clearly showing the formation of nano-crystalline ferrites. The bigger crystallites are obtained through high reaction rates maintained during the synthesis or through annealing after the synthesis.  $\rho_{xrd}$  increases from 5365.4 to 5382.8 Kg/m<sup>3</sup> for the annealed samples which is ascribable to the fact of decrease in the volume of the unit cell overtakes the decrease in mass of the unit cell. Behaviour of hopping length (distance between magnetic ions) for A-site ( $L_A$ ) and B-site ( $L_B$ ) is similar to that of the variation of  $a$ .

Sample name	$a$ (nm)	$D$ (nm)	$\rho_{xrd}$ (Kg/m <sup>3</sup> )	$L_A$ (nm)	$L_B$ (nm)
Dry gel	0.8341	32.15	5365.4	0.361	0.2947
Ann 600°C/3h	0.8332	35.05	5382.8	0.3606	0.2944

**Table 1:** Variation in lattice parameter ( $a$ ), average grain diameter ( $D$ ), X-ray density ( $\rho_{xrd}$ ),  $L_A$  - hopping length for tetrahedral site and  $L_B$  - hopping length for octahedral site of dry gel and annealed samples obtained from the analysis of XRD analysis of NiFe<sub>2</sub>O<sub>4</sub>.

## B. MAGNETIC MEASUREMENTS

Room temperature magnetization studies made for NiFe<sub>2</sub>O<sub>4</sub> dry gel and annealed (at 600 °C for 3hrs) samples are shown in Fig.3. The magnetization behaviour of the sample is of typical ferrimagnets, which can be explained on the basis of changes in exchange interaction between tetrahedral and octahedral sub lattice. However in nano particales of ferrites there is interplay of super- exchange interactions between the projected moments on the surface of nanoparticles [9]. Hence the magnetic property observed in nano NiFe<sub>2</sub>O<sub>4</sub> is a cumulative effect of these interactions. Sample annealed with crystallite size 35.05 nm exhibits a saturation magnetization ( $M_s$ ) of 0.32 Tesla, which is higher than the values for dry gel NiFe<sub>2</sub>O<sub>4</sub> (0.23 Tesla). It is well known that for magnetic nano particals the size has significant influence on their magnetic properties.

Table 2 depicts the values of coercivity ( $H_c$ ), retentivity ( $M_r$ ), saturation magnetization ( $M_s$ ), squareness ratio ( $M_r/M_s$ ) and anisotropy constant ( $K_1$ ). Increased in the value of  $H_c$  can be ascribed to the grain growth.  $M_s$  values are obtained by plotting M versus 1/H and extrapolating the data to 1/H =0 (Fig. 4). For annealed samples  $M_s$  is found to increase which can be ascribed to the increased in the magnetic moment at octahedral site, so the net magnetic moment increases. It has been reported that the squareness ratio at or above 0.5 indicates that the material is the formation of

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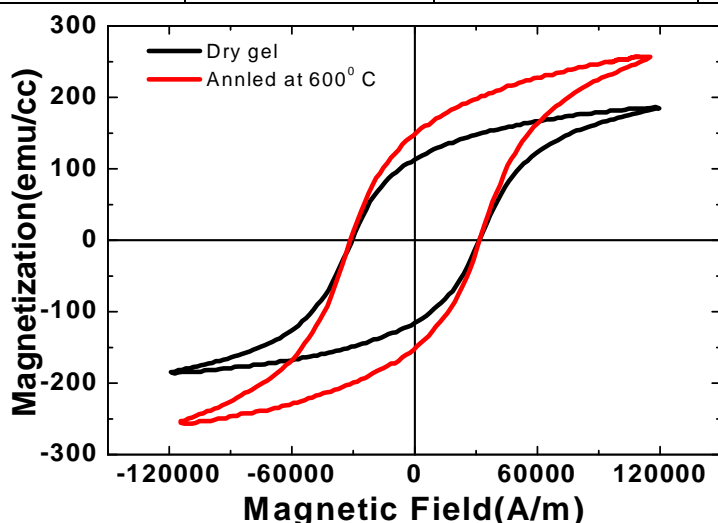
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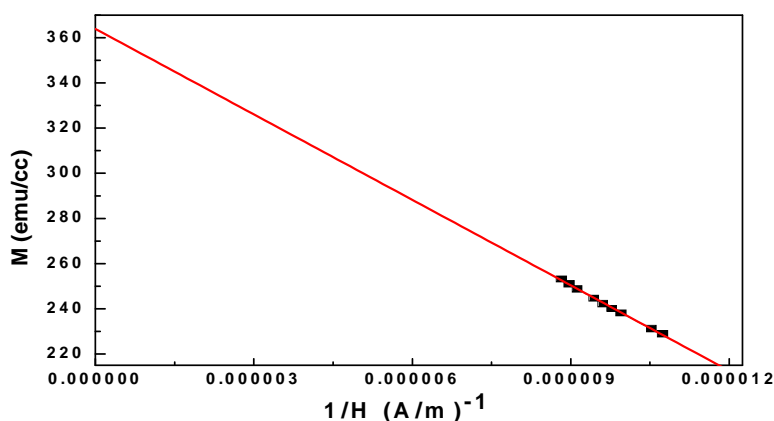
multi-domain structure. The calculated values of squareness ratio of the sample are below 0.5 clearly shows that the nickel ferrite nano-particles synthesized through sol-gel auto combustion method are multi-domain in nature.  $K_1$  follows the same trend as  $H_c$ .

**Table2.** Magnetic data of the studied as burnt and annealed sample for NiFe<sub>2</sub>O<sub>4</sub> showing Coercivity ( $H_c$ ), Retentivity ( $M_r$ ), Saturation magnetization ( $M_s$ ), Squareness ratio ( $M_r/M_s$ ), and  $K_1$  anisotropy constant .

Sample name	$H_c$ (A/m)	$M_r$ (Tesla)/emu/cc	$M_s$ (Tesla)/(emu /cc)	$M_r/M_s$	$K_1 \times 10^4$ (erg/cc)
Dry gel	31177.6	0.15 / 119.37	0.32/255.40	0.62	10.42
Ann 600°C/3h	31650.3	0.19 / 151.20	0.45/363.94	0.59	15.07



**Fig. 3** Hysteresis loops of NiFe<sub>2</sub>O<sub>4</sub> (Dry gel and annealed) samples.



**Fig.4.** M versus 1/H curve showing the extrapolation of the data to  $1/H = 0$  for annealed sample (600 °C for 3Hrs)

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## IV. CONCLUSION

Sol-gel auto-combustion method was used to synthesize nano-crystalline  $\text{NiFe}_2\text{O}_4$  spinel ferrite. The dry gel powder was then annealed at  $600^\circ\text{C}$  for 3hrs in the  $\text{NiFe}_2\text{O}_4$  ferrite sample. XRD of the studied specimens reveals the formation of cubic spinel structure with a secondary phase of  $\beta\text{-Fe}_2\text{O}_3$ . Lattice constant is found to decrease in the case of annealed sample. Behaviour of hopping length for A-site ( $L_A$ ) and B-site ( $L_B$ ) is similar to that of the variation of lattice parameter.  $\rho_{\text{xrd}}$  increases from 5365.4 to 5382.8  $\text{Kg/m}^3$  for the annealed samples. Increased in the value of  $H_c$  can be ascribed to the grain growth. For annealed samples  $M_s$  (obtained by plotting M versus  $1/H$  and extrapolating the data to  $1/H = 0$ ) is found to increase which can be ascribed to the increased in the magnetic moment at octahedral site, so the net magnetic moment increases. The values of squareness ratio of the sample are below 0.5 clearly shows that the nickel ferrite nanoparticles are multidomain in nature.

## V. ACKNOWLEDGMENTS

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