Research Article

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

B. H. Devmunde,¹ A. V. Raut,¹ S. D. Birajdar,² S. J. Shukla,³ D. R. Shengule,¹ and K. M. Jadhav²

¹Vivekanand Arts, Sardar Dalip Singh Commerce and Science College, Aurangabad 431001, India
²Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431001, India
³Department of Physics, P.G. Research Centre, Deogiri College, Aurangabad 431001, India

Correspondence should be addressed to A. V. Raut; dr.avraut@gmail.com

Received 10 October 2015; Revised 7 January 2016; Accepted 13 January 2016

Academic Editor: Raphael Schneider

Copyright © 2016 B. H. Devmunde et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the present investigation structural, electric, magnetic, and frequency dependent dielectric properties of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ ferrite nanoparticles (NPs) (where $x = 0.2, 0.4, 0.6,$ and 0.8) prepared by sol-gel auto-combustion method were studied. The crystallite size ($t$) (46.89–58.40 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 Ni$_{1-x}$Cd$_x$Fe$_2$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 Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs were determined from AC-Susceptibility. Activation energy $\Delta E$ ranges within 0.03–0.15 eV. Decreasing magnetic saturation $M_s$, coercivity $H_c$, and magneton number $n_m$ 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 $+225$°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 Fd3m (O$^{12}_h$) 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 (M$^{2+}$)$_A$ (M$^{3+}$)$_3$BO$_4$ while inverse spinel has the general formula (M$^{3+}$)$_A$ (M$^{2+}$)$_3$BO$_4$. The nonconvergent disorder of cations over the tetrahedral (A) and octahedral [B] sites can be described using an inversion parameter ($\delta$) and the formula $(M^{2+})^{1-\delta}(M^{3+})^\delta[A(M^{2+})_3M^{3+}]_B$BO$_4$, where $\delta = 0$ for an extreme case and $\delta = 1$ for a completely inverse spinel [3, 4]. NiFe$_2$O$_4$ NPs (cubic $a = 8.327$ Å $\pm$ 0.002 Å) ($I^3\bar{4}1/a^2/m$ number 227 in International Tables) [5], $Z = 8$, JCPDS PDF-10-0325, is a semiconductor having a room-temperature resistivity $\sim 1 \Omega$ 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$_2$O$_4$ NPs have widespread applications in recording heads, antenna rods, loading coils, microwave
2 Journal of Nanoparticles 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$_2$O$_4$ 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

$$\left(\text{Cd}^{2+}\text{Fe}^{3+}\right)^{\text{A}}\left[\text{Ni}^{2+}\text{Fe}^{3+}\right]^{\text{B}}\text{O}_4^{2-}$$

(1)

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$_2$O$_4$ NPs synthesised by hydrothermal method [11, 21]. Drmota has described the precipitation in microemulsion method for the controlled particle size of magnetic nanoparticles [22]. Suresh et al. have prepared Ni-Cd NPs with crystal lattice 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 Ni$_{1−x}$Cd$_x$Fe$_2$O$_4$ ferrite powders by sol-gel autocombustion method using EDTA as a complexation agent [25]. In this investigation we have applied sol-gel autocombustion method for the production of fine powder of Ni$_{1−x}$Cd$_x$Fe$_2$O$_4$ NPs. This preparation technique involves the exothermic and self-sustaining thermally induced anodic redox reaction of aerogel, which is obtained from aqueous solution [26].

2. Experimental Details

2.1. Synthesis of Ni$_{1−x}$Cd$_x$Fe$_2$O$_4$ NPs. Ni$_{1−x}$Cd$_x$Fe$_2$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 (Fe(NO$_3$)$_3$·9H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), and cadmium nitrate (Fe(NO$_3$)$_3$·4H$_2$O) (>99%) as starting materials. The metal nitrates were dissolved together in the metal nitrate aqueous solution [26]. Citric acid (C$_6$H$_8$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 (C$_6$H$_8$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 Ni$_{1−x}$Cd$_x$Fe$_2$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 Ni$_{1−x}$Cd$_x$Fe$_2$O$_4$ NPs was granulated with the addition of saturated PVA solution (polyvinyl alcohol (C$_2$H$_4$O)ₙ) 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/cm$^2$ for 5 min in a stainless steel die.

3. Results and Discussion

3.1. X-Ray Diffraction Study of Ni$_{1−x}$Cd$_x$Fe$_2$O$_4$ NPs. X-ray diffraction patterns of Ni$_{1−x}$Cd$_x$Fe$_2$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-Kα radiation ($\lambda = 1.5405$ Å) at room temperature. All the peaks were identified by comparing the “d” spacing with that of JCPDS data of NiFe$_2$O$_4$ and CdFe$_2$O$_4$ 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 Ni$_{1−x}$Cd$_x$Fe$_2$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. 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 Ni$_{1−x}$Cd$_x$Fe$_2$O$_4$ NPs (Table 1) was determined from X-ray data analysis with an accuracy of ±0.002 Å using the formula [28]:

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

(2)

where $a$ is a lattice constant, $(h k l)$ represents the Miller indices, $A$ is a wavelength of X-rays, and $\theta$ 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 Å to 8.491 Å (±0.002 Å) which is attributed to the larger ionic radius of Cd$^{2+}$ (0.97 Å) ions than that of Ni$^{2+}$ (0.78 Å) ions obeying Vegard’s law [12]. Crystallite size ($t$) was determined by using the Scherrer formula [30]:

$$t = \frac{0.89\lambda}{\beta\cos\theta},$$

(3)
Table 1: Cation distribution, hopping length ($L_A$ and $L_B$), and bond length ($R_A$ and $R_B$) of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs.

| Cd (x) | Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ | $I_{(220)}/I_{(440)}$ | $I_{(400)}/I_{(422)}$ | $I_{(440)}/I_{(440)}$ | $L_A$ (Å) | $L_B$ (Å) | $R_A$ (Å) | $R_B$ (Å) |
|--------|-----------------------------|---------------------|---------------------|---------------------|----------|----------|----------|----------|
| 0.2    | (Cd$_{0.2}$Fe$_{0.8}$)$_3^+$[Ni$_{0.8}$Fe$_{0.2}$]$_3^-$ | 0.756 | 0.782 | 1.31 | 1.93 | 0.351 | 0.578 | 3.615 | 2.951 | 1.894 | 2.038 |
| 0.4    | (Cd$_{0.4}$Fe$_{0.6}$)$_3^+$[Ni$_{0.6}$Fe$_{0.4}$]$_3^-$ | 0.912 | 0.776 | 0.74 | 1.09 | 0.250 | 0.464 | 3.621 | 2.956 | 1.897 | 2.041 |
| 0.6    | (Cd$_{0.6}$Fe$_{0.4}$)$_3^+$[Ni$_{0.4}$Fe$_{0.6}$]$_3^-$ | 1.099 | 0.964 | 0.43 | 1.13 | 0.174 | 0.397 | 3.633 | 2.966 | 1.904 | 2.048 |
| 0.8    | (Cd$_{0.8}$Fe$_{0.2}$)$_3^+$[Ni$_{0.2}$Fe$_{0.8}$]$_3^-$ | 1.261 | 1.226 | 0.114 | 0.571 | 0.25 | 0.67 | 3.766 | 3.001 | 1.926 | 2.072 |

Table 2: Lattice constant $a$, crystallite size $t$, X-ray density $d_X$, % porosity $P$, activation energy $\Delta E$, and Curie temperature $T_C$ of Ni$_{1-x}$Cd$_x$Fe$_2$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 Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs for $x = 0.2, 0.4, 0.6, \text{ and } 0.8$.

where $t$ is a crystallite size (nm), $\beta$ is a full width at half maximum of strongest diffraction peak (311), $\lambda$ is a wavelength of X-ray, and $\theta$ is the diffraction angle. Crystallite size of Ni$_{1-x}$Cd$_x$Fe$_2$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.

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]:

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

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 Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs increases with increasing Cd$^{2+}$ content $x$ from 5.592 g/cm$^3$ to 6.017 g/cm$^3$. From X-ray density ($d_X$) and bulk density values ($d_B$) the pore volume distribution ($P$%) was calculated (Table 2) using following relation:

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

Figure 2: Lattice constant $a$ and activation energies $E_P$ and $E_F$ in paramagnetic region and ferrimagnetic region for Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs.
The values of percentage porosity “P” ranges in between 38% to 40%. The variation in P% with increase in Cd^{2+} content x in Ni_{1−x}Cd_{x}Fe_{2}O_{4} NPs is depicted in Table 2.

3.2. Scanning Electron Microscopy. Surface morphology and average grain size of Cd^{2+} substituted Ni_{1−x}Cd_{x}Fe_{2}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 Ni_{1−x}Cd_{x}Fe_{2}O_{4} NPs with vivid pores suggesting it as more advantages for the gas sensing applications. Voids and pores present in Ni_{1−x}Cd_{x}Fe_{2}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 Ni_{1−x}Cd_{x}Fe_{2}O_{4} NPs which is at the base of the magnetic behaviour.

3.3. DC-Resistivity. The resistivity of ferrites ranges from 10^5 Ω cm to 10^9 Ω cm at room temperature. The DC-resistivity in Ni_{1−x}Cd_{x}Fe_{2}O_{4} NPs arises from the contribution of crystallite resistivity as well as the resistivity of crystalline boundaries. This phenomenon can be described by Vervey’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 Ni_{1−x}Cd_{x}Fe_{2}O_{4} NPs was measured by two-point probe technique within the temperature range of 300–900 K and calculated using Arrhenius relation [34]:

$$\rho = \rho_0 \exp^{(\Delta E/K_B T)},$$

where ΔE is an activation energy and K_B is Boltzmann constant (1.38066 × 10^{-23} 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 σ 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 Ni_{1−x}Cd_{x}Fe_{2}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 Fe^{3+} ↔ Fe^{2+} 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 Fe^{3+} ↔ Fe^{2+} 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 Ni_{1−x}Cd_{x}Fe_{2}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 δ) were determined as a function of frequency (100 Hz ≤ f ≤ 10 MHz). In the present investigation Figures 5 and 6 show that ε’ decreases and tan δ 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 Ni_{1−x}Cd_{x}Fe_{2}O_{4}
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 δ with logarithmic frequency range from 3.5 to 4. This behaviour reveals that the resonance occurs between applied frequencies and hopping frequencies of charge carries. 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 Ni_{1-x}Cd_{x}Fe_{2}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 Ni_{1-x}Cd_{x}Fe_{2}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 Ni_{1-x}Cd_{x}Fe_{2}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 \mu_B, n_B^N is given by

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

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

![Figure 4: DC-resistivity plots of Ni_{1-x}Cd_{x}Fe_{2}O_{4} NPs for x = 0.2, 0.4, 0.6, and 0.8.](image)
Table 3: Abortion band frequencies ($\nu_1$ and $\nu_2$), force constant ($K_1$ and $K_2$), saturation magnetization $M_s$, coercivity $H_c$, magneton number $n_B$, and $\alpha_{Y-K}$ angle of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs.

| Cd (x) | $\nu_1$ (cm$^{-1}$) | $\nu_2$ (cm$^{-1}$) | $K_1 \times 10^3$ (dyne/cm) | $K_2 \times 10^3$ (dyne/cm) | $M_s$ (emu/g) | $H_c$ (Oe) | $n_B$ ($\mu_B$) | $\alpha_{Y-K}$ 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 ($\varepsilon'$) verses frequency of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs.

Figure 6: Dielectric loss tangent $\tan \delta$ verses logarithmic frequency of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs.

Figure 7: Magnetic hysteresis loops of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ 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,

$$\mu_B = M_B \cos \alpha_{Y-K} - M_A,$$

(9)

where $\alpha$ is a Y-K angle. In the samples with Cd$^{2+}$ content $x = 0.0$ and $0.2 \alpha_{Y-K}$ was found zero. From $x = 0.4$ to $0.8$, $\alpha_{Y-K}$ increases from $29°30'$ to $77°55'$ which is attributed to the increased triangular spin arrangements on octahedral [B] sites [6]. These dilutions of spin moments weaken the 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$_x$Fe$_2$O$_4$ NPs [45]. Behaviour of coercivity can be explained on the basis of Brown relation [46] $H_c = 2k_1/\mu_B M_s$. 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 $\mu_B$) 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$_x$Fe$_2$O$_4$ spinel ferrite nanoparticles (NPs) were successfully prepared by sol-gel auto-combustion 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 Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs. The dielectric constant ($\varepsilon'$) 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) Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ NPs are synthesised by sol-gel auto-combustion method.
(ii) X-ray diffraction pattern confirmed the formation of spinel structure.
(iii) $\varepsilon'$ 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.

**Acknowledgment**

The authors would like to thank Dr. K. M. Jadhav for his valuable guidance and research facility for the present investigation.

**References**

[1] G. Sabri N, “The outer membrane proteins profiles of *Salmonella enterica* serotypes Enteritidis, Muenster, Florian, Omuna and Noya and their dendrogram analysis,” *International Journal of Advanced Research*, vol. 2, no. 1, pp. 182–187, 2013.

[2] J. L. Martin de Vidales, A. López-Delgado, V. Vila, and F. A. López, “The effect of the starting solution on the physico-chemical properties of zinc ferrite synthesized at low temperature,” *Journal of Alloys and Compounds*, vol. 287, no. 1-2, pp. 276–283, 1999.

[3] C. M. B. Henderson, J. M. Charnock, and D. A. Plant, “Cation occupancies in Mg, Co, Ni, Zn, Al ferrite spinels: a multi-element EXAFS study,” *Journal of Physics: Condensed Matter*, vol. 19, Article ID 076214, 25 pages, 2007.

[4] A. V. Raut, D. V. Kurmude, D. R. Shengule, and K. M. Jadhav, “Effect of gamma irradiation on the structural and magnetic properties of Co-Zn spinel ferrite nanoparticles,” *Materials Research Bulletin*, vol. 63, pp. 123–128, 2015.

[5] D. V. Kurmude, R. S. Barkule, A. V. Raut, D. R. Shengule, and K. M. Jadhav, “X-ray diffraction and cation distribution studies in zinc-substituted nickel ferrite nanoparticles,” *Journal of Superconductivity and Novel Magnetism*, vol. 27, no. 2, pp. 547–553, 2014.

[6] S. K. Nath, K. H. Maria, S. Noor, S. S. Sikder, S. M. Hoque, and M. A. Hakim, “Magnetic ordering in Ni–Cd ferrite,” *Journal of Magnetism and Magnetic Materials*, vol. 324, no. 13, pp. 2116–2120, 2012.

[7] S. M. Ismail, Sh. Labib, and S. S. Attallah, “Preparation and characterization of nano-cadmium ferrite,” *Journal of Ceramics*, vol. 2013, Article ID 526434, 8 pages, 2013.

[8] K. Sinko, E. Manek, A. Meiszterics, K. Havancsák, U. Vainio, and H. Peterlik, “Liquid-phase syntheses of cobalt ferrite nanoparticles,” *Journal of Nanoparticle Research*, vol. 14, no. 6, article 894, 2012.

[9] S. P. Dalawai, A. B. Gadkari, T. J. Shinde, and P. N. Vasambekar, “Effect of sintering temperature on structural and electrical switching properties of cadmium ferrite,” *Advanced Materials Letters*, vol. 4, no. 7, pp. 586–590, 2013.

[10] S. Singh, S. Munjal, and N. I. Khare, “Strain/defect induced enhanced coercivity in single domain CoFe$_2$O$_4$ nanoparticles,” *Journal of Magnetism and Magnetic Materials*, vol. 386, pp. 69–73, 2015.

[11] M. B. Shelar, P. A. Jadhav, S. S. Chougule, M. M. Mallapur, and B. K. J. Chougule, “Structural and electrical properties of nickel cadmium ferrites prepared through self-propagating auto combustion method,” *Journal of Alloys and Compounds*, vol. 476, no. 1-2, pp. 760–764, 2009.

[12] K. S. Lohar, S. M. Patange, M. L. Mane, and S. E. Shiratham, “Cation distribution investigation and characterizations of Ni$_{1-x}$Cd$_x$Fe$_2$O$_4$ nanoparticles synthesized by citrate gel process,” *Journal of Molecular Structure*, vol. 1032, pp. 105–110, 2013.

[13] E. Ranjith Kumar, R. Jayaprakash, T. Arun Kumar, and S. Kumar, “Effect of reaction time on particle size and dielectric properties of manganese substituted CoFe$_2$O$_4$ nanoparticles,” *Journal of Physics and Chemistry of Solids*, vol. 74, no. 1, pp. 110–114, 2013.

[14] B. S. Randhawa, H. S. Dosanjh, and M. Kaur, “Preparation of spinel ferrites from citrate precursor route—a comparative study,” *Ceramics International*, vol. 35, no. 3, pp. 1045–1049, 2009.

[15] M. M. Karanjkar, N. L. Tarwal, A. S. Vaigankar, and P. S. Patil, “Structural, Mössbauer and electrical properties of nickel cadmium ferrites,” *Ceramics International*, vol. 39, no. 2, pp. 1757–1764, 2013.

[16] K. M. Batoor, “Microstructural and Mössbauer properties of low temperature synthesized Ni-Cd-Al ferrite nanoparticles,” *Nanoscale Research Letters*, vol. 6, article 499, 2011.

[17] T. Slatineanu, A. R. Iordan, M. N. Palamaru, O. F. Caltun, V. Gafon, and L. Leontie, “Synthesis and characterization of nanocrystalline Zn ferrites substituted with Ni,” *Materials Research Bulletin*, vol. 46, no. 9, pp. 1455–1460, 2011.

[18] S. S. R. Inbanathan, V. Vaithyanathan, J. A. Chelvane, G. Markandeyulu, and K. K. J. Bharathi, “Mössbauer studies and enhanced electrical properties of R (R=Sm, Gd and Dy) doped Ni ferrite,” *Journal of Magnetism and Magnetic Materials*, vol. 353, pp. 41–46, 2014.

[19] C. Cheng, “Enhanced magnetization and conductive phase in NiFe$_2$O$_4$,” *Journal of Magnetism and Magnetic Materials*, vol. 325, pp. 144–146, 2013.
[20] K. Rafeekali and E. M. Muhammed, “Antibacterial study of cadmium substituted nickel ferrite nano particles,” *International Journal of Engineering Research and General Science*, vol. 3, no. 4, pp. 2091–2307, 2015.

[21] K. Nejati and R. Zabihi, “Preparation and magnetic properties of nano size nickel ferrite particles using hydrothermal method,” *Chemistry Central Journal*, vol. 6, article 23, 2012.

[22] A. Drmota, M. Drofenik, J. Koselj, and A. Žnidaršič, “Microemulsion method for synthesis of magnetic oxide nanoparticles,” in *Microemulsions—An Introduction to Properties and Applications*, R. Najjar, Ed., chapter 10, pp. 191–215, InTech, Rijeka, Croatia, 2012.

[23] R. Suresh, P. Moganavally, and M. Deepa, “Structural and magnetic properties of NiCd ferrites,” *IOSR Journal of Applied Chemistry*, vol. 8, no. 5, pp. 1–5, 2015.

[24] K. B. Modi, M. K. Rangolia, M. C. Chhantbar, and H. H. J. Joshi, “Study of infrared spectroscopy and elastic properties of fine and coarse grained nickel-cadmium ferrites,” *Journal of Materials Science*, vol. 41, no. 22, pp. 7308–7318, 2006.

[25] M. Rahimi, M. Eshraghi, and P. Kameli, “Structural and magnetic characterizations of Cd substituted nickel ferrite nanoparticles,” *Ceramics International*, vol. 40, no. 10, pp. 15569–15575, 2014.

[26] A. Sutka and G. Mezinskis, “Sol-gel auto-combustion synthesis of spinel-type ferrite nanomaterials,” *Frontiers of Materials Science*, vol. 6, no. 2, pp. 128–141, 2012.

[27] F. S. Tehrani, V. Daadmehr, A. T. Rezakhani, R. H. Akbarnejad, and S. Gholipour, “Structural, magnetic, and optical properties of zinc- and copper-substituted nickel ferrite nanocrystals,” *Journal of Superconductivity and Novel Magnetism*, vol. 25, no. 7, pp. 2443–2455, 2012.

[28] A. V. Raut, R. S. Barkule, D. R. Shengule, and K. M. J. Jadhav, “Synthesis, structural investigation and magnetic properties of Zn[2+] substituted cobalt ferrite nanoparticles prepared by the sol–gel auto-combustion technique,” *Journal of Magnetism and Magnetic Materials*, vol. 358-359, pp. 87–92, 2014.

[29] P. B. Belavi, G. N. Chavan, L. R. Naik, R. Somashekar, and R. K. Kotnala, “Structural, electrical and magnetic properties of cadmium substituted nickel-copper ferrites,” *Materials Chemistry and Physics*, vol. 132, no. 1, pp. 138–144, 2012.

[30] A. Mahesh Kumar, P. Appa Rao, M. C. Varma, G. S. V. R. K. Choudary, and K. H. Rao, “Cation distribution in Co_{0.7}Mn_{0.3}Fe_{2}O_{4} (Me = Zn, Ni and Mn),” *Journal of Modern Physics*, vol. 2, pp. 1083–1087, 2011.

[31] Z. Wu, M. Okuya, and S. Kaneko, “Spray pyrolysis deposition of zinc ferrite films from metal nitrates solutions,” *Thin Solid Films*, vol. 385, no. 1-2, pp. 109–114, 2001.

[32] A. Hajalilou, M. Hashim, H. M. Kamari, and M. T. Masoudi, “Effects of milling atmosphere and increasing sintering temperature on the magnetic properties of nanocrystalline Ni_{0.36}Zn_{0.64}Fe_{2}O_{4},” *Journal of Nanomaterials*, vol. 2015, Article ID 615739, 11 pages, 2015.

[33] T. J. Shinde, A. B. Gadkari, and P. N. Vasambekar, “Influence of Nd[3+] substitution on structural, electrical and magnetic properties of nanocrystalline nickel ferrites,” *Journal of Alloys and Compounds*, vol. 513, pp. 80–85, 2012.

[34] S. Kumar, T. J. Shinde, and P. N. Vasambekar, “Study of conduction phenomena in indium substituted Mn–Zn nanoferrites,” *Journal of Magnetism and Magnetic Materials*, vol. 379, pp. 179–185, 2015.

[35] G. N. Chavan, P. B. Belavi, L. R. Naik, R. K. Bammannavar, K. P. Ramesh, and S. Kumar, “Electrical and magnetic properties of nickel substituted cadmium ferrites,” *International Journal of Scientific & Technology Research*, vol. 2, no. 12, 2013.

[36] K. V. Kumar, R. Sridhar, D. Ravinder, and K. Rama Krishna, “Structural properties and electrical conductivity of copper substituted nickel nano ferrites,” *International Journal of Applied Physics and Mathematics*, vol. 4, no. 2, pp. 113–117, 2014.

[37] B. A. Aldar, R. K. Pinjari, and N. M. Burance, “Electric and Dielectric behavior of Ni-Co-Cd Ferrite,” *IOSR Journal of Applied Physics*, vol. 6, no. 4, pp. 23–26, 2014.

[38] A. Ande, S. Thatikonda, R. Dachepalli et al., “Electrical properties of cadmium substitution in nickel ferrites,” *World Journal of Condensed Matter Physics*, vol. 2, pp. 257–266, 2012.

[39] M. B. Shelar and V. Puri, “Dielectric loss and magnetic behavior of combustion synthesized ferrite-ferroelectric composites,” *International Journal of Self-Propagating High-Temperature Synthesis*, vol. 20, no. 2, pp. 128–133, 2011.

[40] C. G. Koops, “On the dispersion of resistivity and dielectric constant of some semiconductors at audiofrequencies,” *Physical Review*, vol. 83, no. 1, pp. 121–124, 1951.

[41] J. C. Maxwell, *Electricity and Magnetism*, Oxford University Press, London, UK, 1973.

[42] K. W. Wagner, “Zur theorie der unvollkommenen dielektrika,” *Annalen der Physik*, vol. 345, no. 5, pp. 817–855, 1913.

[43] K. M. Batoo, S. Kumar, C. G. Lee, and Ali Muhammad, “Influence of Al doping on electrical properties of Ni–Cd nano ferrites,” *Current Applied Physics*, vol. 9, no. 4, pp. 826–832, 2009.

[44] A. Goldman, *Modern Ferrite Technology*, Van Nostrand Reinhold Company, New York, NY, USA, 1990.

[45] M. H. R. Khan and A. K. M. Akther Hossain, “Reentrant spin glass behavior and large initial permeability of Co_{0.5−x}Mn_{x}Zn_{0.5}Fe_{2}O_{4},” *Journal of Magnetism and Magnetic Materials*, vol. 324, no. 4, pp. 550–558, 2012.

[46] J. M. D. Coey, *Rare Earth Permanemt Magnetism*, John Wiley & Sons, New York, NY, USA, 1996.
