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Synthesis and study of Co doped Ni-Cd ferro-spinels by microwave assisted sol-gel auto-combustion method

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ABSTRACT

Cadmium substituted Nickel Ferrite, $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ (x = 0.0, 0. 02) were synthesized by sol-gel auto-combustion technique with microwaves using urea as fuel. The samples were sintered at two different temperatures 600 °C and 800 °C. This paper discusses the effect of sintering temperature on varius structural, morpological, magnetic and optical properties of the syntesized samples. The structural properties such as crystallite size, lattice constant, lattice strain oxygen position parameters, bond lengths and bond angles. Phase analysis of the sample are carried out using XRD measurement. Surface morphology and gualitative and guantitative chemical composition of the samples were done by FE-SEM and energy dispersive X-ray analysis (EDX) measurements respectively. Magnetic properties such as saturation magnetization (Ms), coercivity (H_C) retentivity (Mr), squareness and were obtained from VSM measuements. The variation in the observed and measured magnetic quantities are explained on the basis of YK model. The cation distribution proposed has been discussed based on the observed experimental measured magnetic parameters and it futher discuss spin canting angle and nature of exchange interaction among the magnetic moments of octahedral and tetrahedral sites.

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KEYWORDS

Spinel; superparamagnetic ferrites; sol-gel synthesis; cation distribution; spin canting angle

Introduction

Ferrites are typically ferromagnetic ceramic compounds derived from iron oxides possessing spinel crystal structure (AB₂O₄). It crystallizes in the well known closed packed cubic structure created by oxygen anions, into which each cation is surrounded by four and six, O^{2-} respectively forming two sub-lattices, tetrahedral (A) and octahedral (B) lattices with space group Fd $\overline{3}m$. There are 8 formula units of AB₂O₄ in each unit cell of spinels, with 32 oxygen anions (O²⁻) arranged in a face cantered cubic (FCC) lattice which forms 64 tetrahedral sites and 32 octahedral sites [1, 2]. Ferrites nanomaterials gained immense importance due to their excellent electrical and magnetic properties like high electrical resistance, high magnetic permeability in radio frequency (RF) range, high mechanical strength, high thermal and chemical stability along with low cost which make these materials suitable in numerous applications like electronics and communication technology, magnetic storage media, sensors and catalysts [3–5].

Ferromagnetic materials are normally multi-domain in structures. One of the remarkable property under particular conditions, exhibited by ferromagnetic nanoparticles is superparamagnetism. If the size of the synthesized ferromagnetic nanoparticles is sufficiently small enough, below a threshold value it prevents to favor multi-domain structures and turns into single domain (SD) structure to attain stability which behaves as permanent magnets which offers as excellent media for permanent magnets and magnetic recording applications [6, 7]. If the size is reduced further, below a certain critical size D_c (which is temperature dependant), these single domain nanoparticles losses its stability, looses domain structure due to thermal agitation, and nanoparticles exhibits paramagnetic behavior turning into superparamagnetic nature (SPM) [8]. These superparamagnetic nanoparticles find many applications in biomedical applications such as magnetic hyperthermia and targeted drug delivery [9]. There are various methods to synthesize superparamagnetic nanomaterials: Auto-combustion method, co-precipitation method, sol- gel method, hydro-thermal, mechanical milling, micro-emulsion etc. Sol gel method with microwave auto-combustion method offers many advantages over other conventional methods of short reaction time, high purity, high surface area, simpler, cost effective, energy efficient and favors in ultrafine uniform nanoparticles [10]. Properties of the spinel nanoferrite are highly dependent on composition, preparation methods, and heat treatment during synthesis. In the present study, we have study we have substituted Co²⁺ into Ni-Cd ferrite and its effect on the micro structural and magnetic properties with the composition and heat treatment (calcination).

Experimental

Synthesis of cobalt doped cadmium-nickel ferrite

Cobalt doped cadmium-nickel ferrite, Ni_{0.5}Co_xCd_(0.5-x)Fe₂O₄ (x = 0.0,0.02) were synthesized by sol-gel microwave auto-combustion technique using urea as fuel. Nickel Nitrate, Cadmium nitrate, cobalt nitrate and urea were weighed and mixed in double distilled water and mixed together. The solution was stirred continuously and heated on magnetic stirrer at 80 °C till a gel is obtained. The gel was then fired in a microwave oven so that a floppy ash was obtained which then ground in a mortar pestle for four hours to get fine powder. Half of this powder was then calcined at 600 °C and remaining at 800 °C. The methodology is depicted in the Figure 1. The synthesized samples, Ni_{0.5}Co_xCd_(0.5-x)Fe₂O₄ corresponding to x = 0.0, 0.02 sintered at 600 °C were named as NCC16, NCC56 and those sintered at 800 °C were named as NCC18, NCC58.

Figure 2 show the x-ray diffraction of the Ni_{0.5}Co_xCd_(0.5-x)Fe₂O₄ (x = 0.0, 0.02) samples synthesized and calcined at 600 °C and 800 °C respectively and confirms the formation of spinel ferrites with space group Fd3 m (227). The x-ray diffraction patterns were indexed using MDI Jade 5.0 software with PDF-2 database. All the synthesized samples calcined at 600 °C exhibited the reflection planes (220), (311), (222), (400), (422), (511), and (440) with highest intensity peak at (311), a characteristic feature of cubic spinel ferrites. A small amount of CdO phase presence was observed in the samples calcined at 600 °C. The samples calcined at 800 °C exhibited reflection planes (220), (311), (222), (400), (422), (400), (422), (400), (422), (511), and (440) with improved crystalline nature which is evident from the sharp X-ray diffraction peaks. The cadmium oxide phase is suppressed in the



Figure 1. Synthesis of $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ (x = 0.0,0.02) ferrites.

samples calcined at 800 °C. The average crystallite size for all the samples was calculated using Scherrer's formula $D = \frac{0.9\lambda}{\beta \cos \theta}$, and found in the range 11–25 nm. The crystallite sizes of the prepared samples were found to be influenced by the substitution of Co²⁺ and calcinations temperature. The crystallite side increased due to coarsening and grain boundary wall movement which merges the smaller grains to from bigger grains when the samples were calcined at 800 °C. The lattice parameter (*a*) was obtained from the inter-planer spacing (d) using relation, $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$. The decrease in lattice constant is as per Vegard's law for solid solutions [11]. The lattice parameter decreases with the doping of Co²⁺ which can be attributed to the replacement of Cd²⁺ ions of larger size, $r_{Cd^{2+}} = 0.97A^o$ by the Co²⁺ ions of smaller ionic radii of $r_{Co^{2+}} = 0.82A^o$ A. The X-ray density was estimated using relation $\rho_X = \frac{ZM}{N_AV}$, given by Smit and Wijn [12]. Where M is the molecular weight of the sample, V is the volume of unit cell, N_A is the Avogadro's number (6.023 x 10⁻²³) and Z is number of formula unites in a unit cell of cubic ferrites, here Z = 8.

Characterization of samples

Samples were characterized by XRD, FEG-SEM, and VSM techniques. X ray diffraction study of the $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ samples were carried out on the Rigaku MiniFlex600 X-ray diffractometer (XRD) operating at 600W (40KV, 15mA) with a monochromatic



Figure 2. X-ray diffraction pattern of $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ (x = 0.0,0.02) ferrites.

X-ray source of CuK α radiation ($\lambda = 1.54056$ A) between Bragg angles 10.0° to 80.0° with a step size 0.020°. For the morphological study, the field emission gun scanning electron micrograph (FEG-SEM) and for elemental composition analysis of the samples, the energy dispersive x-ray analysis (EDX) was carried out using JEOL JSM-7600F FEG-SEM operating at 10 KV. Magnetic studies were performed by vibrating sample magnetometry (VSM) using Lakeshore VSM 7410.

Results and discussions

X-ray diffraction study

X-ray density of the sample increases as the Co²⁺ substitution is increased for both the samples. For sample x = 0.0 x-ray density was observed to increase when the sample was calcined at 800 °C. It can be attributed to shrinking of unit cell at high calcinations temperature. For the sample x = 0.02, x – ray density was found to decrease, when the sample was calcined at 800 °C. It can be explained by considering that X-ray density depends on molecular mass as well lattice parameter. Although lattice parameter decreases with the substitution of Co²⁺, the density decreases due to decrease in molecular mass as the Cd²⁺, having larger molar mass (112.411 g/mol.) in the unit cell are replaced with Co²⁺ having smaller molar mass (58.9332 g/mol.) overtaking the effect of decrease of lattice constant. Assuming the particles to be of spherical form, the specific surface area in m²/g of the ferrite powdered sample was evaluated by using the Sauters' relation, $SSA = \frac{6000}{\rho_c \text{ D}}$ where, ρ_x is the X-ray density in g/cm³, D is the

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Sample co-content	Sintering temp. (°C)	Inter-planer spacing (d) (A) ^o	Crystallite size (D) nm	Lattice parameter (a) $(A)^{o}$	Volume, (A) ^o 3	Specific surface areaSSA (m²/g)	X-ray density (g/cm ³)	Lattice strain $\epsilon ~(\times 10^{-2})$	$\begin{array}{c} \text{Dislocation} \\ \text{density} \\ (\times 10^{15}) \end{array}$
x = 0.0	600	2.5790	11.8	8.5535	625.811	10.5	5.545	4.63	4.63
	800	2.5665	23.2	8.5121	616.755	4.63	5.626	2.12	22.6
x = 0.02	600	2.5714	12.0	8.5284	620.301	9.2	5.571	5.22	5.22
	800	2.5663	14.7	8.5115	616.611	5.22	5.604	2.697	35.7

Table 1. Structural parameters crystallite size (D), lattice parameter (a), volume of unit cell (V), Specific surface area (SSA), X-ray density ρ_x , lattice strain (ε) and Dislocation density (δ).

crystallite size in nm. The specific surface area decreases with the substitution of Co^{2+} at lower calcinations temperature 600 °C whereas it increases at 800 °C which can be explained by crystallite size and density of the samples. Average lattice strain was calculated by Stoke-Wilson's equation, $\varepsilon = \frac{1}{4} \times \frac{\text{FWHM}}{\tan\theta}$ [13, 14]. Lattice strain of the samples sample x = 0.02 is more compared to x = 0.0 and with the calcination temperature for both the samples. The length of dislocation lines per unit volume gives number of dislocation density or defect in the crystal lattice is estimated using relation $\delta = \left(\frac{\beta \cos\theta}{0.9\lambda}\right)^2$

[15]. Dislocation density for doped sample x = 0.02 is more than undoped Ni-Cd ferrite sample and increases with the calcination temperature.

Interplaner spacing (d), crystallite size (D), lattice parameter (*a*), volume of unit cell (V), specific surface area (SSA), X-ray density ρ_x , lattice strain (ε) and dislocation density (δ) are listed in Table 1.

Fourier transform infrared analysis

Fourier transform infrared (FTIR) spectra of the samples were recorded in the frequency range 400–4000 cm⁻¹ at room temperature and are shown in the Figure 3. Two absorption frequency bands ν_1 and ν_2 are the characteristic bands of the spinel ferrites corresponding to stretching vibration of metal cation (Me) – oxygen anion (O^{2–}) bond in tetrahedral and octahedral sites. The stretching vibrations of higher frequency band, ν_1 corresponds to tetrahedral site and stretching vibrations of lower frequency band ν_2 corresponds to octahedral site. Broad absorption peak around 3445 cm⁻¹ and somewhat less broad absorption peak around 1625 cm⁻¹ in all the samples corresponds to stretching and bending vibration of O-H interacting via H-bond expected due to absorbed water molecules on the surface [16].

The stretching vibration frequency corresponding to tetrahedral and octahedral sites for the samples calcined at 600 °C and 800 °C are listed in the Table 2. It can be seen that stretching vibration frequency increases with the substitution of Co^{2+} . Cations Ni²⁺ and Co²⁺ in spinel ferrites occupies mainly octahedral site whereas Cd²⁺ seeks tetrahedral site, the substitution of Co²⁺ and reduction of Cd²⁺ causes the replacement of Fe³⁺ from octahedral sites to tetrahedral sites. The net effect is shifting of stretching vibration bands towards higher frequency side. Increased stretched vibration frequency suggests a decrease in the bond lengths and hence strengthening of the bonding between (Me-O) which is further evident from the increased values of force constant F_t and F_o presented in Table 3.

The Debye temperature is a basic property of a solid material which relates elastic properties to the thermodynamic properties of the materials such as specific heat [17, 18]. It is the



Figure 3. FTIR spectra for the samples x = 0.00 and x = 0.02 at 600 °C and 800 °C.

Table 2. Wave number of metal – anion stretching vibration (M-O²⁻) frequency for samples Ni_{0.5}Co_xCd_(0.5-x)Fe₂O₄ for x = 0.0, 0.02, 0.05 calcined at 600 °C and 800 °C.

	ν ₁ (α	:m ⁻¹)	ν ₂ (α	:m ⁻¹)
Sample	600 °C	800 °C	600 ° C	800 °C
x = 0.0	_	585.60		405.88
x = 0.02	592.0	593.27	435.7	420.36

temperature at which lattice vibrations occurs with highest amplitude. According to Waldron, the Debye temperature of the samples can be calculated from the relation [19]

$$\theta_D = \frac{hc\nu_{tO}}{2\pi k_B} = 1.438\nu_{tO}$$

where v_{tO} is the average wave number corresponding to the stretching vibration of the tetrahedral and octahedral sites, $v_{tO} = \frac{v_1 + v_2}{2}$, c is the speed of light in free space (c = 3×10^8 m/s, k_B is the Boltzmann constant $k_B = 1.38 \times 10^{-23} J/K$, h is Planck's constant $h = 6.624 \times 10^{-34} J - s$. The estimated values of the Debye temperatures are listed in Table 3.

Cation distribution

Properties of the synthesized spinel ferrites to a large extent depend upon how the individual cations are distributed over tetrahedral and octahedral interstices. Individual atoms seek the particular sites within the lattice depending upon the size of specific ion,

	$F_t ~(\times 10^5)$	(dyne/cm)	<i>F₀</i> (×10 ⁵)	(dyne/cm)	Debye tempe	erature θ_D (K)
Sample Co	600 °C	800 ° C	600 °C	800 °C	600 °C	800 ° C
x = 0.0	_	2.51	_	1.21	-	712.87
x = 0.02	2.57	2.58	1.39	1.29	736.75	728.80

Table 3. Force constant of Me-O corresponding to tetrahedral (F_t) and octahedral (F_O) sites and Debye temperature.

size of interstice, the orbital preference for specific coordination, electrostatic energy, synthesis methodology adopted, physical condition of synthesis and heat treatment subjected to the material. Nickel and Cobalt ferrites are inverse spinel ferrites with Ni²⁺ and Co²⁺ preferring octahedral sites [20]. On the other hand cadmium ferrite is a normal spinel ferrite where Cd²⁺ prefers to sit on tetrahedral site. However in case of very small nanoparticles these rules of cation distribution may not be strictly followed and Cd²⁺ may occupy octahedral position and Ni²⁺ and Co²⁺ may go to tetrahedral sites. The, general cation distribution for the Ni_{0.5}Co_xCd_{(0.5-x})Fe₂O₄ may be expressed as

$$\left(Cd_{(0.5-x)}^{2+}Fe_{(0.5+x)}^{3+}\right)_{A}[Ni_{0.5}^{2+}Co_{x}^{2+}Fe_{(1.5-x)}^{3+}]_{B}O_{4}^{2-}$$

where parenthesis () and square bracket [] indicated tetrahedral or A-site and octahedral or B-site respectively. In cubic spinel structures, the theoretical lattice spacing can be obtained using relation,

$$a_{th} = \frac{8}{3\sqrt{3}} [(r_A + R_o) + \sqrt{3}(r_B + R_o)]$$

where r_A and r_B are the radius of tetrahedral site, and octahedral site respectively and can be estimated by using the following relations by calculating oxygen positional parameter, *u*. Here R_o is the radius of oxygen ion (O²⁻) as $R_o = 1.38$ Å [21, 22].

$$r_A = \sqrt{3}a_{obs.}\left(u - \frac{1}{4}\right) - R_o$$
$$r_B = a_{obs.}\left(\frac{5}{8} - u\right) - R_o$$

The estimated values of r_A and r_B and theoretical lattice parameter, average bond lengths, A-O = $\langle r_A + R_o \rangle$ and B-O = $\langle r_B + R_o \rangle$, ratio of average bond lengths, $R = \frac{\langle r_B + R_o \rangle}{\langle r_A + R_o \rangle}$, oxygen position parameter $u^{\bar{3}m}$ for samples calcined at 800 °C and 600 °C are listed in the Table 4.

Based on the estimated theoretical lattice parameter the proposed cation distributions at 600 $^{\circ}$ C and 800 $^{\circ}$ C are given in Table 5.

Surface morphological and compositional study

To study the surface morphology of synthesized nano-ferrites and FEG-SEM was conducted for the samples x = 0.0, and 0.02. SEM images (Figure 4(a,b)) show non-uniform mostly spherical shaped, highly agglomerated nanoparticles. Agglomeration of nanoparticles is the natural consequence of the sol-gel autocombustion synthesis method.

Table 4. Microstrctural parameters radii of tetrahedral (r_A) , octahedral (r_B) sites and theoritical (a_{th}) and observed $(a_{obs.})$ lattice constants mean tetrahedral bond length (A-O) and octahedral bond length (B-O) and their ratio (R) and oxygen position parameter u^{3m} .

Sample co-content	Sintering temp. (°C)	$r_A (A)^o$	$r_B (A)^o$	$a_{th} (A)^o$	a _{obs.} (A) ^o	A-0 (<i>A</i>)°	B-O (<i>A</i>)°	$R = \frac{B-O}{A-O}$	u ^{3m} (A)°
x = 0.0	600	0.6386	0.6510	8.5535	8.5421	2.0186	2.0310	1.0061	0.2606
	800	0.5480	0.6990	8.5121	8.5121	1.9280	2.079	1.07832	0.2557
x = 0.02	600	0.6292	0.6526	8.5284	8.5473	2.0092	2.0326	1.0117	0.2607
	800	0.6002	0.6681	8.5115	8.5092	1.9802	2.0481	1.0343	0.2592

Table 5. The proposed cation distributions from the theoretical lattice parameter.

			Catio	n distribution
Co compo-sition (x)	Chemical formula	Calcination temperature $^\circ$ C	A-site	B-site
0.0	Ni _{0.5} Cd _{0.5} Fe ₂ O ₄	800	$(Cd_{0,2}^{2+}Fe_{0,8}^{3+})$	$[Ni_{0.5}^{2+}Cd_{0.3}Fe_{1.2}^{3+}]O_4^{2-}$
		600	$(Cd_{0.5}^{2+}Ni_{0.06}^{2+}Fe_{0.44}^{3+})$	$[Ni_{0.44}^{2+}Fe_{0.1.56}^{3+}]O_4^{2-}$
0.02	Ni _{0.5} Cd _{0.48} Co _{0.02} Fe ₂ O ₄	800	$(Cd_{0.48}^{2+}Fe_{0.52}^{3+})$	$[Ni_{0.5}^{2+}Co_{0.02}^{2+}Fe_{1.48}^{3+}]O_4^{2-}$
		600	$(Cd_{0.38}^{2+}Fe_{0.62}^{3+})$	$[Ni_{0.5}^{2+}Cd_{0.1}^{2+}Co_{0.02}^{2+}Fe_{1.38}^{3+}]O_4^{2-}$

Further, the agglomeration is due to very small size resulting in nanoparticles with high surface energy. Also, the synthesized nanoparticles had permanent magnetic dipoles and nanoparticles agglomerates due to dipolar interaction among them. The crystallite size calculated from the Scherrer's method is much smaller than the observed from the SEM images. It indicates each nanoparticle in the synthesized samples consist of many crystallites. The CdO phase can be identified as the white snow in the SEM image (Figure 4(b)). To confirm the elemental composition of the synthesized samples, energy dispersive x-ray spectroscopic (EDAX) analysis was conducted for the representative samples with x = 0.0 and 0.02. The EDAX spectra are shown in the Figure 5(a,b). The results confirm the stoichiometric presence of each element without loss of elements or presence of impurity in sample x = 0.0. In case of sample x = 0.02, the small doping of Co²⁺ makes it difficult to trace in the synthesized sample.

Magnetic characterization

The enhanced magnetic properties are essesntial for the spinel nanoparticle to be useful in various applications like targeted drug delivery, magnetic hyperthermia, MRI contrast agent, magnetic separation and diagnostic [23, 24]. The decreased particle size and proper heat treatment offers greater possibility to have improved magnetic properties. The samples calcined at 600 °C and 800 °C were studied by room temperature vibrating sample magnetometry (VSM) with the applied field from zero to ± 15 kOe. The room temperature hysterisis loops are shown in the Figure 6 and various parameters were calculated from the VSM data. It is observed that saturation magnetization is strongly influenced by Co²⁺ substitution and heat treatment during synthesis. The narrow hysteresis loop of the samples indicates the of soft ferrite nature. The specific saturation magnetization (M_s) of the synthesized samples decreases for the sample doped with Co²⁺ (x = 0.02,). Further, The Ms also decreases when samples were calculated at 800 °C for both the samples. The decreased value of M_s for the sample x = 0.02 at 800 °C is



(a)



Figure 4. FEG-SEM image for the sample (a) x = 0.00 and (b) x = 0.02 at 600 °C.

attributed to the formation of small non-magnetic CdO phase which decreases the overall M_s . Further, decrease in saturation magnetization may be due to spin disorder at the surface, spin canting effect and/or non-saturation due to arbitrarily dispersed small particles having high magnetocrytalline anisotropy [25, 26]. The higher calcination temperature facilitates the easy diffusion of ions and formation of the intra- granular



(a)



(b)

Figure 5. EDX spectra for the samples (a) x = 0.00 and (b) x = 0.02 at 600 °C.

porosity and inhibiting the domain wall motion inside the grain [27]. The saturation magnetization and magnetic moment, can be explained based on the Neel's two sublattice model, according to which magnetic moments of ions on A (Tetrahedral) and B (oactahedral) sites have collinear structure and are alligned antiparallel to each other [28]. Further, in spinel ferrites magnetic ordering is the result of super exchange interaction between the magnetic ions at A and B sites via an oxygen ion. The net magnetic



Figure 6. Hysteresis curves of the $Ni_{0.5}Co_xCd_{(0.5-x)}Fe_2O_4$ (x = 0.0, 0.02) ferrites.

moment in bohr magneton (μ_B) is therefore given by,

$$\eta_{\rm B}({\rm x}) = {\rm M}_{\rm B}({\rm x}) - {\rm M}_{\rm A}({\rm x})$$

Here $M_A(x)$ and $M_B(x)$ are the magnetic moments of ions at A and B sites respectively obtained from the cation distribution. Applying Neels model, net magnetic moment per formula unit in bohr magneton was calculated using formula,

$$\eta_{\mathrm{B}_{\mathrm{exp}}}(\mathrm{x}) = rac{\mathrm{M}_{\mathrm{w}} imes \mathrm{M}_{\mathrm{S}}(\mathrm{x})}{5585}$$

where M_w is molecular weight in gram and and $M_S(x)$ is specific saturation magnetization in emu/gram. The theoritical (i.e. calcualted) and experimental (observed) magnetic magnetic momemts, ($\eta_{B_{exp}}(x)$ and $\eta_{B_{cal.}}(x)$, retentivity (M_r), coercivity (Hc), squareness ratio, $\frac{M_r}{M_s}$ and anisotropy constant (K_1) for the samples are listed in the Table 6. It can be observed that calculated magnetic moment from the cation distribution doesnot match with the obseved magnetic moment for the samples. Thus, Neels two sub-lattice model with collinear spin is not sufficient to explain the variation in the magnetic moments of samples. The deviation in the observed and calculated magnetic moment can be explaned on the basis of existance of non-collinear arrangement of spins, considering three sab-lattice model (Yafet-Kittel model) proposed by Yafet and Kittel (1952) [28–31]. According to this model, B lattice can be divided into two sublattices, B₁ and B₂, which have magnetic moments in equal magnitude but are canted oppostely, at Yafet-Kittel angle, α_{YK} , with respect to the direction of resultant magnetization at 0 K. Spin or canting angles, Y-K angles, can be calculted from the relation, [28]

$$\eta_{\text{B}_{\text{even}}}(x) = M_{\text{B}}(x) \cos \alpha_{\text{YK}} - M_{\text{A}}(x)$$

The estimated Y-K angles for different samples are presented in Table 6. The ratio of retentivity to the saturation magnetization i.e. squareness, Mr/Ms of the calcined samples at 600 °C increases from 0.0280 for sample x = 0.0 to 0.0530 for the doped sample x = 0.02. When these samples were calcined at 800 °C, the squareness ratio is almost

stant (K ₁), C	Dbserved Magi	netic Moment (η	_B obs.) and ci	alculated mag	netic moment (η_B calc) from	proposed cation distri	ibution.	
		Saturation				Anisotropy		Magnetic moment	
Sample	Sintering	magnetization	Coercivity	Retentivity	Squareness	constant	Magnetic moment	η_B cal (μ_B) calculated	Y-K angles
co content	temp. (°C)	Ms (emu/g)	Hc (G)	Mr (emu/g)	ratio Mr/Ms	K ₁ (×10 ⁴)	$\eta_{B{ m obs.}}$ (μ_{B}) (\pm 0.001)	from cation distribution	α _{YK} (degree)
x = 0.0	600	25.385	34.923	0.7089	0.0280	0.3846	1.1874	6.36	62.26
	800	18.84	68.593	1.202	0.0638	0.2087	1.6668	3.00	98.21
x = 0.02	600	21.47	61.93	1.1372	0.0530	0.5871	0.9958	4.86	77.23
	800	35.633	57.681	2.2738	0.0638	0.1312	0.8777	5.80	67.33

Table 6. Magnetic parameters saturation magnetization (Ms), coercivity (Hc), remanant magnetization (Mr) and squareness ratio (Mr/Ms), Anisotropy con-

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same 0.0638. The smaller values of squareness ratio M_r/M_s less than 0.5, according to Stoner–Wolfarth theory indicate the nanoparticles possess uniaxial anisotropy. The squareness ratio with value 0.83 classifies the materials to having cubic anisotropy. The magnetocrystalline anisotropy constant (K₁) of the nanoparticles obeying uniaxial anisotropy is calculated using Browns relation,

$$K_1 = \frac{H_C M_S}{0.985}$$

The estimated values of magnetocrystalline anisotropy for samples annealed at 800 °C are presented in Table 6. Magnetocrystalline anisotropy of theNi_{0.5}Co_xCd_(0.5-x)Fe₂O₄ increases for all the samples as the Co^{2+} is substituted. It has been observed that anisotropy constant (K_1) decreases at higher calcinations temperature 800 °C. An increase in the magnetic anisotropy indicated stronger dipole-dipole interaction among nanoparticles. The coercivity of the sample is decreases as the calcinations temperature is lowered which can be attributed to the decrease in the saturation magnetization Ms. The smaller value of squareness ratio, reduced coercivity of the samples at lower sintering temperature indicate that although the sample calcined at 600 °C do not posses zero coercivity, however if the calcinations temperature is reduced further the samples may possess near zero coercivity leading to superparamagnetic behavior i.e. $H_C \approx 0$; and $M_r \approx 0$. Further, the non-saturated curves of the samples calcined at 600 °C indicate that the synthesized ferrites samples with nanoparticles of single domain structures having superparamagnetic behavior. The smaller squareness ratio and coercivity indicates that these nanoparticles may be suitable for the magnetic recording and soft ferrites applications including biomedical application such as hyperthermia.

Conclusions

Cadmium substituted Nickel Ferrite, Ni_{0.5}Co_xCd_(0.5-x)Fe₂O₄ (x = 0.0, 0. 02) were synthesized by sol-gel auto-combustion technique with microwaves using urea as fuel. The superparamagnetic nanoparticles of size 11–23 nm were synthesized successfully by solgel microwave assisted autocombustion method. Lattice parameter was found to decreases with Co²⁺ substitution and rising sintering temperature. M_s decreases with Co²⁺ substitution and calcination temperature. The small coercivity and squareness ratio and non-saturation of the samples at even at high applied magnetic fields indicates that the most of the nanoparticles even if not all, are superparamagnetic in nature. The various properties of these nanoparticles studied indicates that they can be of potential applications use in many applied field like MRI contrast agent, magnetic drug delivery and magnetic hyperthermia, data storage, sensores and catalysyts.

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