

Impact of Sm^{3+} and Er^{3+} Cations on the Structural, Optical, and Magnetic Traits of Spinel Cobalt Ferrite Nanoparticles: Comparison Investigation

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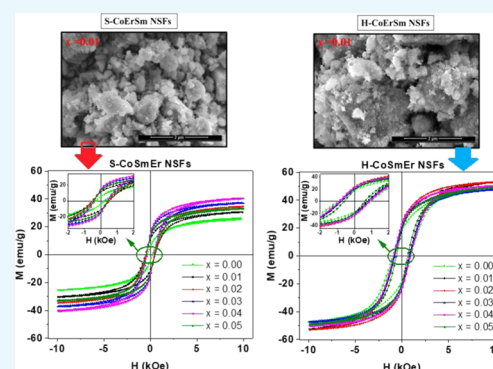
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ABSTRACT: In this study, we investigated a comparison of the structure, morphology, optic, and magnetic (room temperature (RT)) features of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 (CoErSm) nanospinel ferrite (NSFs) ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSFs) and sonochemical (S-CoErSm NSFs) approaches. The formation of all products via both synthesis methods has been validated by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM), along with energy-dispersive X-ray (EDX) and transmission electron microscopy (TEM) techniques. The single phase of the spinel structure (except for the Hyd sample with $x = 0.03$) was evidenced by XRD analysis. The D_{XRD} (crystallite size) values of H-CoErSm and S-CoErSm NSFs are in the 10–14.7 and 10–16 nm ranges, respectively. TEM analysis presented the cubic morphology of all products. A UV–visible percent diffuse reflectance (DR %) study was performed on all products, and E_g (direct optical energy band gap) values varying in the 1.32–1.48 eV range were projected from the Tauc plots. The data of RT magnetization demonstrated that all prepared samples are ferromagnetic in nature. M – H data revealed that rising the contents of cosubstituent elements (Sm^{3+} and Er^{3+} ions) caused an increase in M_s (saturation magnetization) and H_c (coercive field) in comparison to pristine samples. Although concentration dependence is significant ($x > 0.02$), no strict regularity (roughly fluctuating) has been ruled out in M_s values for doped samples prepared via the hydrothermal method. However, sonochemically prepared samples demonstrated that M_s values increase with increasing x up to $x = 0.04$ and then decrease with the further rise in cosubstituent Sm^{3+} and Er^{3+} ions. The calculated values of M_s and H_c were found to be greater in H-CoErSm NSFs compared to those in S-CoErSm NSFs. The present investigation established that the distribution of cations and the variation in crystallite/particle sizes are efficient to control the intrinsic properties of all samples.



1. INTRODUCTION

Nowadays, due to the technological application advantages in various fields such as sensors, catalysts, medicine, magnetic imaging, magnetic recording, microwave devices, and magnetic data storage, research involving spinel ferrite nanomaterials has received much attention.¹ Among all these spinel ferrites, cobalt ferrite has special importance because it is hard due to its high coercivity, high chemical stability, high mechanical hardness, high temperature of magnetic ordering (520 °C), enhanced saturation of magnetization, large magnetocrystalline anisotropy,² and easy synthesis. Cobalt ferrite (CoFe_2O_4) nanoparticles (NPs) can be also used in tomography, magnetic resonance imaging (MRI) (contrast agents of magnetic resonance imaging), and cancer treatment.³ CoFe_2O_4 has an inverse spinel structure, $(\text{Co}_{(x)}^{2+}\text{Fe}_{(1-x)}^{3+})[\text{Co}_{(1-x)}^{2+}\text{Fe}_{(1+x)}^{3+}]\text{O}_4$, where the cations occupy T_d sites and the O_h site.⁴

There are many different approaches for the synthesis of CoFe_2O_4 , including sol-gel autocombustion, sonochemical,

hydrothermal, microemulsion, coprecipitation⁵ etc. Among them, the hydrothermal route is one of the most common due to its compositional control, low-temperature processing, being cheap, and easy process.⁶ Sonochemical synthesis has several advantages. It does not need any reducing agent (as the radicals produced by water irradiation are real reducing agents). Due to this, sonochemical synthesis can be considered as a method of green synthesis.^{7,8}

Doping with rare earth (RE) in cobalt ferrites caused a rising trend of the nanomagnetism phenomenon as well as

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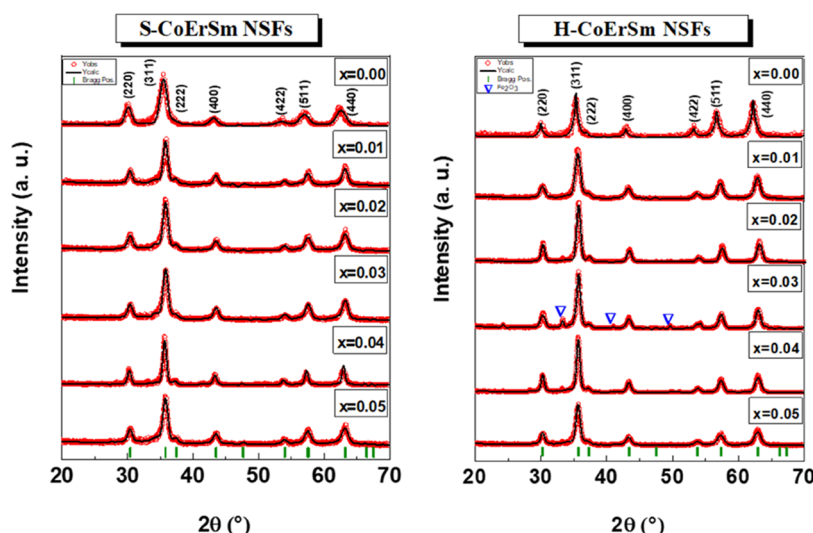


Figure 1. Rietveld refined XRD powder patterns of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSF) and sonochemical (S-CoErSm NSF) approaches.

Table 1. Refined Structural Parameters of Er^{3+} and Sm^{3+} Codoped CoFe_2O_4 Nanospinel Ferrite ($x \leq 0.05$) Synthesized via Hydrothermal (H-CoErSm NSF) and Sonochemical (S-CoErSm NSF) Approaches

S-CoErSm NSF						H-CoErSm NSF				
x	a (Å)	V (Å ³)	D_{XRD} (nm) (± 0.05)	χ^2	R_{Bragg}	a (Å)	V (Å ³)	D_{XRD} (nm) (± 0.05)	χ^2	R_{Bragg}
0.00	8.396(8)	592.10	10.2	1.19	4.78	8.338(2)	588.85	11.90	1.2	4.50
0.01	8.321(7)	576.29	10.84	1.13	0.60	8.361(4)	584.57	10.08	0.95	1.56
0.02	8.319(0)	575.72	11.08	1.02	0.50	8.355(9)	583.41	14.13	1.77	2.67
0.03	8.316(0)	575.10	9.72	1.09	8.48	8.345(0)	581.14	14.66	1.36	1.18
0.04	8.349(9)	582.16	16.12	1.33	0.83	8.348(1)	581.79	14.01	1.88	5.37
0.05	8.323(2)	576.59	9.85	0.88	1.45	8.355(0)	583.23	10.19	1.04	0.46

modification of their properties. These results encourages many researchers to adapt such studies, which showed that the final features had been remarkably affected by the addition of such dopants.^{9,10} Because of this, more work has been performed on CoFe_2O_4 doped with transition and rare earth (RE) elements. Ghorbani et al. studied the impact of Yb doping on the structural and magnetic features of CoFe_2O_4 and found that the H_c increases by increasing the Yb content.¹¹ While Nikmanesh et al. researched the structural magnetic response of CoFe_2O_4 NPs substituted with Sm,¹² Mariosi et al. explored lanthanum-doped cobalt ferrite nanoparticles.¹³ They observed a considerable decrease in coercivity and magnetization with increase in La^{3+} . Kamran et al. improved the transport properties of Ce-doped CoFe_2O_4 for resistive random access memory (RAM) applications.^{14–16} They concluded that the electrical conductivity decreases with increasing Ce^{3+} ions.

In this study, various CoErSm nanospinel ferrites (NSFs) were synthesized by both hydrothermal and ultrasonic approaches, and their different physical properties were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), along with energy-dispersive X-ray (EDX), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM), and diffuse reflectance (DR) UV–vis spectroscopic techniques. Due to the different cation distribution of the products synthesized by these different approaches, there may be a variation of exchange interactions, which may ultimately cause the modification of their magnetic

and functional properties. The results of this study might be useful for practical application of the spinel ferrites.

2. RESULTS AND DISCUSSION

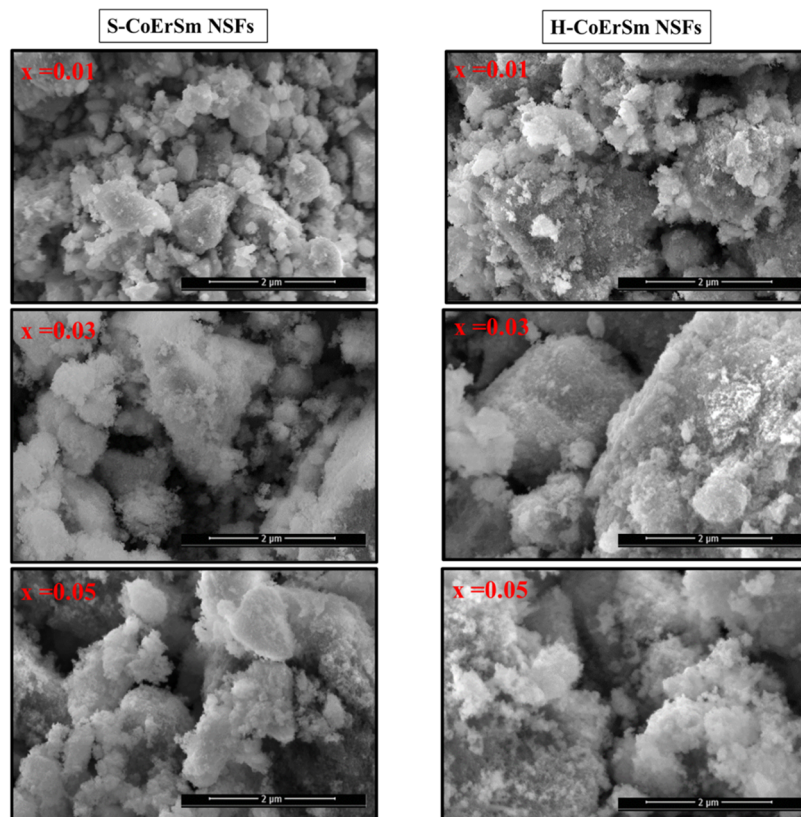
2.1. Structure. Rietveld refined XRD patterns of S-CoErSm and H-CoErSm NSF are given in Figure 1, which confirmed the successful synthesis of both sets of compounds. The XRD pattern of H-CoErSm NSF for $x = 0.03$ substitution showed the minor Fe_2O_3 phase as impurity. The peaks in both XRD powder patterns exhibited broadened peaks, which proved the small crystal size of all products. The structural parameters for both S-CoErSm NSF and H-CoErSm NSF have been computed in Table 1. The values of “ a_o ” obtained by applying Rietveld refinement (Match3! and FullProf) show some fluctuation due to the increase in Eu^{3+} and Sm^{3+} ion concentration in both methods, which shows the redistribution of the ions among the crystals. The D_{XRD} (crystallite size) values of the samples were assessed via Debye–Scherrer equation based on the 311 peak, and were computed within the range 10–16 nm for S-CoErSm NSF and 12–15 nm for H-CoErSm NSF.

The site occupancy of the S-CoErSm NSF and H-CoErSm NSF has been assessed from the XRD patterns.^{16–18} The Bertaut method¹⁹ has been used to define the cation distribution using the below equation

$$\frac{I_{hkl}^{\text{Obs.}}}{I_{h'k'l'}^{\text{Obs.}}} = \frac{I_{hkl}^{\text{Calc.}}}{I_{h'k'l'}^{\text{Calc.}}} \quad (1)$$

Table 2. Cation Distribution in Er³⁺ and Sm³⁺ Codoped CoFe₂O₄ Nanospinel Ferrite ($x \leq 0.05$) Synthesized via Hydrothermal (H-CoErSm NSF) and Sonochemical (S-CoErSm NSF) Approaches

x	S-CoErSm NSFs		H-CoErSm NSFs		impurity
	T_d -site	O_h -site	T_d -site	O_h -site	
0.01	Co _{0.22} Fe _{0.78}	Co _{0.78} Sm _{0.01} Er _{0.01} Fe _{1.2}	Co _{0.2} Fe _{0.8}	Co _{0.8} Sm _{0.01} Er _{0.01} Fe _{1.18}	α -Fe ₂ O ₃
0.02	Co _{0.22} Fe _{0.78}	Co _{0.78} Sm _{0.02} Er _{0.02} Fe _{1.18}	Co _{0.2} Fe _{0.8}	Co _{0.8} Sm _{0.02} Er _{0.02} Fe _{1.16}	
0.03	Co _{0.22} Fe _{0.78}	Co _{0.78} Sm _{0.03} Er _{0.03} Fe _{1.16}	Co _{0.2} Fe _{0.8}	Co _{0.8} Sm _{0.03} Er _{0.03} Fe _{1.14}	
0.04	Co _{0.22} Fe _{0.78}	Co _{0.78} Sm _{0.04} Er _{0.04} Fe _{1.14}	Co _{0.2} Fe _{0.8}	Co _{0.8} Sm _{0.04} Er _{0.04} Fe _{1.12}	
0.05	Co _{0.22} Fe _{0.78}	Co _{0.78} Sm _{0.05} Er _{0.05} Fe _{1.12}	Co _{0.2} Fe _{0.8}	Co _{0.8} Sm _{0.05} Er _{0.05} Fe _{1.10}	

**Figure 2.** SEM images of Er³⁺ and Sm³⁺ codoped CoFe₂O₄ nanospinel ferrite ($x = 0.01, 0.03$ and 0.05) synthesized via hydrothermal (H-CoErSm NSF) and sonochemical (S-CoErSm NSF) approaches.

where $I_{hkl}^{Calc.}$ and $I_{hkl}^{Obs.}$ are the observed and calculated intensities for the reflection (hkl), respectively. The agreement factor (R) is defined in eq 2; the lower value of R indicates the best-simulated structure that matches the actual structure of the sample. The related cation distribution was achieved for every hkl and $h'k'l'$ reflection pair.¹⁹

$$R = \left| \left(\frac{I_{hkl}^{Obs.}}{I_{h'k'l'}^{Obs.}} \right) - \left(\frac{I_{hkl}^{Calc.}}{I_{h'k'l'}^{Calc.}} \right) \right| \quad (2)$$

For the relative integrated intensity (I_{hkl}) of a given diffraction line from powder specimens achieved in a diffractometer with a flat-plate sample holder, the following formula is valid

$$I_{hkl} = |F|_{hkl}^2 PL_p \quad (3)$$

where F is the structure factor, L_p is the Lorentz polarization factor, P is the multiplicity factor, and²⁰

$$L_p = \frac{1 + \cos 2\theta}{\sin 2\theta \cos 2\theta} \quad (4)$$

The cation distribution of the elements present in both S-CoErSm and H-CoErSm NSFs has been calculated using the X-ray diffraction patterns.^{5,21} Table 2 shows the cation distribution of all of the elements. The Co ions occupy both T_d and O_h sites, which is an indication of the random spinel ferrite. The majority of the Co ions occupy the O_h site, which is in accordance with their site preference energy.^{22,23} As expected, rare earth Sm and Er ions occupied the O_h site only, because of their larger ionic radii. As expected, Fe³⁺ ions occupied the O_h site, and their occupancy decreased linearly with the substitution of rare earth Sm³⁺ and Er³⁺ ions. A trace of α -Fe₂O₃ (hematite) as impurity was observed only for $x = 0.03$ substitution (H-CoErSm NSFs).

2.2. Morphology. SEM images of the H-CoErSm and S-CoErSm ($x = 0.01, 0.03$ and 0.05) NSFs are shown in Figure 2. The images exhibited an agglomerate of fine particles due to their magnetic nature. Both H-CoErSm and S-CoErSm NSFs exhibited the same particle shapes. Figure 3 presents the chemical compositions of S-CoErSm NSFs and H-CoErSm

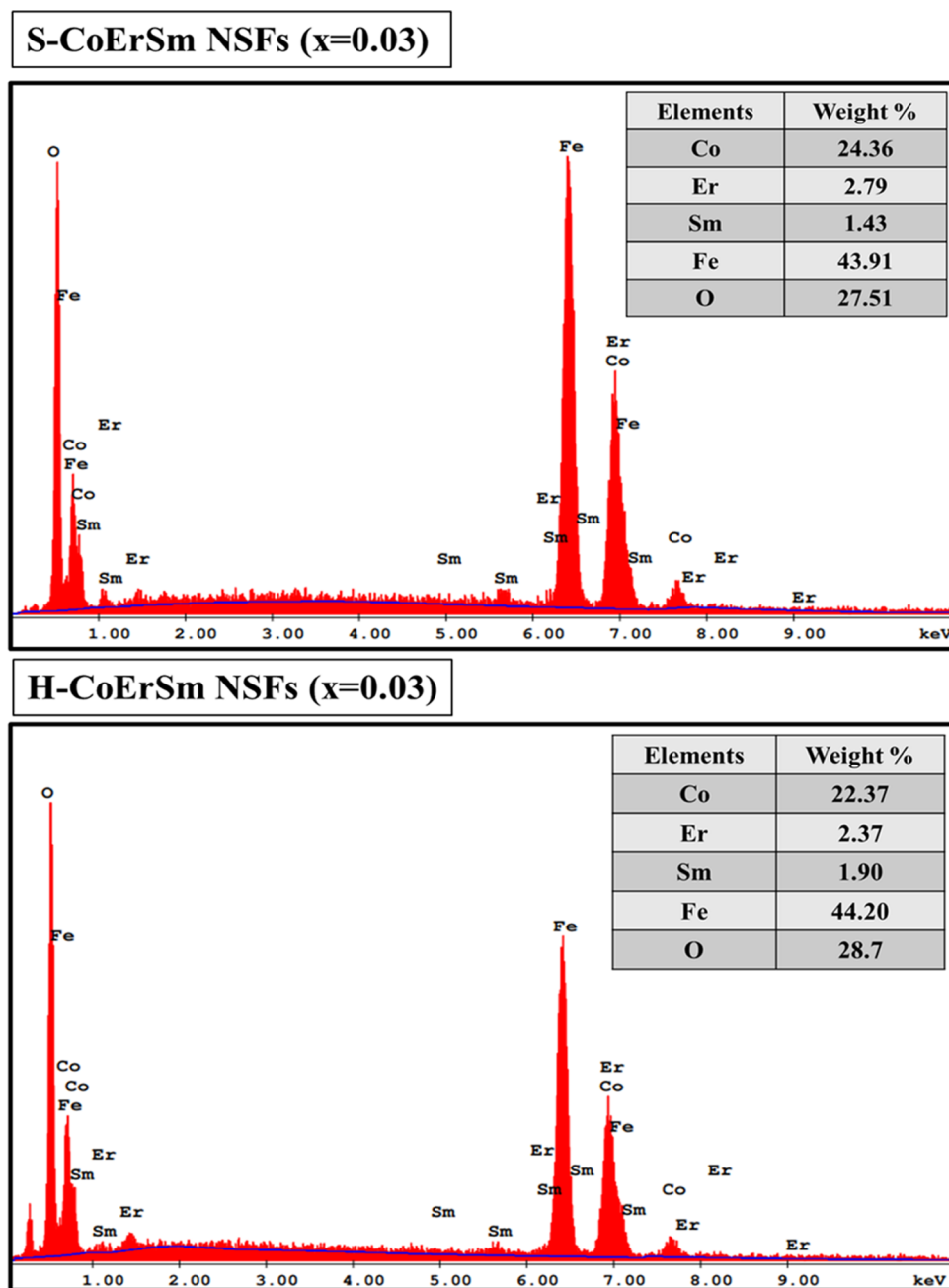


Figure 3. EDX spectrum of Er³⁺ and Sm³⁺ codoped CoFe₂O₄ nanospinel ferrite ($x = 0.03$) synthesized via hydrothermal (H-CoErSm NSF_s) and sonochemical (S-CoErSm NSF_s) approaches.

NSF_s ($x = 0.03$) obtained via EDX. They show the existence of Co, Fe, Er, Sm, and O.

TEM images of the H-CoErSm and S-CoErSm ($x = 0.04$) NSF_s are shown in Figure 4. The particles exhibited a cubic structure and appeared with some agglomeration. However, the individual particles can be seen clearly for each specimen. Both particle size histograms showed a size distribution ranging between 10 and 14 nm. The results of particle sizes were in good agreement with the crystallite sizes calculated by XRD (see Table 1). Selected area electron diffraction (SAED) patterns displayed the well-separated dotted rings indicating the crystalline nature of the particles. The rings of the SAED patterns (starting from inside the ring) were labelled as (220), (311), (400), (511), and (440). It can be noticed that (311)

reflection has the maximum intensity, which is consistent with the XRD pattern shown in Figure 1.

2.3. Optical Properties. The percent diffuse reflectance spectra (DRS %) of both H-CoErSm NSF_s and S-CoErSm NSF_s were recorded using a spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory. Figure 5 indicates the graphs recorded from the samples synthesized via the hydrothermal method on the left and graphs of the samples synthesized via the ultrasonic method on the right in the wavelength region of 190–900 nm. The energy magnitude of the incident radiation corresponds to a value range of 1.377–6.526 eV for decreasing wavelength from maximum 900 nm to minimum 190 nm.

The DRS % values of pristine CoFe₂O₄ samples are between 11.10–16.70% (one via the hydrothermal route) and 12.82–

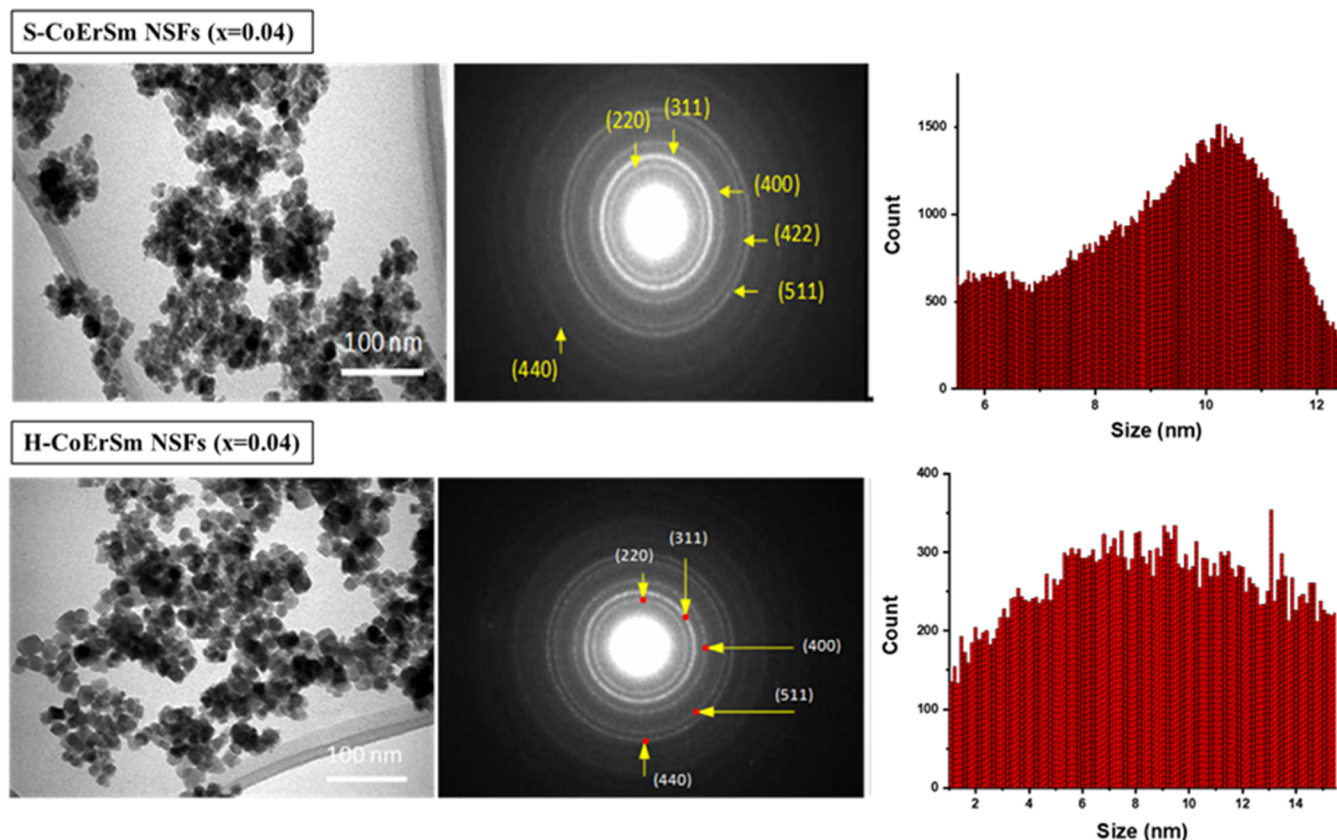


Figure 4. TEM micrographs, SAED patterns, and size distribution histograms of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 nanospinel ferrite ($x = 0.04$) synthesized via hydrothermal (H-CoErSm NSF) and sonochemical (S-CoErSm NSF) approaches.

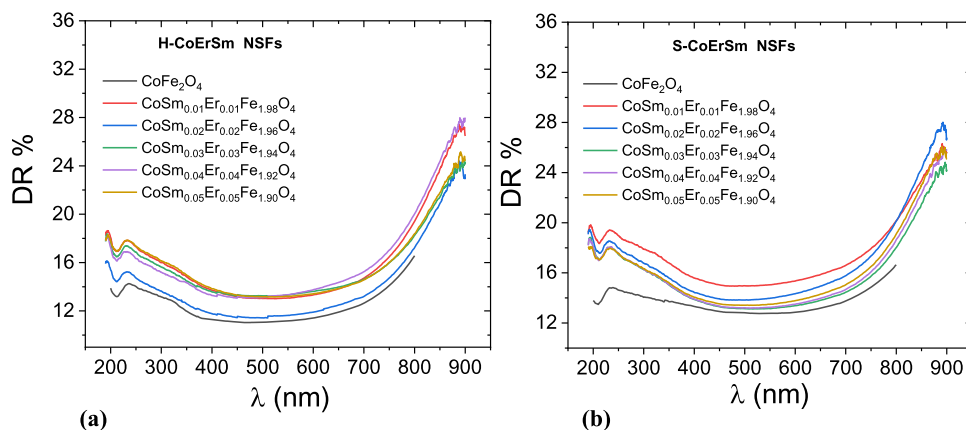


Figure 5. DR % vs λ spectra of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSF) (a) and sonochemical (S-CoErSm NSF) approaches (b).

16.66% (one via the ultrasonic route) in a sweep range of 200–800 nm. Cosubstituted samples with the Sm^{3+} and Er^{3+} rare earth (RE) ions have DR % values between 11.42–27.95% (samples via the hydrothermal route) and 13.06–27.94% (samples via the ultrasonic route) in the wider wavelength region of 190–900 nm. The DR of a layer with infinite thickness (R_∞) is linked with the absorption quantity K and the scattering quantity S by the Schuster–Kubelka–Munk (SKM) theory and related function $F[R_\infty(v)]$

$$F[R_\infty(v)] = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K(v)}{S} = \alpha \quad (5)$$

In the equation, $K = 0.434kc$, k is the molar extinction coefficient (m^2/mol), c is the molar concentration of the absorbing species, and α represents the absorption coefficient. The SKM function transforms the measured reflectance spectra into absorption spectra.²⁴ We use the Tauc and Davis–Mott models to estimate the band-gap energies (E_g)^{25–28}

$$\alpha \propto \frac{(hv - E_g)^n}{hv} \quad (6)$$

$$(ahv)^{1/n} \propto (hv - E_g) \quad (7)$$

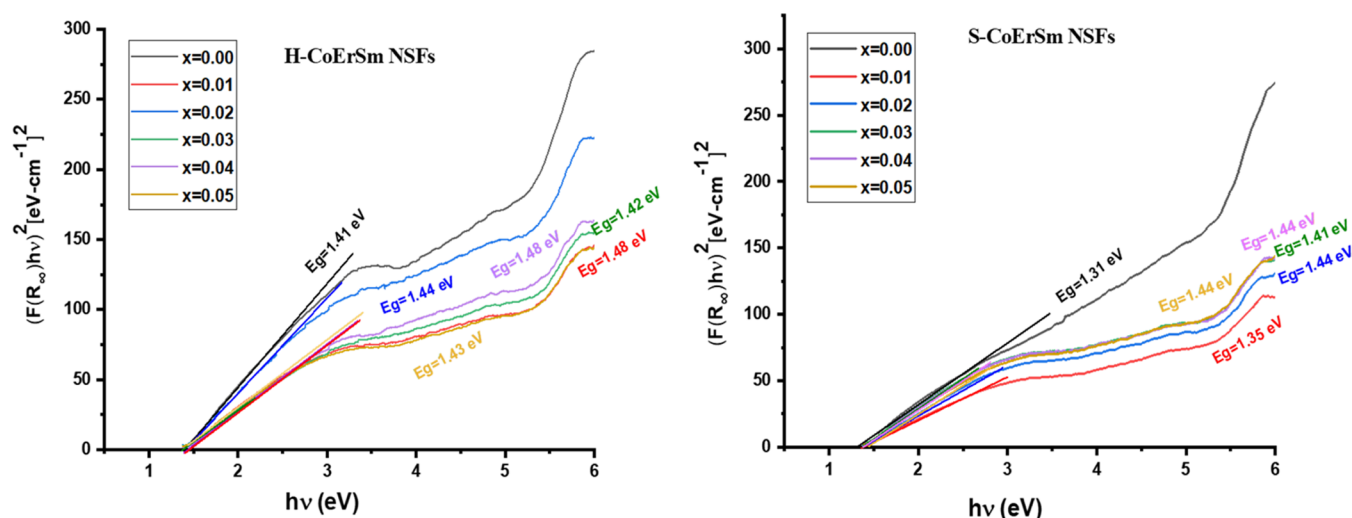


Figure 6. Tauc plots and extrapolated direct E_g data of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSF) and sonochemical (S-CoErSm NSF) approaches.

Here, h is Planck's constant, $n = 1/2$ for direct and allowed band-gap transitions, and ν is the frequency of the incident photon. To plot in the linear range, the equation $y = A(x - B)$ is relevant, where A is a constant of proportionality, B corresponds to E_g , $y = (F(R_\infty)h\nu)^2$, and $x = h\nu$. Direct optical E_g magnitudes are determined by extrapolating the straight part of the Tauc plots, which are the x vs y graphs. All Tauc plots and determined E_g magnitudes belonging to the samples synthesized via the hydrothermal route on the left column and belonging to samples synthesized via the ultrasonic route on the right column are presented in Figure 6.

The pristine H-CoErSm NSF has a direct optical E_g of 1.41 eV. Cosubstitution slightly increases the band-gap magnitudes until $E_{g,\text{max}} = 1.48$ eV for the ion contents of $x = 0.01$ and 0.04. Another pristine Co spinel synthesized via the ultrasonic route has a direct E_g of 1.31 eV. The cosubstitution process increases band-gap magnitudes relatively greater with respect to samples obtained via the hydrothermal method, and $E_{g,\text{max}}$ equals 1.44 eV for $\text{CoSm}_{0.02}\text{Er}_{0.02}\text{Fe}_{1.96}\text{O}_4$. All estimated data can be expected to take place in the semiconductor band-gap range. One can easily say that treatment of codoping with Sm^{3+} and Er^{3+} ions ($x = 0.00$ – 0.05) does not differ the E_g magnitudes of pristine Co spinel NPs obtained via both hydrothermal and ultrasonication methods. In the literature, our group has reported E_g data for CoFe_2O_4 NPs substituted by different single RE ions such as Tb^{3+} , Tm^{3+} , and Eu^{3+} .^{10,22,29,10,22,29} The reported E_g data from those single RE ion-substituted Co spinel NP samples are between 1.37 and 1.64 eV. It seems that the cosubstitution process with Sm^{3+} and Er^{3+} ions produces E_g data almost in the same order. Other research groups have also reported direct or indirect optical E_g data for pristine and substituted CoFe_2O_4 NPs with ions of different elements such as Zn, Ni, and Y.^{30–34} Those studies report the direct or indirect allowed transition values in a wide range of 1.17–4.3 eV. The E_g data for our pristine and cosubstituted CoFe_2O_4 NPs fit well with the direct optical E_g values reported by Ortiz-Quinonez et al.³⁴

2.4. Magnetic Properties. The M – H curves of H-CoErSm NSF and S-CoErSm NSF are given in Figure 7. For comparison, the M – H curves, which are taken from the samples with different Sm^{3+} and Er^{3+} ion concentrations, $x = 0.00, 0.01, 0.02, 0.03, 0.04$, and 0.05 , were plotted together in

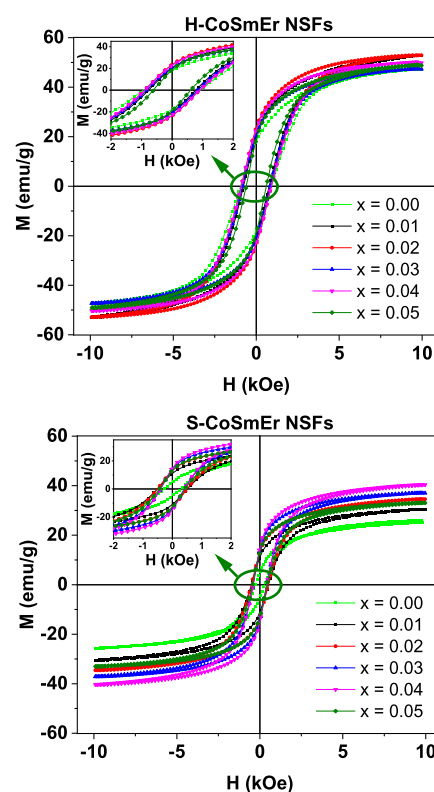


Figure 7. Room-temperature hysteresis loops of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSF) and sonochemical (S-CoErSm NSF) approaches.

two separated figures. Figure 7 shows the room-temperature (RT) hysteresis curves of samples prepared by the two different (hydrothermal and ultrasonic) methods. The curves for each value of x for the Sm^{3+} and Er^{3+} concentrations are indicated by different colors in the figures.

As seen in Figure 7, the hysteresis curves significantly depend on both preparation techniques and Sm^{3+} – Er^{3+} concentrations (x). First, significant hysteresis effects are clearly observed. The observed opened hysteresis loops for all samples indicated the ferrimagnetic nature of different H-

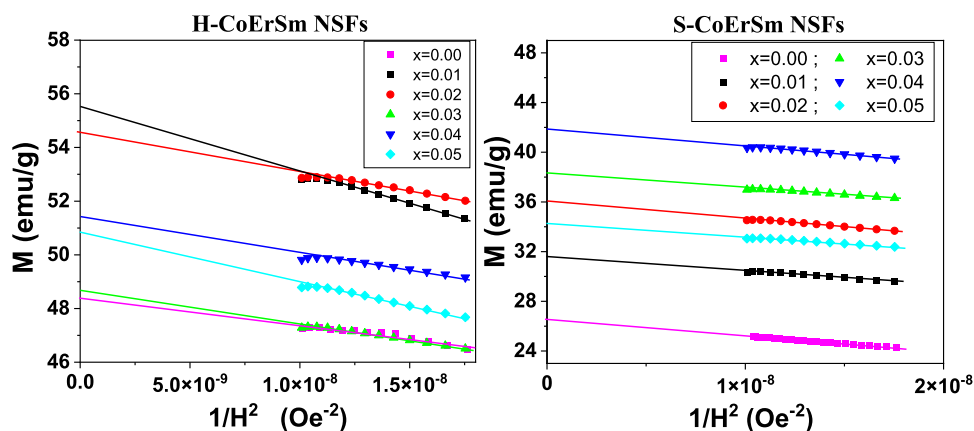


Figure 8. M against $1/H^2$ curve of Er³⁺ and Sm³⁺ codoped CoFe₂O₄ nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSF) (left) and sonochemical (S-CoErSm NSF) approaches (right).

CoErSm NSF and S-CoErSm NSF at RT. Generally, the ferrimagnetic behavior of Co spinel ferrite nanoparticles is observed below the blocking temperature. This indicates that the temperature of measurement is smaller than the blocking temperature of different systems. Both the coercive fields H_c and the saturation magnetizations M_s for the samples prepared by the H-method are significantly higher than those for the samples prepared by the U-S method. But the initial value of the slope of the curves in the vicinity of the zero-field (low-field) region is much higher for the samples prepared by the ultrasonic method as well.

The law of approach to the saturation (LAS) at high external field was applied to determine the technical saturation magnetization of each sample using the formula^{35,36}

$$M = M_s \left(1 - \frac{b}{H^2} \right) \quad (8)$$

The obtained values of saturation magnetization from the M vs $1/H^2$ curve are shown in Figure 8. The technical saturation values of the magnetization are estimated from the intersections of the y-axis with the extrapolated linear curves for each concentration as can be seen in Figure 8. The different products displayed closer saturation magnetizations to their magnetization values at an external field of 10 kOe.

Usually, the global saturation magnetization depends on numerous factors, including chemical composition, temperature, density, synthesis conditions, particle size, domain structures, spin order, etc.^{37,38} The concentration dependences of the values of saturation magnetization (measured at $H = 10$ kOe and estimated from the extrapolation as shown in Figure 8) and the coercive field values (obtained from Figure 7) are summarized in Table 3.

As seen from this table, the measured saturation magnetization (M_s) and coercive field (H_c) values measured at room temperature are significantly higher for the sample obtained by the H-method compared to those obtained by the S-method for each concentration. This could be explained by the difference in crystallite/particle size of the final products.³⁹ Indeed, samples prepared via the hydrothermal method displayed slightly larger crystallite/particle sizes in comparison to those observed in samples synthesized via the sonochemical method. Accordingly, M_s values would be greater in H-CoErSm NSF than in S-CoErSm NSF. In comparison to pristine H-CoErSm NSF with $x = 0.00$, M_s is increased upon Er–Sm doping. Although the concentration dependence is

Table 3. Concentration (x)-Dependence of the Coercivity and Saturation Magnetization Values for Er³⁺ and Sm³⁺ Codoped CoFe₂O₄ Nanospinel Ferrite ($x \leq 0.05$) Synthesized via Hydrothermal (H-CoErSm NSF) and Sonochemical (S-CoErSm NSF) Approaches

x	M_s (emu/g)	$2H_c$ (kOe)
	H/S	H/S
0.00	48.3:26.5	1.8:0.5
0.01	55.7:31.9	1.4:1.0
0.02	54.9:36.2	1.7:1.1
0.03	48.7:38.7	1.5:0.7
0.04	51.4:42.2	1.7:0.8
0.05	50.8:33.2	1.2:0.7

significant, no strict regularity (roughly fluctuate) has been ruled out in M_s values for samples prepared via the hydrothermal method ($x > 0.02$). This peculiarity can be attributed to the complex magnetic structures of the spinel ferrites.⁴⁰ As known, ferrites are ionic crystals, and there are 8 formula units (MFe₂O₄) in the spinel ferrites, where M stands for a divalent positive ion. The crystal structure of iron ferrite is face-centered cubic. The unit cell contains 64 tetrahedra (A site) and 32 octahedra (B site) formed by negative oxygen ions located at those corners.⁴¹ In a unit cell, there are 32 oxygen ions, 8 divalent M²⁺ ions, and 16 three valent Fe³⁺ ions. Depending on the type of the M atom, the positive M²⁺ and Fe³⁺ ions can occupy the center of the tetrahedra or octahedra. In a normal spinel structure, the divalent M²⁺ ions occupy A sites and all Fe³⁺ ions locate at the B sites. But in an inverse spinel ferrite, divalent M²⁺ ions occupy B sites, while half of the Fe³⁺ ions occupy A sites, and the other half occupy B sites. That is, most of the A and B sites do not contain any metallic ions and therefore remain empty. Therefore, the distribution of the positive ions among the A (or B) sites is statistically random, and therefore, the microscopic magnetic structure is not periodic but rather disordered. It must be recalled that the CoFe₂O₄ has an inverse spinel structure. It should be mentioned here that any spinel structure is not purely normal or purely inverse, but it can be composed of partly mixed states, e.g., approximately 90% normal and 10% inverse unit cell, or vice versa.

However, an opposite tendency behavior is observed for sonochemically prepared samples. For the case of samples synthesized via the sonochemical method, it was found that the

M_s value increases with increasing x , showing maximum value at $x = 0.04$, and then decreases with the further rise in x content. In our case, the effective magneton number of the Fe^{3+} is $5 \mu_B$, while Co^{2+} has $3 \mu_B$, where μ_B denotes the Bohr magneton.⁴² In a pure inverse CoFe_2O_4 ferrite, Fe^{3+} and Co^{2+} ions are expected to be distributed between A and B sites. The doping ions Sm^{3+} and Er^{3+} displayed magnetic moments of 1.5 and $9.5 \mu_B$, respectively. It is clear that the magnetic moment of Sm^{3+} ions is smaller, while that of the Er^{3+} ions is higher than those of both Co^{2+} and Fe^{3+} ions. Sm^{3+} and Er^{3+} ions are expected to substitute Fe^{3+} ions to preserve the charge balance. The average value of the magnetic moment of rare earth ions is about $5.5 \mu_B$ (averaged over Sm^{3+} and Er^{3+} moments), which is slightly higher than that of Fe^{3+} ions ($5.9 \mu_B$). Accordingly, when both Sm^{3+} and Er^{3+} ions substitute Fe^{3+} ions, it will provoke a slight increment in the global magnetization, as found in the case samples prepared via the sonochemical method. For the case of H-CoErSm NSF, the Fe^{3+} moments are unbalanced by the insertion of Sm^{3+} and the Er^{3+} moments at the B site must align antiparallel to the Co^{2+} moments, which are the main source of the total magnetization of the mother compound. Thus, the overall magnetization can slightly decrease depending on the substituent concentration x in this case.

The anisotropy (and impurity, dopant)-dependent magnetic coercive field is expected to be influenced by the substituent concentration as well. As is well known, the cobalt spinel structures and the orbital moments of the Co^{2+} ions do not completely quench, and therefore give a large contribution to the magnetic anisotropy field along the $\langle 100 \rangle$ crystallographic direction. This anisotropy originates from the spin and orbit of the metallic ion electrons, which are strongly influenced by the arraignment of the negative oxygen ions. Therefore, the contribution to the anisotropy from the A and B sites becomes different. As a result, the coercive field can be affected by the manner of substituent distribution among the A and B sites, as observed. The variations in coercive fields can be attributed to the rare earth (Sm^{3+} and Er^{3+}) ion doping. The orbits of the inner electrons of the rare earth ions are shielded from the ligand fields by the other shell electrons and their orbits are not quenched. Therefore, the large magnetic anisotropy is induced since it is originated by spin–orbit interactions. This is why the coercive field is large for rare earth ion-doped CoFe_2O_4 compounds.

However, the H_c values (listed in Table 3) that belong to the two kinds of products showed nonmonotonic variations with rising Sm–Er ion content. Generally, the coercive field is the result of the effective anisotropy energy (E_{eff}), and as anisotropy energy becomes higher, the coercivity will also be larger. Usually, the effective anisotropy energy is written as the sum of diverse anisotropy energies, including shape anisotropy (E_1), surface anisotropy (E_2), magnetoelastic anisotropy (E_3), and magnetocrystalline anisotropy energy (E_4). E_1 is correlated to the shape of the nanoparticles. Particularly, sonochemically and hydrothermally prepared nanomaterials displayed nearly spherical shapes with zero-shape anisotropy energy. Moreover, the substitutions of ions do not significantly alter the shapes of the prepared nanomaterials. Therefore, such sort of energy is not expected to present any significant influence to alter the H_c values. E_2 is correlated to the size of the nanoparticles. A smaller size of nanoparticles implies a higher fraction of surface area with respect to the size and higher surface anisotropy. E_3 is correlated to the stress within the crystal lattice. The

incorporation of dopant ions causes mechanical stresses within the crystal lattice and alters the magnetic susceptibility of the nanoparticles. E_4 is correlated to the atomic structures of the crystal host and presents preferential directions for the magnetization. Therefore, the nonmonotonous variations in coercive fields are resulted from the contribution of the three anisotropy energies, namely surface anisotropy (E_2), magnetoelastic anisotropy (E_3), and magnetocrystalline anisotropy energy (E_4), for both sets of prepared samples of H-CoErSm NSFs and S-CoErSm NSFs.⁴³

3. CONCLUSIONS

This study investigated the properties of Er^{3+} and Sm^{3+} codoped CoFe_2O_4 (NSFs) ($x \leq 0.05$) fabricated via hydrothermal and sonication techniques. The spinel ferrite phase was achieved for both compositions with crystallite sizes in the range of 10–14 nm. DR % measurements indicate the strong light-absorption characteristics of all samples especially in the wavelength region of 190–800 nm. Analyses based on SKM theory provided us direct estimates of the E_g magnitudes (between 1.32 and 1.48 eV) in the semiconductor band-gap range for all of the samples synthesized by hydrothermal or ultrasonication methods. Cosubstitution treatment with Sm^{3+} and Er^{3+} ions slightly increased the E_g values of the pristine samples. VSM characterization confirmed the ferromagnetic nature of all of the prepared nanomaterials. Compared to pristine samples prepared via either hydrothermal or sonochemical method, an improvement in M_s and H_c values was observed upon cosubstituting with Sm^{3+} and Er^{3+} ions. For $x > 0.02$, the M_s value fluctuates for codoped samples prepared via the hydrothermal method. Nevertheless, the M_s value increases with increasing cosubstituent Sm^{3+} and Er^{3+} ions up to $x = 0.04$ for the sonochemically prepared samples. A gradual decrease in M_s value was seen with the further rise in cosubstituent Sm^{3+} and Er^{3+} ions ($x > 0.04$). Noteworthy, the calculated M_s and H_c values are greater in H-CoErSm NSFs compared to those in S-CoErSm NSFs. These variations are ascribed to the distribution of cations and the variation in crystallite/particle size.

4. EXPERIMENTAL SECTION

All precursors, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and NH_3 solution were obtained from Merck. Benchtop Miniflex X-ray powder diffraction (XRD, $\text{Cu K}\alpha$ radiation) was used for structural investigation. Both SEM (FEI Titan ST) coupled with the EDX system and TEM (FEI Morgagni 268 microscope) were used for the morphology. UZ SONOPULS HD 2070 with 70 W power and 20 kHz frequency was used for the ultrasonic synthesis. A Quantum Design SQUID with a vibrating sample magnetometer (VSM) head was used for the magnetic measurements.

4.1. Synthesis. **4.1.1. Hydrothermal Approach.** For the particular synthesis of H-CoErSm NSFs ($0.01 \leq x \leq 0.05$), initially, the stoichiometric weight of metal nitrates was thawed in 50 mL of DI H_2O under stirring at RT. The 2 M NaOH solution was dropped into a metal solution to adjust its pH to 11. The obtained solution was transferred to a Teflon-lined autoclave and heated in an oven at 180 °C for 12 h. The obtained solid products were washed with hot DI H_2O , and then dried at 80 °C in air.¹⁵

4.1.2. Sonochemical Approach. For the synthesis of S-CoErSm NSF_s ($0.01 \leq x \leq 0.05$), initially, the required amounts of metal nitrates were dissolved in 50 mL of DI H₂O under stirring at RT. After arranging the pH of the solution to 10.5 using sodium hydroxide solution, it was then exposed to high-intensity ultrasonic irradiation for 60 min. Due to many collisions between the reactants inside the solution, the temperature was measured as 90 °C during irradiation. Finally, the solid product was separated from the solution via a magnet, washed with DI H₂O, and dried at 60 °C for 12 h.¹⁶

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Notes

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