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Effect of neodymium substitution on structural and magnetic properties of magnesium ferrite nanoparticles

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Abstract

The effect of Nd^{3+} substitution on the structural properties of magnesium ferrite prepared by the sol-gel technique was studied in the series $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$, where $x = 0-0.3$ in steps of 0.05. X-ray diffraction analysis revealed the limit for Nd^{3+} doping without any secondary phase appearing along with the spinel phase. Particle size calculation shows that the crystallite sizes of the prepared samples are in the 21–30 nm regime. The decrease in value of the lattice parameter with doping suggests that the shrinkage in unit cell and the crystallite size increase with Nd^{3+} concentration. Fourier transform infrared analysis shows that the substitution of Fe^{3+} ions is in octahedral B-sites by Nd^{3+} ions. X-ray fluorescence results show that the composition of prepared samples is in the expected ratio. Transmission electron microscope micrographs revealed spherical morphology and magnetic interaction of the samples. Magnetic measurements revealed the B-site substitution of Nd^{3+} ions in the series $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$. The variation of magnetic parameters with doping concentration is explained with the help of particle size dependence.

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(Some figures may appear in color only in the online journal)

1. Introduction

Spinel ferrites with the general formula MFe_2O_4 show interesting structural, electrical and magnetic properties that vary with the nature of ions and the site distribution among tetrahedral and octahedral sites. Their characteristics widely vary with the method and the conditions of preparation. Diverse practical applications of spinel ferrites have attracted the attention of researchers for decades. The properties of the ferrites in the nano-regime differ much from the bulk. The study of spinel ferrites in the nano-regime is significant because of their interesting magnetic and electrical properties with chemical and thermal stabilities [1]. Ferrites substituted with different cations prepared by various techniques exhibit interesting applications and involve exciting physics in them. There are several methods for synthesizing nano-sized spinel ferrites, such as co-precipitation, sol-gel, micro-emulsion, hydrothermal and the reverse micelle method [1, 4, 5]. Due to the good stoichiometric control and production of ultrafine

particles in the nano-range at a relatively low temperature, the sol-gel technique is an attractive preparation method [5].

Magnesium ferrite is a typical spinel in which the cation distribution in the crystal lattice site is very much sensitive to heat treatment due to the high diffusibility of Mg^{2+} ions [2, 3]. Magnesium ferrites are used as a humidity sensor [6] and a catalyst [7] and also have magnetic and gas sensing applications [8, 9]. When their crystallite size is below a certain value, MgFe_2O_4 possesses unique superparamagnetic properties at room temperature and has promising potential applications in transformers, ferrofluids and magnetic cores of coils [18–20]. Substitution of rare-earth ions into the spinel structure results in structural distortion and induces strains that significantly modify electrical and magnetic properties [10–12]. Many researchers have investigated the physical and structural properties of such ferrites because substitution of a small proportion of rare-earth elements with large ionic radii in ferrites will drastically modify its

properties. But seldom have studies been reported in Nd^{3+} ions substituted nano-sized magnesium ferrite.

Our investigation on the structural and magnetic properties of Nd^{3+} ions replacing $\text{Fe}^{3+/2+}$ ions in nano-sized magnesium ferrite was able to throw light on the doping concentration limit to obtain single-phase ferrite and the particle size dependence of magnetic properties. Synthesis of nano-sized ferrites was performed using a simple sol-gel technique. X-ray diffraction (XRD), Fourier transform infrared (FTIR) and transmission electron microscope (TEM) analyses were performed for studying the structural characteristics. X-ray fluorescence (XRF) measurements were taken for elemental analysis. Magnetic measurements were taken at room temperature by plotting the $M-H$ curve. XRD analysis reveals a limit for Nd^{3+} concentration to obtain pure $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$ without any extra phase. The FTIR spectrum shows the substitution of Fe^{3+} ions on octahedral B-sites by Nd^{3+} ions. The variation of magnetic parameters with doping concentration is explained by applying the particle size dependence model developed by Chakraverty and Bandyopadhyay [29] in the multi-domain regime.

2. Experiment

2.1. Synthesis of nano-sized magnesium ferrite

The sol-gel combustion method was used for the preparation of magnesium ferrite nanoparticles. Analytical research grade magnesium nitrate, neodymium nitrate and ferric nitrate were used as chemical precursors in ethylene glycol as the solvent. Nitrates in the required stoichiometric ratio were dissolved in a minimum amount of ethylene glycol at room temperature and the sol was heated at 60°C to obtain a wet gel. This gel was dried at 120°C , which self-ignites to form a fluffy product. This is then ground to form fine powders of magnesium ferrite. A series of samples with the formula $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0-0.3$ at step size 0.05) were prepared. The prepared samples were kept at 400°C for 3 hours in a muffle furnace.

2.2. Characterization

Structural characterization was done using an x-ray powder diffractometer (Rigaku make RINT 2000) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) at 40 kV and 30 mA by performing a scan from 20° to 80° at a step size of $0.02^\circ \text{ s}^{-1}$ for each sample. The crystal structure, lattice parameter, crystallite size, x-ray density, bulk density and porosity were determined from the XRD pattern. The FTIR absorption spectra of the samples were recorded using an FTIR spectrometer (Thermo Nicolet, Avatar 370) in the wave number range of $4000-400 \text{ cm}^{-1}$ with potassium bromide (KBr) as the binder. A wavelength dispersive x-ray fluorescence spectrometer (WD-XRF; make: Bruker; model: S4 PIONEER) was used for elemental analysis. Morphological analysis was performed using a TEM (Philips-CM200) operating at 20–200 kV with a resolution of $2.4 \text{ \AA}$. Magnetic measurements were carried out using a Lakeshore VSM 7410 at room temperature.

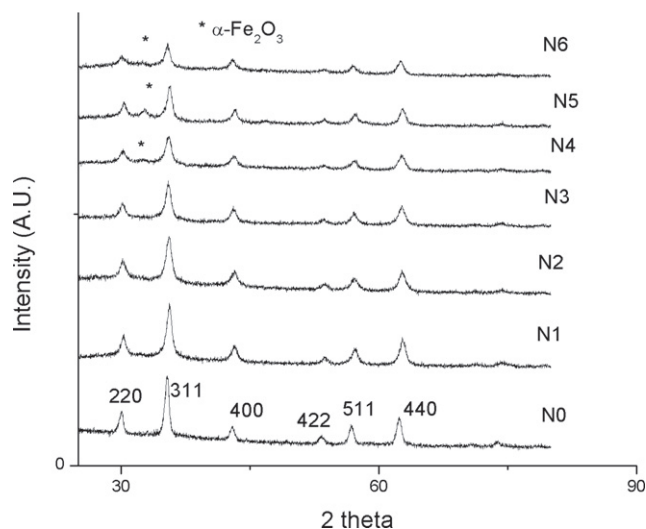


Figure 1. XRD pattern of $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$.

3. Results and discussion

3.1. X-ray diffraction studies

The XRD pattern of the prepared samples (labeled N0, N1, N2, ..., N6 for $x = 0, 0.05-0.3$) of the series is shown in figure 1. The XRD pattern confirms the formation of single-phase fcc spinel structure up to the Nd concentration $x = 0.2$, with no extra lines corresponding to any other crystallographic phase (compared with JCPDS card no. 73-2211). From $x = 0.20$ onwards an extra peak (*) is evolved, which indicates the presence of iron oxide ($\alpha\text{-Fe}_2\text{O}_3$). It is clear from the XRD patterns that the additional phase grows for the composition $x \geq 0.25$. The intensity of the peak decreases with the doping amount of Nd, which suggests difficulty in crystallization with the addition of rare-earth ions with relatively large ion radii.

The lattice constant a is calculated using Bragg's equation

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (1)$$

for a prominent (311) peak. The lattice parameter obtained for MgFe_2O_4 is in good agreement with the reported value of $8.37 \text{ \AA}$ [13, 22].

The average crystallite sizes (D) of all the samples were calculated from the XRD peak broadening of the peaks using the Scherrer formula corrected for micro-strain using Hall-Williamson plots [18, 19].

All peaks were fitted for the Lorentzian curve to determine the angle θ for maximum intensity and full-width at half-maximum (FWHM or β). Instrumental correction in calculating β was done by applying the formula

$$\beta = \beta_{\text{obs}} - \beta_{\text{inst}}, \quad (2)$$

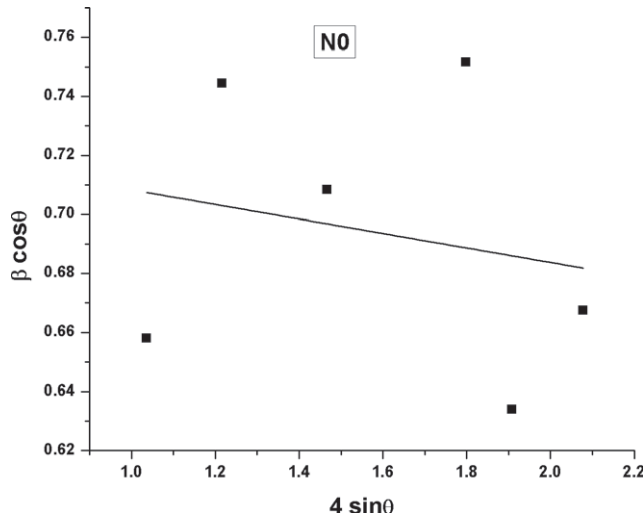
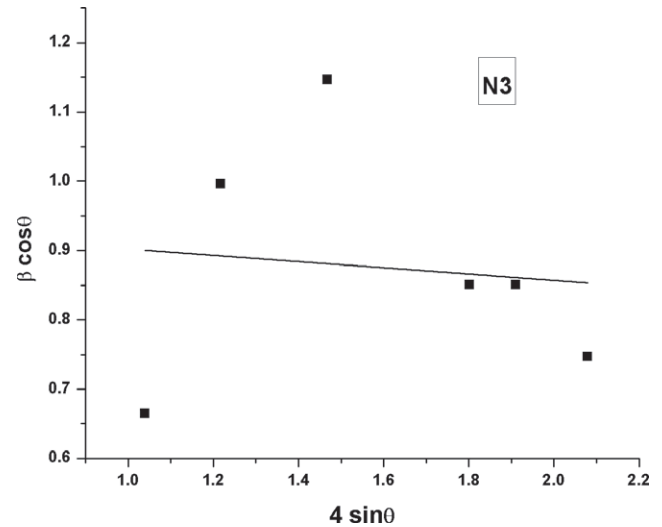
where β_{obs} is the observed FWHM from the XRD pattern and β_{inst} is the FWHM of the standard sample taken.

For the Lorentzian peak shape

$$\beta \cos \theta = \frac{\lambda}{D} + 4\epsilon_{\text{str}} \sin \theta, \quad (3)$$

Table 1. The values of the lattice constant, x-ray density, bulk density, porosity, crystallite size and strain calculated from Hall–Williamson plots for different x values in the series $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$.

x	a (Å)	ρ_x (g cm^{-3})	ρ_m (g cm^{-3})	Porosity (%)	D (nm) from H - W plot	Strain from H - W plot	D (nm) from TEM
0	8.3910	4.4963	1.5165	66.27	21.02	−0.0245	20
0.05	8.3750	4.6209	1.5142	67.23	19.67	−0.0258	22
0.1	8.3704	4.7286	1.1819	75.00	13.01	−0.1505	—
0.15	8.3910	4.7933	1.5923	66.78	16.26	−0.0451	18
0.2	8.3773	4.9168	1.5528	68.40	16.58	−0.0465	—
0.25	8.3568	5.0536	1.5045	70.22	20.11	0.0112	—
0.3	8.4139	5.0498	1.5059	70.17	29.51	0.2255	—

**Figure 2.** Hall–Williamson plots for sample N1.**Figure 3.** Hall–Williamson plots for sample N5.

where ε_{str} is the strain due to imperfection in crystals. A Williamson–Hall analysis was performed by plotting a graph between $\beta \cos \theta$ and $4 \sin \theta$ for all prominent peaks by applying linear best fitting. From the graph particle size D is obtained by

$$D = \frac{\lambda}{\text{intercept}} \quad (4)$$

and the slope gives the strain values.

Since each primitive unit cell of the spinel structure contains eight molecules, the value of x-ray density (ρ_x) was determined according to the relation [19]

$$\rho_x = \frac{8M}{Na^3}, \quad (5)$$

where N is the Avogadro's number and M is the molecular weight of the sample. Bulk density (ρ_m) was calculated using the formula

$$\rho_m = \frac{m}{\pi r^2 h}, \quad (6)$$

where m is the mass, r is the radius and h is the height of the pellet.

Porosity of the samples is calculated using the formula

$$P = \left(1 - \frac{\rho_x}{\rho_m}\right) 100. \quad (7)$$

The values of the lattice constant, x-ray density, bulk density, porosity, crystallite size (D) and strain calculated from Hall–Williamson plots for all the prepared samples are

shown in table 1. Hall–Williamson plots for samples N0 and N3 are shown in figures 2 and 3, respectively.

The values of the lattice parameter for all the doped samples are less than that of the undoped sample, except for the sample with $x = 0.3$. This suggests the shrinkage in unit cell with Nd doping. The decrease in a value with Nd^{3+} concentration is in agreement with the reported tendency of rare-earth doped ferrites [14, 20], which suggests the occupancy of rare-earth ions in B-sites. Rashad *et al* [21] also reported similar structural variations of cobalt ferrite doped with Sm^{3+} ions.

It is noteworthy that the crystallite size decreases with an increase in Nd concentration, which is similar to the reported results [15, 16]. Due to the larger bond energy of $\text{Nd}^{3+}\text{--O}^{2-}$ as compared with that of $\text{Fe}^{3+}\text{--O}^{2-}$ more energy is needed to make Nd^{3+} ions enter the lattice and form $\text{Nd}^{3+}\text{--O}^{2-}$ bonds. So Nd^{3+} -substituted ferrites have higher thermal stability relative to pure magnesium ferrites; but more energy is needed for the Nd^{3+} -substituted samples to complete crystallization and grow grains [15]. The increase in crystallite size for samples with $x > 0.2$ is due to the growth of a new phase in the sample.

Hall–Williamson plots of the samples with $x = 0$ – 0.2 show a negative slope, which indicates a compressive strain on the particles when doped with Nd^{3+} ions of a large ionic radius (98.3 pm) when compared to Fe^{3+} (64.5 pm). The increase in strain value with doping concentration exhibits difficulty in crystallization. The variation of porosity and lattice constant

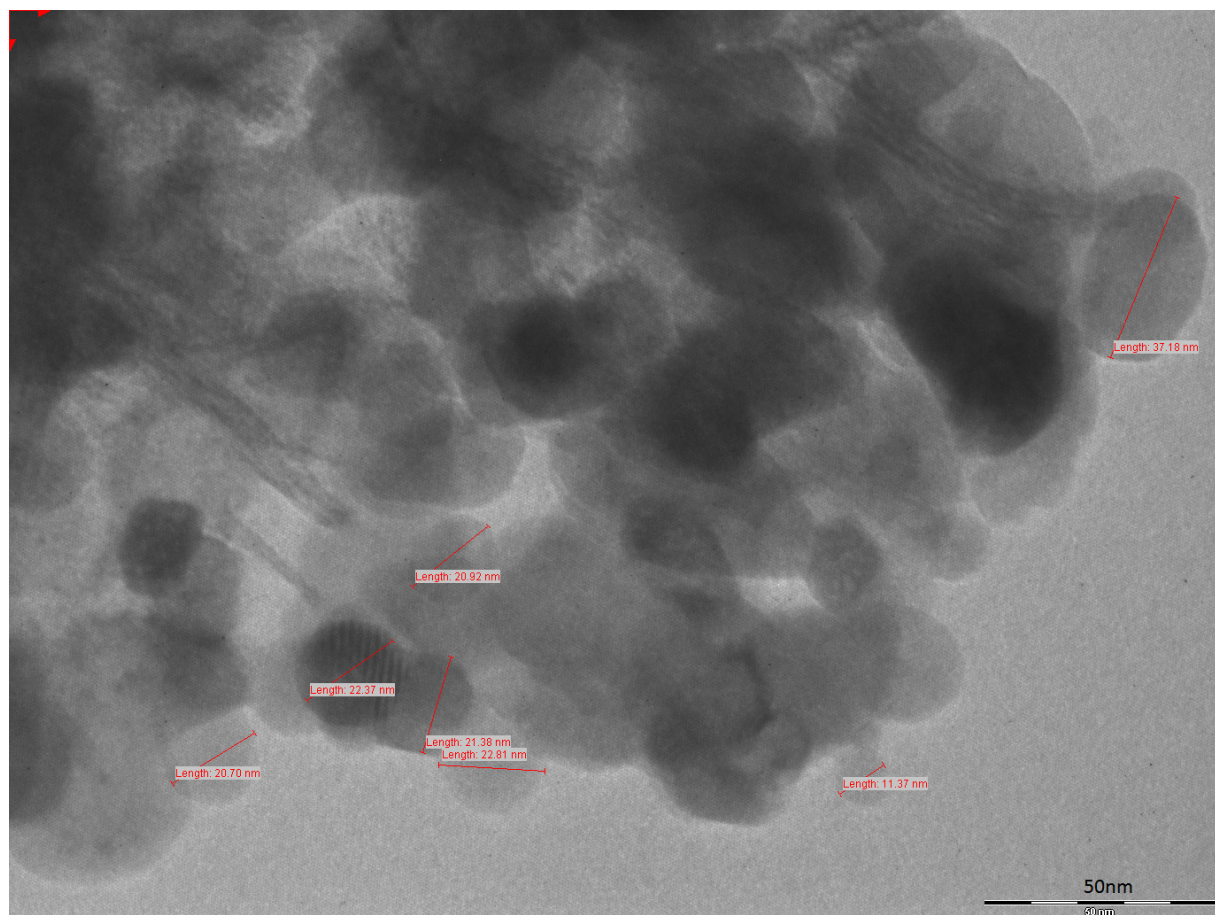


Figure 4. TEM image for sample N0.

with Nd^{3+} ion content shows an inverse relationship, which shows the dependence of lattice constant on the porosity of the sample.

3.2. TEM analysis

Figures 4–6 show the TEM images of N0, N1 and N3, respectively. Most of the nanoparticles are spherical in shape and are agglomerated. The average particle size calculated from the TEM images is given in table 1. The values are almost comparable with the crystallite size obtained from XRD. Magnetic interaction between particles in the samples is visible in the TEM images.

3.3. FTIR spectra

IR spectra of the $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$ ferrite system is shown in figure 7. Two major absorption bands are found in the ranges of 600–550 and 450–385 cm^{-1} . The higher frequency band (ν_1) is due to the stretching vibration of unit cell of the spinel in the tetrahedral (A) site and the lower band (ν_2) is caused by metal–oxygen vibration in octahedral (B) site [17], which are the typical bands of the spinel structure. With Nd concentration the band frequency ν_2 increases and broadens, while ν_1 does not change much and only a slight broadening is observed which may be attributed to the substitution of Fe^{3+} ions on octahedral B-sites by Nd^{3+} ions. An enlarged spectrum of frequency bands ν_1 and ν_2 is shown in the inset of figure 7.

The bands corresponding to 3400 and 1600 cm^{-1} represent stretching and bending vibrations of H–O–H, which indicates the presence of free or absorbed water.

3.4. XRF elemental analysis

The stoichiometry of the powder samples was analyzed using WD-XRF. The composition of elements present in samples N0, N2, N4 and N6 are given in table 2. From the table it is obvious that the samples show concentration values of each element very close to the expected stoichiometry. No trace of impurity was found, which indicates the purity of the sample.

3.5. Magnetic measurements

Magnetic characterizations of the samples were carried out by a vibration sample magnetometer at room temperature with the maximum applied field of 20 kOe. A typical magnetic hysteresis loop of $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$ samples with $x = 0$ –0.3 with step size 0.05 is shown in figure 8. The saturation magnetization (M_s), coercivity (H_c), remanance (M_r) and remanant ratio ($R = M_r/M_s$) of the samples with different Nd^{3+} contents are shown in table 3.

The saturation magnetization value of undoped magnesium ferrite is less than that for bulk MgFe_2O_4 [22, 23]. Its value is almost 25% less than the bulk value (33.4 emu g^{-1} at room temperature). The value of saturation

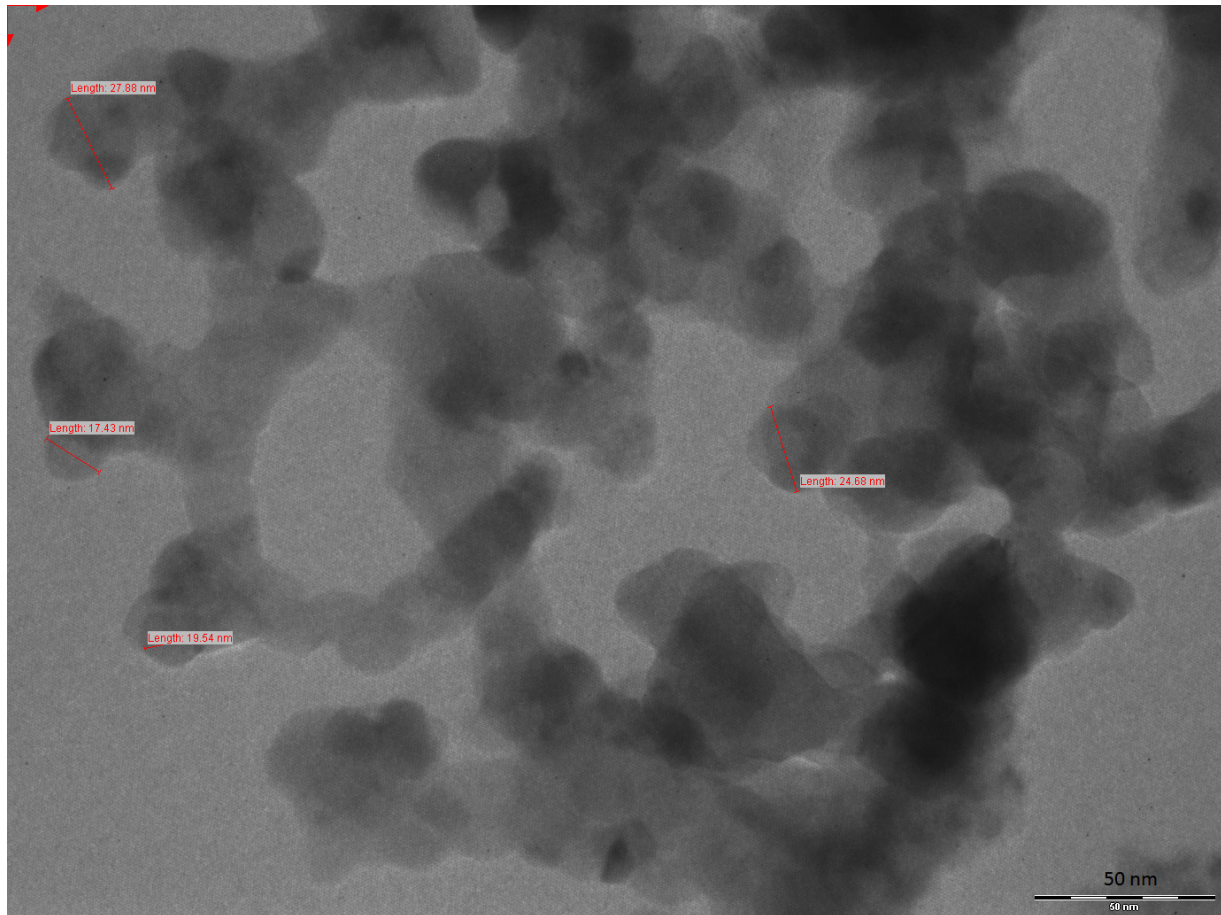


Figure 5. TEM image for sample N1.

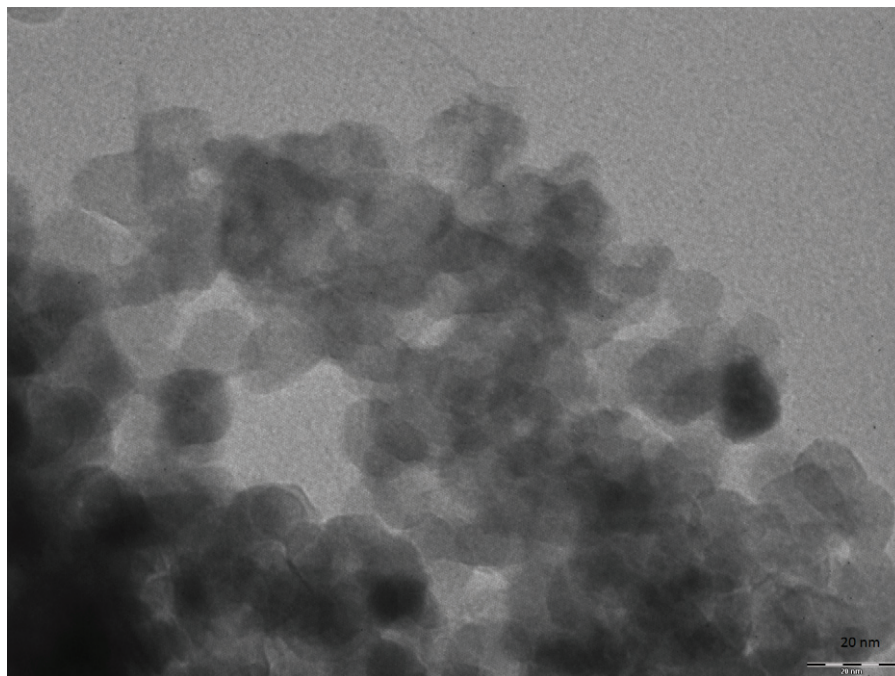


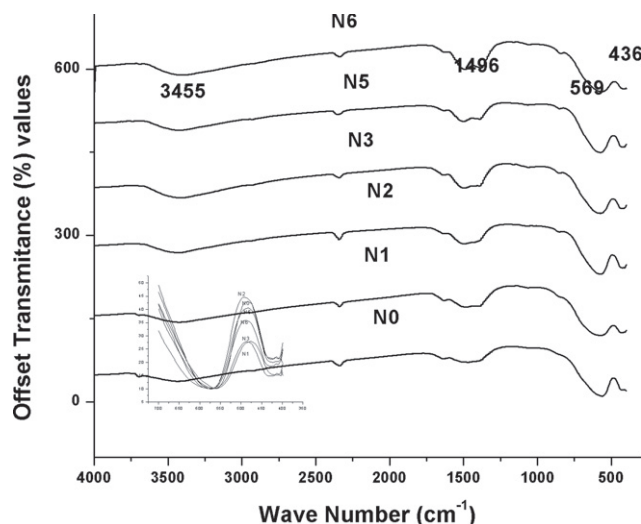
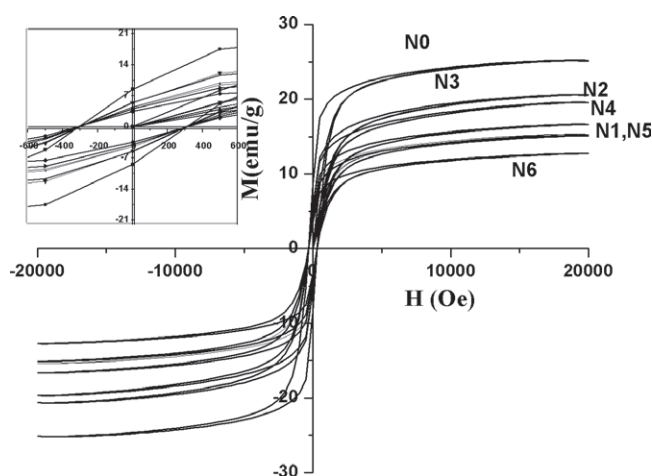
Figure 6. TEM image for sample N3.

magnetization depends on the grain size and preparation temperature [24]. The lower value of M_s may be due to the surface structural distortions and different cation distributions in nano-crystalline magnesium ferrite when

compared with the bulk counterpart [21, 25]. With Nd^{3+} doping the saturation magnetization value decreases from 25.2 to 12.8 emu g^{-1} when x varies from 0 to 0.3. Magnetic moment of Nd^{3+} is predominantly due to the 4f electrons

Table 2. The values of the concentration of each elements present in samples N0, N2, N4 and N6 compared with the expected concentration.

Elements present	Concentration (%) in N0	Expected concentration (%) in N0	Concentration (%) in N2	Expected concentration (%) in N2	Concentration (%) in N4	Expected concentration (%) in N4	Concentration (%) in N6	Expected concentration (%) in N6
Mg	15.780	12	10.840	12	9.500	12	8.908	12
Nd	Nil	0	7.565	7.2	13.710	14.4	19.050	21.6
Fe	51.330	56	50.660	53.2	46.910	50.4	43.080	47.6
O	32.600	32	30.300	32	28.900	32	27.800	32

**Figure 7.** FTIR spectra of $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$ samples.**Figure 8.** Hysteresis loop of $\text{MgNd}_x\text{Fe}_{2-x}\text{O}_4$ samples.

and their magnetic dipolar orientation exhibits a disordered form at room temperature. So Nd^{3+} substitution can be considered as a non-magnetic ion substitution in octahedral B-site. So this reduces the exchange interaction between A- and B-sites, which results in a decrease of magnetization. But we can see that when the concentration varies from $x = 0.05$ to 0.10 , the M_s values increase but when x varies from $x = 0.15$ to 0.3 it decreases. This can be explained by applying the stochastic model of particle size dependence of different magnetic properties of nanomagnetic particles using the non-equilibrium statistical mechanics developed by Chakraverty and Bandyopadhyay [29]. The variation of saturation magnetization (M_s), coercivity (H_c), remanance

Table 3. The saturation magnetization (M_s), coercivity (H_c), remanance (M_r) and remanant ratio ($R = M_r/M_s$) of samples with different Nd^{3+} contents (x).

x	M_s (emu g $^{-1}$)	M_r (emu g $^{-1}$)	$R = M_r/M_s$	H_c (Oe)
0	25.20	9.80	0.3900	299.86
0.05	15.30	5.01	0.3267	305.48
0.1	19.59	6.12	0.3124	316.59
0.15	20.62	5.35	0.2592	315.48
0.2	16.66	5.03	0.3019	318.75
0.25	15.13	4.44	0.3027	320.74
0.3	12.77	3.82	0.2992	283.27

Table 4. The variation of the saturation magnetization (M_s), coercivity (H_c), remanance (M_r) and remanant ratio ($R = M_r/M_s$) of samples with particle size (D).

D (nm)	M_s (emu g $^{-1}$)	M_r (emu g $^{-1}$)	$R = M_r/M_s$	H_c (Oe)
13.01	19.59	6.12	0.3124	316.59
16.26	20.62	5.34	0.2592	315.48
16.58	16.65	5.03	0.3019	318.75
19.67	15.3	5.01	0.3267	305.48
20.11	15.12	4.44	0.3027	320.74
29.51	12.17	3.82	0.2992	283.27

(M_r) and remanant ratio ($R = M_r/M_s$) of the samples with particle size (D) is shown in table 4.

According to this model, in the multi-domain regime at room temperature, as the surface to volume ratio increases, the surface contribution increases and this results in high saturation magnetization. So we can say that M_s decreases as the particle size increases. From table 4, we can see that our result follows this relation in M_s and particle size D for all Nd^{3+} concentrations.

The H_c values of the sample are in the range of 283–316 Oe. This is much greater than for MgFe_2O_4 synthesized by the coprecipitation method (48.86 Oe for 27.2 nm sized nanoparticles) [27] and for MgFe_2O_4 nanofiber synthesized by electrospinning (35.8 Oe for the crystallite size 15 nm) [28]. According to Chakraverty *et al*, above a critical diameter the coercivity decreases as particle size increases in the multi-domain regime. The remanant ratio $R = M_r/M_s$ shows the ease with which the direction of magnetization reorients to the nearest easy axis direction after the field is removed. The low value of R indicates the isotropic nature of the sample [26]. R values also show a decreasing trend with an increase in particle size, similar to H_c .

4. Conclusions

A series of Nd-substituted magnesium ferrites were synthesized by the sol-gel technique. XRD analysis revealed that the prepared samples are single-phasic cubic

spinel till $x = 0.2$. From $x = 0.25$, a secondary phase of iron neodymium oxide appears along with the spinel phase. The value of the lattice parameter for all the doped samples is less than that of the undoped sample, except for the sample with $x = 0.3$, which suggests the shrinkage in unit cell with Nd doping. The decrease of crystallite size with an increase in Nd concentration is due to the higher thermal stability of Nd^{3+} -substituted ferrites relative to pure magnesium ferrites. TEM images show that the samples are spherical in shape and agglomerated. The absorption bands in FTIR are found in the expected range of spinel ferrites and with Nd concentration the band frequency ν_2 increases and broadens, whereas ν_1 does not change much, which indicates the substitution of Fe^{3+} ions on octahedral B-sites by Nd^{3+} ions. The bands corresponding to stretching and bending vibrations of H–O–H point to the presence of free or absorbed water in the samples. XRF elemental analysis shows that the stoichiometry of the prepared samples was in the expected range and no trace of impurity was found, which indicates the purity of the sample. With Nd^{3+} doping the saturation magnetization value decreases, which is due to the non-magnetic ion substitution in the octahedral B-site. The dependence of magnetic parameters on the particle size of the nano-sized particles was explained on the basis of the multi-domain region. These investigations suggest that nano-sized MgFe_2O_4 substituted with Nd rare-earth ions can be manipulated for suitable applications.

Acknowledgments

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