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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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$_2$O$_4$ (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. 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, and easy synthesis. Cobalt ferrite (CoFe$_2$O$_4$) nanoparticles (NPs) can be also used in tomography, magnetic resonance imaging (MRI) (contrast agents of magnetic resonance imaging), and cancer treatment. CoFe$_2$O$_4$ has an inverse spinel structure, ($\text{Co}_{(1-x)}^{2+}\text{Fe}_{(1-x)}^{3+})[\text{Co}_{(1-x)}^{3+}\text{Fe}_{(1+x)}^{2+}]\cdot\text{O}_4$, where the cations occupy $T_d$ sites and the $O_6$ site.

There are many different approaches for the synthesis of CoFe$_2$O$_4$, including sol-gel auto combustion, sonochemical, hydrothermal, microemulsion, coprecipitation 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. 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.

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

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modification of their properties. These results encourage many researchers to adapt such studies, which showed that the final features had been remarkably affected by the addition of such dopants.\textsuperscript{9,10} Because of this, more work has been performed on CoFe\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{4} and found that the $H_c$ increases by increasing the Yb content.\textsuperscript{11} While Nikmanesh et al. researched the structural magnetic response of CoFe\textsubscript{2}O\textsubscript{4} NPs substituted with Sm,\textsuperscript{12} Mariosi et al. explored lanthanum-doped cobalt ferrite nanoparticles.\textsuperscript{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\textsubscript{2}O\textsubscript{4} for resistive random access memory (RAM) applications.\textsuperscript{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 NSFs are given in Figure 1, which confirmed the successful synthesis of both sets of compounds. The XRD pattern of H-CoErSm NSFs for $x = 0.03$ substitution showed the minor Fe$_2$O$_3$ 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 NSFs and H-CoErSm NSFs have been computed in Table 1. The values of $\alpha$ 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 $D_{\text{XRD}}$ (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 NSFs and 12−15 nm for H-CoErSm NSFs.

Table 1. Refined Structural Parameters of Er$^{3+}$ and Sm$^{3+}$ Codoped CoFe$_2$O$_4$ Nanospinel Ferrite ($x \leq 0.05$) Synthesized via Hydrothermal (H-CoErSm NSFs) and Sonochemical (S-CoErSm NSFs) Approaches

| $x$  | $a$ (Å)   | $V$ (Å$^3$) | $D_{\text{XRD}}$ (nm) (±0.05) | $\chi^2$ | $R_{\text{Bragg}}$ |
|------|-----------|-------------|-------------------------------|----------|------------------|
| 0.00 | 8.396(8)  | 592.10      | 10.2 (±1.19)                 | 4.78     | 1.19             |
| 0.01 | 8.321(7)  | 576.29      | 10.84 (±1.13)                | 0.60     | 0.60             |
| 0.02 | 8.319(0)  | 575.72      | 11.08 (±1.02)                | 0.50     | 0.50             |
| 0.03 | 8.316(0)  | 575.10      | 9.72 (±1.09)                 | 8.48     | 1.09             |
| 0.04 | 8.349(9)  | 582.16      | 16.12 (±1.33)                | 0.83     | 0.83             |
| 0.05 | 8.323(2)  | 576.59      | 9.85 (±0.88)                 | 1.45     | 1.45             |

Figure 1. Rietveld refined XRD powder patterns of Er$^{3+}$ and Sm$^{3+}$ codoped CoFe$_2$O$_4$ nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSFs) and sonochemical (S-CoErSm NSFs) approaches.
where \( I_{\text{obs}} \) and \( I_{\text{calc}} \) 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

\[
R = \left| \frac{I_{\text{obs}}}{I_{\text{calc}}} \right| - \left( \frac{I_{\text{calc}}}{I_{\text{obs}}} \right) \tag{2}
\]

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

\[
I_{\text{hlk}} = 4P^2L_p I_p \tag{3}
\]

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

\[
L_p = \frac{1 + \cos 2\theta}{\sin 2\theta \cos 2\theta} \tag{4}
\]

Table 2. Cation Distribution in \( \text{Er}^{3+} \) and \( \text{Sm}^{3+} \) Codoped \( \text{CoFe}_2\text{O}_4 \) Nanospinel Ferrite (\( x \leq 0.05 \)) Synthesized via Hydrothermal (H-CoErSm NSFs) and Sonochemical (S-CoErSm NSFs) Approaches

| \( x \) | \( T_d \)-site | \( O_h \)-site | \( T_d \)-site | \( O_h \)-site | impurity |
|---|---|---|---|---|---|
| 0.01 | \( \text{Co}_{0.22}\text{Fe}_{0.78} \) | \( \text{Co}_{0.78}\text{Sm}_{0.01}\text{Er}_{0.01}\text{Fe}_{1.2} \) | \( \text{Co}_{0.11}\text{Fe}_{0.89} \) | \( \text{Co}_{0.89}\text{Sm}_{0.02}\text{Er}_{0.02}\text{Fe}_{1.16} \) | \( \alpha\text{-Fe}_2\text{O}_3 \) |
| 0.02 | \( \text{Co}_{0.22}\text{Fe}_{0.78} \) | \( \text{Co}_{0.78}\text{Sm}_{0.02}\text{Er}_{0.02}\text{Fe}_{1.18} \) | \( \text{Co}_{0.11}\text{Fe}_{0.89} \) | \( \text{Co}_{0.89}\text{Sm}_{0.03}\text{Er}_{0.03}\text{Fe}_{1.16} \) |
| 0.03 | \( \text{Co}_{0.22}\text{Fe}_{0.78} \) | \( \text{Co}_{0.78}\text{Sm}_{0.03}\text{Er}_{0.03}\text{Fe}_{1.16} \) | \( \text{Co}_{0.11}\text{Fe}_{0.89} \) | \( \text{Co}_{0.89}\text{Sm}_{0.04}\text{Er}_{0.04}\text{Fe}_{1.14} \) |
| 0.04 | \( \text{Co}_{0.22}\text{Fe}_{0.78} \) | \( \text{Co}_{0.78}\text{Sm}_{0.04}\text{Er}_{0.04}\text{Fe}_{1.14} \) | \( \text{Co}_{0.11}\text{Fe}_{0.89} \) | \( \text{Co}_{0.89}\text{Sm}_{0.05}\text{Er}_{0.05}\text{Fe}_{1.12} \) |
| 0.05 | \( \text{Co}_{0.22}\text{Fe}_{0.78} \) | \( \text{Co}_{0.78}\text{Sm}_{0.05}\text{Er}_{0.05}\text{Fe}_{1.12} \) | \( \text{Co}_{0.11}\text{Fe}_{0.89} \) | \( \text{Co}_{0.89}\text{Sm}_{0.06}\text{Er}_{0.06}\text{Fe}_{1.10} \) |

Figure 2. SEM images of Er\(^{3+}\) and Sm\(^{3+}\) codoped CoFe\(_2\)O\(_4\) nanospinel ferrite (\( x = 0.01, 0.03 \) and 0.05) synthesized via hydrothermal (H-CoErSm NSFs) and sonochemical (S-CoErSm NSFs) approaches.

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, Fe\(^{3+}\) ions occupied the \( O_h \) site, and their occupancy decreased linearly with the substitution of rare earth Sm\(^{3+}\) and Er\(^{3+}\) ions. A trace of \( \alpha\text{-Fe}_2\text{O}_3 \) (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.
NSFs ($x = 0.03$) obtained via EDX. They show the existence of Co, Fe, Er, Sm, and O.

TEM images of the H-CoErSm and S-CoErSm ($x = 0.04$) NSFs 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 NSFs and S-CoErSm NSFs 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 CoFe$_2$O$_4$ samples are between 11.10–16.70% (one via the hydrothermal route) and 12.82–
16.66% (one via the ultrasonic route) in a sweep range of 200−800 nm. Cosubstituted samples with the Sm3+ and Er3+ 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 \( (R_\infty) \) is linked with the absorption quantity \( K \) and the scattering quantity \( S \) by the Schuster−Kubelka−Munk (SKM) theory and related function \( F[R_\infty(v)] \)

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

In the equation, \( K = 0.434kc \), \( k \) is the molar extinction coefficient (m²/mol), \( c \) is the molar concentration of the absorbing species, and \( \alpha \) 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 \( (E_g) \)

\[
\alpha \propto \frac{(hv - E_g)^n}{hv}
\]

\[
(\alpha hv)^{1/n} \propto (hv - E_g)
\]
Here, $h$ is Planck’s constant, $n = 1/2$ for direct and allowed band-gap transitions, and $\nu$ 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 $E_g$, $y = (F(R_\infty)\nu)^2$, and $x = \nu$. 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 NSFs have a direct optical $E_g$ of 1.41 eV. Cosubstitution slightly increases the band-gap magnitudes until $E_{g,max} = 1.48$ 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 $E_{g,max}$ equals 1.44 eV for CoSm$_{0.02}$Er$_{0.02}$Fe$_{1.96}$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$_2$O$_4$ NPs substituted by different single RE ions such as Tb$^{3+}$, Tm$^{3+}$, and Eu$^{3+}$.10,22,29,10,22,29 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$_2$O$_4$ NPs fit well with the direct optical $E_g$ values reported by Ortiz-Quinonez et al.14

**2.4. Magnetic Properties.** The $M$−$H$ curves of H-CoErSm NSFs and S-CoErSm NSFs 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 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 6.** Tauc plots and extrapolated direct $E_g$ data of Er$^{3+}$ and Sm$^{3+}$ codoped CoFe$_2$O$_4$nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSFs) and sonochemical (S-CoErSm NSFs) approaches.

**Figure 7.** Room-temperature hysteresis loops of Er$^{3+}$ and Sm$^{3+}$ codoped CoFe$_2$O$_4$ nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSFs) and sonochemical (S-CoErSm NSFs) approaches.
CoErSm NSFs and S-CoErSm NSFs 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\textsuperscript{35,36}

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

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.

The global saturation magnetization depends on numerous factors, including chemical composition, temperature, density, synthesis conditions, particle size, domain structures, spin order, etc.\textsuperscript{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.\textsuperscript{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 NSFs than in S-CoErSm NSFs. In comparison to pristine H-CoErSm NSFs with $x = 0.00$, $M_s$ is increased upon Er–Sm doping. Although the concentration dependence is 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.\textsuperscript{40} As known, ferrites are ionic crystals, and there are 8 formula units ($\text{MFe}_2\text{O}_4$) 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.\textsuperscript{41} In a unit cell, there are 32 oxygen ions, 8 divalent M\textsuperscript{2+} ions, and 16 three valent Fe\textsuperscript{3+} ions. Depending on the type of the M atom, the positive M\textsuperscript{2+} and Fe\textsuperscript{3+} ions can occupy the center of the tetrahedra or octahedra. In a normal spinel structure, the divalent M\textsuperscript{2+} ions occupy A sites, and the other half occupy B sites.

![Figure 8. $M$ against $1/H^2$ curve of Er\textsuperscript{3+} and Sm\textsuperscript{3+} codoped CoFe\textsubscript{2}O\textsubscript{4} nanospinel ferrite ($x \leq 0.05$) synthesized via hydrothermal (H-CoErSm NSFs) (left) and sonochemical (S-CoErSm NSFs) approaches (right).](https://doi.org/10.1021/acsomega.1c06898)

### Table 3. Concentration ($x$)-Dependence of the Coercivity and Saturation Magnetization Values for Er\textsuperscript{3+} and Sm\textsuperscript{3+} Codoped CoFe\textsubscript{2}O\textsubscript{4} Nanospinel Ferrite ($x \leq 0.05$) Synthesized via Hydrothermal (H-CoErSm NSFs) and Sonochemical (S-CoErSm NSFs) Approaches

| $x$  | $M_s$ (emu/g) | $2H_c$ (kOe) |
|------|--------------|--------------|
| 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      |
The average value of the magnetic moment of rare earth ions is about 5.5 μB (averaged over Sm3+ and Er3+ moments), which is slightly higher than that of Fe3+ ions (5.9 μB). Accordingly, when both Sm3+ and Er3+ ions substitute Fe3+ 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 NSFs, the Fe3+ moments are unbalanced by the insertion of Sm3+ and the Er3+ moments at the B site must align antiparallel to the Co5+ 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 Co3+ ions do not completely quench, and therefore give a large contribution to the magnetic anisotropy field along the (100) crystallographic direction. This anisotropy originates from the spin and orbit of the metallic ion electrons, which are strongly influenced by the arrangement 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 (Sm3+ and Er3+) 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 CoFe2O4 compounds.

However, the Hc 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 (Eg), 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 (E1), surface anisotropy (E2), magnetoelastic anisotropy (E3), and magnetocrystalline anisotropy energy (E4). E3 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 Hc values. E4 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. E2 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. Ei 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 (E2), magnetoelastic anisotropy (E3), and magnetocrystalline anisotropy energy (E4), for both sets of prepared samples of H-CoErSm NSFs and S-CoErSm NSFs.43

3. CONCLUSIONS

This study investigated the properties of Er3+ and Sm3+ codoped CoFe2O4 (NSFs) (x ≤ 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 Eg 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 Sm3+ and Er3+ ions slightly increased the Eg 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 Mx and Hc values was observed upon cosubstituting with Sm3+ and Er3+ ions. For x ≤ 0.02, the Mx value fluctuates for codoped samples prepared via the hydrothermal method. Nevertheless, the Mx value increases with increasing cosubstitution Sm3+ and Er3+ ions up to x = 0.04 for the sonochemically prepared samples. A gradual decrease in Mx value was seen with the further rise in cosubstitution Sm3+ and Er3+ ions (x > 0.04). Noteworthy, the calculated Mx and Hc 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, Fe(NO3)3·9H2O, Co(NO3)2·6H2O, Sm(NO3)3·6H2O, and Er(NO3)3·5H2O, and NH3 solution were obtained from Merck. Benchtop Miniflex X-ray powder diffraction (XRD, Cu Ka 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 ≤ x ≤ 0.05), initially, the stoichiometric weight of metal nitrates was thawed in 50 mL of DI H2O 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 H2O, and then dried at 80 °C in air.15
4.1.2. **Sonochemical Approach.** For the synthesis of S-CoErSm NSFs (0.01 ≤ x ≤ 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.\(^{16,16}\)

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**Notes**

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