Effect of Gd\textsuperscript{3+} - Cr\textsuperscript{3+} ion substitution on the structural, electrical and magnetic properties of Ni - Zn ferrite nanoparticles

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Abstract. Gd\textsuperscript{3+} doped nickel zinc nanoceramics with general formula Ni\textsubscript{0.4}Zn\textsubscript{0.6}Cr\textsubscript{0.5}Gd\textsubscript{x}Fe\textsubscript{1.5-x}O\textsubscript{4} (where \(x=0.00, 0.02, 0.04, 0.06\)) were synthesized by solution combustion method using oxylydehydrazine as a fuel. The obtained powder was sintered at 1000°C for 2h. The detailed structural, electrical and magnetic studies were carried out through X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), impedance spectroscopy and vibrating sample magnetometer (VSM). The XRD pattern of as prepared sample confirms the formation of single phase with cubic spinel structure. The average crystallite size was found to be 34 to 19 nm and decreases with increasing Gd\textsuperscript{3+} ion concentration. The IR spectra exhibited two expected absorption bands between 600 to 300 cm\textsuperscript{-1} corresponding to the stretching vibrations of tetrahedral (A) and octahedral (B) metal oxygen vibrations. The variation of room temperature real (\(\varepsilon^\prime\)) and imaginary (\(\varepsilon^\prime\prime\)) part of dielectric permittivity as a function of frequency and composition have been studied in the frequency range from 40Hz to 10MHz. The real and imaginary dielectric permittivity decreases with increase in frequency as well as Gd\textsuperscript{3+} concentration, which is normal behaviour of ferrite material and results have been explained on the basis of Maxwell - Wagner's two layer model. The VSM results showed that the Gd\textsuperscript{3+} concentration had significant impact on the saturation magnetization and coercivity, \(x=0.02\) shows the highest value of dielectric constant and saturation magnetization, thus the material is becoming low loss dielectric and highly resistive and soft magnetic material due to Gd-Cr doping.

1. Introduction

The rare earth substituted Ni-Zn ferrites exhibits remarkable properties such as high resistivity, high saturation magnetization, low eddy current loss, high initial permeability these are the useful properties for low and high frequency applications like electromagnetic interference suppressions, circulators for mobile phone, multilayer chip inductors, transform core, microwave absorption etc., [1]. In general the inverse spinel ferrite structure has two sub -lattice namely tetrahedral (A) and octahedral (B) sites. Distribution of A site are filled by one - eighth of the divalent cations and B site are filled by trivalent cations[2]. A small additives of Gd-Cr ion substitution at B site (Fe\textsuperscript{3+}) site have shown significant enhancement in both electrical and magnetic properties it can be tuned by selecting the proper additives, composition and suitable method of preparation [3]. In this view Gd-Cr ion substitution on Fe\textsuperscript{3+} site produce very good physical and chemical properties in spinel ferrites, rare earth oxides are very good insulators with high electrical resistivity [4-5]. In which selection of suitable rare earth cations can change the electrical and magnetic properties of spinel ferrites and have
large influence on the magnetic anisotropy of the system. There are different methods have been adopted for preparation of Gd doped Ni-Zn ferrites for e. g., solid state reaction , sol-gel method [ 6], chemical co - precipitation method [7], high energy ball milling [8],carboxylic complex precursor method [9], hydrothermal [10], spray pyrolysis method [11] etc. In the present investigation we synthesized by solution combustion method successfully to obtain fine nanosized particles , because solution combustion method attracted much attention of many researchers ,for many advantages due to its cost effective , fast - self sustaining , large scale production of, fine homogeneous crystalline powders, which are free from contamination [12] during synthesis. The effect of Gd-Cr ions on structural ,electrical and magnetic properties of Ni-Zn nanoferrites are prepared by solution combustion method are reporting for the first time in the present investigation.

2. Experimental

Polycrystalline Ni$_{0.4}$Zn$_{0.6}$Cr$_{0.5}$Fe$_{1.5-x}$Gd$_x$O$_4$ (x=0.00, 0.02, 0.04, 0.06) ferrites were prepared by solution combustion method, using stoichiometric amounts of [Ni (No$_3$)$_3$.4H$_2$O] nickel nitrate, [Zn (No$_3$)$_3$.6H$_2$O] zinc nitrate , [Cr (No$_3$)$_3$.5H$_2$O] chromium nitrate, [Fe (No$_3$)$_3$.9H$_2$O] iron nitrate and [Gd (No$_3$)$_3$.6H$_2$O] gadolinium nitrate, as oxidizer and freshly prepared oxylyldehydrazide (C$_2$H$_6$N$_4$O$_2$) as fuel. Stoichiometric compositions of metal nitrates and ODH were calculated based on the ingredients total oxidizing and reducing coefficients for the stoichiometric balance, so that the equivalence ratio ($\phi$) was unity and the energy released was maximum [13]. The compounds were dissolved in de-ionized water and the solution was stirred make use of magnetic stirrer thereby forming a stable solution. The solution kept in a preheated muffle furnace maintained at 450 ± 10°C. The solution mixture boils undergoes thermal dehydration and remain in the form of porous and voluminous powder. The formation Cr - Gd doped nano particle was formed due to the gas phase reaction between decomposition products of metal nitrates and ODH. The complete process take 20 min. whereas the reaction time of the actual ignition flaming was few seconds. The powder was ground in agate pestle mortar and molded into disc shape using a hydraulic press at a pressure of 1.5x10$^8$ N/m$^2$. Finally, the samples were sintered at 1000°C for 2hrs and cooled to RT. The as prepared powder was characterized using Shimadzee X-ray diffractometer with CuKα (1.5401 Å) radiations with detector angle (2θ) range of 10-80° with a step size of 0.02° at room temperature. The formation of spinel phase of nanoferrites sample FTIR transmission spectra were taken on Agilent Infrared spectrometer. Measurements have been done in transmission mode in the range of 2000 to 300 cm$^{-1}$ at room temperature. The magnetic measurements were performed using a vibrating sample magnetometer (VSM Lake Share Model 7404) under applied magnetic field of 15 kOe.

3. Results and discussion

3.1. Structural properties

Figure 1 shows the XRD patterns of as synthesized Ni$_{0.4}$Zn$_{0.6}$Cr$_{0.5}$Gd$_x$Fe$_{1.5-x}$O$_4$ where (x=0.0, 0.2, 0.4 and 0.6) nanoparticles. The XRD patterns of as synthesized sample show cubic spinel structure and confirms presence of (111), (311), (222), (400), (422), (511) (400), (533) planes. Broad diffraction peaks represents the nanoscale crystallite size and the substitution of Gd$^{3+}$ ion concentration attributed to decrease in peak intensity led to decrease in crystallite size. Change in the variation of the structural parameters such as crystallite size (D) lattice constant (a), and hopping length (L$_A$)and (L$_B$) were calculated and tabulated in Table 1. The crystallite sizes of the produced nickel- Zinc ferrite were estimated for the most intense peak (311) plane determined from the X-ray diffraction data using the Debye- Scherer’s formula:
\[ D_{\text{XRD}} = 0.9 \frac{\lambda}{\beta \cos \theta} \]  

Where \( D_{\text{XRD}} \) is the crystallite size, \( k = 0.9 \) is a correction factor to account for a sphere shape particle, \( \lambda \) is the wavelength of the Cu target = 1.5406 Å, \( \beta \) is the full width half maximum (FWHM) of the most intense diffraction peak (311), and \( \theta \) is the Bragg’s angle. The value of the average crystallite size is decreases from 34 to 19 nm by increasing in Gd\(^{3+}\) concentration, this is due to the Gd\(^{3+}\) ions have substituted Fe\(^{3+}\) ions in the host spinel matrix, in spite of Gd\(^{3+}\) higher ionic radius (0.938 Å) as compared to that of Fe\(^{3+}\) (0.645 Å) [14]. Fig.2 represents the enlarged XRD (311) peak, which reveals that the peaks are broadened with increasing the Gd\(^{3+}\) concentration. As a result of incorporation of the trivalent ions in the spinel structure confirms that the studied samples are of ultra-fine nature and small crystallite size. The lattice parameters (a) and distance between adjacent Miller planes (h, k, l) were determined according to Laue and Bragg’s equations for cubic lattice.

\[ a = \lambda \left( h^2 + k^2 + l^2 \right)^{1/2} \div 2 \sin \theta \]

Where \( a \) is lattice constant, (h k l) are the interplanar distance, \( \lambda \) is the x-ray wavelength. The variation in lattice parameter is observed with increase in Gd\(^{3+}\) ion concentration. This variation in lattice parameter is attributed to the larger ionic radii of Gd\(^{3+}\) as compared Fe\(^{3+}\) ions replacing Fe\(^{3+}\) ions on octahedral sides which causes asymmetry in the structure [14]. The distance between magnetic ions (hopping length) in the tetrahedral and octahedral sites is given by,

\[ L_A = a \frac{3}{4} \quad \& \quad L_B = a \frac{3}{2} \]

The dependence of the hopping length (\( L_A \)) and (\( L_B \)) for the A sites and B sites on the Gd\(^{3+}\) content is observed that \( L_A \) and \( L_B \) exhibits similar behaviour as lattice parameters \( a \) \( L_A \) and \( L_B \) increases by increasing Gd\(^{3+}\) ions because Gd\(^{3+}\) ions replaces Fe\(^{3+}\) ions on the B sites in the spinel lattice.

Figure 1. XRD patterns of \( \text{Ni}_{0.4}\text{Zn}_{0.6}\text{Cr}_{0.5}\text{Fe}_{1.5-x}\text{Gd}_x\text{O}_4 \) (x=0.00, 0.02, 0.04, 0.06).
Figure 2. Enlarged (311) XRD peaks of Ni$_{0.4}$Zn$_{0.6}$Cr$_{1.5}$Fe$_{1-x}$Gd$_x$O$_4$ (x=0.00, 0.02, 0.04, 0.06).

3.2. FTIR absorption studies

FTIR is a non-destructive tool to know the position of ions and vibrational modes in the crystal. The transmission spectra of as prepared sample were recorded in the range from 300-2000 cm$^{-1}$ at room temperature, to confirm the formation of spinel cubic structure. Fig. 2. shows the transmission spectra of all the samples. From the figure one can observe that IR spectra shows two prominent absorption bands such as $\nu_1$ and $\nu_2$ at 565 cm$^{-1}$ and 370 cm$^{-1}$ respectively. Absorption band at 565 cm$^{-1}$ is attributed to tetrahedral site and 370 cm$^{-1}$ is assigned to octahedral site. Careful observation of the IR spectra of all the materials implies that substitution of Gd$^{3+}$ - Cr$^{3+}$ ion concentration $\nu_1$ continued to be broaden is attributed to atomic weight and large ionic radius of gadolinium than iron, which affects the Fe$^{2+}$-O$^{2-}$ distance on octahedral site as reported in literature [15]. In the present study $\nu_1$ is not showing any shoulders, hence presence of Fe$^{3+}$ ions at octahedral site is strike out consequently, there is a shift occur in absorption bands $\nu_1$ and $\nu_2$ for both A and B site due to the perturbation occurring in the Fe$^{2+}$-O$^{2-}$ bond by incorporating Gd$^{3+}$ ions [16].
3.3. Dielectric properties

Fig. 4 and 5 show the frequency dependence of real and imaginary part of a relative permittivity ($\varepsilon'$ and $\varepsilon''$) at room temperature for all the studied samples with the frequency range from 40 Hz to 10 MHz. From the figure one can observe that, relative permittivity for all the samples decreases with increase in frequency ten keeping constant at higher frequency. The real and imaginary part of dielectric constant in an AC electric field measure energy loss of the material [15]. Decrease in permittivity become slow at higher frequency and more rapid in low frequency region. Resistivity and permittivity both are electrical properties of spinel ferrites and depends upon the conduction phenomenon of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$. Hopping of electrons is responsible for polarization at grain boundaries due to local charge displacement [16]. Variation of dielectric dispersion in ferrites can be explained by Maxwell-Wagner model [17], and Koop's phenomenological theory [18]. According to this theory the ferrite system is a combination of highly conducting resistive grains separated by poorly conducting grain boundaries. The dispersion in the dielectric permittivity is due to space charge effect arising from $\text{Fe}^{2+}$ ions, oxygen vacancies and grain boundary defects. Relative permittivity and losses increases with increase in $\text{Gd}^{3+}$ ion concentration up to $x=0.06$, this is due to $\text{Fe}^{3+}$ ion concentration at B- site causing low resistivity which gives to high dielectric permittivity, as resistivity and relative permittivity has inverse behaviour to each other[19]
Figure. 4. Real part of permittivity ($\varepsilon'$) as a function frequency of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Cr}_{0.5}\text{Fe}_{1.5-x}\text{Gd}_x\text{O}_4$ ($x=0.00$, 0.02, 0.04, and 0.06)

Figure. 5. Imaginary part of permittivity ($\varepsilon''$) as a function frequency of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Cr}_{0.5}\text{Fe}_{1.5-x}\text{Gd}_x\text{O}_4$ ($x=0.00$, 0.02, 0.04, and 0.06)
3.4. Magnetic properties

Fig. 6. shows the room temperature hysteresis loops for all the studied samples. The 'S' shaped characteristic indicates the soft ferromagnetic nature of the synthesized sample [20]. The magnetic properties such as saturation magnetization ($M_s$), remanent magnetization ($M_r$), and coercive force ($H_c$) are greatly depend on grain size and cation substitution and all the data were tabulated in Table 1.

It can be seen from the figure that $M_s$ value increased up to $x=0.02$ and decreases with increase in Gd$^{3+}$ concentration from 40 emu/g to 16 emu/g and $x=0.02$ composition shows highest saturation magnetization. The initial increase in magnetization and magnetic moment can be explained on the basis of the Neel’s two sub lattice model. The addition of Gd$^{3+}$ forces the same number of Fe$^{3+}$ ions from A-site to occupy B-sites, as a result the magnetic moment of B-site increases and hence $M_s$ increases with increase in gadolinium. However the decrease $M_s$ indicates the non-collinear spin canting structure in the system, which compress the strength of the A-B and B-B interactions [21-22]. Also Gd$^{3+}$ ions have strong preference to occupy B-site, due to large ionic radius. Hence symmetry of crystal will be decreased by substituting Fe$^{3+}$ to Gd$^{3+}$ ions which mean that the distance between Gd$^{3+}$ ions and oxygen ions decreases [23-24], these variation is also depends on 4f spin contribution to the spin up magnetic moment of the ferrite structure [25]. The calculated and observed magnetic properties are good agreement with literature.

| Gadolinium Concentration (X) | Crystallite Size (d) nm | Lattice parameter 'a' (Å) | Octahedral site ($L_A$) | Tetrahedral site ($L_B$) | Saturating Magnetization ($M_s$) in emu/gm | Remanence Magnetization ($M_r$) in emu/gm | Coercivity ($H_c$) in Oe |
|-----------------------------|------------------------|--------------------------|------------------------|--------------------------|------------------------------------------|------------------------------------------|-------------------------|
| 0.00                        | 34                     | 8.348                    | 3.614                  | 7.229                    | 21.25                                    | 15                                       | 136                     |
| 0.02                        | 33                     | 8.352                    | 3.616                  | 7.233                    | 40.45                                    | 29                                       | 102                     |
| 0.04                        | 27                     | 8.324                    | 3.606                  | 7.2120                   | 16.99                                    | 12                                       | 88                      |
| 0.06                        | 19                     | 8.351                    | 3.616                  | 7.2391                   | 16.48                                    | 12                                       | 68                      |
Figure 6. Compositional variation of saturation magnetization of Ni_{0.4}Zn_{0.6}Cr_{0.5}Fe_{1.5-x}Gd_{x}O_{4} (x=0.00, 0.02, 0.04, and 0.06).

4. Conclusion

The effect of trivalent ions on the particle size and magnetic properties of nanocrystalline Ni_{0.4}Zn_{0.6}Cr_{0.5}Fe_{1.5-x}Gd_{x}O_{4} ferrites successfully prepared for the first time by solution combustion method using ODH as a fuel. The PXRD and IR results confirm the single phase cubic spinel structure. Crystallite size of as prepared nano particles decreases with increase in Gd^{3+} content owing to increased ionic radii and atomic weight of gadolinium as compared Fe^{3+}. Dielectric permittivity (real and imaginary) decreases with increase in frequency consequently dielectric constant increases as increase in Gd^{3+} concentration showing that x=0.02 is a low loss dielectric. The saturation magnetization, remanent magnetization and Coercivity increases up to x= 0.02 and decreases by increasing Gd^{3+} concentration due to exchange interaction between A and B site and decreases due to spin canting. In this study, the composition X=0.02 is the best among the four selected compounds at different Gd^{3+} substitutions for wide applications like communication satellites and sensors.

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