Structural, Electrical and Magnetic Studies of Gd $^{3+}$ doped Cobalt Ferrite Nanoparticles

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Abstract

Gd$^{3+}$ doped nanocrystalline Co-ferrites CoGd$_x$Fe$_{2-x}$O$_4$ ($x = 0.0$ to $0.1$) has been prepared by sol-gel auto combustion technique. Structural and morphology studies were performed using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Indexed XRD patterns confirm the formation of pure cubic spinel phase. Average crystallite sizes ranges from $16$ nm to $25$ nm $\pm 2$. Lattice constant ($a$) and crystallite size $D$ ($311$) increases with increase in Gd$^{3+}$ concentration due to large ionic radii ($0.94$nm) of Gd$^{3+}$ replacing Fe$^{2+}$ ($0.64$nm). FT-IR analysis shows the presence of two expected bands attributed to tetrahedral and octahedral metal oxygen vibrations. SEM images show the spherical morphology and uniform size distribution. Room temperature DC electrical resistivity decreases ($\sim 10^8$) for $x=0.025$ then increases up to $x=0.1 \sim (2.67 \times 10^8)$ $\Omega$-cm. Dielectric properties have been studied in the frequency range of $1$ kHz to $5$ MHz. Permittivity and tangent loss ($\tan\delta$) decreases with the substitution of Gd$^{3+}$ in parent crystal structure and have values of $12.4$ and $0.0160$ at $5$ MHz respectively. Complex impedance plots were further studied for complete contribution of grains and grain boundary resistances. Magnetic studies shows that magnetization ($M_s$) decreases with increase in Gd$^{3+}$ concentration from 63 emu/gm to 27.26 emu/gm, thus the material is becoming low loss dielectric, highly resistive and soft magnetic due to Gd$^{3+}$ doping.

Keywords: Rare earth ions, XRD, W-H plots, Dielectric properties, AC conductivity, magneto crystalline anisotropy

1. Introduction

Nano phase ferrites are a class of magnetic materials that have been the most attractive area of the research since the last 5 decades due to its remarkable applications in the high frequency and power devices especially for electromagnetic interference suppression (EMIS), phase shifters and circulators for mobile phones (R. Valenzuela et al., 2012). Spinel ferrites have many versatile electric and magnetic properties owing to its feasibility to make a huge number of solid solutions of different metal cations and a large compositional variability. As the crystal structure of spinel ferrite is cubic closed pack (fcc) with anions ($O^2-$) linked with two sub-lattices namely tetrahedral (A) and octahedral (B). Distribution of divalent and trivalent cations on the A and B sites imparts specific characteristics to a spinel structure (L. B. Tahar et al., 2008). CoFe$_2$O$_4$ is a well known partially inverse spinel, ferromagnetic material with a high specific resistance, low losses in high frequency applications, high coercivity and a moderate saturation magnetization with positive magneto-crystalline anisotropy (M. A. Elkestawy et al., 2010). These exceptional physical properties can be achieved by choosing the method of synthesis, doping of cation in the host crystal structure, size and morphology of the particles. Various methods has been adopted for the synthesis of cobalt ferrites which includes chemical co-precipitation (Y. I. Kim et al., 2003), sol-gel (C. S. Kim et al., 1999), hydrothermal (J. Peng et al., 2011), microemulsion (V. Pillai et al., 1996), solvothermal (W. Cai et al., 2007), reverse micelle (E. E. Sielo et al., 2004), citrate precursor (M. M. Rashad et al., 2008), and solid state reaction (K. S. Rao et al., 2009). Nano scaled cobalt ferrites have attracted much more attention due to above mentioned characteristics in the field of biomedicine (S. C. Goha et al., 2010), ferrofluid technology (V. K. Sankaranarayana et al., 2003), advanced microelectronics (M. Sugimoto et al., 1999), high frequency data storage and microwave absorbing materials (G. Bate et al., 1991). Rare earth oxides are good electrical insulators with high electrical resistivity. In spinel ferrites the proper choice of rare earth cation can alter the electrical and magnetic properties and have a large influence upon the magnetic anisotropy of the system. Doping the parent spinel ferrite with rare earth
ions leads to structural disorder and lattice strain, thereby enhancing the electrical and magnetic parameters (S. E. Jacobo et al., 2004; F. X. Cheng et al., 1999) have studied the effect of rare earth ion substitution on Curie temperature. (B. R. Kumar et al., 2002) have studied the thermolectric properties of spinel ferrites doped with Gd$^{3+}$ (K. K. Bharathia et al., 2009) have studied the magneto-electric properties of Gd$^{3+}$ doped ferrites. (A. Rana et al., 2011) have demonstrated the affect of Gd$^{3+}$ substitution on dielectric properties of cobalt ferrite. Dielectric parameters of cubic ferrite spins are important in understanding the electrical conduction, behavior of localized charge carrier’s, and polarization phenomenon. Impedance spectroscopy is another important way to completely analyze all contributions to resistance in nano materials. According to different studies (D. Ravinder et al., 2001; K. V. Kumar et al., 2002) the concentration of rare earth doping in the ferrites is important while describing the electrical and magnetic properties of these ferrites. These unique characteristics of rare earth doped systems are due to 4fn electronic states (A. Maqsood et al., 2009).

In the present work we aimed to study the influence of a rare earth ion (Gd$^{3+}$) on structural, electrical and magnetic properties of Co-ferrites. We have successfully synthesized spinel type nano ferrites CoGd$_x$Fe$_{2-x}$O$_4$ (x=0.0 to 0.1) by sol-gel auto combustion followed by heat treatment and characterization is done by XRD, FTIR, SEM, VSM, and LCR meter. We report a comprehensive treatment and characterization is done by XRD, FTIR, SEM, VSM, and LCR meter. We report a comprehensive treatment and characterization is done by XRD, FTIR, SEM, VSM, and LCR meter.

2. Experimental techniques

2.1. Synthesis

A nominal composition of CoGd$_x$Fe$_{2-x}$O$_4$ with x ranging from 0.0 to 0.1 has been prepared by sol-gel auto combustion technique. All the chemicals purchased were of analytical grade and used as received. Aqueous solutions of Iron nitrate Fe(NO$_3$)$_3$·9H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O were prepared by dissolving stoichiometric amounts of nitrate salts in de-ionized water. Molar ratio of Mg$^{2+}$ and Fe$^{3+}$ were kept 2:1. Aqueous nitrate were then mixed with a magnetic stirrer. Aqueous solution of citric acid were prepared with the ratio of Nitrate/citric acid=1/1.5 and mixed with the nitrate solution. The mixed solution was magnetically stirred for 1 hr. The solution were then neutralized with aqueous ammonia and heated at 100°C till the liquid turns to a gel. Gel then automatically converted to fluffy powders by self ignition. Prepared powders were then dried further in an electric oven at 100°C for few hours. As synthesized material were then ground and palletized into disc shaped using a hydraulic press under a load of 6 tons. Disc shaped pellets and powder were sintered at 600°C for 4 hrs in a muffle furnace for further characterization.

2.2. Characterization

The crystallographic information (Crystallite size, D (311), lattice constant, (a); X-ray density, (D), and porosity (P), were found using indexed XRD patterns of the studied samples. XRD patterns were recorded using X-ray diffraction analysis (STOE-Seifert X’Pert PRO) at room temperature using CuKα (λ=1.5406 Å) radiation with 2-theta in the range of 20° to 80°. The crystallite sizes were calculated and compared using the sherrer’s formula and Williamson–Hall plots. W-H plots are usually drawn to see the strain effect in crystal structure. According to Williamson-Hall method (A. Ahlawat et al., 2011) the width of individual reflections can be expressed as follows,

\[ \beta \cos \theta = k \lambda / D + 4 \varepsilon \sin \theta \]  
\[ \beta = \sin \theta / \tan \theta \]  
\[ \varepsilon^\prime = C / \varepsilon^\prime \]  
\[ \varepsilon'' = \tan \theta \varepsilon^\prime \]  
\[ \sigma_{AC} = 2 \pi \varepsilon^\prime \varepsilon'' \tan \theta \]  

Complex impedance plane plots were drawn to study the electrical properties of CoGd$_x$Fe$_{2-x}$O$_4$. The real (Z’) and imaginary (Z”) parts of impedance were calculated using the relations (K. M. Batoo et al, 2009),

\[ Z = Z \cos \theta \]  
\[ Z'' = Z \sin \theta \]

where \( \theta \) is the phase angle measured from impedance meter.

3. Results and Discussion

3.1. Structural Characterizations

The powder XRD patterns of Gd$^{3+}$ doped Co-ferrites for
\( x = 0.0 \) to \( x = 0.1 \) have been presented in Fig.1. All the patterns can be easily indexed to cubic spinel crystal structure (Fd3m) of \( \text{CoFe}_2\text{O}_4 \) (ICPDS card 22-1086) with (220), (311), (400), (511) and (440) diffraction peaks. Broad diffraction peaks represent the nanoscale crystallite size. It can be seen from the XRD patterns that crystallinity decreases by increase in the concentration of \( \text{Gd}^{3+} \) attributed to the decreased intensity in the observed peaks. Lattice parameter ‘\( a \)’ for all the samples has been calculated by interplanar spacing (\( d_{hkl} \)) and 2-theta values using the standard relation,

\[
a = d_{hkl}(\sqrt{h^2+k^2+l^2})^{1/2}.
\]

Value of lattice constant for \( x = 0.0 \) comes out to be 8.3865\( \text{Å} \), well in agreement with reported value (Y. C. Mattei et al., 2009). Lattice constant has increased monotonically with increment in \( \text{Gd}^{3+} \) concentration as shown in Table.1. This increase can be easily explained due to substitution of large ionic radii of \( \text{Gd}^{3+} \) \((0.94\text{Å})\) in place of smaller \( \text{Fe}^{3+} \) \((0.67 \text{Å})\) ions. Also rare earth ions are usually present at grain boundaries that cause hindrance in the grain growth, therefore crystal size and unit cell parameters increases. Peak broadening (FWHM) has been used to determine the crystallite sizes using the sherrer’s formula. Average crystallite size calculated for most intense (311) peak comes out to be 16 nm to 25 nm \( \pm 2 \text{nm} \). It is observed that crystallite size also increased by increase in the \( \text{Gd}^{3+} \) concentration. This increase in lattice parameter and crystallite size induces a lattice strain in the crystal structure. This may be explained on the basis of defects present in the parent \( \text{CoFe}_2\text{O}_4 \) which allows the absorption of lattice strain caused by the higher dopant amounts (J. Peng et al., 2011). The value of theoretical density has been calculated by the relation, \( D_t = 8M/\text{Na}^3 \), where \( a_j \) is unit cell volume. Theoretical density \( (D_t) \) and measured density \( (D_m) \) calculated from weight and dimensions both increases with increase in \( \text{Gd}^{3+} \) due to increase atomic weight of gadolinium ion. All the values of crystallite sizes, lattice constant and lattice strain have been presented in Table.1.

Fig.2 (a,b). Shows the W-H plots for \( x = 0.0 \) and \( x = 0.1 \) respectively. These plots have been drawn to measure the crystallite sizes and lattice strain and compared with the crystallite sizes calculated by sherrer’s formula. The positive slopes of the Gaussian fit to the peak broadening shows a tensile strain present in the prepared samples that increases with increases in \( \text{Gd}^{3+} \) concentration owing to lattice distortion in the host crystal structure by \( \text{Gd}^{3+} \). The behavior of the W-H plots also confirm the increase in crystallite size by doping of larger ion \( \text{Gd}^{3+} \) in Co-ferrites as more the positive slope larger is the crystallite size (A. Ahlawat et al., 2011).

### 3.2. FT-IR Characterization

Fig.3 shows the FT-IR spectra for the studied sample at room temperature in a wave number range of 350 cm\(^{-1}\) to 1000 cm\(^{-1}\). It can be observed that the entire spectrum in the described range shows to distinct peaks, one around 600 (\( \nu_1 \)) and the other near 375 (\( \nu_2 \)). The high frequency peak (\( \nu_1 \)) shows the metal oxygen vibration at tetrahedral sub-lattice (A-sites) and the low frequency peak (\( \nu_2 \)) attributes to the intrinsic vibrations of metal oxygen bond at octahedral sub-lattice (B-sites) (M. Shrivastava et al., 2009). These two absorption bands are expected for the spinel structure of present ferrites synthesized by sol-gel auto combustion method. These vibrational bands for \( \text{Gd}^{3+} \) doped Co-ferrites are in a range of 559 cm\(^{-1}\) to 580 cm\(^{-1}\) for \( \nu_1 \) and 370cm\(^{-1}\) to 381cm\(^{-1}\) for \( \nu_2 \) as shown in Table.1. It has been observed that substitution of \( \text{Gd}^{3+} \) with \( \text{Fe}^{3+} \) causes shifts of band (\( \text{Fe}^{3+} \text{O}^2^- \)) towards higher frequency side due to increased bond length at B-sites and lattice distortion. This also suggests the occupancy of \( \text{Gd}^{3+} \) at B-sites for the present studied samples.

### 3.3. SEM Characterization

SEM images (fig.4) shows the surface morphology and grain size for the prepared sample \( x = 0.0 \) and \( x = 0.1 \). It is clear from the image that uniformly distributed; less agglomerated and homogenous spherical particles have been formed in a controlled environment by sol-gel auto combustion technique. Micrographs also confirm the increase in grain size with \( \text{Gd}^{3+} \) doping in the parent crystal structure. The homogeneity of shape and grain size largely affects the electrical and magnetic properties of ferrites.

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**Figure.1 Indexed XRD patterns of \( \text{CoGd}_{x}\text{Fe}_{2-x}\text{O}_4 \) (\( x = 0.0 \) to \( x = 0.1 \)) nanoparticles synthesized by sol-gel auto combustion method**
3.4. AFM study

Atomic force microscopy is another excellent technique to study the morphology of the nano particles in the dispersed form. In support of the particle sizes observed from SEM, the particle sizes for the sample \(x = 0.025\) have been observed by AFM also as shown in the fig 5. It can be observed the well dispersed uniformly distributed and spherical morphology of the nano particles in the micrograph and the average particle sizes lies in the range of 23nm to 36 nm well in agreement with SEM data.

3.5. Electrical Characterization

3.5.1. Variation of DC electrical resistivity

Fig 6 (a) shows the DC electrical resistivity of CoGd\(_{x}\)Fe\(_{2-x}\)O\(_4\) with composition \((x=0.0\) to \(x=0.1)\) of the dopant at room temperature. Co-ferrite is a highly resistive material with high activation energy. Method of synthesis, type and substitution of doped cations at A and B site, particle size and morphology and sintering temperatures largely affects the electrical properties of spinel ferrites (S. A. Mazen et al., 2007). This can be observed from the graph that DC electrical resistivity decreases up to a concentration of \(x=0.025\) but then increases with increase in Gd\(^{3+}\) concentration. There is a significant increase in the DC electrical resistivity with Gd\(^{3+}\) substitution \((x=0.1)\). DC electrical resistivity was measured also in the temperature range of 368K to 573K fig 6 (b) using a Cu electrode and found a decrease in the resistivity due to increase in the temperature that confirms the semiconducting nature of Gd\(^{3+}\) doped cobalt ferrites. According to the Arrhenius relation,

\[
\rho = \rho_0 e^{\Delta E/KB T} 
\]

Where \(\Delta E\) is the activation energy measured from the slope of resistivity temperature plots, and \(K_B\) is the Boltzman constant. Resistivity decreases linearly with increase in temperature due to increase in the mobility of charge carriers by thermal agitation. Electrical conduction in spinel ferrites can be easily explained by Verwey mechanism (E. J. W. Verwey et al., 1935) and is mainly due to electron hopping between Fe\(^{2+}\) and Fe\(^{3+}\).
(Co²⁺₀.₅Gd³⁺₁₋₀.₅)₂O₄. Gd³⁺ ion substitution in place of Fe³⁺ at octahedral (B site) decreases the number of Fe³⁺ ions at B sites which also decrease the hopping tendency between Fe³⁺↔Fe²⁺ ion pairs, thereby reducing the conductivity and increasing the DC electrical resistivity. The DC electrical resistivity variations with Gd³⁺ substitution can be explained as for x=0.025, Gd³⁺ ions occupy A site replacing Fe³⁺ due to which number of Fe³⁺ ions at B-site increases and thus Fe²⁺. This may happen due to lattice distortion caused by doping a concentration of x=0.025. A low concentration of Gd³⁺ causes a severe change in centro-symmetric FCC structure of parent crystal that causes an increase in hopping of electron and a net electric polarization (M. Z. Said et al., 1998). This reason is reflected in the high dielectric parameters and a sharp decrease in saturation magnetization for x=0.025.

Fig.5 AFM micrograph for CoGdₓFe₂₋ₓO₄ (x=0.025) nanoparticles synthesized by sol-gel auto combustion method

3.5.2. Dielectric study

As nanocrystalline spinel ferrites are good dielectric materials, depending upon the particle size, cation distribution and method of synthesis. Therefore different studies (M. A. Ahmed et al., 2003) and (F. Muthafar et al., 2011) have been provided relating the dielectric parameters of Gd³⁺ doped ferrites. Dielectric properties (real and imaginary parts of relative permittivity, dielectric loss tangent) for the prepared series of CoGdₓFe₂₋ₓO₄ (x=0.0 to x=0.1) have been studied in the frequency range 1 kHz to 5MHz at room temperature. Figs 7 and 8 show the real (ε') and imaginary (ε'') part of relative permittivity with frequency at room temperature.

It can be observed from the figure that relative permittivity for all the samples decreases with increase in frequency and ultimately becomes constant at higher frequencies (~MHz). This decrease in permittivity is more rapid in the low frequency region but this decrease becomes sluggish as the applied frequency becomes higher. This behavior is subjected to dielectric polarization under the application of AC field. Permittivity and Resistivity both are electrical properties of ferrites and depends upon the conduction phenomenon. Hopping of electron between Fe²⁺ and Fe³⁺ is responsible for this conduction. This hopping is responsible for polarization at grain boundaries due to local charge displacement. Such kind of dielectric dispersion in ferrites can be explained by Maxwell-Wagner model (R. M. Mohamed et al., 2010) and koops theory (C. G. Koop’s et al., 1951), which suggests that ferrite system consist of a combination of highly conducting grains separated by poorly conducting grain boundaries.

Figure 6 (a) Variation of DC electrical resistivity (ln ρ) with composition x (Gd³⁺) for CoGdₓFe₂₋ₓO₄ (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method.

Figure 6 (b) Variation of DC electrical resistivity (ln ρ) with inverse of temperature 1/K_BT (eV) for CoGdₓFe₂₋ₓO₄
(x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method

![Figure 7 Variations of Permittivity ε' (real part) with ln f for CoGd₂Fe₂O₄ (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method](image)

Electrons by hopping pile up at grain boundaries due to high resistance and polarization takes place there. At high frequencies this hopping frequency does not follow up the field variation thereby making the relative permittivity a constant. Room temperature dielectric parameters have been presented in Table 1. It can be seen from the tabulated data that relative permittivity and losses increases with increase in Gd⁺³ concentration x=0.025 but after this concentration decreases to 12 for x=0.1. As dielectric polarization in ferrites is due to electron exchange Fe²⁺ ↔ Fe³⁺, magnitude of which depends upon the percentage of Fe²⁺ and Fe³⁺ ion pairs at A and B sites. Fe²⁺ ions concentration largely affects the conduction phenomenon and depends upon type of cation substituting, synthesis route, sintering time and sintering temperatures. In the present case relative permittivity (ε' and ε'') both increases for Gd³⁺ concentration x=0.025. Which can be explained by low Fe³⁺ ion concentration at B-site causing a low value of resistivity and hence a high value of dielectric parameter. As resistivity and relative permittivity has inverse behavior to each other (I. H. Gul et al., 2008).

![Figure 8 Variations of Permittivity ε'' (imaginary part) with ln f for CoGd₂Fe₂O₄ (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method](image)

![Figure 9 Variations of Dielectric loss tangent (tanδ) with ln f for CoGd₂Fe₂O₄ (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method](image)

Fig.9 shows the variation of tanδ with frequency. It can be seen that dielectric loss tangent has the same trend as permittivity. It decreases with increase in frequency and becomes constant up to 5 MHz due to decreased polarization at high AC fields. This dielectric behavior reversed the trend that has been observed for DC-electrical resistivity. Dielectric losses in ferrite system usually reflect in DC electrical resistivity. Low loss dielectric material will be a highly resistive as well. Also observed that for x=0.025, a small peak is present owing to the relaxation phenomenon in ferrites (A. Verma et al., 2011). Sample with x=0.1 shows a low loss dielectric behavior which allows its use in high frequency data reading/writing in electronic structures. Fig.10 shows the variation of AC conductivity for CoGd₂Fe₂O₄ as a function of frequency (1 kHz-5 MHz) for composition x=0.0 to x=0.1. It can be observed that AC conductivity increases linearly with frequency. This linear increase in AC conductivity relates with conduction by electron exchange between the ions of same element but difference valence states. As ferrites structure is cubic close pack lattice with cations at octahedral (B) site and tetrahedral (A) site. The exchange of electric charge between A-B sites is more important as compared to B-B exchange. On the application of AC field this electron exchange increases thereby increasing the AC conductivity (K. M. Batoo et al., 2011). Usually AC conductivity can be represented as,

\[ \sigma_{AC} = \sigma(T) + \sigma(\omega, T) \]  

(8)

which is a combination of frequency independent term \( \sigma(T) \) called as DC conductivity and frequency dependent term \( \sigma(\omega, T) \) called as AC conductivity due to hopping of electrons at octahedral site. AC conductivity can be shown as,

\[ \sigma_{AC} = A\omega^n \]  

(9)

where A is term having units of conductivity and n is the slope of AC conductivity (lnσ(AC) vs lnω plots Fig.10). Along with the increase in hopping phenomenon, the AC field promotes the formation of different charge carriers from different localized states. The charge centers help in increasing conductivity. According to (M. G. Chourashiya et al., 2008), AC conductivity increases
linearily for structures consisting of grains and grain boundaries but for large polarons it decreases with increase in applied AC field.

![Figure 10 Variations of lnσAC with lnω for CoGdFe2−xO4 (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method](image)

**3.5.3. Impedance study**

Impedance analysis is useful to completely understand the electrical properties of spinel type ferrites and give us the data for both resistive (real part) and reactive (imaginary part) contribution to conductivity on the application of AC field (A. M. M. Farea et al., 2008). Complex impedance plot also called as Nyquist diagrams gives a complete contribution of microstructure (grains and grains boundary) resistances. Fig.11 (a) and (b) shows the variations of real and imaginary parts of complex impedance with applied frequency (1 kHz to 5MHz). Both the resistance (Z) and reactance (Z′) decreases with increase in AC field showing the conduction is promoted by applied AC field. Fig.11 (c) shows the complex impedance plane plots (Cole-Cole) for all the studied samples. These complex plane plots help to distinguish the grain and grain boundary resistances and interfacial resistance of conducting electrodes. It is clear from the Nyquist plot that only one semi circle is present for all the studied samples in the low frequency region. As it’s shown in different studies (H. Ya et al., 2008) and (W. Chen et al., 2010) that there are two consecutive semi circles in complex impedance diagrams, one in low applied fields showing the grain boundary resistances and the other in high field side shows the grains contribution.

Only one quarter circle in low field region confirms the predominance of grain boundary resistance for the present studied samples of Gd3+ doped Co-ferrite and grain resistance is not well resolved. It can also be seen from complex plane plot that grain boundary resistance increases with increase in Gd3+ concentration for x=0.1.

**3.6. Magnetic study**

To study the effects of Gd3+ doping on magnetization, coercivity, remanent magnetization (Mr) and magnetocrystalline anisotropy (Hk) of Co-ferrite, M-H hysteresis loops were recorded using VSM under the applied magnetic field of 10 k Oe at room temperature. Fig.12 (a) shows the hysteresis curves for all the samples under investigation. It is clear that all the samples show a fine s shape loops with a decrease in magnetization (Ms) and

![Figure 11 (a) Variations of Impedance ′ (real part) with ln f](image)

![Figure 11 (b) Z′ (imaginary part) for CoGdFe2−xO4 (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method](image)

![Figure 11 (c) Complex impedance plane plots for CoGdFe2−xO4 (x=0.0 to x=0.1) nanoparticles synthesized by sol-gel auto combustion method](image)
coercivity ($H_c$) with increase in Gd$^{3+}$ concentration. This is due to the substitution of Gd$^{3+}$ in place of Fe$^{3+}$ at B-sites. Gd$^{3+}$ ions have a higher magnetic moment (7 $\mu_B$) in place of Fe$^{3+}$ that has 5 $\mu_B$. The order in magnetic moments of rare earth ions is below room temperature (J. Peng et al., 2011) due to this at room temperature Gd ion behaves as non magnetic that cause a decrease in saturation magnetization and coercivity. This substitution causes a lattice distortion that alters the magnetic characteristics of materials. Magnetic properties of ferrite materials largely based upon the grain size, cation substitution, and A-B exchange interactions (K. K. Bharathi et al., 2009). Increase in the grain size and decrease of A-B super exchange interaction causes cantiing spins at the surface of nano particles that decreases the magnetic characteristics of the present samples as shown in fig.12 (b). Spin arrangement for the Co-Gd ferrites were analyzed by measuring the value of Bohr’s magnetron by the relation,

$$n_B = (\sigma/5585)M_w$$  

(10)

Using the calculated magnetic moment Yafet-Kittel (Y-K) angles was studied to see the spin arrangement in present ferrite system by the relation (K. Lawrence et al., 2011),

$$n_B = (6+x) \cos K - 5(1-x)$$  

(11)

where $x$ represents the composition of doping ion. All the magnetic data including Y-K angles were presented in Table.2. Y-K angle increases with increase in Gd$^{3+}$ concentration owing to triangular spin arrangement of ions and results in decreased A-B interactions (Y. Yafet et al., 1952). In order to analyze the Gd$^{3+}$ influence on magnetic anisotropy of Co-ferrites, value of anisotropy constant ($K_i$) is determined using Law of approach (LA) to saturation (fig.13). Cubic anisotropy constant ($K_i$) and anisotropy field ($H_i$) can be calculated by following equations (K. Maaz et al., 2007).

$$H_i = 2K_i/\mu_o M_s$$  

(12)

$$K_i = \mu_o M_s (105b/8)^{1/2}$$  

(13)

where $\mu_o$ is the permeability of the free space, $M_s$ is saturation magnetization from the fit, b is the parameter obtained from the fit. Data for anisotropy constant and anisotropy field ($H_i$) is mentioned in Table.2. Our results are in comparable to earlier reported values for Co-ferrites (L. Zhao et al., 2006).

It is clear from the data that cubic anisotropy decreases with increase in gadolinium concentration. Pure cobalt ferrite is has high anisotropy constant and field due to occupation at B-sites. It decreases due to Gd$^{3+}$ occupation at B-sites. Cubic anisotropy constant also decreased doping gadolinium showing a decrease in coercivity for present studied samples. The anisotropy parameters (anisotropy constant and field) are not decreasing monotonically but more abruptly due to differing concentration of doping ion. This behavior is showing a strong lattice distortion due to Gd$^{3+}$ substitution. Nano particles synthesized by sol-gel auto combustion method

Figure.12 (a) $M$-$H$ loops for CoGd$_x$Fe$_{2-x}$O$_4$ ($x$=0.0 to $x$=0.1)

Figure.12 (b) Variation of Coercivity ($H_c$) with $x$=0.0 to $x$=0.1

Figure.13 Fit to LA for CoGd$_x$Fe$_{2-x}$O$_4$ ($x$=0.1) nanoparticles synthesized by sol-gel auto combustion method
Table 1. Crystallite size ($D_{311}$) Sherrer’s method, Crystallite size D (W-H) method, lattice parameter ($a$), X-ray density ($D_x$), measured density ($D_m$). Porosity ($P$), FTIR vibrational Waver numbers ($\nu_1$ and $\nu_2$), Dielectric constant ($\varepsilon$), Dielectric loss factor ($\varepsilon''$), and tangent loss (tanδ), AC conductivity ($\sigma_{AC}$), $n$ (conductivity parameter).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$x=0.0$</th>
<th>$x=0.025$</th>
<th>$x=0.05$</th>
<th>$x=0.075$</th>
<th>$x=0.1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant ‘a’ (Å)</td>
<td>8.3865</td>
<td>8.3874</td>
<td>8.3947</td>
<td>8.3954</td>
<td>8.4162</td>
</tr>
<tr>
<td>$D(311)$ nm</td>
<td>16.92</td>
<td>16.99</td>
<td>21.75</td>
<td>21.93</td>
<td>22.54</td>
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<tr>
<td>$D_m$ (gm/cm$^3$)</td>
<td>2.47</td>
<td>2.48</td>
<td>2.511</td>
<td>2.523</td>
<td>2.57</td>
</tr>
<tr>
<td>$D_\ell$ (gm/cm$^3$)</td>
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<td>5.35</td>
<td>5.38</td>
<td>5.41</td>
<td>5.45</td>
</tr>
<tr>
<td>$P$ (%)</td>
<td>53.3</td>
<td>53.6</td>
<td>53.3</td>
<td>53.4</td>
<td>53.2</td>
</tr>
<tr>
<td>$\nu_1$ (cm$^{-1}$)</td>
<td>559.21</td>
<td>561.13</td>
<td>563</td>
<td>572.54</td>
<td>578.98</td>
</tr>
<tr>
<td>$\nu_2$ (cm$^{-1}$)</td>
<td>370.35</td>
<td>370.87</td>
<td>377.9</td>
<td>378.3</td>
<td>380.76</td>
</tr>
<tr>
<td>$\rho$ (Ω·cm)</td>
<td>3.45x10$^7$</td>
<td>1.29x10$^6$</td>
<td>2.10x10$^7$</td>
<td>9.31x10$^7$</td>
<td>2.67x10$^8$</td>
</tr>
<tr>
<td>$\varepsilon$ (1MHz)</td>
<td>15.2</td>
<td>34.9</td>
<td>16.1</td>
<td>15.1</td>
<td>13.6</td>
</tr>
<tr>
<td>$\varepsilon''$ (1MHz)</td>
<td>1.19</td>
<td>11.9</td>
<td>2.81</td>
<td>2.41</td>
<td>0.4</td>
</tr>
<tr>
<td>tanδ (1MHz)</td>
<td>0.077</td>
<td>0.3463</td>
<td>0.1750</td>
<td>0.1568</td>
<td>0.043772</td>
</tr>
<tr>
<td>$\varepsilon$ (5 MHz)</td>
<td>14.2</td>
<td>22.3</td>
<td>14.8</td>
<td>14.1</td>
<td>12</td>
</tr>
<tr>
<td>$\varepsilon''$ (5 MHz)</td>
<td>0.473</td>
<td>7.86</td>
<td>0.97</td>
<td>0.842</td>
<td>0.156</td>
</tr>
<tr>
<td>tanδ (5 MHz)</td>
<td>0.0324</td>
<td>0.3520</td>
<td>0.0654</td>
<td>0.0598</td>
<td>0.0160</td>
</tr>
<tr>
<td>$\sigma_{AC}$ (5 MHz)</td>
<td>1.31x10$^{-4}$</td>
<td>2.17x10$^{-3}$</td>
<td>2.34x10$^{-4}$</td>
<td>2.7x10$^{-4}$</td>
<td>7.14x10$^{-5}$</td>
</tr>
<tr>
<td>$n$</td>
<td>0.4</td>
<td>0.85</td>
<td>0.39</td>
<td>0.42</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 2. Saturation magnetization ($M_s$), Remanance ($M_r$), Coercivity ($H_c$), Remanance ratio ($M_r/M_s$), Magnetic moments ($n_B$), Yeffit-Kittel angle ($\alpha_{y-k}$), Magnetic anisotropy constants ($K_1$), Anisotropy field ($H_k$).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$x=0.0$</th>
<th>$x=0.025$</th>
<th>$x=0.05$</th>
<th>$x=0.075$</th>
<th>$x=0.1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_s$</td>
<td>63</td>
<td>34.5</td>
<td>28.73</td>
<td>33.32</td>
<td>27.26</td>
</tr>
<tr>
<td>$H_c$</td>
<td>2929</td>
<td>1096</td>
<td>2308</td>
<td>1078</td>
<td>1779</td>
</tr>
<tr>
<td>$M_r$</td>
<td>34.52</td>
<td>14.03</td>
<td>13.49</td>
<td>11.99</td>
<td>10.03</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.55</td>
<td>0.40</td>
<td>0.47</td>
<td>0.36</td>
<td>0.37</td>
</tr>
<tr>
<td>$n_B$</td>
<td>1.017</td>
<td>0.59</td>
<td>0.49</td>
<td>0.57</td>
<td>0.46</td>
</tr>
<tr>
<td>$\alpha_{y-k}$</td>
<td>0</td>
<td>24.74</td>
<td>29.97</td>
<td>31.17</td>
<td>35.52</td>
</tr>
<tr>
<td>$K_1$ (erg/cm$^3$)</td>
<td>0.35x10$^6$</td>
<td>0.1x10$^6$</td>
<td>0.13x10$^6$</td>
<td>0.108x10$^6$</td>
<td>0.12x10$^6$</td>
</tr>
<tr>
<td>$H_k$ (KOe)</td>
<td>11.55</td>
<td>7.245</td>
<td>12.96</td>
<td>8.067</td>
<td>10.424</td>
</tr>
</tbody>
</table>
4. Conclusions

In summary nano sized CoGd$_3$Fe$_{2-x}$O$_4$ with x ranging from 0.0 to 0.1 has been synthesized by sol-gel auto combustion. All the studied samples are pure cubic spinel type ferrites without any impurity phase. Lattice constant and crystallite size increases with increase in Gd$^{3+}$ concentration, owing to increased ionic radii and atomic weight of gadolinium as compared to Fe$^{3+}$. Substitution of Gd$^{3+}$ ion in parent crystal causes a lattice distortion that can be observed by increased lattice strain in W-H plots. DC electrical resistivity increases significantly to $2.67 \times 10^8$ with Gd$^{3+}$ substitution except for $x=0.025\ (~10^8)$. Dielectric properties (real and imaginary relative permittivity and dielectric loss tangent), decreases with increase in the dopant concentration showing that the material with $x=0.1$ is a low loss dielectric. AC conductivity increases with increase in Gd$^{3+}$ composition showing a lattice disorder due to replacing Fe$^{3+}$ by Gd$^{3+}$. Also a linear rise in conductivity with applied field indicates small polaron conduction mechanism. Impedance study reveals that the grain boundary are offering more resistance to conduction showing that smaller grains with more grain boundaries are formed for present samples. Gd$^{3+}$ substitution have tailored the magnetic properties of Co-ferrites due to influence on A-B exchange of electrons. Saturation magnetization, coercivity and remanance all decreases with increase in dopant concentration. Yeffit-Kittel angles increases with $x$, showing a triangular spin arrangement for present ferrite system. Magnetic anisotropy of Co-ferrites decreases with increase in Gd$^{3+}$ concentration ($x$). Thus the rare earth (Gd$^{3+}$) doped Co-ferrites found an application as high resistivity and low loss dielectric material in radio and microwave frequency applications.

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The authors would like to acknowledge TWAS, Italy, Higher Education Commission (HEC) Islamabad Pakistan project No.1326, for providing financial support for this work and Pakistan science foundation (PSF) project No.147.

References


