Research Article

Structural, Electrical, Dielectric, and Magnetic Properties of Cd^{2+} Substituted Nickel Ferrite Nanoparticles

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In the present investigation structural, electric, magnetic, and frequency dependent dielectric properties of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ferrite nanoparticles (NPs) (where $x = 0.2, 0.4, 0.6$, and 0.8) prepared by sol-gel autocombustion method were studied. The crystallite size (t) ($46.89\sim 58.40$ nm) was estimated from X-ray diffraction data with the postconfirmation of single phase spinel structure. Spherical shaped, fused grain nature with intergranular diffusion in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs was observed in scanning electron micrographs. The value of loss tangent ($\tan \delta$) decreases exponentially with an increasing frequency indicating normal Maxwell-Wagner type dielectric dispersion due to interfacial polarization. Decreasing values of Curie temperature (T_C) from 860°C to 566°C with increasing Cd^{2+} content x in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs were determined from AC-Susceptibility. Activation energy ΔE ranges within $0.03\sim 0.15$ eV. Decreasing magnetic saturation M_s , coercivity H_c , and magneton number n_B values show the effect on nonmagnetic Cd^{2+} ions over magnetic Ni^{2+} and Fe ions.

1. Introduction

With the striking feature of “ferrimagnetism” nanocrystalline ferrites have attracted special attention of researchers in the field of electronic technology. Ceramics of ferrite have a wide temperature range of -40 to $+225^\circ\text{C}$ and greater values of specific resistivity and dielectric constant than that of the metals [1]. The unit cell contains eight formula units and is usually referred to as space group $\text{Fd}\bar{3}\text{m}$ (O_h^7) with the cations occupying special positions 8a and 16d. The ideal structure consists of cubic close packing of oxygen atoms ($32e$) in which one-eighth of the tetrahedral (A) and half of the octahedral [B] interstices are occupied [2]. The unit-cell geometry is controlled by only the metal-oxygen bond lengths for the tetrahedral (A–O) and octahedral [B–O] sites (Hill et al. 1979) [3]. In normal spinel structure the cation distribution is proposed as $(\text{M}^{2+})^A(\text{M}^{3+}\text{M}^{3+})^B\text{O}_4$ while inverse spinel has the general formula $(\text{M}^{3+})^A(\text{M}^{2+}\text{M}^{3+})^B\text{O}_4$. The nonconvergent

disorder of cations over the tetrahedral (A) and octahedral [B] sites can be described using an inversion parameter (δ) and the formula $(\text{M}^{2+}_{1-\delta}\text{M}^{3+}_{\delta})^A[\text{M}^{2+}_{\delta}\text{M}^{3+}_{2-\delta}]^B\text{O}_4$, where $\delta = 0$ for an extreme case and $\delta = 1$ for a completely inverse spinel [3, 4]. NiFe_2O_4 NPs (cubic $a = 8.327 \text{ \AA} \pm 0.002 \text{ \AA}$) ($F^4_{1/4}32/m$ number 227 in International Tables) [5], $Z = 8$, JCPDS PDF-10-0325, is a semiconductor having a room-temperature resistivity $\sim 1 \text{ k}\Omega \text{ cm}$ and shows soft ferromagnetic order below 850 K with a relatively low magnetization of $2 \mu_B$ per formula unit, that is, about 300 emu cm^{-3} . Cd^{2+} is a nonmagnetic ($0 \mu_B$) divalent ion that shows almost similar substitution behaviour as that of Zn^{2+} substitution in ferrites [6]. Mixed Cd-ferrites (JCPDS-79-1155 [7]) are technically important due to their high resistivity, high permeability, and comparatively low magnetic losses making them more suitable for the electrical switching applications [8–10]. Cd^{2+} substituted NiFe_2O_4 NPs have widespread applications in recording heads, antenna rods, loading coils, microwave

devices [1, 7], multilayer chip inductor (MLCI) [11], high frequency transformer cores, phase shifter, resonators, computers, TVs, and mobile phones [12–16]. The spinel structure of NiFe_2O_4 NPs is constructed by filling the FCC sublattice of relatively larger oxygen ions and the cation distribution is strongly dependent on ionic radii as well as concentration of the substituted divalent metal ions [17]. The entire Ni^{2+} cations occupy the [B]-site while the Fe^{3+} cations distribute equally between (A)-site and [B]-sites. Angle A–O–B is closer to 180° than the angles B–O–B and A–O–A; therefore, the AB pair (Fe–Fe) has a strong antiferromagnetic superexchange interaction [18]. Postsubstitution site preferences of Cd^{2+} ions are towards the tetrahedral (A) site suggesting the distribution of cations as

Several possible cation distributions and various magnetic orders can be studied at A, B1, and B2 sites [19]. Nath et al. have studied the magnetic orders in Ni–Cd ferrite [6]. In recent days, variety of chemical and physical methods has been employed for the preparation of well-defined, magnetic Ni–Cd ferrite NPs with specific shape and size. Rafeek et al. have synthesised Ni–Cd NPs by sol-gel autocombustion method for the study of the antibacterial effects against microorganism [8, 20]. Nejati et al. have discussed the superparamagnetic nature of NiFe_2O_4 NPs synthesised by hydrothermal method [11, 21]. Drmota has discussed the precipitation in microemulsion method for the controlled size and morphology of magnetic nanoparticles [22]. Suresh et al. have prepared Ni–Cd NPs with crystallite size of 15–23 nm using chemical coprecipitation method [23]. Modi et al. have studied the pre- and postannealing particle size of the Ni–Cd ferrite NPs synthesis by wet-chemical technique [24]. Rahimi et al. have reported the synthesis of nanoscale $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ferrite powders by sol-gel autocombustion method using EDTA as a complexion agent [25]. In this investigation we have applied sol-gel autocombustion method for the production of fine powder of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs. This preparation technique involves the exothermic and self-sustaining thermally induced anionic redox reaction of aerogel, which is obtained from aqueous solution [26].

2. Experimental Details

2.1. Synthesis of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs. $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ spinel ferrite NPs (where $x = 0.2, 0.4, 0.6$, and 0.8) were prepared successfully by sol-gel autocombustion method using stoichiometric proportion of 99.9% pure AR grade ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (>99%) as starting materials. The metal nitrates were dissolved together in the presence of minimum amount of double distilled deionized water. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) is significantly used in wet-chemical methods compared to the other fuels, as it is characteristically weak organic acid having better complexing ability possessing a low ignition temperature (200–250°C). The molar ratio of metal nitrates to citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was taken as 1 : 3. The pH of the solution was maintained at 7 with

the drop by drop addition of ammonia solution. Continuous stirring of the mixed nitrate aqueous solution was performed on a magnetic hot-plate stirrer maintaining the temperature 90°C . During the evaporation stages, solution became viscous in colour and later on formed a viscous brown gel. Finally, a sticky mass began to bubble for few minutes in a same beaker. This gel got ignited automatically and burned with a glowing flint. The decomposition process would not stop before the whole citrate complex was consumed. As a yield product of this reaction, fluffy loose powder of brown coloured ash could be termed as $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ presintered ferrite. The prepared samples were dried and annealed at 800°C for 12 h after thermogravimetric analysis (TGA). Some part of the annealed $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs was granulated with the addition of saturated PVA solution (polyvinyl alcohol ($\text{C}_2\text{H}_4\text{O}$)_x) as a binder. These granulated NPs were used to prepare disc shaped pellets of 10 mm diameter and 3 mm thickness using the hydraulic press by applying pressure of 5 tons/cm² for 5 min in a stainless steel die.

3. Results and Discussion

3.1. X-Ray Diffraction Study of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs. X-ray diffraction patterns of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs were recorded with the X-ray diffractometer (Philips). XRD of all samples were recorded in the 2θ range of 20 – 80° with Cu–K α radiation ($\lambda = 1.5405$ a.u.) at room temperature. All the peaks were identified by comparing the “ d ” spacing with that of JCPDS data of NiFe_2O_4 and CdFe_2O_4 in order to confirm the crystalline phases present. The major lattice planes (220), (311), (400), (422), (511), and (440) in Figure 1 confirm the formation of single phase $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ with a face centred cubic spinel structure, space group Fd3m. Accordingly, minor lattice planes (222), (533), (622), and (444) in XRD pattern gave supporting agreement about the powder diffraction of the spinel cubic JCPDS [27]. Cation distribution was estimated from the comparison between observed intensity ratios (I_{obs}) and calculated intensity ratios (I_{cal}) by following the Bertaut method [12]. The values of structural parameters like peak intensity ratios, hopping length (L_A, L_B), and bond length (R_A, R_B) are depicted in Table 1. Lattice constant (a) of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs (Table 1) was determined from X-ray data analysis with an accuracy of $\pm 0.002 \text{ \AA}$ using the formula [28]:

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

where a is a lattice constant, ($h k l$) represents the Miller indices, λ is a wavelength of X-rays, and θ is the glancing angle. It can be noticed from Figure 2 that the value of lattice parameter increased with the increase in Cd^{2+} content [29] from $8.350 \text{ \AA}$ to $8.491 \text{ \AA}$ ($\pm 0.002 \text{ \AA}$) which is attributed to the larger ionic radius of Cd^{2+} ($0.97 \text{ \AA}$) ions than that of Ni^{2+} ($0.78 \text{ \AA}$) ions obeying Vegard’s law [12]. Crystallite size (t) was determined by using the Scherrer formula [30]:

$$t = \frac{0.89\lambda}{\beta \cos \theta}, \quad (3)$$

TABLE 1: Cation distribution, hopping length (L_A and L_B), and bond length (R_A and R_B) of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs.

Cd (x)	$\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$	$I_{(220)}/I_{(440)}$		$I_{(400)}/I_{(422)}$		$I_{(400)}/I_{(440)}$		L_A (Å)	L_B (Å)	R_A (Å)	R_B (Å)
		I_{cal}	I_{obs}	I_{cal}	I_{obs}	I_{cal}	I_{obs}				
0.2	$(\text{Cd}_{0.2}\text{Fe}_{0.8})^{\text{A}}[\text{Ni}_{0.8}\text{Fe}_{1.2}]^{\text{B}}$	0.756	0.872	1.31	1.93	0.351	0.578	3.615	2.951	1.894	2.038
0.4	$(\text{Cd}_{0.4}\text{Fe}_{0.6})^{\text{A}}[\text{Ni}_{0.6}\text{Fe}_{1.4}]^{\text{B}}$	0.912	0.776	0.74	1.09	0.250	0.464	3.621	2.956	1.897	2.041
0.6	$(\text{Cd}_{0.6}\text{Fe}_{0.4})^{\text{A}}[\text{Ni}_{0.4}\text{Fe}_{1.6}]^{\text{B}}$	1.099	0.964	0.43	1.13	0.174	0.397	3.633	2.966	1.904	2.048
0.8	$(\text{Cd}_{0.8}\text{Fe}_{0.2})^{\text{A}}[\text{Ni}_{0.2}\text{Fe}_{1.8}]^{\text{B}}$	1.261	1.226	0.114	0.571	0.25	0.67	3.676	3.001	1.926	2.072

TABLE 2: Lattice constant a , crystallite size t , X-ray density d_X , % porosity P , activation energy ΔE , and Curie temperature T_C of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs.

Cd (x)	a (± 0.002 Å)	t (± 1 nm)	d_X (± 0.002 g/cm ³)	$P\%$	E_p (eV)	E_f (eV)	$\Delta E \pm E_p - E_f$ (eV)	T_C °C
0.2	8.350	46.89	5.593	39.20	0.38	0.34	0.04	860
0.4	8.363	48.70	5.811	40.29	0.21	0.18	0.03	797
0.6	8.390	55.30	5.995	39.52	0.4	0.27	0.15	766
0.8	8.491	58.40	6.017	38.17	0.34	0.28	0.06	566

FIGURE 1: X-ray diffraction pattern of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs for $x = 0.2, 0.4, 0.6$, and 0.8 .

where t is a crystallite size (nm), β is a full width at half maximum of strongest diffraction peak (311), λ is a wavelength of X-ray, and θ is the diffraction angle. Crystallite size of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs was lying in the range of 46.89 nm to 58.40 nm (Table 2). There is a common trend of increasing crystallite size t with increase in sintering temperature.

FIGURE 2: Lattice constant a and activation energies E_p and E_f in paramagnetic region and ferrimagnetic region for $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs.

Usually, increasing crystallite size in ferrite nanoparticles decreases the magnetic property because a large grain size leads to a low signal to noise ratio [31]. X-ray density (d_X) was calculated using the relation [32]:

$$d_X = \frac{8M}{(N_A a^3)}, \quad (4)$$

where M is a molecular mass and N_A is Avogadro's number ($N_A = 6.02 \times 10^{23}$). It was clear from Table 2 that X-ray density (d_X) of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs increases with increasing Cd^{2+} content x from 5.593 g/cm³ to 6.017 g/cm³. From X-ray density (d_X) and bulk density values (d_B) the pore volume distribution ($P\%$) was calculated (Table 2) using following relation:

$$P = \left(\frac{d_X - d_B}{d_X} \right) \times 100\%. \quad (5)$$

FIGURE 3: Scanning electron micrographs of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs for the typical samples $x = 0.2$ and 0.6 .

The values of percentage porosity “ P ” ranges in between 38% to 40%. The variation in $P\%$ with increase in Cd^{2+} content x in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs is depicted in Table 2.

3.2. Scanning Electron Microscopy. Surface morphology and average grain size of Cd^{2+} substituted $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs were determined by using analytical scanning electron microscope by selecting 10,000 magnification range. SEM images (Figure 3) of typical samples ($x = 0.2$ and 0.6) shows the nanocrystalline nature of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs with vivid pores suggesting it as more advantages for the gas sensing applications. Voids and pores present in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs can be attributed to the release of gases during the combustion process and lesser the dense nature. Intergranular diffusion can be clearly seen in SEM images of the NPs. Fused grain nature can be seen in $x = 0.2$, whereas $x = 0.6$ looks comparatively more crystalline affecting the spin coupling in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs which is at the base of the magnetic behaviour.

3.3. DC-Resistivity. The resistivity of ferrites ranges from $10^5 \Omega \text{ cm}$ to $10^9 \Omega \text{ cm}$ at room temperature. The DC-resistivity in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs arises from the contribution of crystallite resistivity as well as the resistivity of crystalline boundaries. This phenomenon can be described by Verwey’s hopping mechanism. The electrical conduction in a material takes place due to the ions migration and when an external agency makes the activation of charge carriers. As the (A)-site and [B]-site are energetically not equivalent, conductivity is mostly dependent upon electron exchange between [B]-site cations [33]. The temperature dependence DC-resistivity of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs was measured by two-point probe technique within the temperature range of 300–900 K and calculated using Arrhenius relation [34]:

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{K_B T}\right), \quad (6)$$

where ΔE is an activation energy and K_B is Boltzmann constant ($1.38066 \times 10^{-23} \text{ J K}^{-1}$). In ferrites, the mobility of electron is temperature dependent and it is characterized in terms of activation energies. The values of activation energy in paramagnetic (E_p) and ferrimagnetic region (E_F) with

respect to Cd^{2+} content were calculated from the plots of $\ln \sigma$ versus $1000/T$ using following relation [35]:

$$\Delta E = 1.982 \times \text{slope of the graph.} \quad (7)$$

The low value of activation energy in Ni-Cd ferrites may be attributed to the creation of small number of oxygen vacancies after doping of Cd^{2+} content and the decreasing activation energy may be due to the dominant role of Cd^{2+} in electrical resistivity of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs [36]. Several researchers have justified such behaviour in nickel cadmium ferrites on the basis of role of ferrous ion content in exchange interactions [37]. The minimum value of ferrous ion concentration in octahedral [B] site plays an important role in $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ exchange interaction, which is significantly responsible for the maximum electrical resistivity and low activation energies in this ferrite [38]. It was found that the activation energy in paramagnetic region is maximum compared to that of the ferrimagnetic region. A break separating the curve (Figure 4) in ferromagnetic and paramagnetic region indicates the change in magnetic order which is termed as Curie point (T_C). The substitution of nonmagnetic Cd^{2+} ions in place of magnetic Ni^{2+} ions reduces the active linkage $\text{Fe}_A^{3+} \leftrightarrow \text{Fe}_B^{3+}$ with increase in Cd^{2+} content x ; therefore, Curie temperature of the system decreases with increasing Cd^{2+} substitution which is depicted in Table 2. The value of AC-Susceptibility decreases from 860°C to 566°C with increase in Cd^{2+} content x . An electrical property based application of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs includes transformer cores, inductors, (SMPS), converters, EMI filters, picture tube yoke, rotator, circulator, and phase shifter.

3.4. Dielectric Properties. In general, the dielectric behaviour of a material depends on the strength of electromagnetic interactions between constituent phases, the relative predominance of one phase over the other, and micro structure of phases [39]. The dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) were determined as a function of frequency ($100 \text{ Hz} \leq f \leq 10 \text{ MHz}$). In the present investigation Figures 5 and 6 show that ϵ' decreases and $\tan \delta$ decreases exponentially which corresponds to the decrease in AC-conductivity. More dielectric depression can be observed at the lower frequency region. The dielectric behaviour of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$

FIGURE 4: DC-resistivity plots of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs for $x = 0.2, 0.4, 0.6$, and 0.8 .

NPs can be explained on the basis of Maxwell-Wagner interfacial polarization which is in agreement with Koop's phenomenological theory [40–42]. In Figure 6, the shoulder-like peaks observed in the variation of $\tan \delta$ with logarithmic frequency range from 3.5 to 4. This behaviour reveals that the resonance occurs between applied frequencies and hopping frequencies of charge carriers. The maximum values of dielectric constant ϵ' at lower frequencies may be attributed to the polarization due to inhomogeneous dielectric structure, namely, porosity and grain boundaries [43]. The decrease in polarization with increase in frequency may be due to the fact that beyond a certain frequency of electric field the electron exchange cannot follow the alternating field and therefore the real part of the dielectric constant decreases with increase in frequency [24].

3.5. Magnetic Properties. Room-temperature magnetic properties of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs were measured using pulse

field hysteresis loop tracer technique by applying a magnetic field of 1000 Oe. Using M - H plots (see Figure 7) of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs the saturation magnetization (M_s), remanence magnetization (M_r), coercivity (H_c), and squareness ratio (M_r/M_s) were determined. From Table 3 it is evident that magnetic parameters of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs decrease as a function of cadmium content x which is associated with linkage between (A) and [B] sites. It may be due to the fact that nonmagnetic Cd^{2+} ions ($0 \mu_B$) replace magnetic Ni^{2+} ions ($2 \mu_B$) [44]. The magneton number increases up to $x = 0.4$ and then decreases with increasing Cd^{2+} content x . According to Neel's two-sublattice model of ferrimagnetism magnetic moment per formula in μ_B , n_B^N is given by

$$n_B^N(X) = M_B(X) - M_A(X), \quad (8)$$

where M_A and M_B are the [B] and (A) sublattice magnetic moment in μ_B and the values of magnetic moments of Fe^{3+} ,

TABLE 3: Abortion band frequencies (ν_1 and ν_2), force constant (K_t and K_0), saturation magnetization M_s , coercivity H_c , magneton number n_B , and α_{Y-K} angle of $Ni_{1-x}Cd_xFe_2O_4$ NPs.

Cd (x)	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	$K_t \times 10^5$ (dyne/cm)	$K_0 \times 10^5$ (dyne/cm)	M_s (emu/g)	H_c (Oe)	n_B (μ_B)	α_{Y-K} angle (degree)
0.2	579.40	469.78	1.3355	1.7179	97.03	13	2.58	0
0.4	583.34	475.12	1.3592	2.0347	94.22	19	2.57	29°30'
0.6	579.19	477.66	1.3669	2.2950	66.11	32	1.90	53°43'
0.8	—	—	—	—	13.73	20	0.42	77°55'

FIGURE 5: Dielectric constant (ϵ') verses frequency of $Ni_{1-x}Cd_xFe_2O_4$ NPs.

FIGURE 6: Dielectric loss tangent $\tan \delta$ verses logarithmic frequency of $Ni_{1-x}Cd_xFe_2O_4$ NPs.

Ni^{2+} , and Cd^{2+} were taken as $5 \mu_B$, $2 \mu_B$, and $0 \mu_B$, respectively. Neel's model of two sublattices does not hold good for the variation in magneton number with Cd^{2+} content x . According to the Yafet-Kittel model,

$$\mu_B = M_B \cos \alpha_{Y-K} - M_A, \quad (9)$$

FIGURE 7: Magnetic hysteresis loops of $Ni_{1-x}Cd_xFe_2O_4$ NPs.

where α is a Y-K angle. In the samples with Cd^{2+} content $x = 0.0$ and 0.2 α_{Y-K} was found zero. From $x = 0.4$ to 0.8 , α_{Y-K} increases from $29^\circ 30'$ to $77^\circ 55'$ which is attributed to the increased triangular spin arrangements on octahedral [B] sites [6]. These dilutions of spin moments weaken the in A-B interaction as Cd^{2+} content x increases. Fe^{3+} ions have no magnetic neighbours and hence spins become uncoupled decreasing the saturation magnetization (M_s) from 94.22 to 13.73 (emu/g) which is in agreement with Suresh et al. [23]. This shows the size dependent behaviour of $Ni_{1-x}Cd_xFe_2O_4$ NPs [45]. Behaviour of coercivity can be explained on the basis of Brown relation [46] $H_c = 2k_1/\mu_0 k M_s$. For $x = 0.2-0.6$ H_c increases which is attributed to the uniform grain growth of single domain particle in which the absence of domain wall makes the magnetization process more difficult [4]. The values of magneton number n_B (saturation magnetization per formula unit in μ_B) are depicted in Table 3. For $x = 0.6$ maximum value of n_B was recorded; otherwise, decreasing nature of n_B was observed for other samples from $2.58 \mu_B$ to $0.42 \mu_B$ with Cd^{2+} content x which is associated with a decrease in A-B interaction.

4. Conclusions

$Ni_{1-x}Cd_xFe_2O_4$ spinel ferrite nanoparticles (NPs) were successfully prepared by sol-gel autocombustion technique using citric acid as a fuel. X-ray diffraction results showed the presence of all characteristic reflections (220), (311), (222), (400),

(422), (511), (440), (222), (533), (622), and (444) which confirmed the formation of single phase, cubic spinel structure. Lattice constant (a), X-ray density (d_x), and crystallite size (t) increase with Cd^{2+} substitution. DC-resistivity decreases continuously with the increasing temperature, revealing the semiconducting nature of the prepared Ni-Cd samples. T_C decreases from 860°C to 566°C with increase in Cd^{2+} content x . SEM images show the fused grain nature with intergranular diffusion in $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs. The dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) decrease exponentially which correspond to the decrease in AC-conductivity. Size dependent behaviour of magnetic parameters shows the decrease in saturation magnetization (M_s) from 94.22 to 13.73 (emu/g).

Highlights

- (i) $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ NPs are synthesised by sol-gel auto-combustion method.
- (ii) X-ray diffraction pattern confirmed the formation of spinel structure.
- (iii) ϵ' decreases with frequency and $\tan \delta$ decreases exponentially.
- (iv) SEM confirmed the nanocrystalline nature with intergranular diffusion.
- (v) Magnetic parameters decrease with increasing Cd^{2+} substitution.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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