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Research Article

Keywords:

Posted Date: September 22nd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10911415/v1>

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Additional Declarations: No competing interests reported.

Influence of La doping on the electrochemically active surface area of single-phase $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ nanoparticles.

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ABSTRACT

Lanthanum-doped cobalt ferrite nanoparticles, $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ ($x = 0.00, 0.04, 0.06$, and 0.10), were synthesized by a protein-assisted sol-gel route using hydrolyzed gelatin as the organic precursor. The structural, thermal, magnetic, and electrochemical properties of the resulting materials were systematically investigated to elucidate the effect of La^{3+} incorporation on their functional performance. X-ray diffraction and Raman spectroscopy confirmed the formation of a well-preserved cubic spinel structure with $Fd\bar{3}m$ symmetry for all compositions, while the thermal analyses demonstrated the stability of the crystallized ferrite phase. The magnetic measurements revealed pronounced temperature-dependent magnetic relaxation, with a progressive decrease in the blocking temperature from above 300 K for the undoped sample to approximately 180 K for $x = 0.10$, indicating the enhancement of superparamagnetic behavior upon La^{3+} incorporation. At room temperature, the nanoparticles exhibited very low coercive fields, confirming their favorable soft-magnetic and thermally activated magnetic response. Electrochemical characterization by cyclic voltammetry demonstrated a systematic increase in the electrochemically accessible surface with increasing La content. The double-layer capacitance increased from 0.6481 to 1.0452 mF cm^{-2} , resulting in an increase in the electrochemically active surface area (ECSA) from 16.20 to 26.13 cm^2 and in the roughness factor from 228.21 to 368.01 for $x = 0.10$. Overall, the results demonstrate that La^{3+} incorporation provides an effective strategy for tailoring the structural and magnetic properties of CoFe_2O_4 while simultaneously increasing the electrochemically accessible surface and the number of available surface active sites. The $\text{CoFe}_{1.90}\text{La}_{0.10}\text{O}_4$ composition therefore exhibits the most favorable combination of nanoscale, magnetic, and electrochemical characteristics, highlighting its potential as a multifunctional material for magnetic and electrocatalytic applications.

INTRODUCTION

Cobalt ferrite (CoFe_2O_4 , CFO) is a widely investigated inverse spinel ferrite known for its high magnetocrystalline anisotropy, chemical stability, and tunable transport properties at the nanoscale. Its structure can be inverse or mixed and is described by the formula $(\text{Co}_x\text{Fe}_{1-x})_A[\text{Co}_{1-x}\text{Fe}_{1+x}]_B\text{O}_4$, where x indicates the fraction of Co ions at the tetrahedral A-sites. Crystallographically, it exhibits a cubic spinel structure belonging to the $Fd\bar{3}m$ space group, in which metal ions occupy the tetrahedral (A) and octahedral [B]

46 sites of the lattice formed by O ions.

47 Cobalt ferrite is a magnetically hard material; it stands out for its high magnetocrystalline anisotropy
48 ($K = 20 \times 10^5 \text{ erg/cm}^3$), high coercivity ($H_c = 750 - 980 \text{ Oe}$), moderate saturation magnetization (M_s
49 $= 80 \text{ emu/g}$), and high Curie temperature (793 K). It also exhibits good mechanical strength and high
50 chemical stability.

51 Various studies demonstrate that CoFe_2O_4 typically exhibits overpotentials slightly higher than those
52 of nickel ferrite, approximately 432 mV at $10 \mu\text{A/cm}^{-2}$ [1]. Tafel slopes generally vary between 60
53 and 83 mV/dec^{-1} , indicating slightly slower kinetics compared to nickel ferrite [2]. This difference is
54 often attributed to the lower intrinsic electrical conductivity of cobalt ferrite and the greater difficulty
55 in forming highly oxidized species during anodic polarization. Conversely, CoFe_2O_4 exhibits excellent
56 structural stability, high mechanical strength, and greater resistance to degradation during prolonged
57 testing characteristics that are important for industrial applications.

58 Cobalt ferrite (CoFe_2O_4) nanoparticles can be synthesized via various physical and chemical routes,
59 including solid-state reaction, co-precipitation, sol-gel, combustion, hydrothermal/solvothermal process-
60 ing, thermal decomposition, the polyol method, microemulsion, and sonochemical, electrochemical,
61 mechanochemical, microwave-assisted, and green synthesis methods [3, 4, 5, 6]. The synthesis route
62 strongly influences crystallite size, morphology, surface area, cation distribution, and defect concentration
63 factors, which ultimately determine the magnetic, electrical, and catalytic properties of the resulting ferrite.
64 Although solid-state and mechanochemical approaches are attractive due to their simplicity and scalability,
65 they generally require high temperatures and can promote grain growth and agglomeration [7, 8]. Wet-
66 chemical methods, particularly co-precipitation, sol-gel, hydrothermal, and solvothermal routes—offer
67 greater control over chemical homogeneity, particle size, and morphology [3, 4, 9]. Among these, sol-gel
68 methods are particularly appealing, as the molecular-level mixing of precursor cations allows for effective
69 control over phase formation and crystallization at relatively low temperatures [10, 11]. In particular,
70 protein-assisted sol-gel synthesis using gelatin provides an environmentally friendly route in which the
71 biopolymer acts as a complexing agent and organic matrix former, promoting a homogeneous distribution
72 of cations and facilitating ferrite formation during calcination [12]. Such control over physicochemical
73 characteristics is highly relevant for electrocatalytic applications, where surface area, defect chemistry,
74 particle size, and cation distribution play a decisive role in determining the accessibility and activity of
75 catalytic sites.

76 Recent literature shows that the partial substitution of Fe with rare-earth ions (RE, such as La, Ce, Nd,
77 Sm, Gd, Dy, and Er) is an effective strategy for modifying the structural, magnetic, electrical, and dielectric
78 properties of cobalt ferrite. Due to the large ionic radii of rare-earth elements compared to Fe, their
79 incorporation into the spinel lattice can induce local distortions, variations in the lattice parameter, internal
80 stresses, and changes in crystallite size, in addition to altering cation distribution between tetrahedral
81 and octahedral sites. Comparative studies involving Ce, Er, and Sm have demonstrated that even low
82 concentrations of rare-earth elements can significantly alter the physical properties of CoFe_2O_4 , while
83 research involving La, Nd, Sm, Gd, and Dy highlights simultaneous modifications in structural, magnetic,
84 and dielectric properties [13, 14, 15]. In particular, substitution with La whose ionic radius is considerably
85 larger than that of Fe tends to introduce greater lattice distortion and crystalline strain; this can affect the
86 spinel structure inversion, the A - B site superexchange interaction, and, consequently, the magnetization,
87 coercivity, and superparamagnetic behavior of the nanoparticles. More recent results also indicate that the
88 combined incorporation of Sm, Gd, and Nd preserves the cubic spinel structure but modifies the local
89 chemical environment and electronic structure, demonstrating that rare-earth doping is an efficient tool
90 for tuning the functional properties of CoFe_2O_4 [13, 16].

91 Among rare-earth dopants, La^{3+} is particularly interesting because its large ionic radius can induce
92 significant crystal lattice distortion and modify cation distribution, potentially offering an effective way to
93 tune the magnetic, electrical, surface, and catalytic properties of CoFe_2O_4 nanoparticles [17, 18].

94 From a structural standpoint, the partial substitution of Fe^{3+} with La^{3+} in $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ (Lax-CFO)
95 alters the spinel lattice due to the larger ionic radius of La^{3+} . In general, this substitution leads to a
96 moderate increase in the lattice parameter and microstrain, while also promoting a reduction in crystallite
97 size in powders obtained via the sol-gel method. Studies on CFO prepared by sol-gel or autocombustion
98 report similar trends for substitution with La and other rare earths, including in some cases the appearance
99 of small amounts of a secondary perovskite phase, such as LaFeO_3 , at higher x values or after more intense
100 calcination. Therefore, this effect should be monitored using Rietveld and FTIR analyses [17, 19, 20].

101 These structural changes are associated with the redistribution of cations between the A and B sublattices,
102 a process that directly influences magnetic behavior and charge transport [17, 21].

103 On the other hand, nanoscale CFO typically exhibits frequency-dependent permittivity governed
104 by interfacial polarization (Maxwell-Wagner/Koops) arising from semiconducting grains separated by
105 more resistive grain boundaries [22]. In La-modified systems, various studies indicate a reduction in
106 AC conductivity and dielectric losses with increasing La content—consistent with the suppression of
107 small-polaron hopping between $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions at octahedral sites and the reinforcement of barrier layers
108 at grain boundaries. In the context of Jonscher's power-law behavior for $\sigma(\omega)$, this manifests as a
109 lower $\tan \delta$ value at low-to-intermediate frequencies, a desirable characteristic for high-frequency and
110 microwave components.

111 From a magnetic perspective, CFO nanoparticles synthesized via the sol-gel method can be engineered
112 to operate in the superparamagnetic (SPM) regime when the particle diameter falls below the critical
113 single-domain size, resulting in negligible coercivity and remanence above the blocking temperature
114 (T_B). La substitution, by modifying surface anisotropy and grain growth kinetics, often aids in size
115 control and allows for the fine-tuning of saturation magnetization (M_s) and coercivity (H_c) through
116 cation redistribution and structural strains; in SPM La-CFO samples, the room-temperature hysteresis
117 curve narrows substantially, while ZFC/FC curves reveal a distinct T_B that varies with size and doping.
118 Such behavior is advantageous for dispersible magnetic adsorbents and separation media, where high
119 magnetization combined with low remanence minimizes agglomeration after the magnetic field is removed.

120 METHODS

121 Lanthanum-doped cobalt ferrite nanoparticles ($\text{CoFe}_{2-x}\text{La}_x\text{O}_4$) were prepared by a protein-based sol-gel
122 route using hydrolyzed gelatin as an organic precursor[23, 24, 25]. Cobalt(II) nitrate hexahydrate, iron(III)
123 nitrate nonahydrate, and lanthanum(III) nitrate hexahydrate were employed as metal sources, maintaining
124 the stoichiometric ratio $\text{Co:Fe:La} = 1:(2-x):x$.

125 The salts were individually dissolved in distilled water, each solution was mixed with gelatin, and
126 subsequently combined under magnetic stirring to obtain a homogeneous precursor solution. The mixture
127 was stirred for 2 h, dried at 373 K for 24 h to yield a xerogel, and then ground into a powder. Calcination
128 was performed at 623 K for 4 h (10 K/min heating rate), producing $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ nanoparticles.

129 X-ray measurements were performed on a Panalytical X'Pert PRO diffractometer, model MPD, set up
130 in Bragg-Brentano configuration, utilizing monochromatic cobalt radiation ($\lambda = 1.78896 \text{ \AA}$) at 40 kV and
131 40 mA. The apparatus featured a parallel beam, a Hybrid@Monochromator, and a $1/4^\circ$ divergence slit. A
132 spinning sample holder was employed, with a diffracted beam path containing a 0.02° Soller slit. Data
133 collection spanned a 2θ range of 20° to 80° , with incremental steps of 0.013° . The lattice parameters
134 were refined using the Rietveld method available in the GSAS II software [26]. Elemental composition of
135 the samples was determined via a ZSXMini II-Rigaku X-ray fluorescence spectrometer, operating at 40
136 kV and 1.2 mA, equipped with a Palladium (Pd) tube.

137 Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) measurements were performed
138 using a Netzsch STA 449F3 Jupiter simultaneous thermal analysis instrument. Approximately 10 mg
139 samples were placed in partially closed alumina crucibles under an inert nitrogen atmosphere (50 mL/min)
140 and heated from room temperature to 1273 K. The measurement data were processed using Protheus
141 Thermal Analysis software to extract characteristic temperatures, reaction enthalpies, and thermograms
142 for the analyzed materials.

143 Magnetization and magnetic susceptibility measurements were performed using a Physical Property
144 Measurement System (PPMS, from Quantum Design) equipped with a VSM module, covering applied
145 external magnetic fields (H) in the range of $\pm 100 \text{ kOe}$ and temperatures (T) between 2 and 300 K.
146 Magnetization was measured during warming at a fixed value of H, following two procedures: (1) the
147 sample was initially cooled in the absence of an applied magnetic field (zero-field-cooled, or ZFC) before
148 the application of H, and (2) the sample was initially cooled with H already applied (field-cooled, or FC).

149 Raman spectroscopy analyses were performed in a LabRAM HR 800 HORIBA equipped with a
150 N_2 -cooled CCD system. Measurements were conducted using a 488nm laser, a 10×VIS objective, and
151 an 1800 grooves mm^{-1} diffraction grating. Spectra were acquired over the range of $150\text{-}1000 \text{ cm}^{-1}$,
152 with a spectral resolution of 5.2 cm^{-1} and an acquisition time of 180s per accumulation, totaling five
153 accumulations per sample.

In the electrochemical measurement, a glassy carbon electrode (GCE) with a geometric area of 0.071 cm² was used as the working electrode. Before use, the electrode surface was polished with α -Al₂O₃ pastes (1.0, 0.3 and 0.05 μ m), washed with ultrapure water and subjected to ultrasonic treatment in ethanol and water. CoFe_{2-x}La_xO₄ nanoparticles ($x = 0.00, 0.04, 0.06, \text{ and } 0.10$) were dispersed in a water/ethanol mixture (1:1, v/v) at a concentration of 1 mg mL⁻¹ and subjected to ultrasonic treatment for 1 h. Subsequently, 7 μ L of the suspension was deposited onto the GCE surface and dried at 60 °C for 20 min, yielding the CoFe_{2-x}La_xO₄/GCE electrodes.

Electrochemical measurements were performed using a Metrohm Autolab potentiostat/galvanostat in a conventional three-electrode cell, with the modified GCE, Ag/AgCl, and Pt serving as the working, reference, and counter electrodes, respectively. Measurements were carried out in 0.1 M KOH. Cyclic voltammetry (CV) was performed from -0.8 to 0.2 V at scan rates from 5 to 300 mV s⁻¹.

RESULTS AND DISCUSSION

XRD measurement

Figure 1 (a) illustrates the Rietveld refinement was carried using the GSAS software for samples (CoFe_{2-x}La_xO₄) at varying x values of 0.00, 0.04, 0.06, and 0.10. As can be seen in the Figure 1 (a), the diffraction profiles adequately fit the crystallographic pattern (ICSD-29630), as evidenced by the fitting parameters reported in Table 1. In every instance, a single-phase cobalt ferrite with cubic symmetry and belonging to the $Fd\bar{3}mZ$ symmetry space group was confirmed. Moreover, the Rietveld refinement analysis, as derived from ICSD-29630 (Table 1), revealed that the lattice parameters decrease progressively with the increased doping of La³⁺ ions in the B site originally occupied by Fe³⁺ ions. This reduction in lattice parameters is also associated with a decrease in crystallite size. The reduction in both crystallite size and/or lattice strain correlates with a broadening of the primary diffraction peaks (311), as shown in Figure 1 (b).

La³⁺ ions have an ionic radius of 1.06 Å, which is larger than the 0.67 Å ionic radius of Fe³⁺, making the direct substitution of La³⁺ into CoFe₂O₄ spinel ferrite nanoparticles challenging. Consequently, La³⁺ ions are typically found at the grain boundaries, where their larger size exerts pressure, hindering grain growth. As a result, the crystallite size of the cobalt ferrite nanoparticles tends to decrease with an increase in La³⁺ content. Another important observation in the patterns is the reduced intensity of diffraction peaks for the doped ferrites (Figure 1 (b)), suggesting a crystallization challenge due to the large ionic size of La³⁺.

The broadening of diffraction peaks in powder X-ray diffraction (XRD) patterns arises from two principal contributions: the finite crystallite size and the presence of microstrain within the lattice (The contribution of instrumental effects to the full width at half maximum was corrected using the LaB₆ NIST standard). The total broadening (considering size and microstrain distribution dominated by Lorentzian), β (in radians), after correction for instrumental effects, can be expressed as

$$\beta_{\text{total}} = \beta_{\text{size}} + \beta_{\text{strain}}. \quad (1)$$

According to the Scherrer relation, the size-induced broadening is inversely proportional to the crystallite size D :

$$\beta_{\text{size}} = \frac{K\lambda}{D \cos \theta}, \quad (2)$$

where K is the shape factor (typically $K \approx 0.9$), λ ($K_{\alpha\text{Co}} = 1.789 \text{ \AA}$) is the X-ray wavelength, and θ is the Bragg angle. The strain-induced broadening is given by

$$\beta_{\text{strain}} = 4\varepsilon \tan \theta, \quad (3)$$

where ε is the micro-strain. Combining these contributions leads to the Williamson-Hall equation in its linearized form:

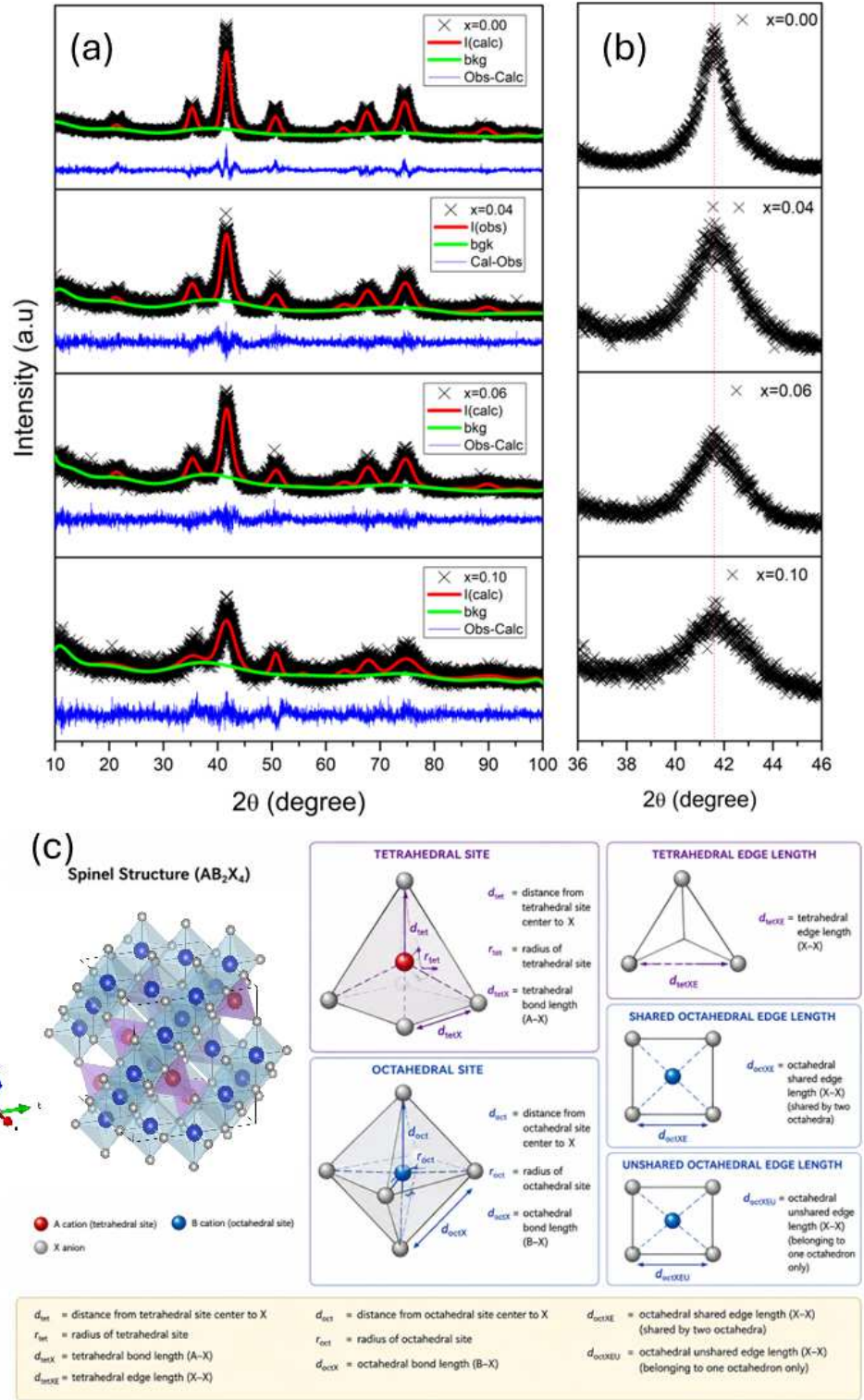


Figure 1. (a) Rietveld refinement of lanthanum-doped cobalt ferrite nanoparticles ($\text{CoFe}_{2-x}\text{La}_x\text{O}_4$) with $x=0.00, 0.04, 0.06, \text{ and } 0.10$, respectively, (b) magnification of the region of the most intense peak corresponding to the (311) plane, and (c) schematic representation of the spinel-type structure.

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta. \quad (4)$$

A plot of $\beta \cos \theta$ versus $4 \sin \theta$ yields a straight line whose intercept gives the crystallite size D and whose slope corresponds to the micro-strain ε .

An alternative and often more reliable method is the Size–Strain plot (SSP) approach [27], which assumes Gaussian-type peak broadening and provides a weighted least-squares estimate of the size and strain. The SSP relation is given by

$$\left(\frac{d_{hkl} \beta \cos \theta}{\lambda}\right)^2 = \left(\frac{K}{D}\right) \left(\frac{d_{hkl}^2 \beta \cos \theta}{\lambda}\right) + \left(\frac{\varepsilon}{2}\right)^2, \quad (5)$$

where d_{hkl} is the interplanar spacing for the (hkl) reflection. A plot of $(d_{hkl} \beta \cos \theta / \lambda)^2$ versus $(d_{hkl}^2 \beta \cos \theta / \lambda)$ produces a straight line, from which the slope yields the microstrain ε and the intercept provides the crystallite size D . The SSP methods are powerful tools for quantifying microstructural parameters in nanocrystalline and polycrystalline materials. The results of this analysis are summarized in Table 1.

The Figure 1(c) schematically shows the distances between ions at tetrahedral (d_{tet}) and octahedral (d_{oct}) sites; the radii of the tetrahedral (r_{tet}) and octahedral (r_{oct}) sites; the tetrahedral and octahedral bond lengths (d_{tetX} and d_{octX}); and the tetrahedral edge length, as well as the lengths of the shared and unshared octahedral edges (d_{tetXE} , d_{octXE} , d_{octXEU}). In this case, the red cations occupy site A (associated with the tetrahedral site), the blue cations occupy site B (associated with the octahedral site), and the gray spheres represent oxygen anions.

Table 1 also summarizes the hopping distances between ions at tetrahedral (d_{tet}) and octahedral (d_{oct}) sites, the radii of tetrahedral sites (r_{tet}) and octahedral sites (r_{oct}), the tetrahedral and octahedral bond lengths (d_{tetX} and d_{octX}), as well as the tetrahedral edge, and the shared and unshared octahedral edge lengths (d_{tetXE} , d_{octXE} , d_{octXEU}). These quantities were calculated from the experimental lattice parameter (a), the oxygen positional parameter ($u = 0.381 \text{ \AA}$), and the oxygen ion radius ($R_0 = 1.32 \text{ \AA}$) using the following equations.

$$d_{tet} = \left(\frac{a}{4}\right)\sqrt{3} \quad ; \quad d_{oct} = \left(\frac{a}{4}\right)\sqrt{2} \quad (6)$$

$$r_{tet} = (u - 0.25)a\sqrt{3} - R_0 \quad ; \quad r_{oct} = (0.625 - u)a - R_0 \quad (7)$$

$$d_{tetX} = a\sqrt{3}\left(u - \frac{1}{4}\right) \quad ; \quad d_{tetXE} = a\sqrt{2}\left(2u - \frac{1}{2}\right) \quad (8)$$

$$d_{octX} = a\left[3u^2 - \frac{11}{4}u + \frac{43}{64}\right]^{1/2} \quad ; \quad d_{octXE} = a\sqrt{2}(1 - 2u) \quad ; \quad d_{octXEU} = a\left[4u^2 - 3u + \frac{11}{16}\right]^{1/2} \quad (9)$$

It is evident from Table 1 that the ion-hopping distances at tetrahedral (d_{tet}) and octahedral (d_{oct}) sites decrease with La content (x). It is worth noting that d_{tet} and d_{oct} represent the separation between cations at the A and B sites.

Thermal analysis

The thermal behavior of the La-doped cobalt ferrite nanoparticles was investigated by simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses in flowing air from room temperature to 1273 K at a heating rate of 10 K min^{-1} . Figure 2 shows that all compositions exhibit similar thermal profiles, indicating that lanthanum incorporation does not significantly alter the thermal decomposition pathway of the spinel ferrite.

Table 1. Rietveld refinement parameters. Crystallite size determined using the Scherrer, Williamson - Hall, and SSP methods. Spontaneous magnetization, remanence, coercive field, and anisotropy constant obtained from magnetic isotherm curves. Blocking temperatures, irreversibility temperature, and effective anisotropy estimated from ZFC susceptibility curves. Raman-active vibration modes for one, two, and three dimensions.

Parameters	x=0.00	x=0.04	x=0.06	x=0.10
a (Å)	8.36(19)	8.34(15)	8.34(00)	8.30(75)
V (Å ³)	584.(7)	580.(4)	580.(1)	573.(4)
ρ (g/cm ³)	5.331	5.522	5.601	5.821
χ^2	1.33	1.31	1.31	1.32
R_{Wp}	0.2014	0.1958	0.1910	0.2001
R_p	0.1517	0.1489	0.1453	0.1515
$D_{Scherrer}$ (nm)	5.92	4.82	4.65	3.51
D_{W-H} (nm)	7.51	6.99	6.16	-
D_{SSP} (nm)	6.64	5.74	5.27	1.37
ϵ_{W-H} ($\times 10^{-3}$)	4.14	7.35	5.95	-
ϵ_{SSP} ($\times 10^{-2}$)	4.97	7.46	6.54	20.5
d_{tet} (Å)	3.6208	3.6119	3.6113	3.5972
d_{oct} (Å)	2.9563	2.9491	2.9485	2.9371
r_{tet} (Å)	0.5773	0.5726	0.5723	0.5649
r_{oct} (Å)	0.7203	0.7153	0.7149	0.7070
d_{tetX} (Å)	1.8973	1.8926	1.8923	1.8849
d_{octX} (Å)	4.7487	4.7371	4.7362	4.7178
d_{tetXE} (Å)	3.0982	3.0907	3.0901	3.0782
d_{octXE} (Å)	2.8144	2.8076	2.8070	2.7961
d_{octXEU} (Å)	2.9580	2.9508	2.9502	2.9388
3K				
M_s (emu/g)	53.30	37.63	31.81	20.33
k_1 ($\times 10^6$ J/m ³)	1.033	1.230	1.146	0.928
M_r (emu/g)	29.82	15.82	12.52	7.16
H_c (kOe)	17.50	17.63	16.61	18.05
300K				
M_s (emu/g)	48.49	31.32	25.85	18.04
k_1 ($\times 10^6$ J/m ³)	1.686	1.333	1.159	0.923
M_r (emu/g)	3.42	0.66	0.40	0.14
H_c (kOe)	0.25	0.13	0.12	0.09
T_B (K)	> 300	$\approx$ 250	$\approx$ 225	$\approx$ 180
T_{irr} (K)	> 300	$\approx$ 299	$\approx$ 299	$\approx$ 292
K_{eff} V (J)	$> 1.05 \times 10^{-19}$	8.80×10^{-20}	7.87×10^{-20}	6.29×10^{-20}
K_{eff} (J/m ³)	$> 6.84 \times 10^5$	8.89×10^5	1.03×10^6	4.68×10^7
T _{2g} (1)	266.51	269.03	269.84	267.83
E _g	321.13	329.57	329.97	328.16
T _{2g} (2)	480.58	481.49	479.76	482.68
T _{2g} (3)	572.02	569.77	574.66	570.92
A _{1g}	678.53	682.84	684.24	681.13

226 The TG curves reveal a relatively small total mass loss, ranging from approximately 7.2 to 8.2%, with
227 residual masses between 91.15 and 92.78% at 1273 K. The first mass-loss event (approximately 4.3-6.4%)
228 occurs below 473 K and is attributed to the evaporation of physically adsorbed water and residual moisture
229 trapped on the particle surface. A second mass-loss stage, accounting for approximately 1%, is observed
230 between 473 and 973 K and is associated with the decomposition of residual organic species derived
231 from the gelatin precursor as well as the oxidation of carbonaceous residues formed during the polymeric

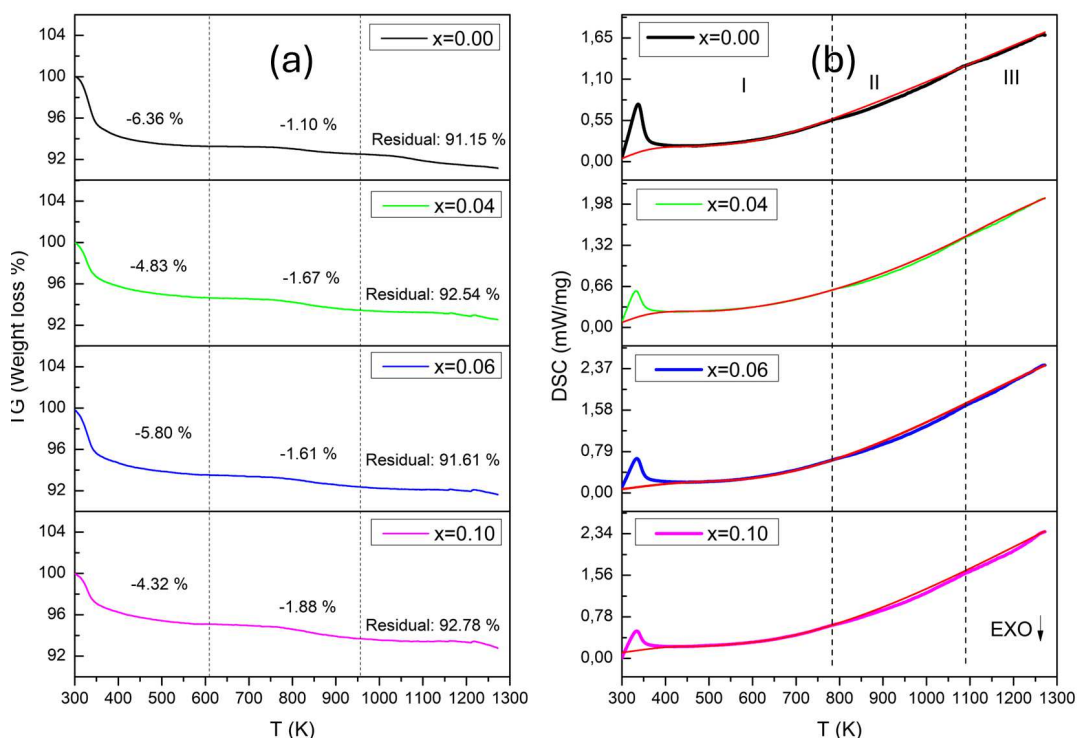


Figure 2. (a) TG and (b) DSC measurement for lanthanum-doped cobalt ferrite nanoparticles ($\text{CoFe}_{2-x}\text{La}_x\text{O}_4$) with $x = 0.00, 0.04, 0.06$, and 0.10 , respectively.

sol-gel process. Above 973 K, only a slight additional mass variation ($<2\%$) is detected, indicating that the spinel phase is thermally stable and that no significant decomposition occurs up to 1273 K.

The DSC curves exhibit three characteristic thermal events. The first broad endothermic peak, centered between 300 and 400 K, is attributed to the removal of physisorbed water and the dehydration of hydroxyl groups weakly bonded to the particle surface. A second thermal event is observed at approximately 750-1080 K for all compositions. This exothermic process is assigned to the combustion of residual organic matter together with the crystallization and ordering of the cobalt ferrite spinel structure. Similar crystallization temperatures have been reported for cobalt ferrites synthesized by polymeric precursor and sol-gel methods, where the decomposition of the organic matrix is followed by rapid nucleation of the inverse spinel phase [28, 29].

A third exothermic peak appears between approximately 1080 and 1250 K. This high-temperature event is associated with structural rearrangements involving cation redistribution between tetrahedral and octahedral sites, accompanied by improved crystallinity and a reduction of lattice defects. In the samples studied, there is no significant shift in this peak with increasing lanthanum concentration, suggesting that La^{3+} ions do not influence diffusion kinetics during the final stage of spinel ordering. This supports our assumption that La^{3+} ions are accommodated at the grain boundaries. Otherwise, given that the ionic radius of La^{3+} (1.16 Å) is considerably larger than that of Fe^{3+} (0.645 Å), lanthanum incorporation would introduce local lattice distortions requiring higher thermal energy for complete structural relaxation; such behavior has been reported for rare-earth-doped spinel ferrites, where dopant-induced lattice strain retards cation redistribution while preserving the thermal stability of the ferrite phase [28, 15, 17].

The combination of TG and DSC results demonstrates that the synthesized $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ nanoparticles possess excellent thermal stability after crystallization, with negligible mass loss above 473 K. Consequently, calcination temperatures around 623 K are sufficient to obtain a well-crystallized spinel structure while avoiding unnecessary grain growth that typically occurs at higher temperatures. Furthermore, the preservation of the thermal behavior after lanthanum substitution indicates that the rare-earth

257 dopant does not modify the local crystal structure without compromising the intrinsic thermal stability of
 258 cobalt ferrite.

259 Magnetic measurement

260 The magnetic measurements (M–H isotherms) recorded at 3 K and 300 K are shown in Figure 3. The
 261 saturation magnetization M_s and the magnetocrystalline anisotropy constant K_1 were determined from the
 262 M–H isothermal magnetization curves for each sample at 3 K and 300 K by fitting the high-field region
 263 using the law of approach to saturation (equation 10).

$$M(H) = M_s \left(1 - \frac{a}{H} - \frac{b}{H^2} \right) \quad (10)$$

264 where a is a constant related to the structural defect in a non-magnetic inclusion, b is the parameter that
 265 couples to calculate the magnetic anisotropic constant, and H is the applied magnetic field. The estimated
 266 values of magnetocrystalline anisotropy K_1 and M_s are shown in Table 1 using $k_1 = M_s \sqrt{105b/8}$.

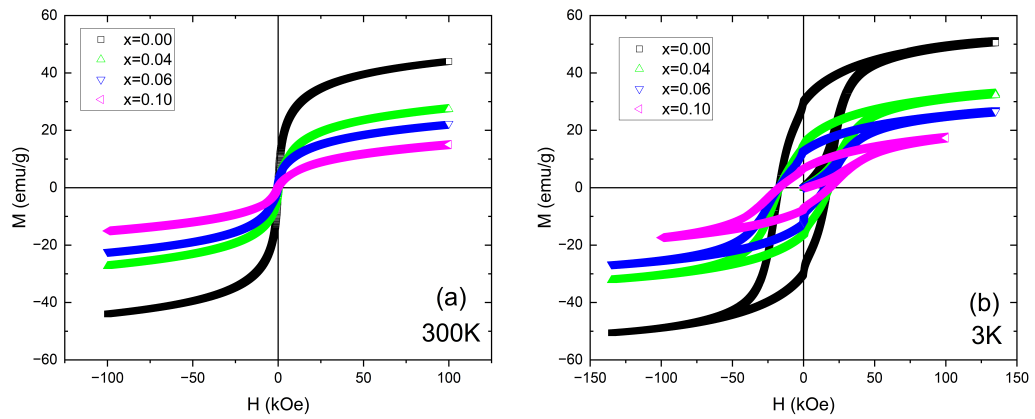


Figure 3. M-H isotherm of (a) temperature of the 300 K and (b) temperature of the 3K, for lanthanum-doped cobalt ferrite nanoparticles ($\text{CoFe}_{2-x}\text{La}_x\text{O}_4$) with $x = 0.00, 0.04, 0.06$, and 0.10 , respectively.

267 At room temperature (300 K), Figure 3 (a), the nanoparticles exhibit superparamagnetic behavior,
 268 as evidenced by a reversible magnetization curve. Upon cooling to approximately 3 K Figure 3(b),
 269 the intrinsic magnetic response of the nanoparticles becomes dominant. Under these conditions, the
 270 magnetization curves display well-defined hysteresis loops characteristic of magnetically hard systems,
 271 with coercive fields of 17.50, 17.63, 16.61, and 18.05 kOe for compositions $x = 0.00, 0.04, 0.06$, and 0.10 ,
 272 respectively. Such behavior indicates that a significant fraction of the particles remains in a magnetically
 273 blocked, nonequilibrium state.

274 In contrast, at 300 K the coercive fields for the same compositions decrease to 0.25, 0.13, 0.12, and
 275 0.09 kOe, respectively. This pronounced reduction is attributed to thermally assisted magnetic relaxation,
 276 which effectively weakens exchange-mediated spin alignment and promotes superparamagnetic reversal.

277 ZFC and FC magnetic measurements

278 The temperature-dependent magnetic susceptibility of the $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ nanoparticles was investigated
 279 through zero-field-cooled (ZFC) and field-cooled (FC) measurements in the temperature range from 3
 280 to 300 K under an applied magnetic field of 100 Oe, as shown in Figure 4. The ZFC and FC curves
 281 exhibit a pronounced irreversibility over a broad temperature range, indicating the presence of thermally
 282 activated magnetic relaxation and a distribution of magnetic energy barriers among the nanoparticles.
 283 Such behavior is characteristic of nanoparticulate ferrites, for which the magnetic moments can undergo
 284 a transition between blocked and superparamagnetic states depending on the relationship between the
 285 thermal energy and the magnetic anisotropy energy [30, 31].

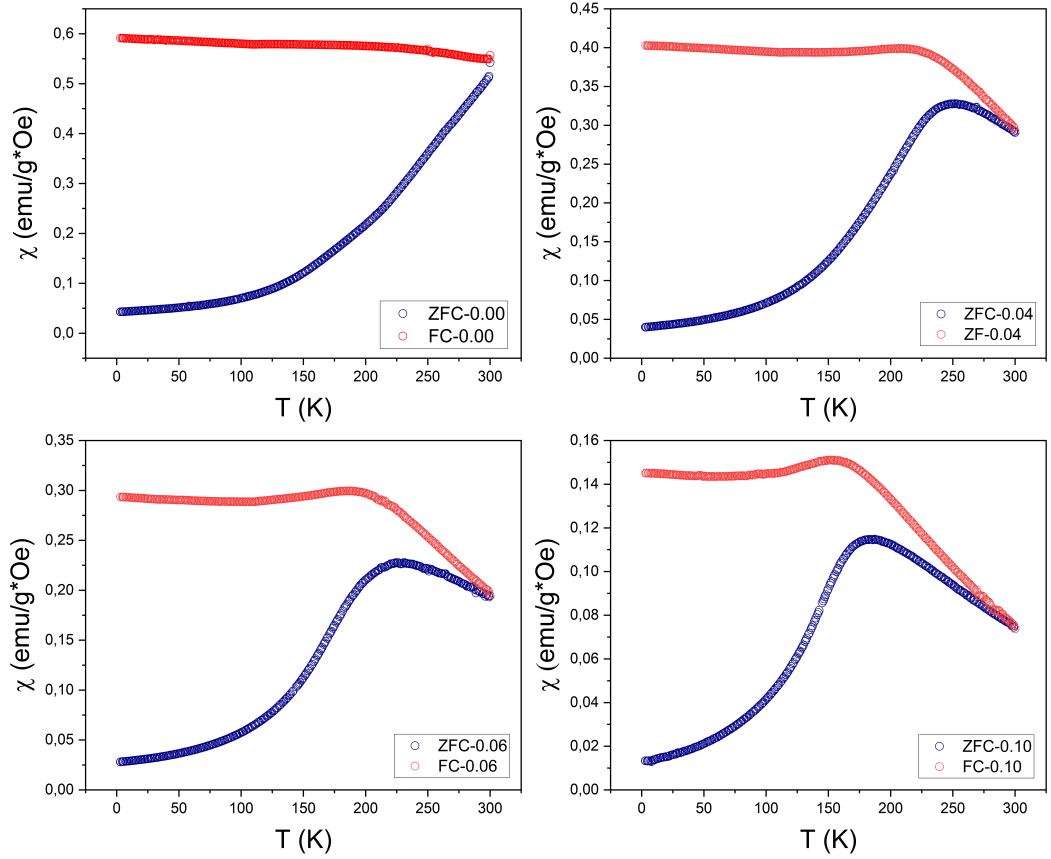


Figure 4. ZFC (red circles) and FC (blue circles) measurements for $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ samples with $x = 0.00, 0.04, 0.06$, and 0.10 , respectively

The blocking temperature (T_B) was initially estimated from the temperature corresponding to the maximum of the ZFC susceptibility curve, following the conventional procedure adopted for superparamagnetic nanoparticle systems [30]. For a system with a distribution of particle sizes and anisotropy energies, the maximum of the ZFC curve represents an effective or mean blocking temperature rather than a unique microscopic transition temperature. In the present case, the estimated values are approximately $T_B \approx 300$ K for $x = 0.00$, $T_B \approx 250$ K for $x = 0.04$, $T_B \approx 225$ K for $x = 0.06$, and $T_B \approx 180$ K for $x = 0.10$. For the undoped sample, however, the ZFC curve continues to rise up to the upper limit of the measurement range. Therefore, the value obtained for $x = 0.00$ should be considered a lower limit that is, $T_B > 300$ K.

A clear decrease in T_B of approximately 120 K is observed with increasing La^{3+} content. The reduction in blocking temperature indicates that La substitution modifies the magnetic anisotropy energy and/or the effective magnetic volume of the nanoparticles, as evidenced by M vs. H and XRD measurements; specifically, the $k_1 (\times 10^6 \text{ J/m}^3)$ value decreases from 1.686 to 0.928 as the La concentration increases, accompanied by a reduction in crystallite size (SSP) from 6.64 to 1.37 nm.

The progressive reduction of T_B is also evident from the evolution of the ZFC curves. The undoped CoFe_2O_4 sample exhibits a ZFC susceptibility that increases continuously across the investigated temperature range, whereas the La-doped samples display a well-defined maximum at progressively lower temperatures. The approximate values extracted from the curves are summarized in Table 1. The decrease in T_B from above 300 K for $x = 0.00$ to approximately 180 K for $x = 0.10$ demonstrates that the incorporation of La^{3+} promotes the transition to the superparamagnetic regime at lower temperatures.

Above T_B , the thermal energy becomes sufficiently large to overcome the magnetic anisotropy energy barrier, allowing the magnetic moments of individual nanoparticles to fluctuate rapidly relative to the experimental time scale. Consequently, the system exhibits superparamagnetic behavior. Below T_B , the

magnetic moments become blocked along preferential directions defined by the magnetic anisotropy, resulting in an irreversible separation between the ZFC and FC curves. Similar ZFC/FC behavior has been reported for CoFe₂O₄ nanoparticles, where the blocking temperature depends strongly on particle size, crystallinity, magnetic anisotropy, and interparticle interactions [32, 30, 31].

The strong dependence of the blocking temperature on the La³⁺ concentration demonstrates that rare-earth substitution offers an effective means of tuning the magnetic relaxation of cobalt ferrite. In particular, the composition with $x = 0.10$ exhibits a $T_B \approx 180$ K and displays superparamagnetic behavior at room temperature, whereas the undoped CoFe₂O₄ sample remains partially or predominantly in the blocked regime at 300 K, although M vs. H measurements in this case do reveal superparamagnetic-like behavior, as the particle size is below the critical size. Therefore, the incorporation of La significantly modifies the temperature at which the magnetic nanoparticles undergo the transition from the blocked state to the superparamagnetic state.

The blocking temperature exhibits a systematic decrease with increasing La³⁺ content, from $T_B > 300$ K for the undoped CoFe₂O₄ sample to approximately 250, 225, and 180 K for $x = 0.04, 0.06$, and 0.10 , respectively. In contrast, the irreversibility temperature remains close to room temperature, with $T_{irr} \approx 299$ K for $x = 0.04$ and 0.06 and approximately 292 K for $x = 0.10$. Consequently, the separation between T_B and T_{irr} progressively increases with La content, indicating a broadening of the magnetic energy-barrier distribution. This behavior is consistent with an increasing contribution from particle-size dispersion, surface anisotropy, structural disorder, and interparticle magnetic interactions.

Within the Néel-Brown approximation, $K_{eff}V = k_B T_B \ln(\tau_m/\tau_0)$, the estimated magnetic energy barrier decreases from values above 1.05×10^{-19} J for $x = 0.00$ to 8.80×10^{-20} , 7.87×10^{-20} , and 6.29×10^{-20} J for $x = 0.04, 0.06$, and 0.10 , respectively. This trend confirms that La incorporation progressively facilitates thermally activated reversal of the nanoparticle magnetic moments. Considering the average crystallite diameters and assuming spherical magnetic volumes, the estimated effective anisotropy constants are $K_{eff} > 6.84 \times 10^5$ J m⁻³, 8.89×10^5 J m⁻³, 1.03×10^6 J m⁻³ and 4.68×10^7 J m⁻³ for $x = 0.00, 0.04, 0.06$ and 0.10 , respectively. These results suggest that, although the magnetic energy barrier decreases with La substitution, the effective anisotropy may increase as the particle volume is reduced.

Raman measurement

Figure 5 shows the Raman spectra of CoFe_{2-x}La_xO₄ samples with La concentrations $x = 0.00, 0.04, 0.06$, and 0.10 , respectively, and the deconvolution into individual Lorentzian peaks. Cobalt ferrite (CoFe₂O₄), an inverse spinel oxide exhibiting magnetic ordering, was investigated by Raman spectroscopy at room temperature using a 488 nm excitation wavelength as the excitation source in the interval 150-750 cm⁻¹. The recorded spectrum for the undoped composition shows five active Raman modes, in agreement with the factor group analysis for the Fd $\bar{3}$ m space group, which predicts five active Raman phonon modes, A_{1g} + E_g + 3T_{2g}.

The A_{1g} mode (~ 678 -685 cm⁻¹) originates from the symmetric stretching vibrations of oxygen atoms with respect to the metal ions at tetrahedral sites and serves as a reliable probe of lattice integrity. The T_{2g}(3) mode (~ 569 -575 cm⁻¹) is attributed to the symmetric bending of Fe/Co/La-O bonds in octahedral coordination, whereas the T_{2g}(2) mode (~ 478 -483 cm⁻¹) is associated with asymmetric stretching vibrations of oxygen, and the T_{2g}(1) mode (~ 265 -269 cm⁻¹) is related to the translational motion of metal cations (Fe³⁺, Co²⁺) of the tetrahedron. In addition, the E_g mode (~ 321 -330 cm⁻¹) is ascribed to the symmetric bending of O-Fe-O bonds. Here, A, E and T are for one dimensional, two dimensional and three dimensional representations, respectively.

The observed Raman peak positions and their relative intensities are consistent with a structurally well-preserved spinel lattice, exhibiting only limited cation inversion. The moderate broadening of the vibrational features suggests the presence of nanoscale effects and/or localized lattice strain. Furthermore, the use of a 488 nm excitation line effectively reduces background fluorescence, thereby enabling a more accurate resolution and assignment of the vibrational modes.

Electrochemical measurement

The electrochemical behavior of the CoFe_{2-x}La_xO₄ nanoparticles was investigated by cyclic voltammetry (CV) at different scan rates ranging from 5 to 300 mV s⁻¹, as shown in Figure 6. The measurements were performed in the potential window from approximately -0.8 to 0.2 V. For all compositions, the current response increased progressively with the scan rate, indicating a significant contribution of capacitive processes associated with the electrochemical double layer. The approximately symmetric evolution of

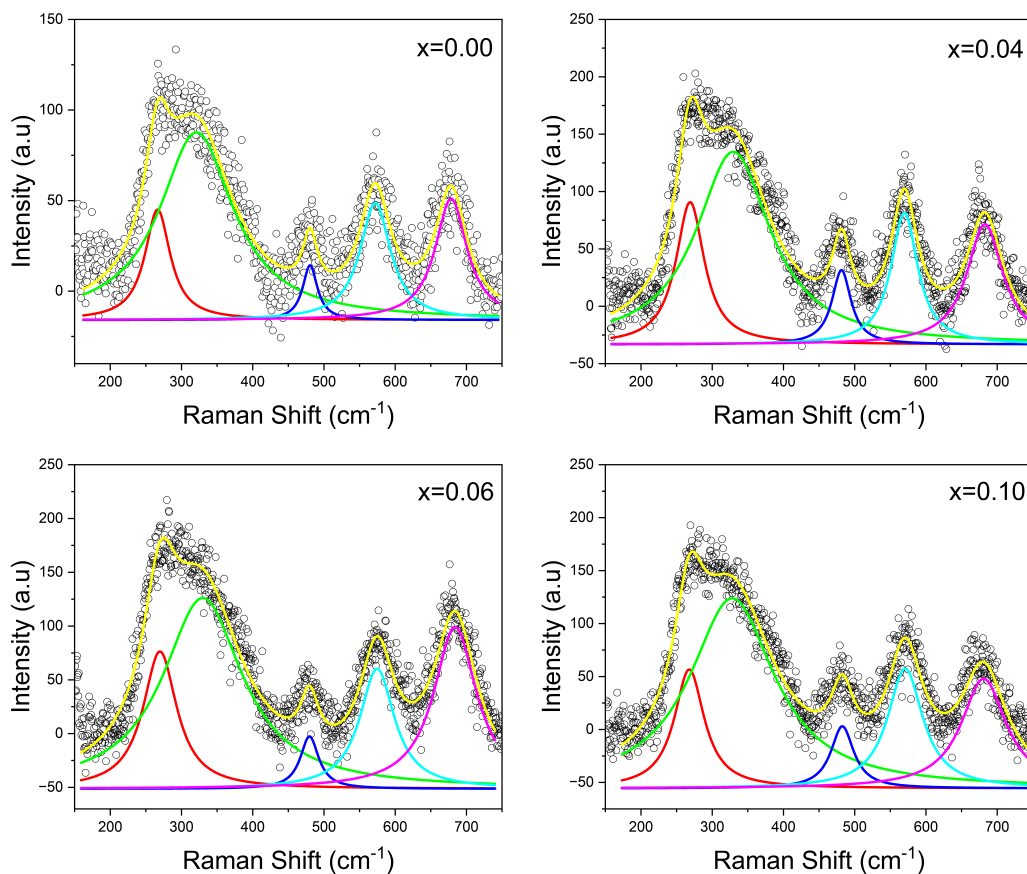


Figure 5. Raman measurement and deconvoluted spectral of samples $\text{CoFe}_{2-x}\text{La}_x\text{O}_2$ with $x=0.00$, 0.04 , 0.06 , and 0.10 , respectively

the anodic and cathodic current branches also indicates good electrochemical reversibility of the surface processes. However, the presence of broad redox features, particularly around -0.3 V, suggests that surface faradaic reactions also contribute to the overall current response. Such behavior is characteristic of transition-metal oxides, in which surface redox processes involving different oxidation states of Co and Fe may coexist with double-layer charging.

A systematic increase in the current density with increasing scan rate is observed for all samples, while the overall shape of the voltammograms is maintained. This behavior indicates that the electrochemical response is strongly influenced by the accessible surface of the electrode and by the kinetics of ion/electron transport at the electrode/electrolyte interface. Importantly, the magnitude of the capacitive current changes with La^{3+} incorporation, demonstrating that the dopant concentration modifies the electrochemically accessible surface of the $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ nanoparticles. Similar behavior has been reported for cobalt ferrite-based electrocatalysts, where changes in synthesis conditions, composition, and surface structure lead to significant variations in double-layer capacitance and electrochemically active surface area (ECSA) [33, 34].

The electrochemically active surface area was estimated from the double-layer capacitance (C_{dl}) obtained from CV measurements performed at different scan rates. In the non-faradaic region, the capacitive current is approximately proportional to the scan rate according to

$$j = C_{dl}v, \quad (11)$$

where j is the capacitive current density and v is the scan rate. Experimentally, C_{dl} was determined from the slope of the linear relationship between the capacitive current and the scan rate (Figure 7). This

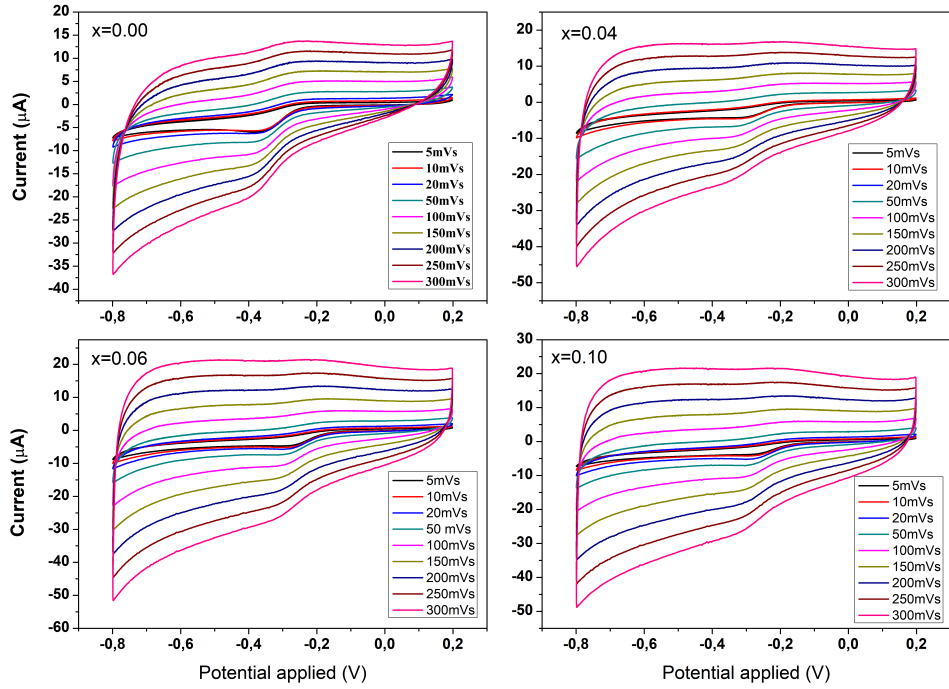


Figure 6. Cyclic voltammograms at different scan rates (5, 10, 20, 50, 100, 150, 200, 250 and 300 mVs^{-1}) of samples $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ with $x=0.00, 0.04, 0.06$, and 0.10 , respectively

approach is widely employed to estimate the electrochemically accessible surface of transition-metal oxide electrocatalysts [33, 34]. The ECSA was subsequently calculated according to

$$ECSA = \frac{C_{dl}}{C_s}, \quad (12)$$

where C_s represents the specific capacitance of a smooth reference surface. Following the convention commonly adopted for metal-oxide electrocatalysts in alkaline media, a value of $C_s = 0.040 \text{ mF cm}^{-2}$ was employed [34]. The roughness factor (R_f), which provides an estimate of the ratio between the electrochemically accessible and geometric electrode areas, was calculated from

$$R_f = \frac{ECSA}{A_{geo}}, \quad (13)$$

where $A_{geo} = 0.071 \text{ cm}^2$ is the geometric area of the working electrode.

Table 2. Electrochemical parameters obtained from cyclic voltammetry for $\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ nanoparticles.

x	C_{dl} (mF cm^{-2})	ECSA (cm^2)	R_f	A_{geo} (cm^2)
0.00	0.6481	16.203	228.21	0.071
0.04	0.8016	20.039	282.24	0.071
0.06	1.0335	25.839	363.93	0.071
0.10	1.0452	26.129	368.01	0.071

The electrochemical parameters obtained from the CV measurements are summarized in Table 2. progressive increase in the double-layer capacitance is observed with increasing La^{3+} content, from 0.6481

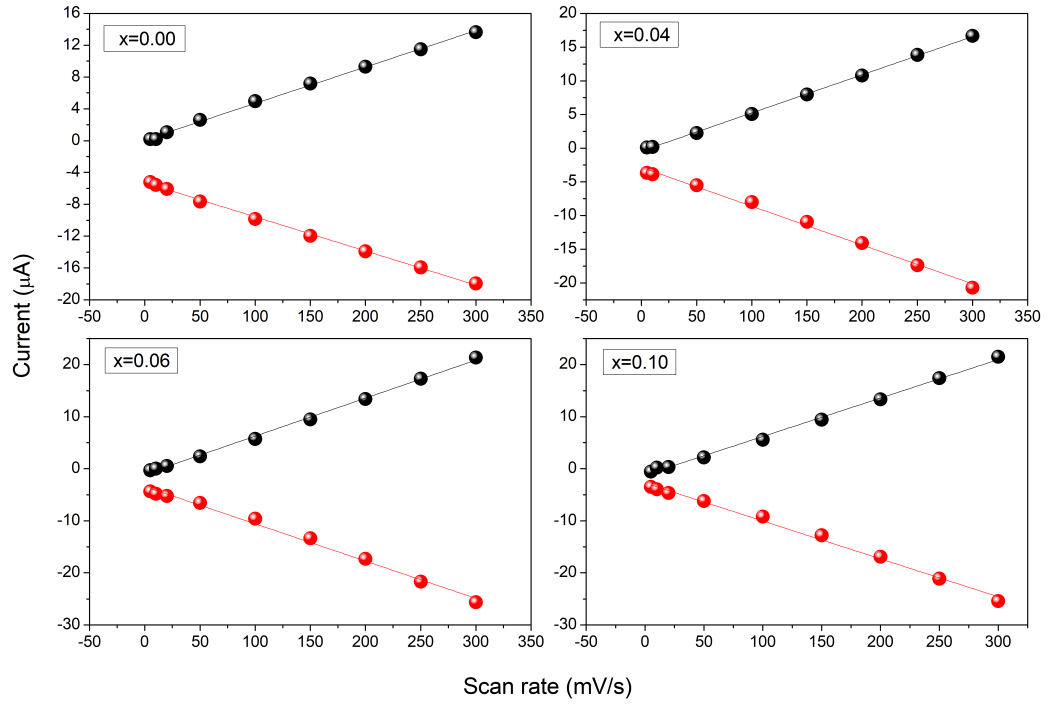


Figure 7. Double layer capacitance calculate by plotting the difference between the anodic and cathodic current density as a function of the scan rate from the cyclic voltammograms of samples $\text{CoFe}_{2-x}\text{La}_x\text{O}_2$ with $x=0.00, 0.04, 0.06$, and 0.1 , respectively

mF cm^{-2} for the undoped CoFe_2O_4 ($x = 0.00$) to $1.0452 \text{ mF cm}^{-2}$ for $\text{CoFe}_{1.90}\text{La}_{0.10}\text{O}_4$ ($x = 0.10$). Considering a specific capacitance of $C_s = 0.040 \text{ mF cm}^{-2}$, the corresponding ECSA values increase from 16.20 to 26.13 cm^2 . Consequently, the roughness factor increases from 228.21 to 368.01 , considering a geometric electrode area of 0.071 cm^2 . These results indicate that La^{3+} incorporation progressively increases the electrochemically accessible surface of the cobalt ferrite electrodes.

The increase in ECSA is particularly pronounced for the samples containing higher La^{3+} concentrations. Compared with the pristine CoFe_2O_4 , the $x = 0.10$ composition exhibits an approximately 61.3% increase in C_{dl} and ECSA. This behavior suggests that La^{3+} incorporation modifies the surface characteristics of the ferrite, potentially through changes in crystallite size, particle morphology, surface defects, and local lattice distortion. The larger ECSA implies a greater electrochemically accessible area and, consequently, a larger population of surface sites available for interfacial charge transfer and catalytic reactions.

1 CONCLUSIONS

$\text{CoFe}_{2-x}\text{La}_x\text{O}_4$ ($x = 0.00, 0.04, 0.06$, and 0.10) nanoparticles were successfully synthesized through a protein-assisted sol-gel method using hydrolyzed gelatin. The combined structural and spectroscopic characterization confirmed the formation of the cobalt-ferrite spinel phase with cubic $Fd\bar{3}m$ symmetry for all investigated compositions, demonstrating the effectiveness of the adopted synthesis route for obtaining high-quality La-modified cobalt ferrite nanoparticles. The Raman spectra further confirmed the preservation of the characteristic vibrational modes of the spinel lattice, while the thermal analyses indicated satisfactory thermal stability after crystallization.

The magnetic characterization demonstrated that La^{3+} incorporation provides an effective means of controlling the magnetic relaxation of the nanoparticles. The blocking temperature progressively decreased from $T_B > 300 \text{ K}$ for pristine CoFe_2O_4 to approximately $250, 225$, and 180 K for $x = 0.04, 0.06$, and 0.10 , respectively. This evolution, together with the strong reduction of the coercive field

at room temperature, indicates an increasing contribution of thermally activated magnetic reversal and superparamagnetic behavior with increasing La concentration. At 300 K, the coercive field decreased from 0.25 kOe for the undoped material to only 0.09 kOe for $x = 0.10$, evidencing the favorable soft-magnetic response of the La-substituted nanoparticles.

From an electrochemical perspective, La^{3+} incorporation produced a clear and systematic enhancement of the electrochemically accessible surface. The double-layer capacitance increased from 0.6481 mF cm^{-2} for pristine CoFe_2O_4 to 1.0452 mF cm^{-2} for $x = 0.10$. Consequently, the estimated electrochemically active surface area increased from 16.20 to 26.13 cm^2 , while the roughness factor increased from 228.21 to 368.01. Thus, the $x = 0.10$ composition exhibited an approximately 61% increase in C_{dl} and ECSA relative to the undoped ferrite. The increase in accessible surface is particularly relevant for electrocatalytic applications because it implies a larger population of exposed surface sites capable of participating in electrode/electrolyte charge-transfer and catalytic reactions.

Overall, the results demonstrate that La^{3+} substitution is an effective strategy for tailoring the functional properties of cobalt ferrite nanoparticles. The preservation of the spinel structure, excellent thermal stability, favorable room-temperature magnetic response, and, most importantly, the significant enhancement of the electrochemically active surface establish the La-doped materials as promising multifunctional candidates for magnetic and electrocatalytic applications. Among the investigated compositions, $\text{CoFe}_{1.90}\text{La}_{0.10}\text{O}_4$ presented the most favorable combination of nanoscale characteristics, magnetic relaxation, and electrochemical surface accessibility, highlighting the beneficial role of La^{3+} incorporation in improving the catalytic potential of cobalt ferrite.

ACKNOWLEDGMENTS

The authors thank CNPq (Process: 402561/2007-4) MCT/CNPq Notice No. 10/2007. Also, thank FUNCAP/CNPq, Process number DC3-0235-00058.01.00/24; NUP No. 31052.000213/2025-16, Call for Proposals: FUNCAP/CNPq Regional Scientific and Technological Development Program (PDCRT) 07/2024. We also thank the Telecommunications and Materials Science and Engineering Laboratory (LOCEM), Structural Crystallography Laboratory (LabCrES) and X-ray Diffraction Laboratory (LRX) of the Department of Physics at the Federal University of Ceará (UFC) for laboratory support.

FUNDING

The authors are grateful to the Brazilian Agencies: Funcap (Grant numbers 31052.000213/2025-16) and CNPq for financial support.

COMPETING INTEREST

The authors declare that they have no competing financial interests.

AUTHOR CONTRIBUTIONS

All authors contributed to the study conception and design. Material preparation, data collection and analysis, and the first draft of the manuscript were written by Dr. Yosdan Martínez Camejo. All authors read and approved the final manuscript.

AVAILABILITY OF DATA AND MATERIAL

Data can be made available upon request.

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