INFLUENCE OF GADOLINIUM DOPED IN NICKEL NANO FERRITE ON MAGNETIC AND OPTICAL PROPERTIES PREPARED BY SOL-GEL TECHNIQUE

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A B S T R A C T

Gadolinium (Gd^{2+}) doped in Nickel (Ni^{2+}) nano ferrite as $NiGd_xFe_{2-x}$ O_4 (were x=0.025,0.050,0.075,0.1,0.125,0.15) were synthesized by a simple and cost effective method involving sol-gel auto combustion method. Synthesized samples were sintered at 600^0C temperature. The Gadolinium, Nikel ,and ferric nitrates are used analytical Grade as a raw materials Citric acid is used as fuel 1:3 and ethylene glycol added for uniform formation of particle size. The powders resulting from this synthesis were characterized by X-ray diffraction (XRD). The grain size was found to be in the range of nanometer and structural properties it was found spinel crystalline nature. It The Magnetic properties are studied using hysteresis loop tracer field of 10 kOe. The magnetization of the prepared nanoparticles was investigated and the saturation magnetization (M_s), remanence (M_r), and coercivity (H_c) were derived from the hysteresis loops. The results revealed that as the (Co^{2+}) Gadolinium substitution in (Ni) nickel nano ferrite increases the magnetic properties remanence (M_r), and coercivity (H_c)goes on decreasing, the saturation magnetization (M_s), first it is increases upto x = 0.075 and then decreases for higher Gd^{2+} substitution such changes in magnetic properties may be due to the exchange interaction between the tetrahedral and the octahedral sites. From the magnetic properties it is clear that the synthesized materials shifted from hard to soft ferrite. From UV–Vis absorbance spectra band gap energy were calculated and it is in the range of semiconductor materials.

Keywords: : Ni, Gd nanoferrite, sol-gel, VSM, UV

1. Introduction:

Nanoparticles research has recently become an important field and widely used in material science. When particles are prepared at nano scale, their physical, chemical and biological properties changed. The properties at nanoscale are different from bulk due to two effects known as surface effects and finite size effects [1]. With decrease in particle size number of particles on surface will increase. Due to this, surface effects and interface effects become more important. For example,. Hence, the contribution of surface spins becomes more important to determine magnetization of nanoparticles [2,3]. Saturation magnetization depends on strength of dipole moment of the atoms and also depends on how densely the atoms are packed. Saturation magnetization will change with temperature [4]. Ferrites are those ceramic compounds that consist of iron oxide and one or more other metals in chemical combination [5]. The molecular formula of ferrites is $M^{2+}Fe_2{}^{3+}O_4$where M stands for divalent metal like Mn, Co, Ni, Cd, Mg, Zn, Cu. Ferrites are the metal oxide which contains magnetic ions grouped in such a manner that it produces spontaneous magnetization [6].Ferrites are chemically stable and show high electrical resistivity. Due to high chemical stability, ferrite materials exhibit interesting properties such as optical, electrical, chemical and magnetic [7]. Ferrites are used in magnetic recording media, permanent magnets, memory chips, antenna rods, transformer cores, microwave, computer technology, drug delivery, magnetic resonance imaging, gas sensors, actuators, transformers and in magnetic refrigeration [8,9,10,11].

Ce and Gd doped in Nickel ferrite were studied and reported that the Ce doped samples show smallest crystallite size and largest surface area and the X-ray density was found to be highest for Gd doped samples [12]. Gadolinium-doped cobalt ferrite were synthesized and reported that single crystal spherical shape and also reported the magnetic properties that rare- earth material doping in ferrite are strongly influence on their magnetic properties. [13]

Eu – substitution on Cobalt ferrite influence on thermal behavior, structural, Surface and magnetic properties are reported strongly depends. [14]. Nickel ferrite synthesized and studied the calcinations temperature and magnetic properties and reported that it posses the higher saturation magnetization. [15]

2. Experimental Technique:

Preparation of nanomaterials can be divided into two broad spectrum top down and bottom up, each of which has two directions physical and wet chemical. The most important criteria for preparation of nanoparticles are: Proper size with narrow size distribution well dispersed particles, shape of particles, high purity, and homogeneous composition. Most of the wet chemical methods have common feature that the mixing of components takes place at the atomic or molecular scale. Some of the non-conventional processes are: Sol-gel method, Co-precipitation method, Precursor method, combustion method, Hydrothermal, Spray drying. etc.

In present work a Sol-gel auto combustion technique were used. The raw materials are in the form of Metal nitrates and citric acid were used as oxidizing salts and combustion fuel. All chemicals were of high purity Analytical reagent The Sol-gel auto combustion technique has been proved to be extremely facile, time-saving and energy-efficient route for the synthesis of ultrafine hexaferrite powders.

3. Materials

Raw material are used in experiments are analytical grade nitrate i.e. nickel nitrate($Ni(No_3)_2.6H_2O$),Gadolinium nitrate($Gd(No_3)_2$),ferric nitrate ($Fe(NO_3)_2$) and citric acid ($C_6H_8O_7$) is used as fuel in the ratio 1:3 provided by Merck with ~99 % purity were used as a starting materials without further purification for the synthesis. Using the stoichiometric ratio appropriate amounts of raw materials were dissolved in 100ml distilled water under magnetic stirring. Then citric acid ($C_6H_8O_7$) was mixed in the metal nitrate solution to chalet Ni^{2+} ,Gd^{3+} and Fe^{3+} ions in the solution. The molar ratio of citric acid to total moles of nitrates was maintained at 1:3. A small amount of ammonia was added drop-wise into the solution to adjust pH 7. The solution were continuously stirring with 100 0C til to formation of gel after gel was auto-combustion to take place and obtain fine powder. The resulting powder is crushed in an agate mortar to obtain the nano ferrite particles and was sintered at 600˚C for 4 hours.

Gd^{3+}substituted $NiFe_2O_4$ ferrite with a chemical formula $NiGd_xFe_2O_4$ (where, x = 0.025, 0.05, 0.075, 0.1, 0.125 and 0.1s5) have been synthesized via sol-gel method.

4. Results & Discussion :

Characterization Techniques and Results:

1. X-Ray Diffraction:

Figure 1 shows the XRD patterns for the Gd samples with the Gd concentration of (x = 0.025, 0.050, 0.075, 0.1, 0.125, 0.15) Crystalline phases or Structural studies of Gd substituted $NiFe_2O_4$ were examined by XRD pattern . The pattern was recorded using Cu-Kα radiation (λ = 1.54182 Å) in the 2θ range 20°-80° with step size 0.01°and time/step 2 s. The average crystallite size (t) was calculated using the Debye-Scherrer’s formula;

$$t = \frac{0.9\lambda}{(\beta\cos\theta)\cdot} ----------- (1)$$

Where, λ is wavelength of the Cu-Kα radiation, β is the fullwidth of the half maximum and θ is the Bragg’s angle. Indexed patterns were compared with those in the JCPDS (Joint Committee on Powder Diffraction Standard) data base for phase identification. The lattice parameter “a” was calculated using the equation ,

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

Where d is the interplanar spacing and (hkl) is the index of the XRD reflection peak.

The average crystallite size (t) was calculated using the Debye-Scherrer’s formula. The average crystallite size was found to be in the range of 42–46.8 nm and lattice parameter were calculated.

2. Magnetic Properties:

The magnetic properties were measured by Vibration Sample Magnetometer (VSM). The hysteresis curves of $NiGd_xFe_2O_4$where(x=0.0, 0.025, 0.050, 0.075, 0.100, 0.125) was shown in Fig.2. Table 1 gives the saturation magnetization (Ms), Magnetic remenance (Mr), Magnetic Coercivity (Hc), squareness ratio. The results revealed that as the (Gd^{3+}) Gadolinium substitution in (Ni) Nickel nano ferrite decreases the magnetic remanence (M_r), and coercivity (H_c) goes on increasing upto to 0.075, i.e the optimization point and after that random nature, the saturation magnetization (M_s), first it is decreases upto x = 0.075 and then random nature is obtained (Ms) such changes in magnetic properties may be due to the exchange interaction between the tetrahedral and the octahedral sites. The magnetic remanance is very low. $NiGdxFe_2O_4$ is soft ferrite material, therefore such nanoferrite was recommended for cores and coils of low inductance.

Table 1 : Value of saturation magnetization (Ms), Magnetic remenance(Mr), Magnetic Corecitivity(Hc), Bohr magneton (nB), anisotropy constant (K1)

Concentration	**Hc (Oe)×1000**	**Mr (emu/gm)**	**Ms (emu/gm)**	**Mα**	**K1= Ms*Hc /0.98**	**nB= Mα* Ms /5585**
$NiGd_{0.025}Fe_2O_4$	11222.2	7.8365	16.6101	236.9644	190205.98	0.704747
$NiGd_{0.050}Fe_2O_4$	53444.4	8.0592	15.8197	239.4995	862728.95	0.678390
$NiGd_{0.075}Fe_2O_4$	63333.3	7.5228	13.1854	242.0345	852117.23	0.571408
$NiGd_{0.1}Fe_2O_4$	12222.2	7.1317	16.1982	244.569	202018	0.709324
$NiGd_{0.125}Fe_2O_4$	45666.7	6.3342	15.2204	247.1035	709250.44	0.673414
$NiGd_{0.15}Fe_2O_4$	25444.4	5.9517	12.2484	249.6385	318013.45	0.547479

The magnetic moment decreases with increasing Gadolinium concentration, which is the good agreement with particle size.

3. UV-Visible spectroscopy

Figure 3 shows the UV–Vis absorbance spectra of the Gd^{3+} doped $NiFe_2O_4$ with (x=0.025, 0.05, 0.075, 0.1, 0.125, 0.15) recorded at room temperature. An absorption edge of all sample appears in the range of 750nm to 771.5nm.using the absorption edge one can determine the energy gap (E=hc/λ).where h is planck constant ($h=6.602\times10^{-34}$), c is velocity of light and λ is wavelength of absorption edge. By using above relation obtained band gap for all the ferrites is listed in

Table 2: Optical band gap energy (Eg) of $NiGd_xFe_2O_4$

Sr No.	**Composition**	**Absorption Wavelength (λ)nm**	**Band gap (ev)**	**By Tauc Method Band Gap (eV)**
1	NiGd0.025Fe2O4	753.11	1.6496	1.6367
2	NiGd0.050Fe2O4	771.15	1.6110	1.5735
3	NiGd0.075Fe2O4	757.5	1.6408	1.6367
4	NiGd0.1Fe2O4	763	1.6281	1.6212
5	NiGd0.125Fe2O4	757	1.6408	1.6367
6	NiGd0.15Fe2O4	763	1.6281	1.614

Figure 4. **S**hows Tauc plot for Gd^{3+} doped $NiFe_2O_4$ with (x=0.025, 0.05, 0.075, 0.1, 0.125, 0.15). The optical band gap obtained by Tauc relation and is found to be nearly same as obtained by relation E=hc/λ. It observed that increasing of Gd^{2+} Concentration the band gap first decreases up to concentration x=0.050 then random nature .As Gd^{3+} replaces Fe^{3+}, impurity bands are created due to the formation of the impurity levels inside the gap. Burstein–Moss effect is the phenomenon of which the apparent band gap of a semiconductor is increased as the absorption edge is pushed to higher energies as a result of all states close to the conduction band being populated. Apparent band gap = Actual band gap + Moss-Burstein shift. It may be due to decrease in grain size with increasing Gd^{3+} (x>0.3) concentration and as grain size decreases band gap increases.

5. Conclusions:

Gadolinium substituted Nickel ferrite nanoparticles ($NiGdxFe_2O_4$ with x = 0.025, 0.050, 0.075, 0.1, 0.125 and 0.15) were synthesized via sol-gel auto combustion route. From x-ray analysis, it has been found that the average crystallite size is in the range of 46.8–42.2 nm. All the peaks are well matched with standard JCPDS data for $NiFe_2O_4$ (01-074-2081). lattice parameter is in the range from 8.32596 Å to 8.36544 Å. From UV–Vis absorbance spectra it was found that an absorption edge of samples appears in the range of 650nm to 771nm.It observed that with increasing concentration of Gd^{3+} band gap between the1.5 to 1.55eV. Gd^{3+}Gadolinium substitution in (Ni) Nickel nano ferrite decreases the magnetic remanence (M_r), and coercivity (H_c)goes on increasing upto to 0.075, and after that random nature. The saturation magnetization (M_s), first it is decreases upto x = 0.075 and then random nature is obtained (Ms) such changes in magnetic properties may be due to the exchange interaction between the tetrahedral and the octahedral sites. The magnetic moment decreases with increasing Gadolinium concentration, which is the good agreement with particle size.

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REFERENCES

[1] F. Gazeau, J. C. Bacri, F. Gendron, R. Perzynski, Y. L. Raikher, V. I. Stepanov, E. Dubois, *"Magnetism and Magnetic Materials"*, **186**(1998)175

[2] A. H. Lu, E. L. Salabas, F. Schuth, *"Magnetic Nanoparticles"*Wiley-VCH verlagGmbh& Co. KGaA, Weinheim, (2007)1223

[3] B. N. Pianciola, E. L. Jr., H. E. Troiani, L. C. C. M. Nagamine, R. Cohen, R. D. Zysler, *"Magnetism and Magnetic Materials"* **377**(2015)44

[4] M. Houshiar, F. Zebhi, Z. J. Razi, A. Alidoust, Z. Askari, *"Magnetism and Magnetic Materials"*, **371**(2014)43

[5] M. Mozaffari, J. Amighian, E. Darsheshdar, *"Magnetism and Magnetic Materials"*, **350**(2014)19

[6] M. Meshram, N. K. Agarwal, B. Sinha, P. S .Mishra, *"Magnetism and Magnetic Materials"*, **271**(2004)207

[7] K. Maaz, G. H. Kim, *"Materials Chemistry and Physics"*, **137**(2012)359

[8] M. A. Ahmed, A. A. E. Khawlani, *"Magnetism and Magnetic Materials"*,**329**(2009)1959

[9] L. Kumar, P. Kumar, A. Narayan, M. Kar, *"International Nano Letters"*, **3**(2013)8

[10] S. Rana, J. Philip, B. Raj, *"Materials Chemistry and Physics"*, **124**(2010)264

[11] K. Maaz, A. Mumtaz, S. K. Hasanain, A. Ceylan, *"Magnetism and Magnetic Materials"*, **308**(2007)289.

[12] Gagan Dixit, JitendraPalSingh, R.C.Srivastava , H.M.” Journal of Magnetism and Magnetic Materials 324 (2012) 479–483

[13] Jianhong Peng , BaoweiCao, JuanWang, HongWu, Journal of Magnetism and Magnetic Materials 323 (2011) 133–138

[14] Aiman Zubair , Zahoor Ahmad , Azhar Mahmood , Weng-Chon Cheong , Irshad Ali , Results in Physics 7 (2017) 3203–3208

[15] J. Azadmanjiri , S.A. Seyyed Ebrahimi , H.K. Salehani Ceramics International 33 (2007) 1623–1625

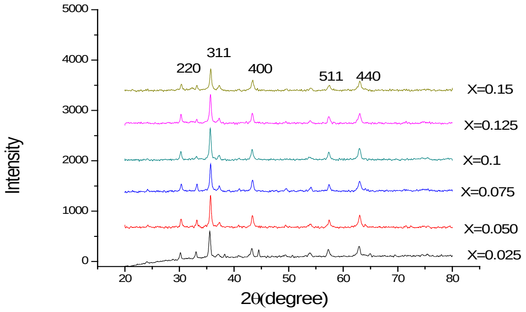

Figure.1 stacked XRD patterns for the Gd substituted $NiFe_2O_4$ samples

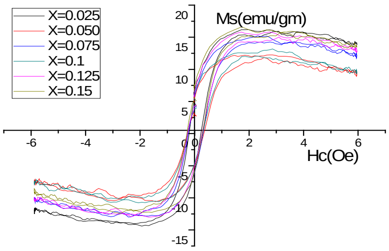

Fig.2:-Hysteresis of $NiGd_xFe_2O_4$nanoferrite with the Gd concentration of x = 0.025, 0.05, 0.075, 0.1, 0.125, 0.15.

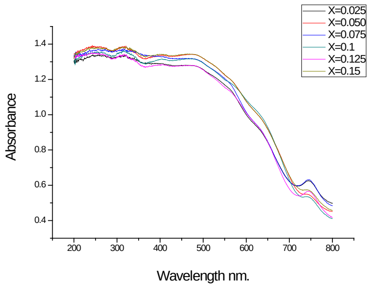

Figure 3. UV absorption spectra Gd^{3+} doped $NiFe_2O_4$ with(x=0.025, 0.05, 0.075, 0.1, 0.125, 0.15)
(recorded at room temperature).

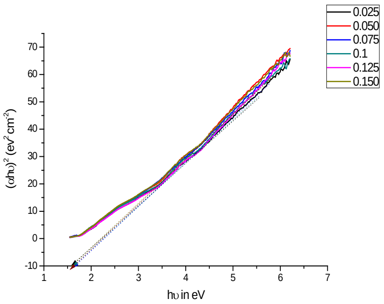

Figure 4. Tauc plot for Gd^{3+} doped $NiFe_2O_4$ with x=0.025, 0.05, 0.075, 0.1, 0.125, 0.15.