Synthesis and characterization of electrospun $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ nanofibers

F. Alahmari^a, M.A. Almessiere^{b,*}, Y. Slimani^{b,*}, H. Güngüneş^c, Sagar E. Shirsath^d, S. Akhtar^b, M. Jaremko^e, A. Baykal^a

^a Department of Nanomedicine, Institute for Research and Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, P.O. Box 1982, 31441 Dammam, Saudi Arabia

^b Department of Biophysics, Institute for Research and Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, P.O. Box 1982, 31441 Dammam, Saudi Arabia

^c Department of Physics, Hitit University, 19030 Çevre Yolu Bulvarı-Çorum, Turkey

^d School of Materials Science and Engineering, University of New South Wales, Sydney NSW 2052, Australia

^e King Abdullah University of Science and Technology (KAUST), Biological and Environmental Sciences & Engineering Division (BESE), Thuwal, 23955-6900, Saudi Arabia

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ABSTRACT

We report here the production of novel $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ nanofibers (NFs) ($0.00 \leq x \leq 0.25$) via electrospinning method with using polyvinylpyrrolidone (PVP) as a polymer agent. The investigation of the partial substitution effect of Co by Cd ions in $\text{Co}_{0.5}\text{Ni}_{0.5}\text{Fe}_{1.78}\text{Nd}_{0.02}\text{O}_4$ NFs on their morphological, structural and magnetic properties was performed. The XRD confirmed the successful formation of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs with cubic structure. The hyperfine parameters were determined from the analysis of Mössbauer results. The hyperfine magnetic field of both sites was not much affected by the substitution. Mössbauer analysis indicated that the Cd^{2+} ions strongly occupy A site and the Fe^{3+} ions emigrated from A site to B site, and hence the content of Co^{2+} ions diminished at B site. Room temperature (RT; $T = 300\text{K}$) and 10 K magnetization curves were investigated via vibrating sample magnetometer (VSM). All prepared samples displayed ferrimagnetic behavior at both measured temperatures. The saturation magnetization (M_s) enhances from $x = 0.00$ to 0.05 and thereafter reduces with the further increase in Cd^{2+} ion contents. All the Cd-substituted samples displayed higher M_s values than that of the non-substituted sample. The improvement in M_s values with Cd substitution is largely ascribed to the surface spins effects and cations distribution on T_d and O_h sites. Magnetic moments, remanence (M_r) and coercivity (H_c) were determined and investigated.

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1. Introduction

Spinel ferrite nanoparticles (SFNPs) are one of the most significant nanomaterials. They are being used in most modern life applications such as in electronics [1], telecommunications [2], magnetic recordings [3], catalytic and wastewater treatment applications [4–6]. The general composition of the spinel ferrites is AB_2O_4 where A represents the M^{2+} cations and B represents the M^{3+} cations occupying tetrahedral (T_d) and octahedral (O_h) sites, respectively, in normal spinel structures [7]. It is proven that the characteristics of spinel ferrites including the structure, magnetic and electrical features are extremely altered by the chemical composition, types and distribution of cations on T_d and O_h crystallographic sites, the disparity in their ionic radii and doping ratio along with other important parameters such as the synthesis method and conditions, microstructure, grains size and morphology [8]. Altering the electromagnetic features of these nanomaterials is a key factor for electronics growth indus-

try. Thus, SFNPs have been considered as ideal candidates for such advance field due to their capability to engineer their properties [9].

Cobalt ferrites (CoFe_2O_4), as renowned hard magnetic materials, are widely investigated owing to their desirable magnetic traits including high M_s , large magnetocrystalline anisotropy, great coercivity (H_c), and outstanding physical and chemical stabilities [10,11]. The nickel ferrite (NiFe_2O_4) is a soft ferrite, which possess large electrical resistivity but very weak magneto-crystalline anisotropy [12]. Because the magnetic moment of the smaller size Co^{2+} ions is greater than that of Ni^{2+} ions, the substitution between these cations increases the total magnetic moment among the unit cell and lead to outstanding magnetic, electric and dielectric features [13]. Thus, the improved electrical and magnetic features nominate the Ni-Co ferrite NPs as an optimum choice for telecommunication and high-frequency electronics applications [14].

There are many studies reporting that transition metals substituted Co–Ni ferrites, mainly focused on Zn, Mn, Cu influenced greatly their structure, magnetic and electrical behaviors. Many experiments have been performed by substituting Cd ions in other spinel structure of ferrite. Cd ions substituted NiMg spinel ferrites were prepared via sol–gel approach [15]. It was found that the M_s value increases with Cd^{2+} content, whereas, the M_r and H_c values decrease with Cd sub-

* Corresponding authors.

Email addresses: malmessiere@iau.edu.sa (M.A. Almessiere); yaslimani@iau.edu.sa (Y. Slimani)

Fig. 1. XRD patterns of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$).

Table 1

Refined structural parameters for $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$).

x	a (Å)	V (Å) ³	D _{XRD} (nm) ± 0.04	χ ² (chi ²)	R _{Bragg}
0.00	8.3584	583.94	17.5	3.1	26.5
0.05	8.3618	584.66	19.3	1.9	27.5
0.15	8.3661	585.56	13.2	2.5	25.8
0.20	8.3690	586.17	11.4	1.8	22.1
0.25	8.3812	588.72	10.5	2.6	26.7

Table 2

Cations distribution of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$).

x	Tetrahedral A-site	Octahedral B-site	Secondary phases (hematite)
0.00	$\text{Ni}_{0.05}\text{Co}_{0.05}\text{Fe}_{0.9}$	$\text{Ni}_{0.45}\text{Co}_{0.45}\text{Nd}_{0.02}\text{Fe}_{1.08}$	—
0.05	$\text{Ni}_{0.05}\text{Co}_{0.05}\text{Cd}_{0.05}\text{Fe}_{0.85}$	$\text{Ni}_{0.45}\text{Co}_{0.40}\text{Nd}_{0.02}\text{Fe}_{1.13}$	—
0.15	$\text{Ni}_{0.05}\text{Co}_{0.05}\text{Cd}_{0.15}\text{Fe}_{0.75}$	$\text{Ni}_{0.45}\text{Co}_{0.30}\text{Nd}_{0.02}\text{Fe}_{1.23}$	α-Fe ₂ O ₃
0.20	$\text{Ni}_{0.05}\text{Cd}_{0.20}\text{Fe}_{0.75}$	$\text{Ni}_{0.45}\text{Co}_{0.30}\text{Nd}_{0.02}\text{Fe}_{1.23}$	α-Fe ₂ O ₃
0.25	$\text{Ni}_{0.05}\text{Cd}_{0.25}\text{Fe}_{0.70}$	$\text{Ni}_{0.45}\text{Co}_{0.25}\text{Nd}_{0.02}\text{Fe}_{1.28}$	α-Fe ₂ O ₃

stitution. M. Rahimi et al. [16] investigated the structural and magnetic properties of Cd substituted Ni ferrite nanoparticles, $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.3, 0.5$, and 0.7), prepared via sol-gel auto-com-

Table 3

Mossbauer fitting parameters for $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$).

x	Assignment of sites	I.S. (± 0.002) (mm s ⁻¹)	Q.S. (± 0.004) (mm s ⁻¹)	B _{hf} (± 0.02) (T)	Area (%)
0.00	Sx-B1: Fe ³⁺	0.378	-0.071	51.751	26.566
	Sx-A: Fe ³⁺	0.272	0.014	49.057	35.911
	Sx-B2: Fe ³⁺	0.291	-0.042	47.259	18.459
0.05	Sx-B3: Fe ³⁺	0.333	-0.077	42.599	19.064
	Sx-B1: Fe ³⁺	0.386	-0.021	51.181	13.339
	Sx-A: Fe ³⁺	0.284	0.021	48.435	34.686
0.15	Sx-B2: Fe ³⁺	0.283	-0.021	46.077	22.54
	Sx-B3: Fe ³⁺	0.336	-0.023	41.451	29.435
	Sx-B1: Fe ³⁺	0.378	-0.05	51.607	24.988
0.20	Sx-A: Fe ³⁺	0.281	0.036	48.944	33.406
	Sx-B2: Fe ³⁺	0.324	-0.096	47.265	18.664
	Sx-B3: Fe ³⁺	0.369	0.041	42.902	22.942
0.25	Sx-B1: Fe ³⁺	0.371	-0.11	51.572	19.466
	Sx-A: Fe ³⁺	0.28	0.015	48.489	29.092
	Sx-B2: Fe ³⁺	0.287	-0.056	46.059	19.933
0.25	Sx-B3: Fe ³⁺	0.364	-0.061	40.957	31.51
	Sx-B1: Fe ³⁺	0.371	tmin0.11	51.686	18.002
	Sx-A: Fe ³⁺	0.279	0.014	48.78	25.725
0.25	Sx-B2: Fe ³⁺	0.273	-0.024	46.855	26.324
	Sx-B3: Fe ³⁺	0.369	-0.033	41.959	29.95

bustion approach. The M_s value at RT was found to increase with Cd²⁺ ions content up to $x = 0.3$ and then decrease for $x > 0.3$.

Although Cd-substituted Co-Ni ferrites are less investigated, it is confirmed that Cd substitution on spinel ferrites resulted in increasing their dielectric constants [8,17,18]. Moreover, the insertion of rare earth ions into spinel ferrites is expected to initiate 3d-4f interactions coupling, which usually provide further adjustment mainly for the magnetic properties. Many studies reported the effect of Lanthanide element (Ln^{3+}) ions (e.g. Ce, Gd, Dy and La) substitution on the magnetic features of Co-Ni ferrites [19,20]. Among other Ln^{3+}

Fig. 2. SEM images of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($x = 0.00, 0.15$ and 0.25) NFs. (a) before calcination, and (b) after calcination.

Fig. 3. TEM images of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs.

ions, Nd^{3+} doping has a reduction influence on the saturation magnetization and coercivity on ferrite NPs [21]. Only few reports are available to evaluate the role-played by Nd as a dopant on the properties of Co-Ni ferrite NPs [22,23]. Nowadays, substantial progress has been carried out for producing nanosized one-dimensional (1D) magnetic materials, including nanofiber, nanoribbon and nanotube structures. The driving force for such great efforts is to investigate their magnetization and the configurations of their magnetic domains in order to develop new nanoscale devices for electromagnetic applications [24]. The electrospinning technique is certified to be an economic, simple and adaptable method to produce various 1D nanosized structures. Nanofibers exhibit large shape anisotropy, high surface/volume ratio, and high facet ratio in comparison with bulks or even nanoparticle materials [25].

To the best of our knowledge, there is no report available detailed the impact of different proportion of Cd^{2+} on the structural, morphological and magnetic properties of Co-Ni spinel ferrite nanofibers prepared through the electrospinning technique. The current study presents the electrospinning synthesis, structure, morphology and magnetic properties of nanofiber samples of Cadmium substituted Ni-Co ferrites wherein low Cd content as substituting element in Co sites was considered.

2. Experimental

2.1. Synthesis

High purity metal nitrates (nickel, cobalt, cadmium, iron and neodymium nitrates) and polyvinylpyrrolidone (PVP, average $M_w \sim 1,300,000$) were obtained from Merck. For the synthesis of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs, metal precursor solution was prepared by dissolving stoichiometric amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in a mixture of 10 ml absolute ethyl alcohol and 7 ml deionized water. The mixture was magnetically stirred until the salts were completely dissolved before adding 1.4 g of the PVP polymer and kept stirring for 2 h until getting a clear viscous gel. The prepared gel was loaded into 20 ml plastic syringe, which was fixed on a syringe pump with stainless-steel needle tip. The electrospinning system was occupied with an adjustable voltage (up to 30 kV) to generate the required voltage difference between the needle tip and the collector to induce the electrospun fibers to diffuse. The collector plate was covered by aluminum foil uniformly and the needle tip was located in 12 cm away from the collector. The flowing rate of the electrospinning solution was 1.5 ml/h at applied voltage of 25 kV. The collected samples of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$) were dried in air at 75 °C for overnight before the calcination process at 650 °C for 2 h.

Fig. 4. EDX spectra and elemental mapping for $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($x = 0.00, 0.15$ and 0.20).

2.2. Characterization

The structure of NFs was identified by a (XRD; Rigaku Benchtop Miniflex, Tokyo, Japan) X-ray powder diffractometer (XRD). The morphology of obtained products before and after calcination were performed via (SEM/TEM; FEI Titan 80–300 kV FEI/TEM, Hillsboro, OR, USA). The presence of various incorporated elements and their ratios were confirmed by EDX analysis. The Mössbauer spectra were performed at room temperature using a conventional Mössbauer spectrometer (Fast Com Tec PC-moss II, Oberhaching, Germany) under constant accelerations mode using ^{57}Fe in Rh matrix with an approximate activity of 10 m Ci. The recorded spectra were analyzed and fitted to inbuilt Win-Normos fitting software (WISSEL company, Germany). A vibrating sample magnetometer (VSM) Quantum Design SQUID-PPMS vibrating sample magnetometer (PPMS Dyna-

Cool, Quantum Design, San Diego, CA, USA) was utilized for magnetization measurements.

3. Result and discussion

3.1. Crystal structure

The successful preparation of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs was verified through XRD patterns as exposed in Fig. 1. The main XRD peaks are characteristics of the inverse spinel ferrite phase. A minor phase of Fe_2O_3 has been detected at and above $x = 0.15$. The XRD experimental data was analyzed via Rietveld refinement by using Full-proof software to deduce the structural parameters (Table 1). The lattice parameter " a_0 " is raised with growing the quantity of Cd. The crystallites size (D_{XRD}) was estimated by using Scherrer formula [26]. D_{XRD} values are within 18

Fig. 5. Mössbauer spectra of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$).

Fig. 6. Variations of Mössbauer parameters with respect to Cd concentration.

to 10 nm range. Compared to unsubstituted sample, the DXRD value enlarged for $x = 0.05$ and afterward reduced with further increasing the ratio of Cd ions [27].

Bertaut method [28] is utilized to estimate the cations distribution in $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs. The distribution of mixed valance cations through the available T_d and O_h sites was assessed from the ratio of I_{220}/I_{440} and I_{422}/I_{400} XRD lines that are most likely sensitive to the distribution of cations [29]. The cations showed nearly linear dependencies of substitution and composition (Table 2

). The majority of Ni^{2+} and Co^{2+} cations accommodated by the O_h site (B). However, very small percentage of these ions occupy T_d site (A) as well. Depending on the single-ion model, Co^{2+} cations in the exact inverse spinel structure should occupy the O_h site (B) [28,30] which are the case for all presented samples while Cd^{2+} cations occupied the T_d site only. It is noticed that the Fe^{3+} cations migrated from T_d to O_h sites with increasing Cd^{2+} substitution ratio. At the same time, the % of the Co^{2+} cations at the A and B site decreased with increasing Cd^{2+} substitution ratio. Secondary phases such as α -

Fig. 7. M - H hysteresis curves of different $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Fe}_{1.78}\text{Nd}_{0.02}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs at (a, b) $T = 300$ K and (c, d) $T = 10$ K.

Fig. 8. Variations in the various magnetic parameters as a function of Cd content: (a) M_s , (b) M_r , (c) H_c , and (d) experimental (n_{exp}) and theoretical (n_{th}) magnetic moment at RT and 10 K.

Fe_2O_3 (hematite) have been clearly observed at higher substitution level of Cd^{2+} ions mainly because of the off-stoichiometry composition of the prepared samples and the inclusion of rare earth Nd ions in the composition (see Table 3).

3.2. Morphology

The microstructural analyses of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($x = 0.00, 0.015$ and 0.25) NFs obtained before and after calcination steps are displayed in Fig. 2(a) and (b), respectively. Fig. 2(a), referred to the samples obtained before calcination, showed

the nanofiber shapes wherein the diameter is decreasing with increasing the content of Cd. However, Fig. 2(b) illustrated the assemblage of multi-particles in polygon forms wherein the grains size is decreasing with increasing x content. Fig. 3 revealed the TEM images of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($0.00 \leq x \leq 0.25$) obtained after calcination step. These images demonstrated a homogeneous nanofiber structure consisting of dispersed nano-grains with lengths in ranges of hundred nanometers, but the diameters are decreased with increasing the amount of substitution ions. EDX spectra and elemental mapping of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ NFs ($x = 0.00, 0.15$ and 0.20) are presented in Fig. 4. They illustrated the presence of differ-

Fig. 9. Example of M vs. $1/H^2$ plot at both RT and 10 K for $x = 0.00$ composition. The solid line shows the fitting according to law of approach to saturation (LAS) approximation.

ent Ni, Co, Cd, Nd, Fe and O elements, and confirmed the construction of the desired compositions.

3.3. Magnetic investigations

3.3.1. Mössbauer analysis

Mössbauer spectra of $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs measured at RT have been depicted in Fig. 5. The spectra were fitted using three sextets, which one sextet for the tetrahedral A site and other two for octahedral B positions. The largest hyperfine with greater isomer shift is distinguished for Fe^{3+} cations at two different environments in O_h sites, while the lower values of both parameters are associated with the Fe^{3+} cations in T_d site [31]. The $\alpha\text{-Fe}_2\text{O}_3$ phase detected sample for $x \geq 0.15$ and added to spectra. The isomer shift is originated from the nuclear radius deference. The electronic interaction between nucleus and s electron density leads to isomer shift. The isomer shift was correlated to the oxidation state of Fe at T_d and O_h sites [32]. The isomer shift (I.S) of B site is larger than that of A site because of bond length among $\text{Fe}^{3+}\text{-O}$. It is found that the I.S values of A and B magnetic patterns are varying between 0.274 and 0.388 mm/s. Such isomer shifts values are associated to the characteristics Fe^{3+} in high spin charge state [33]. As seen in Fig. 5, the isomer shift of A site raised with the inclusion of Cd ions ($x = 0.05$) and then become unchanged. The isomer shift of B₁ site increased with the addition of Cd ions up to $x=0.15$ then decreased, while that of B₂ site hardly even changed. These show that the electron density of A site was not influenced by the substitution. The existence of non-zero quadrupole splitting (Q.S) reveals that there are chemical disorders in the crystal structure. Hence, the values of Q.S are providing information about the crystal lattice symmetry and its local distortions. The chemical disorder could produce a distribution of EFG of varying magnitude, asymmetry, sign and direction. Consequently, the sign of Q.S could be changed [34]. The Q.S values of obtained components with respect to substitution are negligible. This proves that the cubic symmetry of O^{2-} ions around Fe^{3+} ions is unaffected by the substitution of Cd ions in the cubic ferrite structure.

The change of hyperfine magnetic field of all sites with respect to x content is shown in Fig. 6. The hyperfine magnetic field value of all sites decreases with rising Cd^{2+} ions. The reason of this decreasing maybe the nonmagnetic Cd^{2+} ions increased by replacing Fe^{3+} ions of higher magnetic moment, $5 \mu_B$, and reduce the average number of magnetic bond of $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ and consequently Fe^{3+} nuclei experience a decrease in the magnetic field at both the sub lattices. The hyperfine magnetic field of A site decreases from 48.875 to 48.176 T, whereas that of B site decreases from 51.746 to 51.282 T with increasing of Cd^{2+} content from $x = 0.0$ to $x = 0.25$. On most Cd doped ferrite systems, nonmagnetic Cd^{2+} ions are preferably occupying

A site [35,36]. In our Cd^{2+} doped ferrite systems, the hyperfine magnetic field of both sites was not much affected by the substitution. According to Fig. 4, the relative area of B site increases, whereas that of A site decreases continuously with increasing of Cd^{2+} content. This shows that Fe^{3+} ions emigrated from A site to B site. The Cd^{2+} ions strongly occupy A site. Therefore, the content of Co^{2+} ions diminished at B site.

3.3.2. Magnetization against magnetic field

Magnetization M - H hysteresis loops at both 300 and 10 K for various $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) compounds are shown in Fig. 7. The different prepared compounds show S-type shape in M - H curves with opened hysteresis loops at both measured temperatures, indicating ferrimagnetic behavior. The deduced magnetic parameters for all the compounds are presented in Fig. 8. As obvious in Fig. 7, the magnetization of all produced compounds is not well saturated even up to a field of 70 kOe. The law of approach to saturation at high-field parts by linear fits of M vs. $1/H^2$ plots was used to obtain M_s values, as shown in Fig. 9. The experimental values of magnetic moment ($n_B\text{_{exp}}$) in Bohr magneton were determined via the following formula [37]:

$$n_{B_exp} = \frac{Mw \times M_s}{5585} \quad (1)$$

where Mw is the molecular weight and M_s is the saturation magnetization. The measurements at very low temperature ($T = 10$ K) showed M_s values superior than those at high temperature ($T = 300$ K). This is predominantly resulted from the reduction in the thermal fluctuations and magneto-crystalline anisotropy effects at very low temperatures [38,39]. Moreover, the M_s magnitudes attained in the current study (in the range of 42.8–48.9 emu/g at RT) are smaller than those of bulk NiCo ferrites. This reduction in M_s values could be elucidated on the basis of cations distribution. Additionally, several other influences described in previous reports could explain the decrease of M_s in NPs. The lower M_s values in NPs can be ascribed to the occurrence of arbitrary spins canting on surface of particles produced by competing antiferromagnetic exchange interactions because of asymmetries in the spins' environment [40,41]. Besides, the smaller M_s magnitudes are resulted from the non-saturation effects due to the arbitrary distribution of the tiny nanoparticles with improved magnitudes of magnetocrystalline anisotropy as reported by Q.A. Pankhurst et al. [42]. The influence of size in NPs could provoke a decrease in the M_s values compared to the bulk counterpart. Greater surface to volume ratio characterized tinier grains [43]. Particularly, if surface to volume become large, the surface spins disorder of the NPs will rise. Consistent with the morphology of core-shell NPs, ferrimagnetic aligned spins characterize the core and disordered spins are perceived at the surface. The application of a magnetic field tends to align the magnetic moments in the core, and then these magnetic moments become saturated at specific higher magnetic field amplitudes. The additional intensification of magnetic field will have an influence only on the surface, which cause a slow-down of magnetization. This is the purpose that the various products in the present study do not attain the saturation under applied fields of 70 kOe.

The non-substituted compound showed M_s values of about 42.8 and 53.2 emu/g at 300 and 10 K, respectively. It is noticed that the M_s values at both measured temperatures increase from $x = 0.00$ to 0.05 and then decrease with further increase x . The highest M_s values at $x = 0.05$ level is equal to 48.9 and 60.2 emu/g at 300 and 10 K, respectively. Nevertheless, all the Cd-substituted products displayed higher M_s values than in unsubstituted product. P.P. Hankare et al. [44] reported analogous kind of variation. The obtained M_s

magnitudes in these compounds are larger than in $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nanosized ceramics produced mechanochemically via high energy ball milling technique [45], in NiCo ferrite NPs prepared through sol-gel auto-combustion method [46], Gd^{3+} substituted NiCo ferrite NPs formed through sol-gel auto-combustion approach [47]. Comparable magnitudes were found in NiCo ferrite NPs prepared via a one-pot modified-solvothermal approach followed by annealing stage [48]. The improvement in M_s values with Cd substitution is largely ascribed to the surface spins effects and cations distribution on A and B sites [49]. In the spinel ferrite lattice, the theoretical magnetic moment (n_{B_th}) is provided by the vector sum of magnetic moments of A and B sublattices:

$$n_{th}(x) = n_{th}(B) - n_{th}(A) \quad (2)$$

where $n_{B_th}(A)$ and $n_{B_th}(B)$ are the magnetic moments at T_d and O_h sites, respectively. The different magnetic moments for various Co^{2+} , Ni^{2+} , Cd^{2+} , Nd^{3+} and Fe^{3+} ions are about 3.87, 2.83, 0, 2.5 and 5 μ_B , respectively. The theoretical and experimental values of magnetic moments were plotted in Fig. 8(d). The theoretical value of magnetic moment (n_{B_th}) is increasing with increasing Cd^{2+} ions content. Whereas, the experimental value of magnetic moment (n_{B_exp}) increases initially from $x = 0.00$ to 0.05 and thereafter decreases with further rising Cd^{2+} ions content. The decrease in n_{exp} value at higher content is principally owing to the formation of secondary phases (impurities) for $x \geq 0.15$. The enhancement in magnetization with Cd substitution is mainly resulted from the tendency of the nonmagnetic Cd^{2+} ions to occupy the T_d site [50]. Whereas, Ni^{2+} , Co^{2+} and Fe^{3+} ions occupy both T_d and O_h sites [49,51]. The inclusion of non-magnetic divalent Cd^{2+} ions (which prefer to occupy T_d site) in ferrite systems diminishes the content of Co^{2+} ions in O_h site. This pushes same content of Fe^{3+} ions to move from T_d to O_h sites. As a result, the concentration of Fe^{3+} ions increases in B site. Consequently, the magnetic moment at the B site increases while that on T_d site decreases. This results in a global increase in magnetization of the product, which is in line with the evolution in the theoretical values of magnetic moment (n_{B_th}). Interestingly, n_{B_exp} values increase initially for $x = 0.05$ and thereafter decrease with further rising Cd^{2+} content. Nevertheless, all the Cd-substituted products displayed higher n_{B_exp} values than in the non-substituted product. It is obvious that the n_{B_exp} and M_s values presented analogous trend regarding Cd^{2+} content at both 300 and 10 K. The evolution in M_s and n_{B_exp} values with Cd^{2+} ions substitution could be elucidated based on Neel's model [49]. Consistent with this model, there exist three exchange interactions, namely A–A, B–B and A–B. Among them, the A–B super-exchange interaction is the strongest and most effective. The A–B interactions are strengthened with the occupation of Cd^{2+} ions on A site followed by a transfer of Fe^{3+} ions from A to B site. This is responsible for the improvement in M_s and n_{B_exp} values. We note that all the Cd-substituted products displayed higher M_s and n_{B_exp} values than in unsubstituted product. The lower M_s and n_{B_exp} values in $x \geq 0.15$ compared to those in $x = 0.05$, is greatly affected by formation of secondary phases (impurities) for $x \geq 0.15$.

The non-substituted sample displayed H_c values of about 366.1 and 5389.7 Oe at 300 and 10 K, respectively. Compared to $x = 0.00$ product, H_c magnitudes decreased at both measured temperatures for $x = 0.05$ and thereafter increased for much higher Cd content. The variation in H_c in nanocrystalline products is greatly inversely linked to their sizes. In the present study, an increase in crystallites size was discerned at lower Cd^{2+} ion content and then a reduction in crystallites size was perceived with further rising Cd^{2+} ions content.

4. Conclusion

The presented $\text{Ni}_{0.5}\text{Co}_{0.5-x}\text{Cd}_x\text{Nd}_{0.02}\text{Fe}_{1.78}\text{O}_4$ ($0.00 \leq x \leq 0.25$) NFs were synthesized by electrospinning technique using PVP as a polymer. The microstructure of the prepared NFs was revealed via XRD, SEM and TEM. Mössbauer results showed that the Cd^{2+} ions strongly occupy A site, leading the Fe^{3+} cations to emigrate from A site to B site with increasing the nonmagnetic Cd^{2+} content. RT and 10 K magnetization curves recorded at RT and 10 K, revealed the ferromagnetic behavior for all prepared NF samples. It is observed that the M_s and n_{B_exp} values increase from $x = 0.00$ to 0.05 and thereafter decrease with the further increase in Cd^{2+} ion contents. All the Cd-substituted samples displayed higher M_s values than the non-substituted sample. The highest M_s and n_{B_exp} values belong to $\text{Ni}_{0.5}\text{Co}_{0.45}\text{Cd}_{0.05}\text{Fe}_{1.78}\text{Nd}_{0.02}\text{O}_4$ NPs with values of 48.9 emu/g and 1.59 μ_B at $T = 300$ K and 60.2 emu/g and 2.39 μ_B at $T = 10$ K, respectively. The improvement in the magnetization (M_s and M_r) values with Cd substitution is largely ascribed to the surface spins effects, cations distribution on A and B sites, and strength of A–B super-exchange interactions. The nonmagnetic Cd^{2+} cations are preferably occupying the tetrahedral sites (A), whereas, Ni^{2+} and Co^{2+} ions are occupying the octahedral B site and Fe^{3+} ions are occupying both A and B sites. As a result, the concentration of Fe^{3+} ions increases in B sites due to their transfer from A to B site, resulting in an increase in the magnetic moment at the B sites which is responsible for the enhancement of the total magnetization of the NFs.

CRedit authorship contribution statement

F. Alahmari: Conceptualization. **M.A. Almessiere:** Methodology.

Y. Slimani: Methodology. **S. Akhtar:** Writing - review & editing.

M. Jaremkko: Methodology. **A. Baykal:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Kebede K. Kefeni, Titus A.M. Msagati, Bhekile B. Mamba, Ferrite nanoparticles: Synthesis, characterisation and applications in electronic device, Mater. Sci. Eng. B 215 (2017) 37–55.
- [2] Abdul Same Fawzi, A.D. Sheikh, V.L. Mathe, Structural, dielectric properties and AC conductivity of $\text{Ni}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ spinel ferrites, J. Alloys Compd. 502 (2010) 231–237.
- [3] N. Sivakumar, A. Narayanasamy, J.M. Grenèche, R. Murugaraj, Y.S. Lee, Electrical and magnetic behaviour of nanostructured MgFe_2O_4 spinel ferrite, J. Alloys Compd. 504 (2010) 395–402.
- [4] K.K. Kefeni, B.B. Mamba, Photocatalytic application of spinel ferrite nanoparticles and nanocomposites in wastewater treatment: Review, Sustain. Mater. Technol. 23 (2020), e00140.
- [5] Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environ. Sci. Pollut. Res. 27 (2020) 26681–26693.
- [6] Tetiana Tatarchuk, Ivan Mironyuka, Volodymyr Kotsyubynsky, Alexander Shyichuk, Mariana Myslin, Volodymyra Boychuk, Structure, morphology and adsorption properties of titania shell immobilized onto cobalt ferrite nanoparticle core, J. Molecular Liquids 297 (2020), 111757.

- [7] J. Xiang, et al., Electrospinning preparation, characterization and magnetic properties of cobalt-nickel ferrite (co_{1-x}ni_xfe₂o₄) nanofibers, *J. Colloid Interface Sci.* 376 (1) (2012) 57–61.
- [8] N. Hamdaoui, et al., Cd-doping effect on morphologic, structural, magnetic and electrical properties of ni_{0.6-x}cd_xmg_{0.4}fe₂o₄ spinel ferrite (0 ≤ x ≤ 0.4), *J. Alloys Compd.* 803 (2019) 964–970.
- [9] M.d. S. Amarante, et al., Sintering behavior and electromagnetic properties of a ni-co ferrite/nio biphasic ceramic, *Mater. Res. Express* 6 (7) (2019), 076110.
- [10] V.L. Mathe, A.D. Sheikh, Magnetostrictive properties of nanocrystalline co-ni ferrites, *Physica B* 405 (17) (2010) 3594–3598.
- [11] M. Houshiar, et al., Synthesis of cobalt ferrite (cofe₂o₄) nanoparticles using combustion, coprecipitation, and precipitation methods: A comparison study of size, structural, and magnetic properties, *J. Magn. Magn. Mater.* 371 (2014) 43–48.
- [12] Z. Wang, et al., Preparation of ferrite mfe₂o₄ (m = co, ni) ribbons with nanoporous structure and their magnetic properties, *J. Phys. Chem. B* 112 (36) (2008) 11292–11297.
- [13] V.L. Mathe, R.B. Kamble, Electrical and dielectric properties of nano crystalline ni-co spinel ferrite, *Mater. Res. Bull.* 48 (4) (2013) 1415–1419.
- [14] K. Ashok, et al., Effect of sn on magnetic and dielectric properties of ni-co spinel ferrite over LF and MF range, *Trans. Indian Ceram. Soc.* 78 (3) (2019) 131–136.
- [15] N. Hamdaoui, Y. Azizian-Kalandaragh, M. Khelifi, L. Beji, Cd-doping effect on morphologic, structural, magnetic and electrical properties of ni_{0.6-x}cd_xmg_{0.4}fe₂o₄ spinel ferrite (0 ≤ x ≤ 0.4), *J. Alloys Compd.* 803 (2019) 964–970.
- [16] M. Rahimi, M. Eshraghi, P. Kameli, Structural and magnetic characterizations of cd substituted nickel ferrite nanoparticles, *Ceram. Int.* 40 (2014) 15569–15575.
- [17] D. Saha, M. Hakim, Resistivity and curie temperature of co doped cdni permivar ferrite, *J. Bangladesh. Acad. Sci.* (2009) 32.
- [18] G. Sathishkumar, C. Venkataraju, K. Sivakumar, Magnetic and dielectric properties of cadmium substituted nickel cobalt nanoferrites, *J. Mater. Sci., Mater. Electron.* 24 (3) (2013) 1057–1062.
- [19] S. Dwevedi, K.K. Bharathi, G. Markandeyulu, Magnetoreactance studies in rare earth-doped Ni ferrite, *IEEE Trans. Magn.* 45 (10) (2009) 4253–4256.
- [20] R. Samad, et al., Dielectric and magnetic properties of rare-earth-doped cobalt ferrites and their first-order reversal curve analysis, *Appl. Phys. A* 125 (8) (2019) 503.
- [21] M.A. Almessiere, et al., Nd³⁺ ion-substituted Co_{1-2x}Ni_xMn_xFe_{2-y}Nd_yO₄ nanoparticles: Structural, morphological, and magnetic investigations, *J. Inorg. Organomet. Polym. Mater.* 29 (3) (2019) 783–791.
- [22] M.K. Kokare, et al., Effect of nd³⁺ doping on structural and magnetic properties of ni_{0.5}co_{0.5}fe₂o₄ nanocrystalline ferrites synthesized by sol-gel auto combustion method, *J. Alloys Compd.* 748 (2018).
- [23] M.A. Almessiere, et al., Effect of nb(3+) substitution on the structural, magnetic, and optical properties of co(0.5)ni(0.5)fe₂o₄ nanoparticles, *Nanomater. (Basel, Switzerland)* 9 (3) (2019) 430.
- [24] P. Jing, et al., Width-controlled m-type hexagonal strontium ferrite (srfe₂o₁₉) nanoribbons with high saturation magnetization and superior coercivity synthesized by electrospinning, *Sci. Rep.* 5 (1) (2015) 15089.
- [25] L. Pan, et al., A novel method to fabricate CoFe₂O₄/SrFe₂O₁₉ composite ferrite nanofibers with enhanced exchange coupling effect, *Nanoscale Res. Lett.* 10 (1) (2015) 131.
- [26] V.G. Patil, S.E. Shirsath, S.D. More, S.J. Shukla, K.M. Jadhav, Effect on zinc substitution on structural and elastic properties of cobalt ferrite, *J. Alloy. Compd.* 488 (2010) 199–203.
- [27] F. Alahmari, S. Rehman, M. Almessiere, F.A. Khan, Y. Slimani, A. Baykal, Synthesis of Ni_{0.5}Co_{0.5-x}Cd_xFe_{1.78}Nd_{0.02}O₄ (x ≤ 0.25) nanofibers by using electrospinning technique induce anti-cancer and anti-bacterial activities, *J. Biomol. Struct. Dyn.*, <http://dx.doi.org/10.1080/07391102.2020.1761880>.
- [28] S.E. Shirsath, et al., Chemical tuning of structure formation and combustion process in cody_{0.1}fe_{1.9}o₄ nanoparticles: influence@ph, *J. Nanoparticle Res.* 15 (10) (2013) 1976.
- [29] S.E. Shirsath, et al., Ferrites obtained by sol-gel method, In: *Handbook of Sol-Gel Science and Technology*, Springer, Cham, 2018, pp. 695–735.
- [30] S.E. Shirsath, et al., Switching of magnetic easy-axis using crystal orientation for large perpendicular coercivity in cofe₂o₄ thin film, *Sci. Rep.* 6 (1) (2016) 30074.
- [31] R. Justin Joseyphus, et al., Synthesis and magnetic properties of the size-controlled mn-zn ferrite nanoparticles by oxidation method, *J. Phys. Chem. Solids* 67 (7) (2006) 1510–1517.
- [32] S.P. Yadav, et al., Distribution of cations in co_{1-x}Mn_xFe₂O₄ using xrd, magnetization and Mössbauer spectroscopy, *J. Alloys Compd.* 646 (2015) 550–556.
- [33] H. Kumar, et al., Structural and magnetic study of dysprosium substituted cobalt ferrite nanoparticles, *J. Magn. Magn. Mater.* 401 (2016) 16–21.
- [34] H.N. Ok, B.J. Evans, Collective electron description of the conduction mechanism in m_xFe_{3-x}O₄, m = cd, zn, *Phys. Rev. B* 14 (7) (1976) 2956–2965.
- [35] S. Kumar, et al., Mössbauer studies of Co_{0.5}Cd_xFe_{2.5-x}O₄ (0.0 ≤ x ≤ 0.5) ferrite, *Physica B* 403 (19) (2008) 3604–3607.
- [36] M.M. Karanjkar, et al., Structural, Mössbauer and electrical properties of nickel cadmium ferrites, *Ceram. Int.* 39 (2) (2013) 1757–1764.
- [37] E. Gorter, Magnetization in ferrites: saturation magnetization of ferrites with spinel structure, *Nature* 165 (4203) (1950) 798–800.
- [38] M. Almessiere, et al., The effect of nb substitution on magnetic properties of bafe₂o₁₉ nanohexaferrites, *Ceram. Int.* 45 (2) (2019) 1691–1697.
- [39] M. Almessiere, et al., Investigation of the effects of tm³⁺ on the structural, microstructural, optical, and magnetic properties of sr hexaferrites, *Results Phys.* (2019), 102166.
- [40] J.M.D. Coey, Noncollinear spin structures, *Can. J. Phys.* 65 (10) (1987) 1210–1232.
- [41] Y. Slimani, et al., Effect of bimetallic (Ca, mg) substitution on magneto-optical properties of nife₂o₄ nanoparticles, *Ceram. Int.* 45 (5) (2019) 6021–6029.
- [42] Q. Pankhurst, R. Pollard, Origin of the spin-canting anomaly in small ferrimagnetic particles, *Phys. Rev. Lett.* 67 (2) (1991) 248.
- [43] M. Almessiere, et al., Nd³⁺ ion-substituted co_{1-2x}ni_xmn_xfe_{2-y}nd_yo₄ nanoparticles: structural, morphological, and magnetic investigations, *J. Inorg. Organomet. Polym. Mater.* 29 (3) (2019) 783–791.
- [44] P.P. Hankare, et al., Effect of zinc substitution on structural and magnetic properties of copper ferrite, *J. Alloys Compd.* 501 (1) (2010) 37–41.
- [45] M.D. Chermahini, et al., Low temperature sintering of magnetic ni_{0.5}co_{0.5}fe₂o₄ ceramics prepared from mechanochemically synthesized nanopowders, *Ceram. Int.* 45 (5) (2019) 5491–5495.
- [46] F. Saffari, et al., Effects of co-substitution on the structural and magnetic properties of nicox_{0.2}co_{0.8} ferrite nanoparticles, *Ceram. Int.* 41 (6) (2015) 7352–7358.
- [47] D.B. Pawar, L. Ravangave, Sol-Gel Auto Combustion Synthesis of Gd₃Doped Ni_{0.5}Co_{0.5}Fe₂O₄ Nanoparticles and Examinations of Magnetic Properties.
- [48] G. Datt, et al., Observation of magnetic anomalies in one-step solvothermally synthesized nickel-cobalt ferrite nanoparticles, *Nanoscale* 8 (9) (2016) 5200–5213.
- [49] P. Belavi, et al., Structural, electrical and magnetic properties of cadmium substituted nickel-copper ferrites, *Mater. Chem. Phys.* 132 (1) (2012) 138–144.
- [50] S. Patil, et al., Structure and magnetic properties of cd and ti/si substituted cobalt ferrites, *Mater. Chem. Phys.* 57 (1) (1998) 86–91.
- [51] C.V. Reddy, et al., Effect of calcination temperature on cobalt substituted cadmium ferrite nanoparticles, *J. Mater. Sci., Mater. Electron.* 26 (7) (2015) 5078–5084.