Influence of Rare Earth (Gd$^{3+}$) on Structural, Gigahertz Dielectric and Magnetic Studies of Cobalt ferrite

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Abstract. A series of 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) and Scanning Electron Microscopy (SEM). Indexed XRD patterns confirm the formation of pure cubic spinel phase. Average crystallite sizes ranges from 16 nm to 25 nm ±2, were calculated from Sherrer’s formula and Williamson Hall plots. Crystal strain increases with increase in doping amount of trivalent Gd ion. Lattice constant ($a$) and crystallite size D (311) increases with increase in Gd$^{3+}$ concentration due to large ionic radii (0.94nm) of Gd$^{3+}$ replacing Fe$^{3+}$ (0.64nm ). SEM images show the spherical morphology and uniform size distribution. Room temperature DC electrical resistivity decreases (~10$^6$) for $x=0.025$ then increases up to $x=0.1$ ~ (4.5x10$^7$). Dielectric properties have been studied using RF Impedance/material analyzer in the frequency range of 1 MHz to 1GHz. All the studied samples show a semi-conducting behavior as Permittivity and tangent loss (tanδ) decreases with the substitution of Gd$^{3+}$ in parent crystal structure and have values of 4.92and 0.016 at 1 GHz respectively. Complex impedance and Complex electric modulus plots were further studied for complete contribution of grains and grain boundary resistances to conduction and resonance frequencies respectively. Magnetic studies by Vibrating Sample Magnetometer (VSM) shows that magnetization (Ms) decreases with increase in Gd$^{3+}$ concentration from 63 emu/gm to 27.26 emu/gm. Coercivity (Hc) first decreases for $x=0.025$, after which it increases to 2308 Oe for $x=0.1$.

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) [1]. 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. Cobalt ferrite is a hard spinel with high saturation magnetization, coercive field, mechanical hardness and high magneto crystalline anisotropy [2]. 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. CoFe$_2$O$_4$ is known as partially inverse spinel with ferromagnetic behavior having a high specific resistance and low eddy current losses in high frequency applications [3]. 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 [4], sol-gel [5], hydrothermal [6], microemulsion [7], solvothermal [8], reverse micelle [9], citrate precursor [10], and solid state reaction [11]. Nano scaled cobalt ferrites have attracted much more attention due to above mentioned characteristics in the field.
of biomedicine, ferrofluid technology, advanced microelectronics, high frequency data storage, microwave absorbing materials (circulators, phase shifters, isolators) [12-15]. 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 making the spinel ferrite an excellent option in place of hexa ferrites or garnets.

Doping the parent spinel ferrite with rare earth ions (Y³⁺, Gd³⁺, Ho³⁺, Sm³⁺, Nd³⁺) leads to structural disorder and lattice strain, thereby increasing the electrical and magnetic parameters [16]. Cheng. et al [17] have studied the effect of rare earth ion substitution on Curie temperature. B. Ravi [18] has studied the thermoelectric properties of spinel ferrites doped with Gd³⁺. K.K. Bharathia [19] has studied the magnetoelectric properties of Gd³⁺ doped ferrites. A. Rana [20] has demonstrated the effect of Gd substitution on dielectric properties of cobalt ferrite. Dielectric parameters of cubic spinel ferrites are important in understanding the electrical conduction, behavior of localized charge carrier’s, and polarization phenomena. Impedance and electric modulus studies are another important way to completely analyze all contributions to resistance in nano materials and to observe the relaxation behavior. According to different studies [21-22] 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 4f electronic states [23].

In the present work we aimed to study the influence of a rare earth ion (Gd³⁺) on structural, gigahertz dielectric and magnetic properties of Co-ferrites. We have successfully synthesized spinel type nano ferrites CoGdₓFe₂₋ₓO₄ (x=0.0 to 0.1) by sol-gel auto combustion followed by heat treatment and characterization is done by XRD, SEM, VSM, LCR, , meter bridge and RF impedance/Material Analyzer. We report the complex electric modulus and magneto crystalline anisotropy for gadolinium doped Co-ferrites.

2. Experimental techniques

2.1. Synthesis

A nominal composition of CoGdₓFe₂₋ₓO₄ 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(NO₃)₃.9H₂O, Gd(NO₃)₃.6H₂O and Co(NO₃)₂.6H₂O were prepared by dissolving stoichiometric amounts of nitrate salts in de-ionized water. Molar ratio of M³⁺ and M²⁺ were kept 2:1. Aqueous nitrates were then mixed with a magnetic stirrer. Aqueous solution of citric acid were prepared with the ratio of Nitrates/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 characterizations.

2.2. Characterization

The crystallographic information (Crystallite size (D311), lattice constant, (a); X-ray density, (Dₐ), 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 20⁰ to 80⁰. 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 [24] the width of individual reflections can be expressed as follows,

\[ \beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \]  

(1)

where \( \beta \) is the width of peaks, \( D \) is the crystallite size, \( \lambda \) is the wavelength of Cu Kα radiation and \( \varepsilon \) is the crystal strain effect. The morphology and grain size was analyzed using SEM (JEOL-instrument JSM-6490A). A vibrating sample magnetometer was used to study the magnetic properties. DC electrical resistivity (\( \rho \)) were measured using two probe method at room temperature. Pellets (13mm
in diameter) of samples were used for measuring the impedance and electric modulus properties using precision impedance analyzer (Wayne Kerr 6500B) at room temperature. The complex relative permittivity ($\varepsilon$, $\varepsilon''$) was measured by RF impedance/Material analyzer (Agilent E4991A). The dielectric tangent loss (tanδ) factor measured directly from the impedance analyzer using pellets of 10mm in diameter.

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 [25],

$$Z' = Z \cos \theta$$

$$Z'' = Z \sin \theta$$

where $\theta$ is the phase angle measured from LCR meter.

Complex electric modulus was calculated from the standard relations [26].

$$M* = \varepsilon'' Z*$$

Magnetic measurements were done at room temperature using a vibrating sample magnetometer (VSM) under an applied field of 10 kOe.

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 (a). All the patterns can be easily indexed to cubic spinel crystal structure (Fd$3$m) of CoFe$_2$O$_4$ (JCPDS 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 Gd$^{3+}$ attributed to the decreased intensity in the observed peaks.

![Figure 1. Indexed XRD patterns of CoGd$_x$Fe$_{2-x}$O$_4$ ($x=0.0$ to $x=0.1$) nanoparticles synthesized by sol-gel auto combustion method.](image)

Lattice parameter ‘a’ for all the samples has been calculated by interplanar spacing ($d_{hkl}$) and 2-theta values using the standard relation, $a=d_{hkl}(h^2+k^2+l^2)^{1/2}$. Value of lattice constant for $x=0.0$ comes out to be 8.3865Å, well in agreement with reported value [27]. Lattice constant has increased monotonically with increment in Gd$^{3+}$ concentration as shown in Fig.2. This increase can be easily explained due to substitution of large ionic radii of Gd$^{3+}$ (0.94Å) in place of smaller Fe$^{3+}$ (0.67 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 [6]. 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 ±2nm. It is observed that crystallite size also increased by increase in the 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 CoFe$_2$O$_4$, which allows the absorption of lattice strain caused by the higher dopant amounts [4]. The value of theoretical density has been calculated by the relation, $D_x = \frac{8M}{N a^3}$ where $a^3$ is unit cell volume. $D_x$ and measured density ($D_{m}$) calculated from weight and dimensions both increases with increase in 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.

**Figure 2.** Variation of lattice constant and $D_x$ with composition ($x$) for CoGd$_x$Fe$_{2-x}$O$_4$

Fig.3 Shows the W-H plot only for $x=0.1$. 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 Gd$^{3+}$ concentration owing to lattice distortion in the host crystal structure by Gd$^{3+}$. The behavior of the W-H plots also confirm the increase in crystallite size by doping of larger ion Gd$^{3+}$ in Co-ferrites as more the positive slope larger is the crystallite size [24].
3.2. Morphology Analysis

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 Gd\(^{3+}\) doping in the parent crystal structure. The homogeneity of shape and grain size largely affects the electrical and magnetic properties of ferrites.

Figure 4. SEM images for CoGd\(_x\)Fe\(_{2-x}\)O\(_4\) (\(x=0.0\)) and (\(x=0.1\)) 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 ($P$), dielectric constant ($\varepsilon$), dielectric loss factor ($\varepsilon'$), and tangent loss ($\tan\delta$), Relaxation time.

| Composition | x=0.0 | x=0.025 | x=0.05 | x=0.075 | x=0.1 |
|-------------|-------|---------|--------|---------|-------|
| Lattice     | 8.3865 | 8.3874  | 8.3947 | 8.3954  | 8.4162 |
| $a$'         |        |         |        |         |       |
| $D_{311}$ (nm) | 16.92 | 16.99   | 21.75  | 21.93   | 22.54 |
| $D_m$ (gm/cm$^3$) | 2.47  | 2.48    | 2.511  | 2.523   | 2.57  |
| $D_x$ (gm/cm$^3$) | 5.29  | 5.35    | 5.38   | 5.41    | 5.45  |
| $P$ (%)      | 53.3  | 53.6    | 53.3   | 53.4    | 52.8  |
| $\rho$ (Ω·cm) | 3.45x10$^7$ | 1.29x10$^8$ | 1.03x10$^7$ | 4.5x10$^7$ | 9.5x10$^7$ |
| $\varepsilon'$ (1MHz) | 15.2  | 34.9    | 16.1   | 15.1    | 13.6  |
| $\varepsilon''$ (1MHz) | 1.19  | 11.9    | 2.81   | 2.41    | 0.7   |
| $\tan\delta$ (1MHz) | 0.077 | 0.3463  | 0.1750 | 0.1568  | 0.043772 |
| $\varepsilon'$ (1 GHz) | 6.20  | 5.96    | 5.86   | 5.22    | 4.92  |
| $\varepsilon''$ (1 GHz) | 0.473 | 7.86    | 0.97   | 0.842   | 0.256 |
| $\tan\delta$ (1 GHz) | 0.0324 | 0.3520  | 0.0654 | 0.0598  | 0.0160 |
| $\tau_r$ (sec) | 9.88x10$^{-7}$ | 4.99x10$^{-6}$ | 8.6x10$^{-6}$ | 2.54x10$^{-5}$ | 2.1x10$^{-5}$ |

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

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

3.3. Electrical Characterization
3.3.1. Variation of DC electrical resistivity
Fig.5 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 [28]. 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 ($x=0.1$). Electrical conduction in spinel ferrites can be
easily explained by Verwey mechanism [29] and is mainly due to electron hopping between Fe$^{2+}$ and Fe$^{3+}$. The suggested cations distribution for the present samples of CoGd$_{x}$Fe$_{2-x}$O$_{4}$ can be written as: 

$$(\text{Co}^{2+}_{0.5}\text{Fe}^{3+}_{0.5})_A(\text{Co}^{2+}_{0.5}\text{Gd}^{3+}_{x}\text{Fe}^{3+}_{1.5-x})_B\text{O}_4.$$ 

Gd$^{3+}$ ion substitution in place of Fe$^{3+}$ at octahedral (B site) decreases the number of Fe$^{3+}$ ions at B sites which also decrease the hopping tendency Fe$^{3+}$↔Fe$^{2+}$, thereby reducing the conductivity and increasing the DC electrical resistivity. The DC electrical resistivity variations with Gd$^{3+}$ substitution can be explained as for $x=0.025$, Gd$^{3+}$ ions occupy A site replacing Fe$^{3+}$ due to which number of Fe$^{3+}$ ions at B-site increases and thus Fe$^{2+}$. This may happen due to lattice distortion caused by doping a concentration of $x=0.025$. A low concentration of Gd$^{3+}$ 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 [30]. This reason is reflected in the high dielectric parameters and a sharp decrease in saturation magnetization for $x=0.025$.

![Graph](image)

**Figure 5.** Variation of DC electrical resistivity ($\ln \rho$) with composition $x$ (Gd$^{3+}$) for CoGd$_{x}$Fe$_{2-x}$O$_{4}$ ($x=0.0$ to $x=0.1$) nanoparticles synthesized by sol-gel auto combustion method

3.3.2. Dielectric study

Dielectric behavior of nano spinel ferrites mainly depends upon the nature and distribution of metal cations on A-sites and B-sites in the spinel lattice. Spinel Cobalt ferrites are considered good dielectric materials and the high frequency dielectric behavior is mainly dependent upon the particle size and method of synthesis of nano particles [31]. Different studies have been provided relating the dielectric parameters of Gd$^{3+}$ doped ferrites [32-33]. Dielectric parameters (real and imaginary parts of relative permittivity, dielectric loss tangent) for the prepared series of CoGd$_{x}$Fe$_{2-x}$O$_{4}$ ($x=0.0$ to $x=0.1$) have been studied in the frequency range 1 MHz to 1GHz at room temperature. Figs.6 (a,b) show the real ($\varepsilon'$) and imaginary ($\varepsilon''$) 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 (~GHz). This decrease in permittivity is more rapid in the low frequency region and becomes sluggish as the applied frequency increases. This behaviour is subjected to dielectric polarization under the application of AC field [34].
Permittivity and Resistivity both are electrical properties of ferrites and depend upon the conduction phenomenon. Hopping of electron between Fe$^{2+}$ and Fe$^{3+}$ 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 [35] and koops theory [36] which suggests that ferrite system consist of a combination of highly conducting grains separated by poorly conducting grain boundaries. 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.2. It can be seen from the tabulated data that imaginary relative permittivity increases with increase in Gd$^{3+}$ concentration $x=0.025$ but after this concentration decreases till $x=0.1$. As dielectric polarization in ferrites is due to electron exchange Fe$^{2+} \leftrightarrow$Fe$^{3+}$, magnitude of which depends upon the percentage of Fe$^{2+}$ and Fe$^{3+}$ ion pairs at A and B sites. Fe$^{2+}$ 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 ($\varepsilon'$ and $\varepsilon''$) both decreases for Gd$^{3+}$ concentration $x=0.1$. Which can be explained by low Fe$^{2+}$ 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 [37].
Fig. 7 shows the variation of $\tan\delta$ with frequency. It can be seen that dielectric loss tangent has the same trend as permittivity losses. It decreases with increase in frequency and becomes constant up to 1GHz 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 slight increase in the loss tangent due to lattice distortion at $x=0.025$ [38]. Sample with $x=0.1$ shows a low loss dielectric behavior which allows its use in high frequency data reading/writing in electronic structures.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Variations of Dielectric loss tangent ($\tan\delta$) with $\ln f$ for CoGd$_x$Fe$_{2-x}$O$_4$ ($x=0.0$ to $x=0.1$) nanoparticles synthesized by sol-gel auto combustion method

3.3.3. Complex Impedance/Complex electric modulus study

Complex impedance and electric modulus studies were performed at room temperature using the LCR meter in the frequency range of 1KHz to 5 MHz. 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 [39]. Complex impedance plot also called as Nyquist diagrams gives a complete contribution of microstructure (grains and grains boundary) resistances. Fig.8 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 its shown in different studies [40-41] 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 Gd$^{3+}$ 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 Gd$^{3+}$ concentration for $x=0.1$. 
Electric modulus were plotted to see the relaxation behavior and resonance frequencies of the prepared samples. To see the influence of Gd$^{3+}$ on the resonance frequencies of cobalt ferrite, cole-cole type diagrams of $M^*$ were plotted as the AC data of impedance ($Z^*$) was poorly resolved into semi circle arc in the cole-cole diagram of complex impedance. This possibly could happen for the samples where the change in resistance is dominant as compared to capacitance of the material [42]. Fig.9 (a) shows the imaginary part of the electric modulus variation with applied field. The observed peaks in the plots show that the relaxation phenomenon is occurring in the samples under study. These peaks are due to dielectric relaxation where $\omega \tau = 1$, where $\tau$ is the relaxation time inverse of relaxation frequency $f_r$. It can also be observed that the peak shifts to lower frequency side with increase in Gd$^{3+}$ concentration.

Showing that relaxation and associated resonance losses are in low frequency region and no resonance is observed for the material at high frequencies. Fig.9 (b) shows the real part of the electric modulus with frequency. Onset frequency also shifts to low frequency region showing the grain boundary resistance is higher for the samples with higher composition of Gd$^{3+}$. Clearly resolved semi circles have been observed for cole-cole diagram of electric modulus ($M'_r$ vs $M'_c$) fig.9 (c). Sample with $x=0.025$, show two semi circle arcs one in the high frequency side and other in low frequency region corresponding to grain and grain boundary resistance respectively.

**Figure 8.** Complex impedance plane plots for CoGd$_x$Fe$_{2-x}$O$_4$ ($x=0.0$ to $x=0.1$) nanoparticles synthesized by sol-gel auto combustion method.
3.4. Magnetic study
To study the effects of Gd$^{3+}$ doping on magnetization, coercivity, remanent magnetization ($M_r$) and magneto-crystalline anisotropy ($H_K$) of Co-ferrite, M-H hysteresis loops were recorded using VSM under the applied magnetic field of 10 kOe at room temperature. Fig.10 (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 ($M_s$) and 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 [4], 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 [17]. Increase in the grain size and decrease of A-B super exchange interaction causes canting spins at the surface of nano particles that decreases the magnetic characteristics of the present samples. Spin arrangement for the Co-Gd ferrites were analyzed by measuring the value of Bohr’s magnetron by the relation,

\[ n_B = \frac{\sigma s}{5585} M_w \]  \hspace{1cm} (5)

using the calculated magnetic moment Yafet-Kittel (Y-K) angles were studied to see the spin arrangement in present ferrite system by the relation [43],

\[ n_B = (6 + x)\cos \alpha_{Y-K} - 5(1 - x) \]  \hspace{1cm} (6)

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 [44]. In order to analyze the Gd\(^{3+}\) influence on magnetic anisotropy of Co-ferrites, value of anisotropy constant \( K_1 \) is determined using Law of approach (LA) to saturation (Fig.10 (b)). Cubic anisotropy constant \( K_1 \) and anisotropy field \( H_k \) can be calculated by following equations [45-46]

\[ K_1 = \mu_0 M_s \sqrt{105b/8} \]  \hspace{1cm} (7)

\[ H_k = \frac{2K_1}{\mu_0 M_s} \]  \hspace{1cm} (8)

where \( \mu_0 \) 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 \( H_k \) is mentioned in Table.2. Our results are in comparable to earlier reported values for Co-ferrites [45]. 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 behaviour is showing a strong lattice distortion due to Gd\(^{3+}\) substitution.
4. Conclusions
Nano spinel CoGd$_x$Fe$_{2-x}$O$_4$ with $x$ in step increment of 0.025 has been synthesized by sol-gel auto combustion. All the studied samples are pure cubic spinel phase ferrites without any impurity metal oxides. Lattice constant and crystallite size increases with increase in Gd$^{3+}$ concentration, owing to increase 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 to 9.5x10$^7$ with Gd$^{3+}$ substitution except for $x=0.025$ ($\sim 10^6$). Dielectric constant and loss tangent decreases to 4.92 and 0.016 respectively with increase in the dopant concentration showing that the material with $x=0.1$ is a low loss dielectric. Complex impedance and electric modulus 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 relaxation behavior making the resonance frequencies lower than the pure cobalt ferrites. Magnetic properties of Gd$^{3+}$ doped Co-ferrites decrease due to influence on A-B exchange interactions and canted spins of electrons on nano particles surface. Saturation magnetization, coercivity and remanance all decreases with increase in dopant concentration. Yefft-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 in high frequency devices and power supply due to high resistivity and low losses.

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