

Influence of Co²⁺ Ions on Structural, Optical, and Magnetic Properties of Inverse Spinel Lithium Ferrite Nanoparticles

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Abstract

The Co-doped lithium ferrite (LiCo_xFe_{1-x}O₄) compound is made using a sol-gel auto-combustion process with metal nitrates and citric acid as fuel. The characterization techniques, including X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy, UV-Vis spectroscopy, vibrating sample magnetometry, cyclic voltammetry, galvanostatic charge/discharge, and impedance, provide an idea about the Co²⁺ content on structural, microstructural, physical, and electrochemical properties. The crystallinity decreases to 13.72 nm as the Co²⁺ concentration increases, and when the Co²⁺ circumstances change, the magnetic characteristics improve as well and change from soft to hard magnetic material. FE-SEM micrographs clearly show defined grain development as the grain size decreased from 10 to 20 nm. The crystallite sizes observed in the XRD data are in good agreement with the TEM's estimate of the particle sizes, which range from 15 to 20 nm.

Categories: Advanced Materials, Nano Materials, Nanotechnology

Keywords: lithium ferrite, cobalt doping, sol-gel auto-combustion, crystallite size, vsm

Introduction

In the inverse spinel ferrite structure, half of the octahedral sites (B) are occupied by divalent metal ions (A²⁺), while the other half are filled by trivalent ions (B³⁺) [1]. The sol-gel auto-combustion method is a cost-effective technique for synthesizing ferrites, producing high-purity powders at low temperatures (Sol-gel auto combustion synthesis and characterizations of cobalt ferrite nanoparticles: Different fuels approach). It provides the ability to control crystallinity and phase purity, making it suitable for the development of advanced materials with customized properties [2]. Cobalt ferrite (CoFe₂O₄) is a magnetic compound recognized for its robust properties and stability. It features an inverse spinel structure, where Co²⁺ ions predominantly occupy octahedral sites, while Fe³⁺ ions are distributed across both tetrahedral and octahedral sites, contributing to its enhanced magnetic characteristics [3]. Cobalt ferrite is advantageous for various magnetic applications due to its low coercivity, high electrical resistivity, and excellent thermal stability, making it effective in minimizing eddy current losses [4,5]. Researchers are exploring the use of lithium ferrite in lithium-ion batteries and other energy storage devices due to its electrochemical characteristics. By introducing lithium in cobalt or altering the synthesis conditions, the properties of lithium ferrite can be adjusted to meet specific requirements [6].

Preeti Thakur et al. used the citrate precursor technique to produce cobalt-doped lithium ferrites. They verified the development of the α-phase using X-ray diffraction (XRD) and observed frequency shifts with different levels of cobalt doping using Fourier-transform infrared spectroscopy (FTIR) [7]. Using sol-gel combustion, M. K. Shobana synthesized lithium-doped cobalt ferrites with an average particle size of 15-20 nm. When lithium concentration increased, conductivity values somewhat dropped due to charge carrier mobility [8]. Cobalt-doped lithium ferrite nanoparticles were produced using the sol-gel process by Manish Srivastava et al. The evolution of distinct size and structural morphologies of the nanoparticles was shown to be significantly influenced by the fluctuation in pH during the production process [9]. Sameen Aslam and associates formed Li-NiCo ferrites by doping with neodymium (Nd) and praseodymium (Pr) using the micro-emulsion process. It has been approximated that Pr³⁺ and Nd³⁺ concentrations affect the magnetic structure and characteristics of lithium ferrite [10]. S. Malathi et al. developed lithium ferrite and lithium vanadium ferrite using a sol-gel method. It was reported that the average particle size of lithium ferrite is 22 nm, while vanadium-doped lithium ferrite has an average particle size of 29 nm [11].

The study aims to explore the impact of Cobalt doping on lithium ferrite for potential supercapacitor

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applications. Using a cost-effective sol-gel auto-combustion method, Cobalt doping lithium ferrite was synthesized. The research indicates that doping lithium enhances the properties of cobalt ferrite, which holds promise for energy storage applications and future supercapacitors.

Materials And Methods

Sol-gel auto-combustion was used to synthesize the $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ ferrite with varying x values, i.e., 0.0, 0.025, 0.050, and 0.075, as shown in Figure 1. Ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), lithium nitrate hexahydrate ($\text{LiNO}_3 \cdot 6\text{H}_2\text{O}$), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), and cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are produced by Merck Chemical Company in India. High-purity AR grades of these chemicals were used as the starting materials. Citric acid and nitrates were maintained at a stoichiometric ratio of 1:3. Each nitrate and citric acid were separately dissolved in double-distilled water to produce clear aqueous solutions. These solutions were then combined and stirred continuously to achieve a homogeneous mixture. Ammonium hydroxide (30%) solution was added gradually to adjust the pH of the mixture to 7. The mixture was then stirred and heated gradually to 100°C . Constant heating led to the formation of a thick gel, which solidified as all water molecules evaporated. The dry gel self-ignited, producing fine ash. The ash was then ground in a mortar to create a uniform powder. After annealing at 500°C , the finished powder samples were used for further characterization.



FIGURE 1: Experimental detail of synthesis of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

Characterizations

XRD examination is used to determine the structural properties of the produced $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$. A scanning electron microscopy (SEM) is used for structural analysis, and an energy-dispersive X-ray analysis (EDAX), which is connected to the SEM, is used for elemental analysis. Transmission electron microscopy (TEM) was used to analyze the size and shape of the nanoparticles. FTIR was used to determine the chemical composition and confirm the results. UV-Vis absorption spectroscopy was used to investigate the optical characteristics. Using a maximum applied field of 17,500 Oe at room temperature, the hysteresis loop, saturation magnetization, and coercivity of the nanocomposites were accurately measured with a

vibrating sample magnetometer (VSM) [12].

Results

X-ray diffraction

Figure 2 displays the XRD patterns for $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ at different ($0.0 \leq x \leq 0.075$). The pattern was recorded in the 2θ range of 20° – 80° using Cu-K α radiation ($\lambda = 1.54182 \text{ \AA}$). All the diffraction peaks could be attributed to reflections from the planes (220), (311), (222), (400), (422), (511), (440), and (440). These reflections could all be indexed to a face-centered cubic. Indexed patterns were compared to those in the databases JCPDS 22-1086 [13] and 41-0971 [14] for phase identification [15]. The XRD pattern's lack of extra peaks suggests that the $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ is single-phase and free of impurity phases.

Crystallite size 'D', lattice constant 'a', X-Ray density 'dx', dislocation density 'pD', and microstrain 'ε' were calculated using Equations (1) to (5) [16,17];

$$D = \frac{0.9\lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

$$a = d\sqrt{h^2 + k^2 + l^2} \dots \dots \dots (2)$$

$$d_x = \frac{8M}{Na^3} \dots \dots \dots (3)$$

$$\rho_D = \frac{1}{D * D} \dots \dots \dots (4)$$

$$\varepsilon = \frac{\beta \cos \theta}{4} \dots \dots \dots (5)$$

where λ is the wavelength of the Cu-K α radiation, β is the full breadth of the half maximum of Bragg's angle θ , (hkl) is the XRD reflection peak index, N denotes Avogadro's number, M is sample molecular weight, and d is the interplanar separation.

The lattice parameters varied from 9.244 to 9.188 Å, whereas the average crystallite size was determined to be between 18 and 13 nm. During the synthesis, Li⁺ ions replace Co²⁺ ions. This replacement modifies the lattice constant by shifting the positions of the cobalt ions inside the crystal lattice, which in turn modifies the arrangement of the atoms [18]. It is the degree of ion substitution and the resulting lattice distortions caused by the variations in ionic radii between Co and Li ions that will define the exact influence on the diameters of the crystallites. The structure of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ allows for the presence of Co²⁺ and Fe³⁺ ions in both tetrahedral and octahedral locations [19]. Moving to octahedral locations causes the lithium ions to arrange more compactly, resulting in smaller crystallites. In contrast, migration to tetrahedral positions produces larger crystallites. The X-ray density (dx) [20] increases from 3.044 to 3.671 gm/cc, almost linearly with the amount of Co²⁺ doping [21]. The microstrain and dislocation density [22] are 0.00207 to 0.00273 % and 0.0145 to 0.0186 line/m², respectively. This occurs when a larger mass of Co²⁺ ions replaces the Fe³⁺ ions on the octahedral sites. Furthermore, microstrain values increase with Co²⁺ concentration, which can be attributed to grain size's impact on the material's overall stress [23]. Here, structural parameters are given in Table 1.

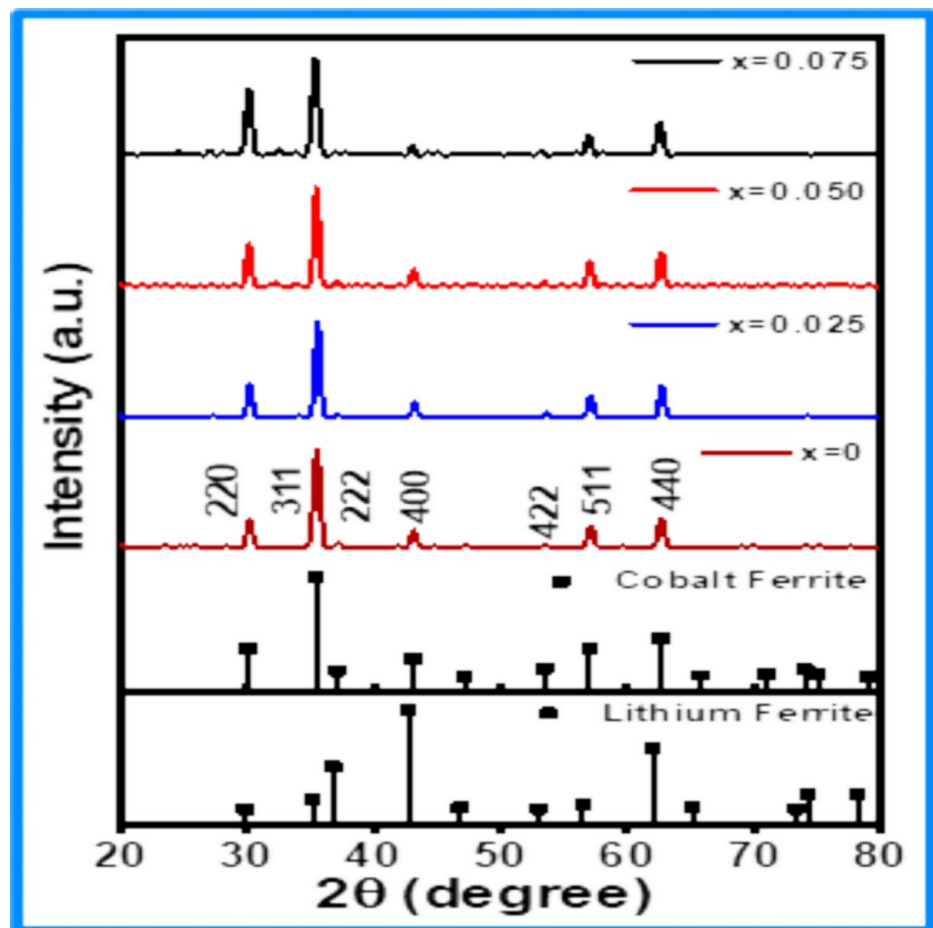


FIGURE 2: XRD analysis of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

XRD, X-ray diffraction

Field emission scanning electron microscopy (FE-SEM)

With the aid of Windows®-based Smart SEM control software, FE-SEM investigation of a sample of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ at $x = 0.075$ was carried out using the Carl Zeiss Model Supra 55 (Germany) with an installation of Windows®-based Smart FE-SEM control software. Figure 3A displays the $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticle's FE-SEM micrographs, which in some regions exhibit nearly spherical-shaped particles and in others, a structure like a flower. Figure 3C displays the histogram of the acquired FE-SEM image. It displays that the material's mean grain size is 287.55 nm. Figure 3B displays the EDAX spectrum of the sample under study, allowing for the identification and characterization of the constituent elements and their relative quantities. It shows that the primary elements present are iron, lithium, cobalt, and oxygen; no indication of contamination from other elements is found. The peaks in the EDAX spectrum properly reflect the true composition of the item under investigation. Table 2 provides an analytical analysis of the EDAX spectra and shows the relative proportions of the components. Furthermore, EDAX mapping is provided for the composition of the produced $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ with $x = 0.075$, as seen in Figure 3D-G. It seems from the image that each component is distributed equally. Fe, O, Co, and Li are represented by the colors brown, red, blue, and yellow, in that order.

Name of samples	Crystallite size (nm)	Lattice constant (Å)	X-ray density gm/cc	Dislocation density line/nm ²	Microstrain %
LiCo _x Fe _{2-x} O ₄ S ₁	15.45	9.244	3.044	0.00145	0.0024
LiCo _x Fe _{2-x} O ₄ S ₂	18	9.221	3.274	0.00308	0.0020
LiCo _x Fe _{2-x} O ₄ S ₃	17.7	9.246	3.424	0.00319	0.0021
LiCo _x Fe _{2-x} O ₄ S ₄	13.72	9.188	3.671	0.00531	0.0027

TABLE 1: Values of crystallite size, lattice constant, X-ray density, dislocation density, and microstrain of LiCoxFe2-xO4

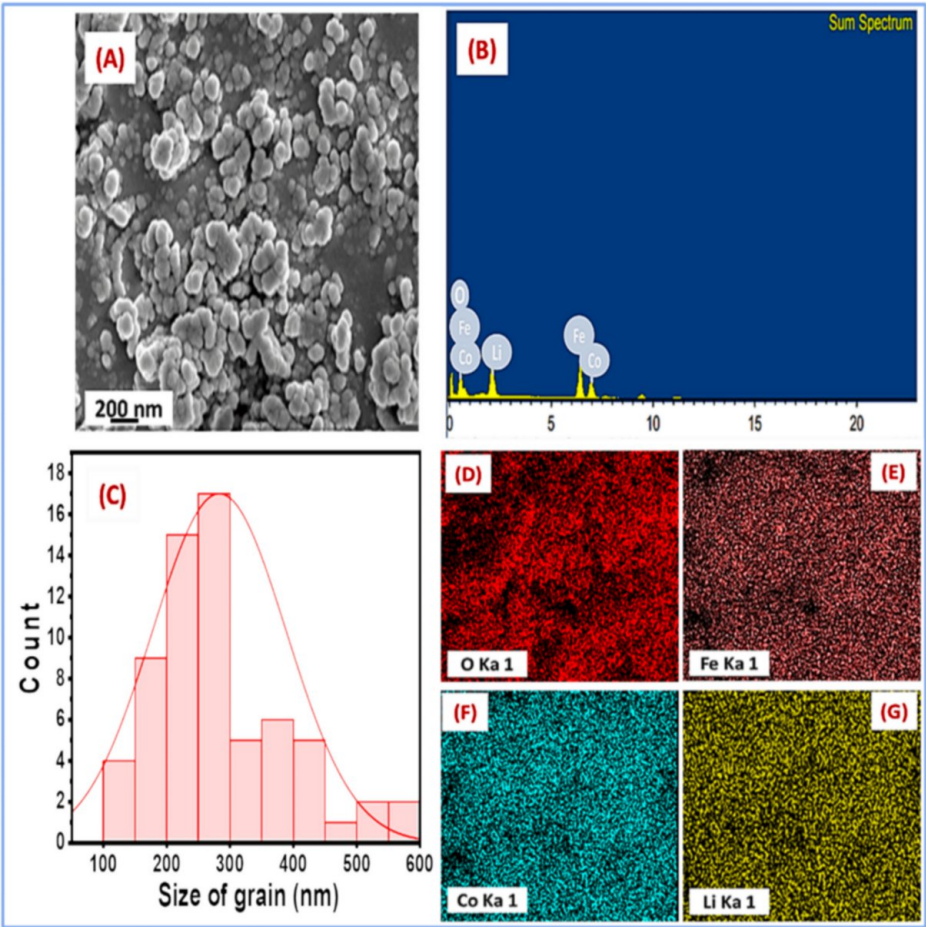


FIGURE 3: (A) FE-SEM image, (B) EDAX analysis, (C) histogram from FE-SEM image, and (D-G) mapping of O, Fe, Co, and Li of LiCoxFe2-xO4 at x = 0.075

FE-SEM, field emission scanning electron microscopy; EDAX, energy-dispersive X-ray analysis

Elements	Weight %	Atomic weight %
Li K	30.01	23
O K	14.52	40.37
Co K	26.76	15.74
Fe K	28.71	20.89
	100.00	

TABLE 2: EDAX elemental analysis of LiCoxFe2-xO4 (x = 0.075)

EDAX, energy-dispersive X-ray analysis

High-resolution transmission electron microscopy (HR-TEM)

The HR-TEM image of LiCoxFe2-xO4 at x = 0.075 is shown in Figure 4A. It showed that there was some little agglomeration in the sample and that surface energy during preparation gave the sample a roughly spherical form. Figure 4B provides evidence that the predicted particle size ranges between 16 and 21 nm, which closely matches the crystallite sizes given in the XRD data. With the use of an HR-TEM, the selected area electron diffraction pattern of LiCoxFe2-xO4 at x = 0.075 is displayed in Figure 4C, displaying a superimposed bright spot that denotes the polycrystalline nature of the nanoparticles. This result confirms the particle dispersion seen in the XRD study.

UV-Vis spectra

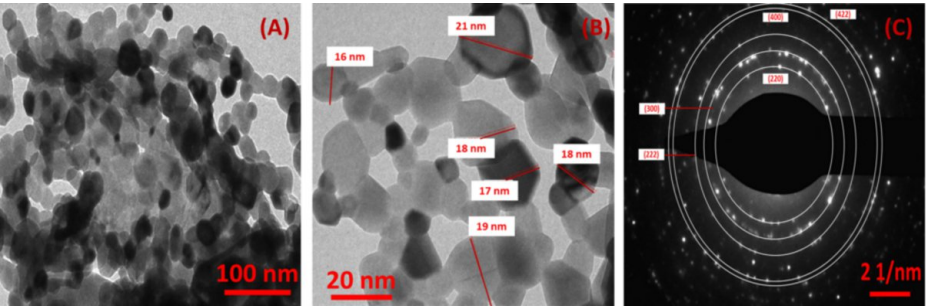


FIGURE 4: (A and B) HR-TEM image and (C) SAED pattern of LiCoxFe2-xO4 at x = 0.075

HR-TEM, high-resolution transmission electron microscopy; SAED, selected area electron diffraction

Figure 5A displays the wavelength-dependent UV-Vis absorption spectra of LiCoxFe2-xO4 (x = 0 to 0.075) nanoparticles synthesized via sol-gel auto-combustion in the 200-800 nm wavelength range. The band gap energy was calculated using the direct formula 6 [24].

$$E_g = \frac{1239}{\lambda}.....(6)$$

where λ denotes the wavelength and Eg stands for the band gap energy [25]. The band gap energy obtained from the equation shifts from 2.07 to 1.74 eV as the amount of Co²⁺ increases, as shown in Figure 5 and Table 3. These values show that the obtained material is a semiconductor material. Distortions in the lattice structure can result from the presence of lithium ions because the ionic radii of Li⁺ and Co²⁺ or Fe³⁺ differ, which may be impacted by these instabilities, which may then have an impact on the energy levels of the electronic state and narrow the band gap [26]. The distribution of cations between the tetrahedral (A) and octahedral (B) sites can be changed by lithium, which has an impact on the band structure as a whole and lowers the band gap.

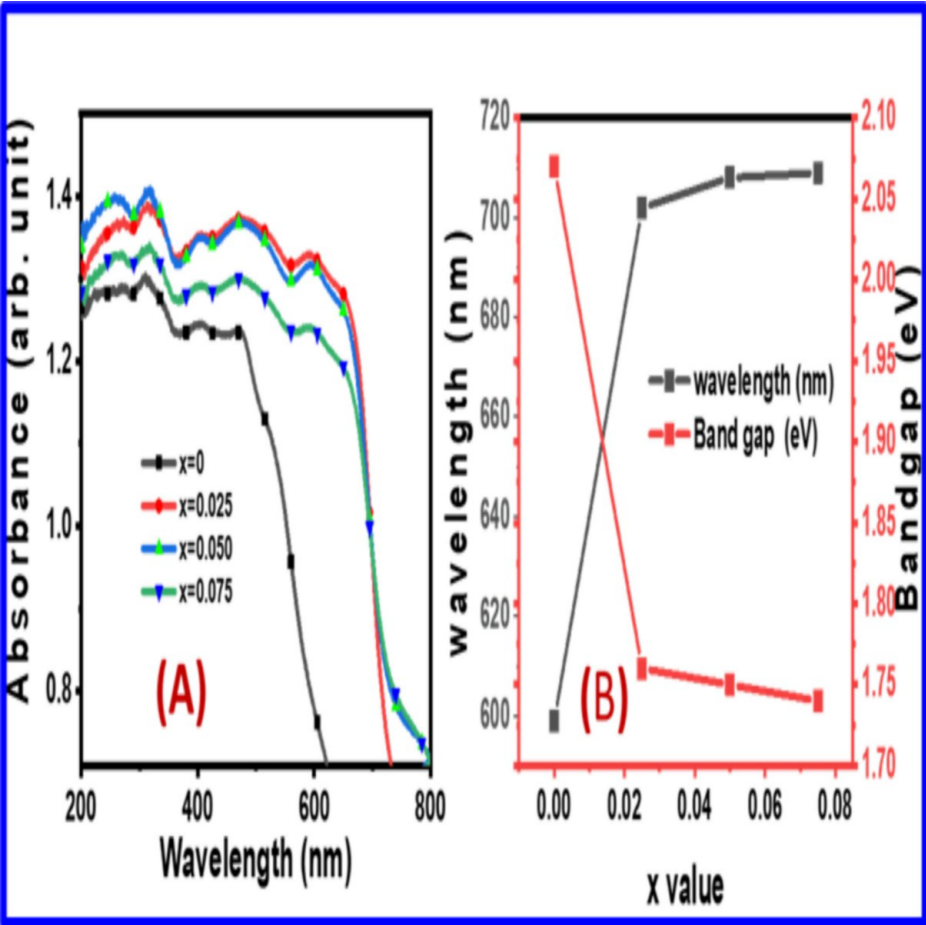


FIGURE 5: (A) UV-Vis absorption spectra and (B) variation of band gap with various concentrations of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

Name of samples	Object wavelength (nm)	Band gap (eV)
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₁	599	2.07
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₂	702	1.76
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₃	708	1.75
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₄	709	1.74

TABLE 3: The variation of band gap for different concentrations of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

Fourier transform infrared (FTIR) spectra

FTIR spectra, which were obtained in the $400\text{--}2000\text{ cm}^{-1}$ wave number range, were used to analyze the structural characteristics of a $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ and are shown in Figure 6A. Two well-defined peaks can be seen in the $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ FTIR spectrum. Tetrahedral complexes (ν_1) are responsible for the peak at roughly $560\text{--}550\text{ cm}^{-1}$, while the high peak at $400\text{--}460\text{ cm}^{-1}$ is caused by the stretching vibrations of octahedral site complexes (ν_2), i.e. metal cation and oxygen [27], given in Table 4. The difference in bond length between the octahedral and tetrahedral positions also affects the band position shift. Force constants at octahedral site K_o , tetrahedral site K_t , and Debye temperatures θ_E [28] are calculated using Equations (7) to (9) [29].

$$k_t = 4\pi^2 c^2 \nu_1^2 \mu \dots\dots\dots(7)$$

$$k_o = 4\pi^2 c^2 \nu_2^2 \mu \dots\dots\dots(8)$$

$$\theta_E = \frac{hc\nu_{av}}{K\beta} \dots\dots\dots(9)$$

In the $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$, the average band wavenumber is ν_{av} , c is the speed of light (2.99×10^{10} cm/s), and μ is the decreased mass of the ions (2.061×10^{-23} g) for Fe^{3+} and O^{2-} . In this case, $K\beta$ stands for the Boltzmann constant, 1.380649×10^{-23} J/K, and h is the Planck constant ($h = 6.626 \times 10^{-34}$ J•s).

The bond length increases when the radius of Li^+ ions is larger than that of Co^{2+} ions, resulting in a decrease in the force constant for both sites, leading to a reduction in electrostatic energy and a lower wavenumber. The FTIR data confirm that Li^+ ions are stabilized in the Oh crystal field as expected, but they occupy Td sites [30]. Analyzing the differences in force constants with Co^{2+} for each $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ sample necessitates a critical examination of the $\text{Fe}^{3+}\text{-O}^{2-}$ band at tetrahedral and octahedral sites. It is observed that the force constants F_t and F_o increase as the concentration of Co^{2+} rises due to the variation in cation-oxygen bond length.

The Debye temperatures (θ_E) of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ vary with increasing Co^{2+} concentration, as shown in Figure 6B and Table 4. The maximum value of θ_E is 687.6278 K at $x = 0.075$. Understanding the conduction mechanism of these ferrites is crucial, and these data point to an enhancement in the lattice vibrations. This suggests that the conduction observed in these samples is most likely the result of n-type electrons. The increase in θ_E is mainly caused by a decrease in the wavenumber of the peak, which is caused by the vibration of the Me-O bond in the tetrahedral site.

Sr. No.	Material	Synthesis method	Crystallite size (nm)	References
1	Vanadium-doped lithium ferrite	Sol-gel	22	[11]
2	Aluminium-substituted lithium nano ferrite	Citrate gel method	27	[31]
3	Cr-doped lithium ferrite	Sol-gel	44	[32]
6	Present work	Sol-gel auto-combustion	13	This work

TABLE 4: Comparison of present work with other ferrite material

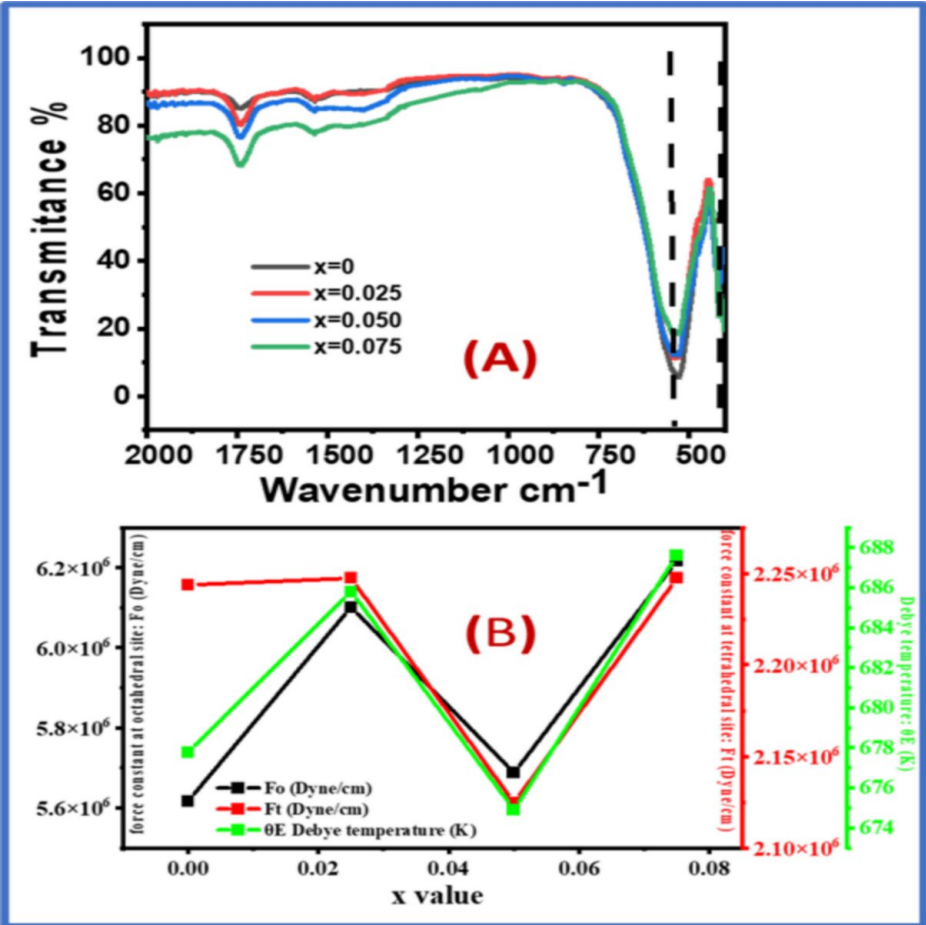


FIGURE 6: (A) FTIR spectra of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075 and (B) variations in the force constant at the octahedral site (F_o), tetrahedral site (F_t), and Debye temperature θ_E of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

FTIR, Fourier transform infrared spectroscopy

Name of samples	$\nu_2 \text{ cm}^{-1}$	$\nu_1 \text{ cm}^{-1}$	F_o (dyne/cm)	F_t (dyne/cm)	Debye temperature (K)
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4 \text{ S}_1$	418.38	526.26	5616646.47	2243671.68	677.783
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4 \text{ S}_2$	418.55	537.27	6101631.96	2247320.58	685.805
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4 \text{ S}_3$	412.72	527.92	5687849.61	2124700.42	674.913
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4 \text{ S}_4$	418.56	539.8	6217376.46	2247535.36	687.627

TABLE 5: Change in force constant of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

Vibrating-sample magnetometry (VSM)

Figure 7 displays the results of the magnetic analysis performed on the $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ samples. The saturation magnetization (M_s), remanence (M_r), and coercivity (H_c) of Cobalt ferrite on Li^+ doping are described here. These results are attributed to Neel's two sublattice models, in which the ions occupying these sites have their magnetic moments organized antiparallely due to exchange energy [33]. The prepared materials convert soft to hard magnetic material as Co^{2+} ions increase. The distribution of Fe^{3+}

and Li^+ ions in the material's A and B sites affects its magnetic behavior. The net magnetic moment is determined by the Li^+ ions, and the total magnetization is influenced by the higher concentration of ions at the B site. The presence of non-magnetic Co^{2+} ions leads to interesting magnetic behavior, causing the magnetization to decrease as Fe^{3+} ions shift from A to B sites due to Co^{2+} 's preference for A sites, thereby increasing magnetization. With an increase in Co^{2+} value, the coercivity (H_c) value rises from 20.89 Oe to 109.1111 Oe before progressively declining. These variations may result from variations in the grain and particle sizes of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$. In $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$, magneto-crystalline anisotropy (K) [34] is calculated by Equation (10),

$$H_c = \frac{2K}{M_s} \dots \dots \dots (10)$$

The anisotropy (K) value increases at $x = 0.025$ and decreases as the concentration of Co^{2+} increases (Table 5). This increase in K is associated with a rise in coercive force, which varies with the Co^{2+} concentration, suggesting that higher Co^{2+} concentrations tend to occupy B -sites, leading to an increase in the K value. This has significant implications for creating novel materials with improved magnetic properties.

$$n\beta = \frac{M_s * \text{MolecularWt}}{5585} \dots \dots \dots (11)$$

The amount of Bohr magnetons [35] is calculated using Equation (11). The non-linear variation in $n\beta$ implies that the magnetization of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ may be influenced by spin canting. The octahedral sites of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ exhibit a triangular spin configuration due to the replacement of Li^+ . The degree of spin canting increases with Co^{2+} in lithium ferrite, demonstrating its effectiveness. When $x = 0.025$, the values of $n\beta$ increase to 1.1357 and subsequently decrease. This research is significant as it shows how spin canting can control magnetization in similar materials and provides insights into magnetization in $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$. The squareness ratio (M_r/M_s) increases with more Co^{2+} ions, going from 0.7199 to 0.3861. When the squareness ratio (R) is less than 0.5 [36], ferrite materials have a multi-domain structure; when it is larger than 0.5, $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ has a single-domain structure. The values of all magnetic parameters are given in the Table 6.

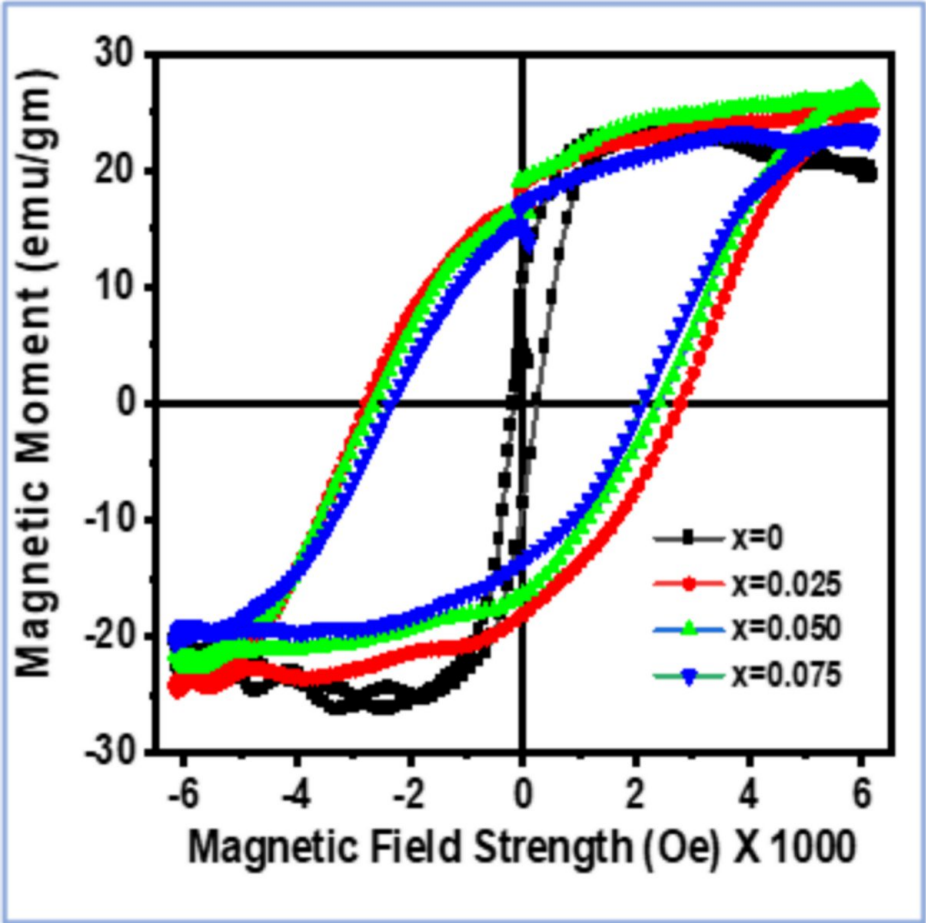


FIGURE 7: The magnetic behavior of of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

Name of samples	Hc (Oe)	Mr (emu/gm)	Ms (emu/gm)	Anisotropy constant K	Bohr magneton (B)	Squareness ratio (Mr/Ms)
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₁	20.89	18.65	27.10	283.00	0.89	0.69
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₂	109.11	18.59	25.82	1408.85	1.14	0.72
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₃	63.89	9.63	24.94	796.59	0.91	0.39
$\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ S ₄	37.44	16.39	24.27	454.31	0.93	0.68

TABLE 6: Change in magnetic parameters concerning of $\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$ where x : 0.0, 0.025, 0.050, and 0.075

Discussion

The findings of the present work consist of increasing cobalt content in lithium ferrite leading to a decrease in crystallite size. Cobalt ions (Co^{2+} and Co^{3+}) replace Fe^{3+} ions in the lattice. The ionic radius of Co^{2+} (0.74 Å) is slightly larger than that of Fe^{3+} (0.64 Å), and Co^{3+} (0.545 Å) is even smaller. This size mismatch causes lattice distortions, hindering crystallite growth and resulting in smaller particles. The strain from the size difference limits lattice expansion, while cobalt doping also introduces defects like vacancies and dislocations, further restricting crystallite growth (Figure 8).

Cobalt’s oxidation state influences crystallite size. Co^{2+} induces more strain than Co^{3+} , disrupting charge distribution and interactions with oxygen ions, which suppresses larger crystallite formation. Co^{2+} also introduces additional electron states near the conduction band, narrowing the band gap. This is due to

interactions between $\text{Co}^{2+}\text{-Fe}^{3+}$ and $\text{Co}^{3+}\text{-Fe}^{3+}$ and the hybridization of Co^{2+} and Fe^{3+} 3d orbitals, which creates intermediate energy levels. These effects lower the energy required for electron transitions and enhance electron delocalization, increasing conductivity.

In summary, cobalt doping reduces crystallite size and narrows the bandgap due to strain, defects, and charge transfer mechanisms that modify the electronic structure and improve conductivity.

The findings show the prepared material can be used in the supercapacitor in the future for supercapacitor application. The specific capacitance will be increased as cobalt is doped in the lithium ferrite.

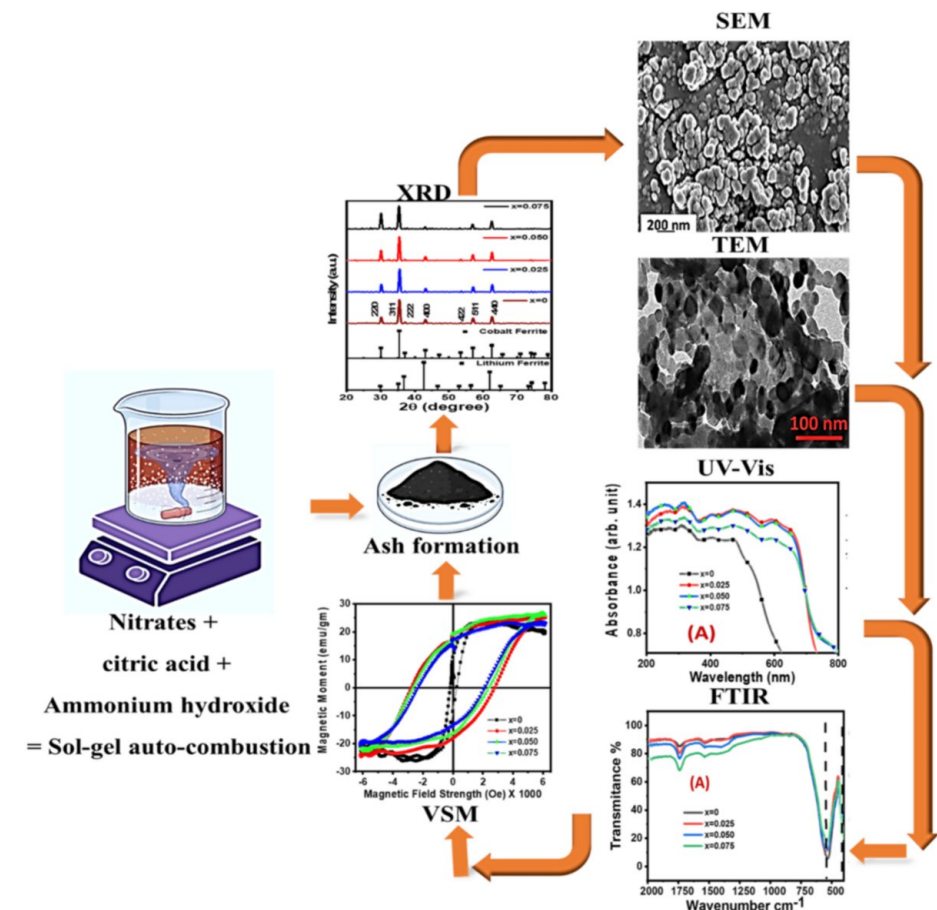


FIGURE 8: Discussion and graphical abstract of the present manuscript procedure and result

SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction; VSM, vibrating sample magnetometry; FTIR, Fourier transform infrared spectroscopy

Conclusions

Lithium ferrites doped with cobalt ($\text{LiCo}_x\text{Fe}_{2-x}\text{O}_4$), where x ranges from 0 to 0.075, were successfully synthesized using the sol-gel auto-combustion method. XRD analysis confirmed a single-phase cubic spinel structure, with crystallite sizes observed between 18 nm and 13.72 nm. As the concentration of Li^+ ions increased in the cobalt ferrite, the lattice parameters expanded from 9.221 to 9.187 Å, which was attributed to the substitution of smaller ions by larger ones. The Raman peaks in the range of 400-460 cm^{-1} corresponded to the stretching vibrations of metal cations and oxygen in octahedral sites, while the peak around 550-560 cm^{-1} was linked to tetrahedral site complexes. FE-SEM images revealed well-defined grain growth, with the grain size reducing from 10 to 20 nm. TEM analysis estimated particle sizes between 16 and 21 nm, which correlated closely with the crystallite sizes obtained from the XRD data. VSM analysis showed that as the lithium content increased, the material transitioned from a soft to a hard ferromagnetic state. Additionally, UV-Vis spectroscopy indicated a trend of increasing optical band gap energy with higher cobalt doping concentrations.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

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Disclosures

Human subjects: All authors have confirmed that this study did not involve human participants or tissue.

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