Sol-gel auto-ignition fabrication of Gd^{3+} incorporated $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ multifunctional spinel ferrite nanocrystals and its impact on structural, optical and magnetic properties

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Abstract

Monophasic nanocrystals of rare earth gadolinium (Gd^{3+}) ion doped nickel–cobalt ferrite, $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y = 0.00, 0.025, 0.050, 0.075, 0.100$ and 0.125) have been synthesized by L-ascorbic acid assisted sol–gel auto-ignition process. Thermogravimetric and differential scanning calorimetry, X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) with selected area electron diffraction (SAED) patterns, ultraviolet–visible spectrophotometry and vibrating sample magnetometer were employed to characterize the microstructure, optical and magnetic properties. Structural investigations verified the presence of cubic spinel phase short of any contamination peak. The average crystallite size was seen in nano-regime dimensions and well confirmed by TEM results. SAED patterns showed bright and intense ring of (311) plane revealed the establishment of spinel ferrite nanocrystals. Lattice constant (a) increases steadily with the rise in Gd^{3+} content following the Vegard's law. FTIR spectra confirmed the creation of spinel ferrite structural geometry. Saturation magnetization (M_s) and a remanence magnetization (M_r) decreased from 29.77 to 20.78 emu/g and 21.62 to 15.79 emu/g, respectively, with increasing the Gd^{3+} content. However, coercivity (H_c) is significantly increased. The highest value of $H_c = 1132$ Oe was found for $y = 0.075$ sample. The reduction in M_s values can be justified owing to the replacement of Fe^{3+} existing at the octahedral [B]-sites by the Gd^{3+} ions which is paramagnetic at room temperature. The elucidation of magnetic parameters with Gd^{3+} doping was attributed to the discrepancy of anisotropy constant, the paramagnetic nature of Gd^{3+} and crystallite size effect.

Keywords Ni–Co ferrite · Sol–gel · Nanocrystals · Rare earth · Magnetic properties

1 Introduction

In the group of ferrites, spinel ferrites are comprehensively studied worldwide by a number of researchers from the academic and technological viewpoint. Nanostructured spinel ferrites have an enormous prospective material for several innovative scientific and technological applications [1–3]. Spinel ferrites are widely used in microwave devices [4], solar cells [5], magneto-strictive sensors [6],

transducers [7], super-capacitors [8], power supplies for a large variety of electronic gadgets [9], drug delivery [10], memory devices [11], catalysis [12] and spintronics devices [13].

Spinel ferrites (AB_2O_4) exhibit a face centered cubic (fcc) geometric structure someplace both trivalent and divalent metal cations are reside in the tetrahedral (A) and octahedral [B] sites occupancy in a cubic closed packing of oxygen (O^{2-}) [14]. Owing to the high level of accessible

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connectivity among the cations in spinel structure, these solid exhibit diversities of physico-chemical characteristics. The properties of spinel ferrites can be altered with approaches of synthesis, microstructure, chemical composition, kinds of dopant elements etc. parameters [15, 16]. Over the years, nano-ferrites have received considerable attention as potential materials owing to their capability to express improved and unique properties in contrast with conventional bulk ferrite materials [17]. The nano-ferrites are synthesized by the different routes such as chemical co-precipitation [18], hydrothermal [19], microemulsion [20], citrate-gel [21], etc. techniques. The sol-gel technique is the utmost adaptable process to produce synthetic nanoparticles of spinel ferrites and having uncountable benefits over other synthesis methods for instance; requires low temperature, ecofriendly, desired nanoarchitecture, chemically stable product formation with desired morphology through modification of synthesis environments and parameters [22–24]. The doping of variability of divalent, trivalent and tetravalent cations (Mg^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , Cr^{3+} , Ga^{3+} , Zr^{4+} , Sn^{4+} , Ti^{4+}) with different molar compositions are another crucial factor that has an effect on physico-chemical properties of spinel ferrite nanoparticles [25–28].

Amongst the spinel ferrites, NiFe_2O_4 and CoFe_2O_4 are the most applicable ferromagnetic solids and widely studied materials which have unique properties for example, vast coercive force, moderate saturation magnetization, high magnetocrystalline anisotropy energy, high Curie temperature, high mechanical, thermal and chemical strength [29, 30]. Moreover, Ni-Co mixed ferrites are considerable electronic materials, which are utilized in electronic appliances suitable for high-frequency devices in the telecommunication sector [31, 32]. The Ni-Co ferrite based materials are economically used in antenna rods, radio-frequency circuits, high-quality filters, transformer cores and read/write memory heads, etc. [33, 34]. The exceptional electric and magnetic properties of these materials make them potential materials for the miniaturization of microwave tunable devices.

The appropriate amount of doping of rare earth RE species in AB_2O_4 ferrites is liable for extraordinary variations in structural, optical, magnetic, electric in addition dielectric behavior [35]. The origin of magnetism in rare earth metals viz. La^{3+} , Ce^{3+} , Pr^{3+} , Gd^{3+} , Dy^{3+} , Ho^{3+} initiates from '4f' orbital electrons that are isolated through '5s' and '5p' shells. Henceforth, their magnetic moments are restricted to the atomic system. In view of these confined '4f' orbital electrons the rare-earth metals have colossal magnetocrystalline anisotropy [36, 37]. Among the lanthanide group, gadolinium (${}_{64}\text{Gd}^{3+}$) having electronic configuration ($[\text{Xe}]4f^7, 5d^1, 6s^2$), has seven valence '4f' electrons, but has magnetocrystalline anisotropy nearby to zero as

a result of symmetric spherical electronic charge distribution [38]. The accurate doping of Gd^{3+} ions in Ni-Co-ferrite can manufacture the product that could be appropriately utilized in microwave tunable devices, magnetic storage and recording device applications [39, 40].

The literature study recommends that fascinating variations in AB_2O_4 ferrites can be done through the incorporation of rare-earth Gd^{3+} cations, in an attempt to fulfil the prerequisites of technological industry [41, 42]. On account of their number of applications and utility in the diverse field, there is a requirement to investigate the mixed nickel-cobalt (Ni-Co) nano-ferrite materials with improved properties which can be achieved through synthesis techniques and using different rare earth dopants.

In the present study, nanocrystalline rare earth gadolinium (Gd^{3+}) doped Ni-Co nano-ferrite with chemical composition $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00, 0.025, 0.050, 0.075, 0.100$ and 0.125) were synthesized consuming sol-gel auto ignition technique and influence of Gd^{3+} doping on the structural, microstructural, optical and magnetic characteristics were systematically investigated.

2 Experimental

2.1 Synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00 - 0.125$) spinel ferrite nanoparticles

2.1.1 Materials

The analytical reagent grade nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), gadolinium nitrate ($\text{Gd}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) procured from Sigma-Aldrich were used as raw materials (with 99.9% purity) and used as received without further purification.

2.1.2 Synthesis

Nanocrystalline $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ with concentration $y=0.00, 0.025, 0.050, 0.075, 0.100$, and 0.125 were effectively produced using sol-gel auto ignition technique and L-ascorbic acid as a fuel. The AR grade nickel nitrate, cobalt nitrate, gadolinium nitrate, ferric nitrate and L-ascorbic acid were dissolved in deionized water separately to attain a homogenous solution. The precursor metal nitrates were liquefied at once with a least volume of deionized water required to attain a transparent solution. The chemical process was done in a normal air atmosphere. The metal nitrates to fuel (L-ascorbic acid) ratio was maintained at 1:4. Liquid ammonia was added dropwise to preserve the pH to 7. The solution is then magnetically stirred at ambient temperature to form a homogeneous solution. The

homogeneous solution is allowed to condense with continuous stirring on a hot plate, at a temperature of about 110 °C till it forms a highly viscous and dried gel. Then the dried viscous gel is further heated on a hot plate until it gets self-ignited. The auto ignition reaction takes place in a few seconds to produce the required product.

The un-calcinated powder samples were sintered at 700 °C for 5 h and afterward utilized for further examinations of structural, microstructural, optical and magnetic properties. The general chemical reaction of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ nanoparticles is described in Fig. 1.

2.1.3 Characterizations

The thermogravimetric (TGA) and differential scanning calorimetry (DTA) analysis for the un-calcinated sample were completed on a thermal analyzer (STA449C/4/MFC/G, Netzsch, Germany) with thermal rate of 10 °C/min. The X-ray diffraction (XRD) technique was employed to check the phase purity and nano-crystalline nature of the prepared samples. The XRD graphs were measured in the 2θ range of '20°–80°' with $\text{Cu-K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation 'RIGAKU-Japan'. The microstructural studies were performed using transmission electron microscopy 'TEM, Philips CM-200' technique accompanied by selected area electron diffraction (SAED) patterns. The fourier transform infrared spectroscopy (FTIR) of synthesized nanoferrites

were analyzed in the region 4500–400 cm^{-1} performed on a spectrophotometer 'Shimadzu-Japan' using KBr as a standard material for verification of molecular components and structure analysis. Optical characteristics were examined by ultraviolet–visible (UV–Vis) absorption measurements noted in the region 200–800 nm by means of a 'Lambda 25-Perkin-Elmer' UV–Vis spectro-photometer. The synthesized samples were dispersed in ethanol solvent and a clear solution was obtained. Absorbance was measured in 1 cm path length of the quartz crystal cuvette and spectral examination was found with the Spectrophotometer. Room temperature magnetic measurements of the materials under consideration were investigated with the vibrating sample magnetometer (VSM) 'Lakeshore VSM 7410' with applied field of 7 kOe.

3 Results and Discussion

3.1 Thermogravimetric and differential thermal analysis (TGA–DTA)

TGA–DTA data of the representative as-prepared $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y = 0.025$) sample was measured from 25 to 800 °C at a continual heating proportion of 10 °C/min. The TGA plot illustrates 0.8% weight loss up to 350 °C which features to the loss of H_2O molecules and

Fig. 1 General chemical reaction of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y = 0.00 - 0.125$) spinel ferrite nanoparticles synthesized by auto-ignited sol–gel method

Fig. 2 TGA–DTA graph of as prepared $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.025$) sample

evaporative organic compounds due to the evaporation process as revealed in Fig. 2. A slow breakdown has happened between 350 and 650 °C because of the chemical decomposition of polymeric molecular fragments with a weight reduction of $\pm 0.02\%$. Additional decay is not detected beyond 650 °C which demonstrates that this solid is thermodynamically stable material. This observed behaviour is in acceptable concurrence to the TGA outcomes reported in the literature [43, 44]. In the DTA plot, an extensive endotherm is noticeable in the temperature scale of 50–300 °C. This wide endotherm resembles to the absorption of external thermal energy for the disintegration of material. At ~ 360 °C, a broad exothermic peak was seen which credits to the liberation of thermal energy that could be utilized for the exact phase formation. While a wide endotherm (400–450 °C) represents the crystallization of the complex organometallic compound [45]. The TGA curve displays that rate of weight loss is nearly continuous after the temperature ~ 650 °C. Therefore, the annealing temperature is kept at 700 °C for the resultant samples.

3.2 X-ray diffraction (XRD) analysis

XRD patterns of the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00, 0.025, 0.050, 0.075, 0.100$ and 0.125) nanoparticles acquired at room temperature are shown in Fig. 3. All the XRD patterns demonstrates the existence of the desired phase of a cubic spinel structure (space group $Fd\bar{3}m$) with no extra peaks of any impurity phases. The observed Bragg's reflections are somewhat broader approving the nanocrystalline nature of the synthesized samples. The existence of (111), (220), (311), (222), (400), (422), (511), (440) and (533) reflection planes in the XRD pattern reveals the

Fig. 3 XRD patterns of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00 - 0.125$) nanoparticles

cubic spinel structural geometry of entire samples [46]. It is also evident that all the reflection peaks are intense and sharp without any impurity peaks thus, the materials are single phase in nature.

The average particle size (t) of the Gd^{3+} substituted Ni–Co ferrite powders was determined by utilizing the most intense peak (311) and by means of the Debye–Scherer's formula [47, 48],

$$t = \frac{0.9\lambda}{\beta \cos \theta} \text{ nm} \quad (1)$$

where λ is wavelength of the 'Cu-K α ' radiation, β is the full width of the half maximum, θ is Bragg's angle. The average particle size assessed by using Debye–Scherer's formula is of the order of 29–35 nm showing nano-regime dimension (Table 1).

The lattice constant (a) of the Gd^{3+} doped Ni–Co ferrites were determined by means of the typical relation and their values are organized in Table 1 [49],

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

where d is interplanar distance; (hkl) is Miller Indices.

Figure 4 illustrates the distinction of lattice constant (a) with Gd^{3+} concentration y . It can be observed from the graph that the values of a increases with Gd^{3+} content y . This can be accredited to the bigger ionic radii of Gd^{3+} (1.05 Å) rare earth ion as related to Fe^{3+} (0.60 Å) ion following the Vegard's law [50]. Our result on the lattice constant is comparable to Gd^{3+} doped Co and Ni ferrite separately [51, 52].

Table 1 Lattice constant (a), unit cell volume (V), X-ray density (d_x), bulk density (d_b), porosity ($\%P$), average particle size (t) from XRD, average particle size (D) from TEM, vibrational band frequency (ν)

y	a (Å)	V (Å ³)	d_x (gm/cm ³)	d_b (gm/cm ³)	P (%)	t (nm)	D (nm)	ν (cm ⁻¹)	E_g (eV)
0.000	8.3449	581.11	5.41	4.2461	21.64	35.5	33.5	545.87	2.72
0.025	8.3496	582.09	5.46	4.2522	22.22	33.3	31.3	549.87	2.59
0.050	8.3499	582.16	5.52	4.2590	22.91	30.3	28.3	550.77	2.55
0.075	8.3525	582.70	5.57	4.6161	17.23	29.3	28.3	557.72	2.48
0.100	8.3572	583.69	5.62	4.6890	16.65	33.4	29.4	563.37	2.42
0.125	8.3631	584.92	5.67	4.7120	16.91	32.5	27.5	571.25	2.20

Fig. 4 Variation of lattice constant (a) and X-ray density (dx) with Gd^{3+} concentration y

The unit cell volume (V) was assessed by using lattice constant. The unit cell volume shows a steady increase with the doping of Gd^{3+} ions (Table 1). The expansion of the unit cell volume is accredited to increase in lattice constant.

The X-ray density (d_x) value was estimated via the relation (3) and values are summarized in Table 1 [53];

$$d_x = \frac{Z \times M}{V \times N_A} \quad (3)$$

where Z is the number of molecules per formula unit ($Z=8$ for spinels), M is molecular mass of the material, V is the unit cell volume, N_A is the Avogadro's number.

X-ray density increases as Gd^{3+} concentration y (Table 1) due to the fact that the rise in molecular weight/mass exceeds the increase in volume. In the current system, both unit cell volume and molecular weight increases resulting increase in d_x values. Figure 4 shows the discrepancy of X-ray density versus Gd^{3+} concentration y .

The bulk density (d_b) of the fabricated pellet samples was found consuming the Archimedes principle using

from FTIR, optical band gap energy (E_g) from UV-Vis spectroscopy of $Ni_{0.5}Co_{0.5}Gd_yFe_{2-y}O_4$ ($y=0.00-0.125$) nanocrystals

xylene as an immersion liquid [54]. It is evident from Table 1 that, similar to X-ray density, bulk density also increases with Gd^{3+} concentration y . The porosity ($\%P$) values were determined using d_x and d_b values and detected to be of the order of 16–22% (Table 1) suggesting the porous nature of the synthesized materials due to evolution of substantive gases during the combustion synthesis.

3.3 Transmission electron microscopy (TEM) with selected area electron diffraction pattern (SAED) analysis

A TEM study demonstrated that sphere-shaped, unvarying nano-crystalline powders were effectively produced. The TEM micrographs along with SAED patterns of the representative 0.00, 0.075 and 0.125 powder samples are represented in Fig. 5. The grains exhibit the agglomerate spherical and cubical shape morphology for the prepared samples. The obtained average crystallite size (D) of the prepared nanoparticles from TEM was in the range of 27–33 nm listed in Table 1. The SAED pattern (Fig. 5) shows a bright, intense ring of (311) plane showing the creation of spinel ferrite sample. Similarly, the diffraction rings of the planes (220), (311), (400), (422), (511), (440), (533) which are permitted planes of cubic structure. The small spots, making up a ring and superimposition of bright spots show the establishment of poly-nanocrystalline nature of the entire prepared materials.

3.4 FTIR spectroscopy

FTIR spectra of the $Ni_{0.5}Co_{0.5}Gd_yFe_{2-y}O_4$ ($y=0.00-0.125$) samples were composed at normal temperature are shown in Fig. 6. As suggested by Waldron (1955), ferrites are the continuously bonded crystals that means it is bonded to all adjacent neighbors through equal forces which may be ionic, covalent or Van der Waal's type [55]. For spinel ferrites, the FTIR spectra validates the twofold distinct absorption bands in the scale of 400–1000 cm⁻¹, the first absorption band (ν_1) is observed at around 400 cm⁻¹ and

Fig. 5 TEM micrographs along with SAED pattern of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ for representative $y=0.00$, 0.075 and 0.125 nanoparticles

second band (ν_2) is around 550 cm^{-1} . These absorption bands resemble to intrinsic oscillations of atoms in a solid of octahedral and tetrahedral coordination compounds in the spinel structure respectively [56, 57].

In Fig. 6, the intense absorption band is observed at $\sim 550\text{ cm}^{-1}$ which shows the characteristic band feature of spinel ferrite geometrical structure. The position of band changes with Gd^{3+} concentration due to structural

changes for the entire prepared samples (Table 1). The absorption band slightly shifts to a higher wave number direction with doping of Gd^{3+} ions and can be ascribed to the rise in bond length of the [B]-site [58]. This recommends that the rare-earth ions reside in the [B]-site. Also, the spectra show the absorption bands nearby 3440 cm^{-1} and 1500 cm^{-1} which are attributed to H–O stretching and bending vibration modes of absorbed and unrestricted

Fig. 6 FTIR spectra of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y = 0.0 - 0.125$) nanoparticles

water molecules. The band position around 2300 cm^{-1} designates the existence of a remaining amount of CO_2 [59]. The FTIR results are analogous to Gd^{3+} doped cobalt ferrite nanoparticles [60].

3.5 UV-Vis absorption spectroscopy

Figure 7a illustrates the UV-Vis absorbance spectra of the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y = 0.00 - 0.125$) nanoparticles recorded at room temperature. The optical band gap energy (E_g) could be predictable from the transformation of absorption coefficient with wavelength using Tauc's relation (4) [61];

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

where α -linear absorption coefficient of the material, h -Planck's constant ($6.6260 \times 10^{-34}\text{ J s}$), ν -photon energy (in eV), A -proportionality constant that relies on the transition probability, and n is a constant associated with allowed indirect or direct transition probability.

As per the reports, spinel ferrites exhibit an optical absorption spectrum ruled by direct electronic transitions [62]. The optical energy band gap is evaluated from the intercept of the linear area in the curve of a plot of photon energy ($h\nu$) on the X-axis versus $(\alpha h\nu)^2$ on the Y-axis as visible in Fig. 7b.

Table 1 provides the optical band gap energy of the synthesized nanocrystals. The optical band gap of the $y = 0.00$ is obtained to be 2.72 eV. Generally, the band gap of semiconducting spinel ferrite changes when foreign impurities are added. With the addition of Gd^{3+} concentration,

Gd^{3+} ions replace the [B] site Fe^{3+} cations which may create impurity bands inside the gap. Once Gd^{3+} content is lower, the separation among the valence band and the lowest impurity band look like effective band structures. As Gd^{3+} dopant content increases, the thicknesses of these impurity bands rise, and these bands might overlap together responsible for reduction in band gap energy (as given in Table 1). Also, the reduction of E_g values with increasing Gd^{3+} concentration could be by reason of variation in the lattice constant, reduction in average crystallite size and modification of surface area to volume ratio [63]. The obtained values of E_g (2.2–2.7 eV) is equivalent to the semiconductor materials. Hence, the prepared nano-ferrite materials show the semiconductor characteristics.

3.6 Magnetic properties

So as to explore the magnetic response of the present materials to an exterior field, we measured the field reliant magnetization of the samples at 300 K using VSM equipment. Figure 8 displays the $M-H$ plots of the produced samples. The $M-H$ plots viewing the ferrimagnetic behaviour of the prepared samples. The magnetic parameters viz. saturation magnetization (M_s), remanence magnetization (M_r), coercivity (H_c) and remanence ratio (M_r/M_s) were determined from $M-H$ plots and are given in Table 2. The results revealed that as the Gd^{3+} concentration increases the values of M_s decrease gradually. The lower values of remanence magnetization recommend the prepared sample is a soft ferrite material, thus such nano-ferrite was suggested for coils and cores of inductance. The magnetic characteristics of the nano-ferrite strongly dependent on the distribution of cations and these properties can be easily tuned by the various dopant elements [64].

In spinel ferrites, three varieties of super-exchange communications amongst the A and B cations of (A) and [B]-occupancy site are conceivable for example 'A-A', 'B-B' and 'A-B'. Out of these, 'A-B' communication is leading because of ideal separations among the A-B cations in addition the bulky degree of distortion amongst 'A-B' cations among with oxygen O^{2-} anions. The spins of cations at (A) and [B] occupancy sites influence the sub-lattice A and B in reverse ways and the variation amongst the moments of B and A species is the total magnetic strength of the spinel ferrite [58]. Therefore, the subsequent saturation magnetization will be, $M_s = M_B - M_A$, where M_A and M_B are the magnetic strength of (A) and [B]-site.

Currently in the case of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ solid, the doped Gd^{3+} ions reside in octahedral [B] site. The magnetic moment of Gd^{3+} ions is i.e. $7.94\text{ }\mu\text{B}$ which is higher related to the Fe^{3+} ions ($5\text{ }\mu\text{B}$). The magnetic moment of Gd^{3+} ion generates from the $4f^7$ shell electrons and is seems meaningfully at lower temperatures only ($\sim 290\text{ K}$). At

Fig. 7 **a** UV-Vis absorption spectra for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00 - 0.125$) nanoparticles. **b** Tauc plots for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00 - 0.125$) nanoparticles

Fig. 8 M - H plots for $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00 - 0.125$) nanoparticles

room temperature (~ 300 K) the dipole moments in Gd^{3+} have undirected alignments, owing to which their impact to magnetic moment contribution is very slight, viewing 'paramagnetic' nature [65]. Hence, the doping of Gd^{3+} ions into Ni-Co ferrite is identical to adding of non-magnetic species to [B]-site, owing to which the total saturation magnetization decreases [66].

The H_c values were found from M - H plots and are presented in Table 2. It can be observed that all the samples show bigger values of coercivity confirming the nanocrystalline nature. The H_c values overall increases with Gd^{3+} doping. The huge enhancement in the values of H_c from 909.4 Oe to 1132 Oe for $y=0.075$ could be owing to gain in anisotropy constant (K) and instantaneous reduction in average crystallite size (33–27 nm). In spinel ferrites, decrease in crystallite size is accountable for amplified coercive force. The decrease in H_c values for $y > 0.075$ (1132–982 Oe) is attributed to reducing values of anisotropy constant. Commonly, the coercivity of ferrites is testified to be tuned by aspects like crystallite size, morphology, micro-strain, porosity, anisotropy, size distribution and the magnitude of the magnetic domain.

The magnetic moment, i.e. magneton number (n_B) of the synthesized samples was calculated by using the relation (5) and their values is presented in Table 2;

$$n_B = \left(\frac{\text{Mol. Weight} \times M_s}{5585} \right) \quad (5)$$

As like saturation magnetization, magneton number of Gd^{3+} doped Ni-Co ferrite decreases as Gd^{3+} content y increases.

The anisotropy constant (K) of ferrites sample was obtained by [67];

$$H_c = \frac{0.96 K}{M_s} \quad (6)$$

where M_s is saturation magnetization and H_c is coercivity. The anisotropy constant quantities are of the order of 21,278.33–28,202.48 erg/cm³ (Table 2). Figure 9 portrays the discrepancy of anisotropy constant (K) and magneton number (n_B) with Gd^{3+} concentration y . The lessening in anisotropy entity might be due to the distortion formed in the lattice of Ni-Co ferrite owed to Gd^{3+} ion doping.

It is well acknowledged fact that, in Ni-Co ferrite the magnetocrystalline anisotropy originates from the existence of Ni^{2+} - Co^{2+} ions at the octahedral sites. As the Gd^{3+}

Fig. 9 Variation of anisotropy constant (K) and magneton number (n_B) with Gd^{3+} concentration y

Table 2 Saturation magnetization (M_s), remanence magnetization (M_r), coercivity (H_c), remanence ratio (M_r/M_s), anisotropy constant (K) and Bohr magneton moment (n_B) of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ ($y=0.00 - 0.125$) nanocrystals

y	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	M_r/M_s	K (erg/cm ³)	n_B (μ_B)
0.000	29.77	21.62	909.4	0.7263	28,202.48	1.25
0.025	28.30	20.80	923.6	0.7350	27,229.26	1.20
0.050	26.83	20.46	971.0	0.7625	27,140.46	1.15
0.075	25.10	19.94	1132	0.7945	29,605.69	1.08
0.100	23.12	18.08	1020	0.7820	24,570.73	1.01
0.125	20.78	15.79	982.8	0.7600	21,278.33	0.91

substitution increases the Co^{2+} ions may be migrated from octahedral sites to tetrahedral sites. However, it is expected that the reduction in Ni^{2+} – Co^{2+} ions in octahedral sites might be reducing the anisotropy constant of Gd^{3+} doped Ni–Co ferrite at higher concentrations. Our results on magnetic properties are analogous to Gd^{3+} doped CoFe_2O_4 spinel ferrite nanoparticles reported in the literature [68].

4 Conclusions

Nanocrystals of gadolinium (Gd^{3+}) doped Ni–Co ferrite for the composition of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Gd}_y\text{Fe}_{2-y}\text{O}_4$ where, $y = 0.00, 0.025, 0.050, 0.075, 0.100$ and 0.125 were effectively synthesized via sol–gel auto ignition technique and L-ascorbic acid as a fuel. Gd^{3+} doping has carried about a noteworthy fluctuation in the structural, microstructural, optical and magnetic characteristics of mixed Ni–Co nano-ferrite. The XRD study confirmed the growth of fine nanocrystals of cubic spinel structure with space group $Fd-3m$ without any impurity phase. The average crystallite size of prepared nanocrystals was estimated by the Debye–Scherer relation which was obtained in the range of 29–35 nm. The lattice constant increases with the Gd^{3+} doping attributed to the larger ionic radii of Gd^{3+} (1.05 Å) rare earth ions as compared to Fe^{3+} (0.60 Å) ions conforming the Vegards law. The X-ray density, unit cell volume and bulk density value increase as Gd^{3+} doping increases resulting in the structural variation. A TEM study demonstrated that spherical, uniform nanocrystalline powders were magnificently synthesized. TEM results also supported the approximate sizes of the nanoparticles (27–33 nm) initially derived from XRD data. SAED pattern shows a bright, intense ring of (311) plane showing the construction of spinel ferrite sample. FTIR study shows a prominent absorption band detected nearby 550 cm^{-1} confirmed to the construction of single-phase cubic spinel structure. The small variation in the band positions has been attributed to the Fe^{3+} – O^{2-} distances in the octahedral and tetrahedral complexes due to Gd^{3+} doping. The optical energy band gap varies with the Gd^{3+} doping. This band gap energy is equivalent to the semiconducting materials. Hence, this prepared ferrite material shows the semiconductor behavior and enhanced optical properties. Gd^{3+} doping has a noteworthy impact on the magnetic characteristics of Ni–Co ferrite nanoparticles. As Gd^{3+} content increases, the M_s and M_r values were found to be decreased and thus resulted in a decrease of magnetic anisotropy constant. The large rise in values of H_c from 909.4 Oe to 1132 Oe for $y = 0.075$ may be attributed to gain in anisotropy constant and a concurrent decrease in crystallite size. Moderate values of coercivity along with saturation magnetization make these fabricated samples

of Gd^{3+} doped Ni–Co nano-ferrites more appropriate for memory devices, magnetic recording instruments and biomedical applications.

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

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