



Lithium-substituted Nickel Ferrite Nanomaterials and Their Structural, Optical and Electrical Properties for Applications in Green Energy Hydroelectric Cells

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ABSTRACT

The development of hydroelectric cells (HECs) has revolutionized the generation of green and sustainable electricity. In this study, lithium-substituted nickel ferrite ($\text{Li}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$, $x=0.0-0.3$) magnetic nanoparticles were synthesized using the sol-gel method for HEC performance. X-ray diffraction analysis confirmed a reduction in crystallite size from 46.79 nm to 40.97 nm with increasing lithium content. The crystallite size of the material decreases with the increase in the concentration of Li^+ . Also, the particle size decreases with the Li^+ , which is evidenced by the SEM micrograph analysis. The micrographs show the porous microstructure of the material. Photoluminescence studies revealed emission wavelengths between 279 and 558 nm, corresponding to defect states and oxygen vacancies, which increased with lithium substitution. The band gap variation followed the Brus effective mass model. Impedance spectroscopy demonstrated a significant reduction in impedance values for Li^+ -substituted ferrites compared to pure nickel ferrite. The presence of defects and nanopores in the material facilitated enhanced water dissociation, leading to efficient electricity generation *via* redox reactions at Zn and Ag electrodes. The V-I polarization curve indicated that the short circuit current of the Li/Ni-based HEC ranged from 7.5 to 16.64 mA, with the highest value observed for $x=0.3$ (16.64 mA and maximum power of 14.98 mW) due to its high porosity, low charge transfer resistance, and increased defect density. Dielectric studies show that ionic and electronic charge movement influences the hydroelectric cell performance and energy output. The present research findings highlight the potential of lithium-substituted nickel ferrite for improving hydroelectric cell efficiency and advancing sustainable energy solutions.

Keywords: Ferrite; Nanomaterials; Alkali metal; Hydroelectric cell; Green Energy.

1. INTRODUCTION

There is a continuous search for clean and sustainable energy. This has led to a lot of research into renewable energy. Solar, wind, and hydropower have great potential, but they also have challenges. These include the space needed for installation, reliance on weather, and effects on the environment. Hydroelectric cells (HECs) are a new option. They produce electricity by breaking down water molecules on metal oxides or ferrites. They do not need outside energy or electrolytes. This process uses the material's natural features, like unsaturated surface cations and oxygen vacancies, to split water into hydronium (H_3O^+) and hydroxide (OH^-) ions. These ions move to the electrodes, producing an electric current. The usual ferromagnetic behavior of nickel ferrite is facilitated by its unique characteristics, which include low conductivity, low eddy current loss, excellent electrochemical stability, and catalytic behavior (Shanmugavel *et al.* 2015; Gore *et al.* 2015; Rahimi *et al.* 2014; Srivastava *et al.* 2016). It has numerous uses in

various industries, including medicinal applications, memory devices, transformer cores, telecommunications, and microwave absorption (Tartaj *et al.* 2003). With Ni^{2+} ions at octahedral sites and Fe^{3+} ions at tetrahedral and octahedral sites, nickel ferrite exhibits an inverse spinel structure. A recently developed hydroelectric cell uses a specifically processed nanoporous, oxygen-deficient $\text{Mg}_{0.8}\text{Li}_{0.2}\text{Fe}_2\text{O}_4$ combination to dissociate water molecules to produce energy (Tartaj *et al.* 2003; Kargar *et al.* 2016; Atif *et al.* 2011; Aakash *et al.* 2015; Bharathi *et al.* 2009; Jacobo *et al.* 2016; Mozaffari *et al.* 2011). By collecting these ions at the silver and zinc electrodes, a redox process produces electricity (Atif *et al.* 2011). It has also been found that hydroelectric cells based on less resistive magnetite (Fe_3O_4) have higher output current values than those based on magnesium oxide ($\text{Mg}_{0.8}\text{Li}_{0.2}\text{Fe}_2\text{O}_4$) (Nandapure *et al.* 2012). Hydroelectric cells built on several defective oxides, including Al_2O_3 , TiO_2 , SnO_2 , ZnO , SiO_2 , and MgO , have also demonstrated hydroelectric cell performance (Raju *et al.* 2014). Numerous spinel ferrites have been investigated

for use in the production of hydroelectric cells. Several uses for spinel ferrites exist, including high-capacity batteries, rechargeable battery electrodes, water splitting, gas sensing, magnetic and electric characteristics, wastewater cleaning, and photocatalysis (Assar *et al.* 2014a; Assar *et al.* 2014b; Kaiwen *et al.* 2015; Rashad *et al.* 2012). The spinel ferrites have been investigated as solar-powered photocatalysts for water splitting (Rashad *et al.* 2012). For water splitting, lithium ferrite has been employed as a photoanode (Assar *et al.* 2014a). Ni^{+2} (0.72 Å) replacement at Li^{+1} (0.76 Å) is justified by the lower/higher valence and ionic radius. Oxygen vacancies are caused by strain in the lattice due to valence and ionic radius mismatches (Kannan *et al.* 2016).

Adding Ce to magnesium ferrite created a defective structure that could be used to produce hydroelectricity (Ishfaq *et al.* 2023). The Williamson-Hall (WH) plot confirmed that these defects caused compressive strain in the materials, and the presence of oxygen vacancies in the ferrite material caused water to dissociate on its surface. These Ce-based HECs generated a maximum offload current of 5.2 mA and 8.4 mA for $\text{Ce}_x\text{MgFe}_{2-x}\text{O}_4$ and at other concentration cells with an open circuit voltage of 0.86 V and 0.76 V, respectively. Ag- MgFe_2O_4 nanocomposite was used to investigate the green energy generation process via hydroelectric cells by the dissociation of water molecules (Vivek *et al.* 2024). Mesoporosity inside the produced nanocomposite was also confirmed by BET analysis. A large surface area in Ag- MgFe_2O_4 facilitates efficient water adsorption. Ag inclusion enhances electrical conductivity and charge transport, while the linked mesopores speed up ion diffusion and water dissociation. In the meantime, there are plenty of active sites for proton conduction in the MgFe_2O_4 matrix. These characteristics improve electrochemical kinetics, which raises the output voltage. The Ag- MgFe_2O_4 nanocomposite-based hydroelectric cell's voltage-current (V-I) polarization diagram displayed an output power of 25.27 mW, an open circuit voltage of 1.404 V, and an offloading current of 18 mA. When compared to traditional energy generation technologies, the Ag- MgFe_2O_4 nanocomposite has a comparatively small environmental impact. The synthesis process uses low-temperature, solution-based processing, which is consistent with green chemistry principles by lowering energy consumption and avoiding the use of dangerous reagents. Furthermore, the hydropower cell runs in ambient circumstances without the requirement for additional fuel inputs, combustion, or greenhouse gas emissions. X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) data have been used to find that defects exist and their concentration decreases as the pre-sintering temperature rises (Saini *et al.* 2022a). Using LNFO pellets pre-sintered at 750 and 800°C, the hydroelectric cell produced output current densities of 3.8 and 3.6 mA/cm², respectively. The PL and XPS spectra demonstrate that the decrease in defect concentration is the cause of the

output current drop. The generated current densities are twice as high as those seen in hydroelectric cells based on alkali metal substitution (1.7 mA/cm²) (Kumar *et al.* 2020). One of the objectives of the current study is to synthesize Li^{+} -substituted NiFe_2O_4 using an affordable sol-gel method and then measure its properties using advanced tools such as FTIR, SEM, XRD, UV-visible spectroscopy, and PL spectroscopy for its application. Another key goal of this research is to manufacture hydroelectric cells employing these materials and examine V-I polarization properties and electrochemical impedance to gain a better knowledge of green energy production.

2. EXPERIMENTAL MATERIAL AND METHOD

High-purity $\text{LiNO}_3 \cdot x\text{H}_2\text{O}$ (Alfa Aesar), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), and citric acid (Sigma Aldrich) with assays exceeding 99% were utilized. Metal nitrates were combined in an aqueous solution according to their respective ratios. To achieve a uniform, stable, and clear solution, citric acid was dissolved in deionized water and employed as a chelating agent. The resulting mixture was thoroughly blended using a magnetic stirrer. Ammonia Solution (35% Assay Merck) was added dropwise, maintaining the sample's pH at 7. Once the pH reached 7, the temperature was held at 800 °C, and the sample underwent continuous stirring for approximately 5 hours until a viscous gel formed. The gel slurry was then oven-dried. This process yielded a lightweight, porous mass of fragile, flake-like powder. Fig. 1 illustrates the material synthesis process in a flow chart. The final product was subsequently annealed at a temperature of 750 °C for 8 hours. To form a uniform powder, the pre-sintered powders were ground for 15 minutes. Using polyvinyl alcohol (PVA) as a binder, these uniform powders were formed into square pellets measuring 2.54 cm in both dimensions. After that, these pellets were sintered for two hours at a temperature of 950 °C. These pellets were pasted with a zinc plate on one face and silver glued in a comb pattern on the other side.

3. CHARACTERIZATION

The performance of the hydroelectric cell was tested using contacts made from the two electrodes, which are silver and zinc. Using $\text{Cu}(\text{K}\alpha)$ radiation, the structural characterization of LNFO samples was performed at room temperature using an X-ray diffractometer (Bruker D8 Advance) throughout a broad Bragg's angle range (20–80°). A Perkin Elmer LS55 was used to obtain the photoluminescence spectrum. A PerkinElmer FT-IR spectrometer Frontier was used to obtain FTIR spectra. A Zeiss SEM has been used to investigate surface morphology. The Perkin Elmer Scan Lambda 950 was used to gather optical parameters, and the Tauc Plot was used to assess the band gap. A Keithley source meter was used to obtain the HEC voltage-current performance curve.

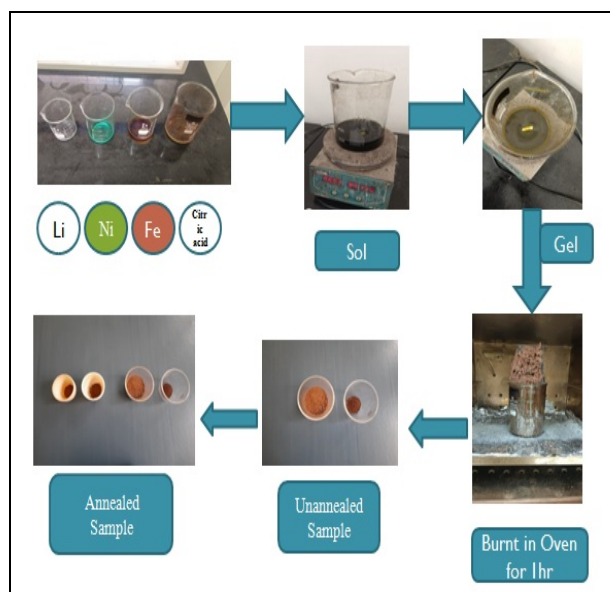


Fig. 1: Flow chart of synthesis of Li substituted nickel ferrite nanomaterials

4. RESULTS AND DISCUSSION

4.1 XRD Measurement and W-H Analysis

The crystallographic phase and crystal structure parameters of the samples were determined through XRD measurements. Fig. 2 shows XRD patterns for the $\text{Ni}_{1-x}\text{Li}_x\text{Fe}_2\text{O}_4$ Samples with $x = 0, 0.1, 0.2$, and 0.3 . All the observed peaks corresponding to planes (220), (311), (400), (422), (511), and (440) are for the cubic spinel structure with Fd-3m space group. It reveals that the Li substitution does not change the crystal symmetry. Similar results have been reported by other researchers (Kumar *et al.* 2020). The prominent (311) peak further

substantiates the spinel phase formation, a common feature in ferrite materials (Naagar *et al.* 2021). As lithium doping (x) increases, a subtle shift in peak positions is noted. Alterations in lattice parameters can explain this due to the replacement of Ni^{2+} (ionic radius = $0.69 \text{ \AA}$) with Li^+ (ionic radius = $0.76 \text{ \AA}$). The average crystallite size can be calculated by using Debye-Scherrer's equation, based on full width at half maximum (FWHM). Typically, lithium doping causes variations in crystallite size due to structural modifications (Saini *et al.* 2022b). Alterations in the relative intensity of diffraction peaks indicate changes in crystallinity and phase purity. The cation distribution between tetrahedral (A) and octahedral (B) sites in the spinel structure is affected by lithium doping, influencing the diffraction patterns (Sharma *et al.* 2021). The observed patterns and peak shifts suggest that while lithium substitution causes slight lattice distortions, it does not disrupt the spinel structure. This observation aligns with previous studies showing that doping impacts the magnetic and electrical properties of ferrites through structural changes (Sandeep *et al.* 2022). From Table 1, it is seen that the average crystallite size increases to 52.98 nm for $x=0.1$ from 46.79 nm for $x=0$, which may result from improved average crystalline growth facilitated by the introduction of lithium ions. This is consistent with observations in doped ferrites, where minor doping promotes enhanced nucleation and reduced microstructural defects (Patil *et al.* 2021). For $x=0.2$ and $x=0.3$, the crystallite size decreases to 39.56 nm and 40.97 nm , respectively. This reduction may be due to increased lattice distortion caused by the substitution of Li^+ ions ($0.76 \text{ \AA}$) for Ni^{2+} ions ($0.69 \text{ \AA}$), leading to strain and disruption in the crystal structure (Kumar *et al.* 2020). The lattice strain for increases from 13 ($x=0.0$) to 13.3 and 14.6 for $x=0.1$ and $x=0.2$, respectively.

Table 1. Structural parameters of lithium doped nickel ferrite ($\text{Ni}_{1-x}\text{Li}_x\text{Fe}_2\text{O}_4$) samples

Sample	FWHM	d(A)	a=b=c(A)	V($\text{\AA}^3$)	Average Crystallite size(nm)	Lattice Strain (10^{-4})
X=0	0.18622	2.512	8.3313	578.28	46.79	13.0
X=0.1	0.16449	2.506	8.3114	574.14	52.98	13.3
X=0.2	0.22028	2.511	8.3280	577.59	39.557	14.6
X=0.3	0.21266	2.513	8.3340	578.84	40.97	12.5

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ions ($0.69 \text{ \AA}$), leading to strain and disruption in the crystal structure (Kumar *et al.* 2020). The increase in lattice strain could be due to the rearrangement of cations within the octahedral and tetrahedral sites of the spinel ferrite structure, resulting in partial relaxation of the lattice (Devsharma *et al.* 2024).

The microstructural characteristics of nickel ferrite are influenced by lithium doping, as evidenced by the observed patterns in crystallite dimensions and lattice

strain. Higher strain values correlate with reduced crystallite sizes, resulting from lattice distortions and defects. This relationship significantly affects the material's magnetic and physical attributes, offering potential uses in catalytic processes and spintronics applications (Yang and Wu, 2022).

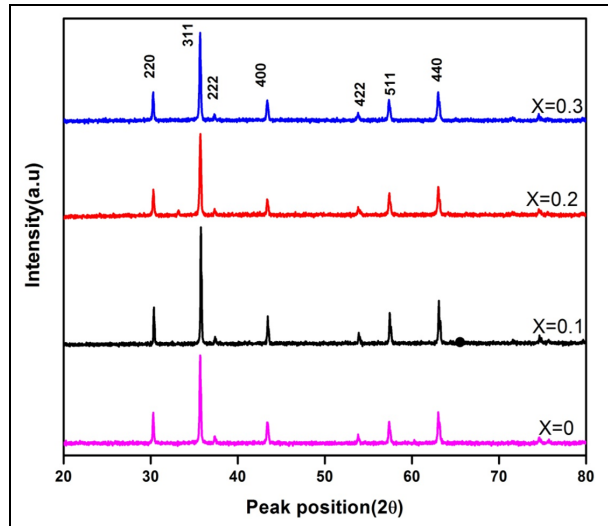


Fig 2: XRD pattern of lithium-substituted nickel ferrite sample annealed at 750°C

The average crystallite size and microstrain have been evaluated using the Williamson-Hall (W-H) equation (Eqn 1), respectively.

$$\beta_{hkl} \cos \theta_{hkl} = \frac{K\lambda}{D} + 4\varepsilon \sin \theta_{hkl} \quad \dots (1)$$

Here, D is the average crystallite size, K is the constant having a value of 0.94 for circular grain, λ is the wavelength of the Cu-K α radiation (0.154 nm), β_{hkl} is the full width at half maxima (in radians), θ_{hkl} is the diffraction angle (in radians), and ε is the micro strain. The Williamson-Hall plot in Fig. 3, which displays $\beta_{hkl} \cos \theta_{hkl}$ on the vertical axis and $4 \sin \theta_{hkl}$ on the horizontal axis, with β_{hkl} representing the full width at half maximum of X-ray diffraction peaks and θ_{hkl} denoting the Bragg's angle. A linear equation was employed to analyze the data points. The gradient of the line correlates with lattice microstrain, while its y-intercept provides insights into average crystallite dimensions.

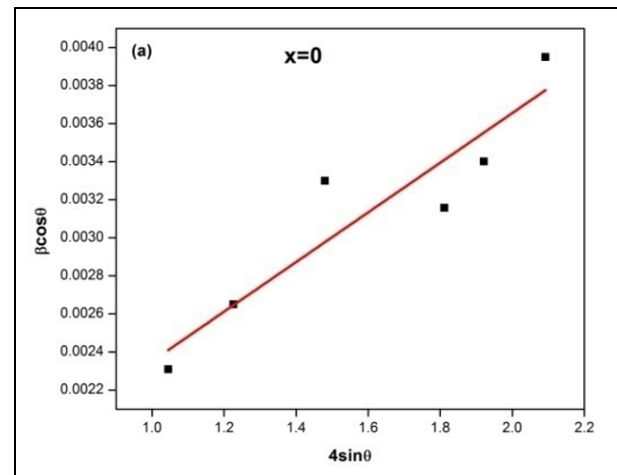
The graph indicates that both microstrain and crystallite size influence XRD peak broadening. Compared to the undoped sample, lithium incorporation appears to modify the W-H parameters, suggesting structural changes in the nickel ferrite lattice. The Williamson-Hall technique is widely employed to distinguish between size-induced and strain-induced broadening in X-ray diffraction analyses. Lithium doping

in nickel ferrite causes structural modifications, potentially due to ionic radius differences between Li^+ and Ni^{2+} , leading to changes in microstrain and crystallite dimensions. The strain calculated from the W-H method is listed in Table 1. The Rietveld refinement analysis of Li^+ substituted NiFe_2O_4 has been carried out, and the refined patterns are depicted in Fig. 4. The XRD patterns for all the samples can be analyzed by considering the cubic spinel structure with Fd-3m space group. Consistent Bragg position alignment and negligible peak splitting indicate that lithium incorporation maintains the single-phase spinel structure. The lattice constant shows a systematic increase with higher lithium doping. This occurs because Li^+ ions (0.76 Å ionic radius) substitute Ni^{2+} ions (0.69 Å ionic radius) at octahedral sites. This linear lattice parameter increase indicates successful nickel-lithium substitution. The refinement also elucidates changes in crystallite size and microstrain.

These distortions create strain within the crystal lattice, leading to smaller crystallites that enhance surface area, beneficial for hydroelectric cell applications. Lithium ions preferentially occupy octahedral sites, displacing some nickel and iron cations. This redistribution significantly affects magnetic and electrical properties, enhancing the material's suitability as functional materials at the nanoscale. Refinement metrics (χ^2) indicate high-quality refinement.

4.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy has been used to study the surface morphology. Average particle size has been evaluated using ImageJ software, with $x=0$, $x=0.1$ and $x=0.2$ having an average grain size of 215, 174 and 138 nm, respectively. The SEM micrographs are shown in Fig. 5, illustrating the surface morphology of NiFe_2O_4 with varying lithium doping concentrations: (a) $x=0$ (undoped), (b) $x=0.1$, and (c) $x=0.3$.



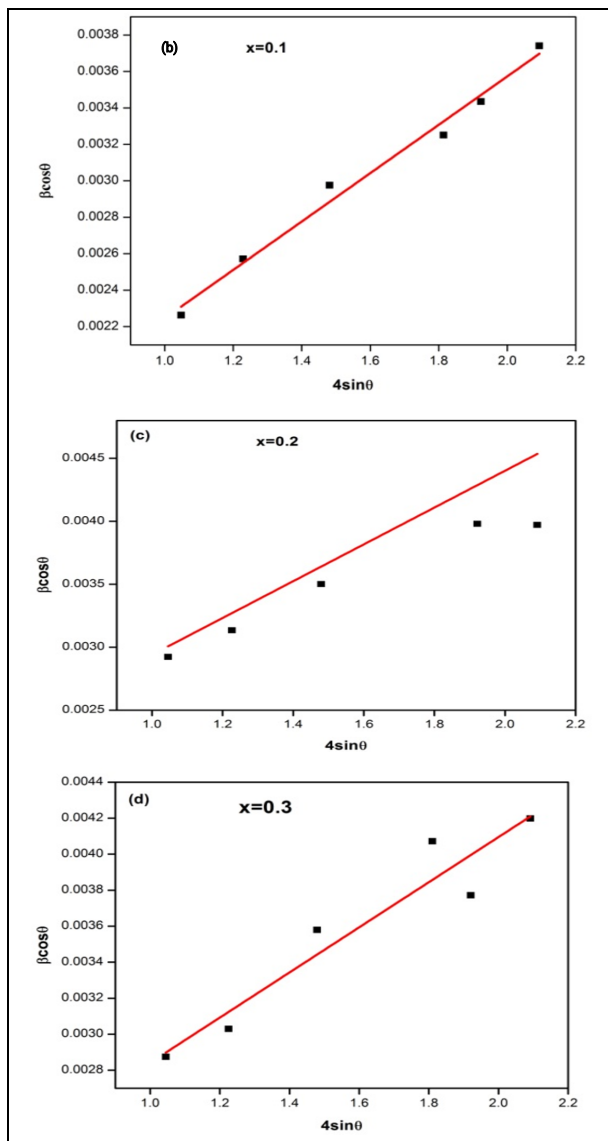
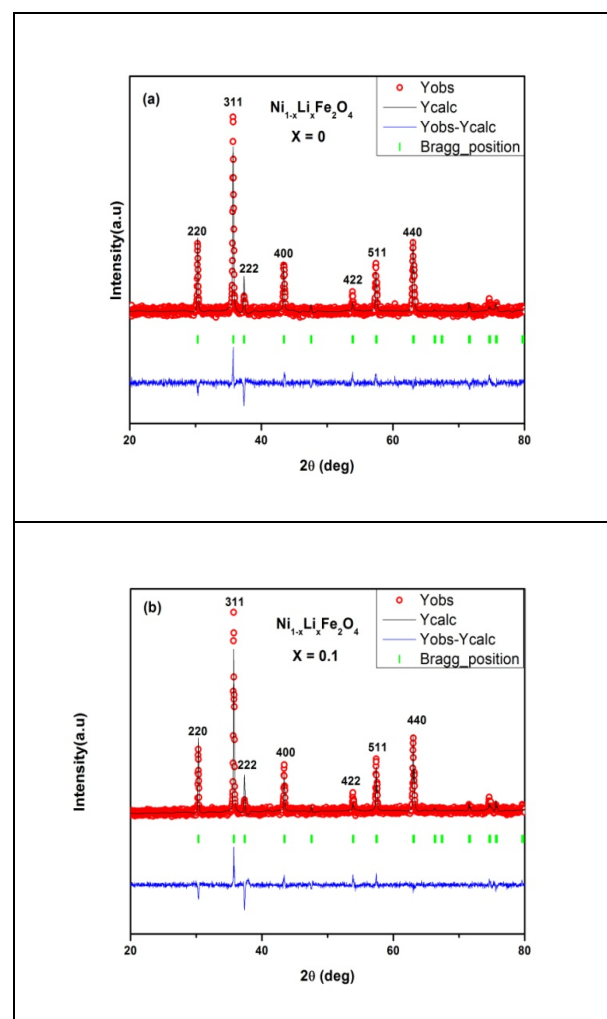


Fig. 3: W-H plots of lithium lithium-substituted nickel ferrite sample annealed at 750°C

The SEM micrograph of the undoped nickel ferrite ($x = 0$) in Fig. 5 (a) shows the largest grain size of 215 nm with a relatively uniform structure. The surface morphology exhibits closely packed grains, providing a lower surface area due to the larger grain size. The SEM image of nickel ferrite doped with lithium at $x = 0.1$ in Fig. 5 (b) demonstrates a noticeable reduction in grain size (174 nm), leading to moderately increased surface roughness. The impact of Li^+ ions on the diffusion kinetics and grain growth mechanisms during synthesis and sintering is responsible for the observed decrease in grain size with increasing Li^+ concentration. Li ions typically occupy interstitial or substitutional lattice sites due to their reduced ionic radius, which causes lattice deformation and increases internal strain inside the crystal structure. Grain growth is suppressed by this

distortion because it prevents grain border migration. Li^+ inclusion can also prevent mass movement and decrease cation mobility during sintering, leading to the creation of finer grains. Grain coarsening is thus successfully inhibited by the higher Li^+ level, resulting in a systematic decrease in grain size. This structural change contributes to enhanced active sites for water dissociation, a crucial mechanism in hydroelectric cells. The intermediate grain size strikes a balance between sufficient conductivity and high surface area, making this material potentially more efficient for HECs than the undoped sample (Bhakar *et al.* 2025). For $x = 0.3$ in Fig. 5 (c), the SEM micrograph pore sizes confirm the mesoporosity in the material. These features are advantageous for hydroelectric cells, as a higher surface area generally improves electrochemical performance. Small grains may increase grain boundary resistance, which could slightly limit overall efficiency (Parry *et al.* 2024). Overall, as the lithium concentration increases ($x = 0$ to $x = 0.3$), the grain size decreases, enhancing surface activity and potentially improving the hydroelectric cell's performance.



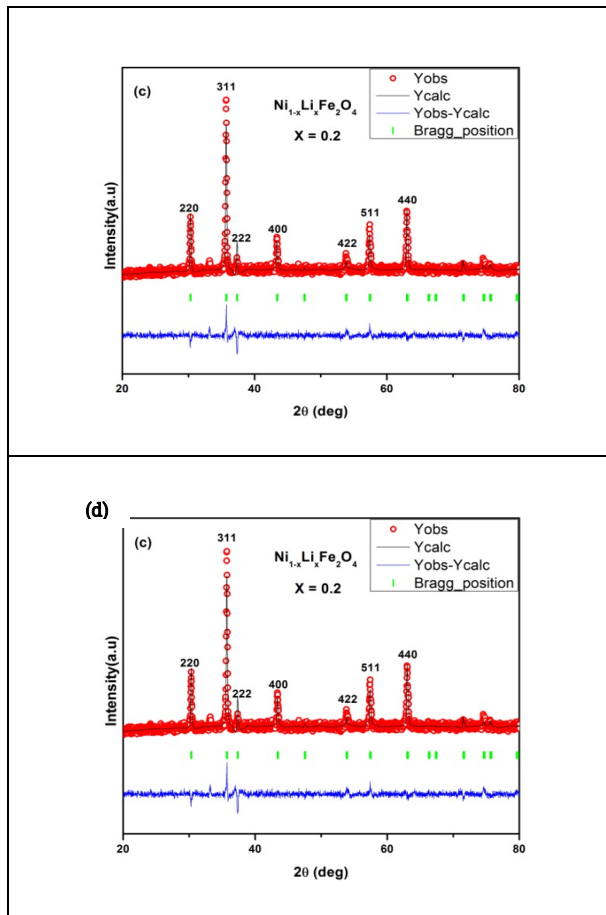


Fig 4: Rietveld refinement of li-substituted nickel ferrite sample annealed at 750°C for (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$

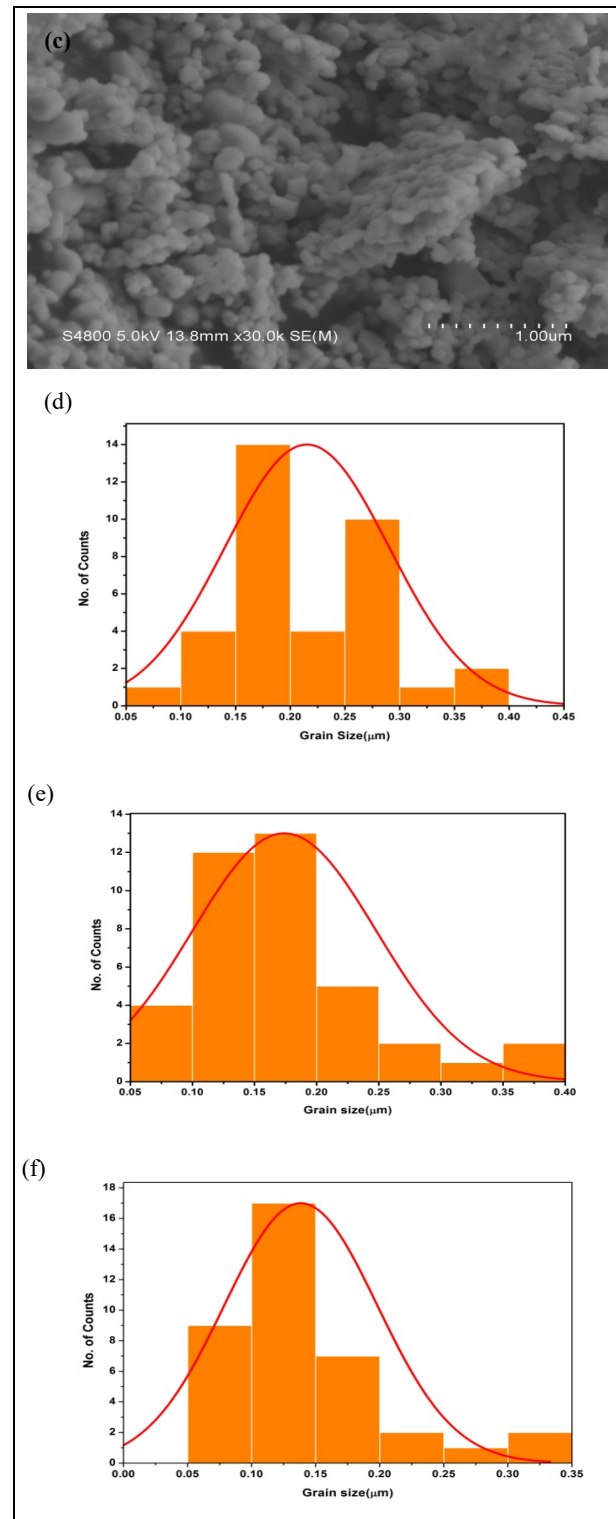
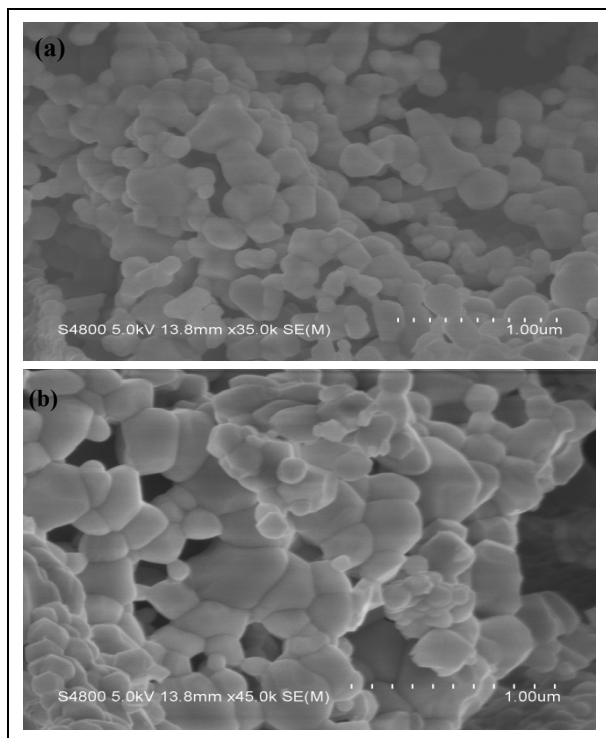


Fig 5: SEM micrographs of Li-substituted nickel ferrite sample annealed at 750°C: (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.3$. Histograms are shown for (d) $x = 0$, (e) $x = 0.1$ and (f) $x = 0.3$

4.3 FTIR Measurement

The FTIR spectra for lithium-doped nickel ferrite (Li^+ substituted NiFe_2O_4) samples show

characteristic absorption bands that provide insights into the structural and compositional changes due to doping.

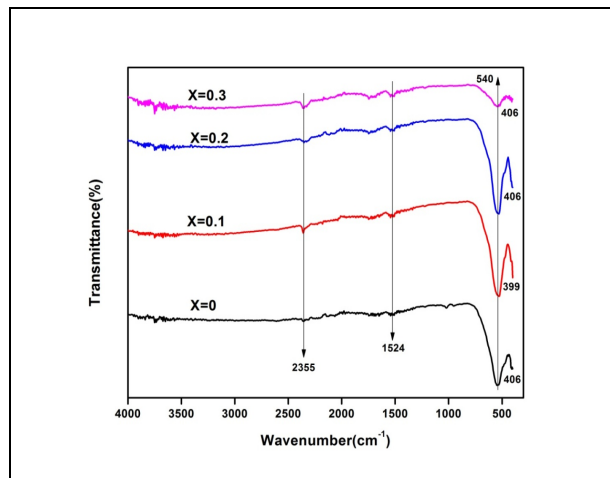


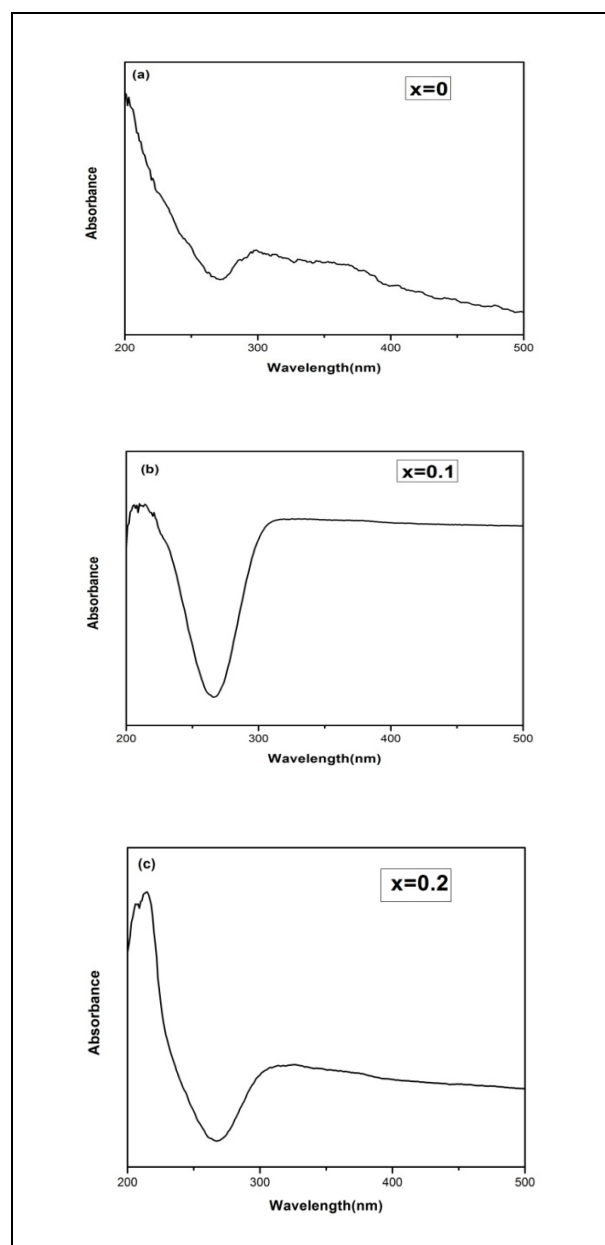
Fig. 6: FTIR plots of lithium substituted nickel ferrite samples annealed at 750°C

Spinel ferrites exhibit characteristic peaks in the 400–700 cm^{-1} range (Fig. 6), attributed to metal-oxygen stretching vibrations. The higher-frequency band, approximately 600 cm^{-1} , represents metal-oxygen bond stretching in tetrahedral sites, such as Ni-O or Li-O bonds (Kotnala *et al.* 2022). The lower-frequency peak (400–500 cm^{-1}), is associated with metal-oxygen bonds in octahedral sites, primarily Fe-O vibrations [30]. Incorporating lithium ions (x) into the nickel ferrite lattice alters the local bonding environment, potentially resulting in subtle peak position shifts or intensity changes, indicative of crystal structure modifications (Das *et al.* 2020). The weak peaks in the 1400–1600 cm^{-1} region may be attributed to bending vibrations of carbonate species or adsorbed carbon dioxide (CO_2) on the surface (Nishant *et al.* 2020). These peaks are commonly observed in ferrite materials exposed to atmospheric conditions. Increasing lithium content leads to changes in vibration modes due to differences in ionic radii and charge distribution among Ni^{2+} , Li^+ , and Fe^{3+} ions. These observations align with studies on lithium-doped ferrites, which report comparable peak shifts and intensity variations. The stretching vibrations of octahedral sites are represented by the lower frequency absorption band located at 412 cm^{-1} and 411 cm^{-1} . Li-O complexes at octahedral sites are demonstrated by the middle frequency absorption band seen at 479 cm^{-1} in both instances.

4.4 UV-vis Spectroscopy Measurement

The UV-visible absorption spectra of lithium-doped nickel ferrite ($\text{Ni}_{1-x}\text{Li}_x\text{Fe}_2\text{O}_4$) shown in Fig. 7 indicate a significant impact on its optical and electronic properties with increasing lithium concentrations ($x = 0, 0.1, 0.2, 0.3$). The shift in the absorption edge with increasing lithium doping (x) suggests changes in the

bandgap energy. A lower bandgap allows the material to effectively absorb visible light, facilitating electron excitation and enabling interactions with water molecules. The increase in absorbance intensity at higher doping levels implies that lithium substitution introduces additional defect states or modifies the electronic structure of the ferrite. These defect states may act as active sites for the adsorption and dissociation of water molecules. Enhanced absorption in the UV-visible range improves the material's ability to interact with water, a key requirement for efficient hydroelectric cell operation. The characteristic peaks observed in the spectra correspond to electronic transitions of Ni^{2+} , Fe^{3+} , and possibly Li^+ associated states. These transitions indicate a robust electronic environment for the movement of charge carriers, crucial for generating a sustainable current in hydroelectric cells.



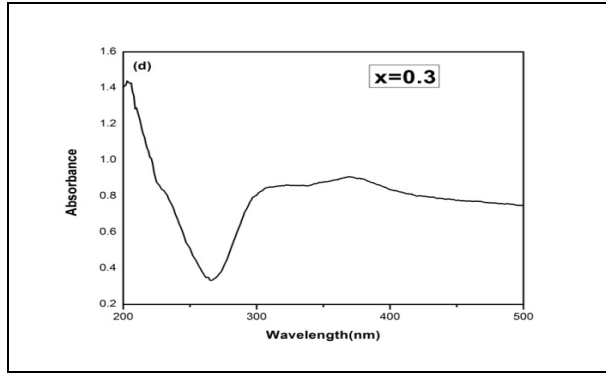


Fig. 7: UV-vis spectra of Li-substituted nickel ferrite samples annealed at 750°C

Additionally, the increased absorbance intensity at higher doping levels reflects the introduction of defect states that act as active sites for water adsorption and dissociation. This behavior, coupled with transitions of Ni^{2+} and Fe^{3+} ions, facilitates charge carrier mobility, thereby improving energy conversion efficiency in hydroelectric cells. The inclusion of lithium ions introduces lattice distortions and boosts conductivity, which may be critical for optimizing the performance of hydroelectric cells (Rakesh *et al.* 2021; Etim *et al.* 2021). In semiconductor materials with a direct band gap, the conduction band's lowest energy point and the valence band's highest energy point align at the same momentum value (k-value) within the electronic band structure.

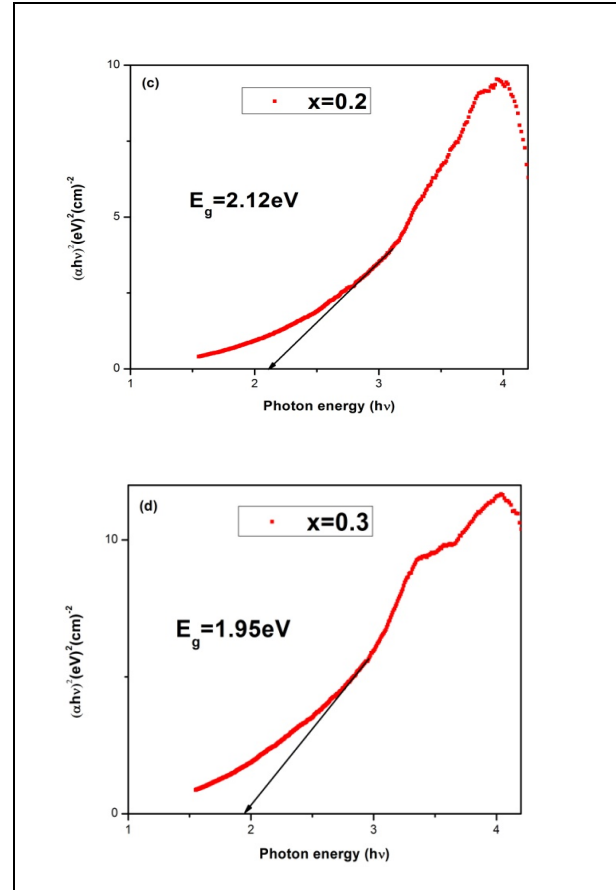
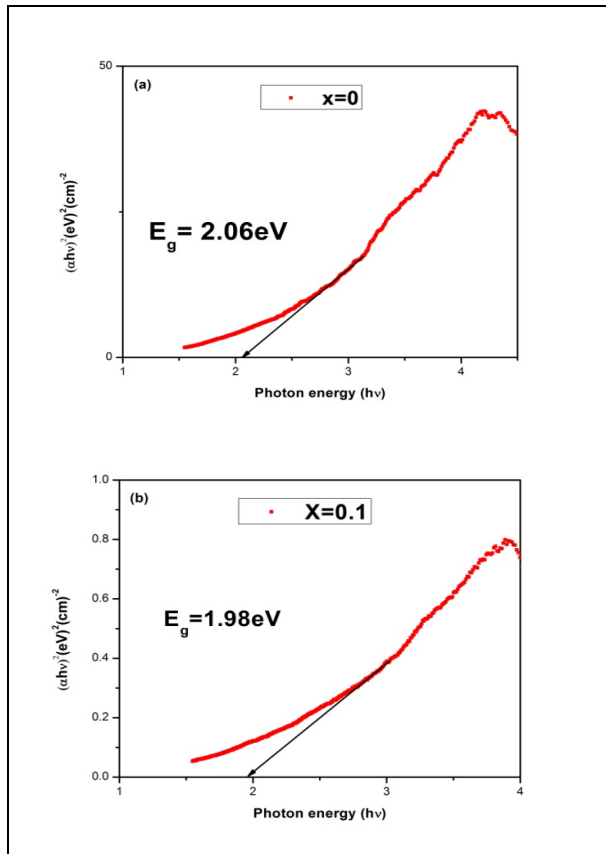


Fig. 8: Direct band gap of ni1-xLixFe₂O₄ annealed at 750 °C

The graphs in Fig. 8 illustrate the direct band gap energy of $\text{Ni}_{(1-x)}\text{Li}_x\text{Fe}_2\text{O}_4$ across various lithium doping concentrations $x=0, 0.1, 0.2$ and 0.3 are 2.06 eV, 1.98 eV, 2.12 eV, 1.95 eV, respectively. These energy values calculated using the relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$) as described by Tauc's equation (Eqn 3) (Kashyap *et al.* 2023), offer valuable information about the material's electronic characteristics.

$$\alpha h\nu = (h\nu - E_g)^n \quad \dots (3),$$

where, α = Absorption coefficient, $h\nu$ = Photon energy, E_g = Optical band gap energy, n = A factor that depends on the nature of the electronic transition, $n=1/2$ for direct allowed transitions and $n=2$ for indirect permitted transitions. The band gap energy exhibits variations with different lithium doping levels. At $x=0.1$ in Fig. 8 (b), E_g measures 1.98 eV, rising to 2.12 eV when $x=0.2$ in Fig. 8 (c), and then slightly decreasing to 1.95 eV at $x=0.3$ in Fig. 8 (d). These changes indicate that the amount of lithium doping substantially affects the electronic structure of Li^+ substituted NiFe_2O_4 , potentially through alterations in the density of states and the presence of localized defects. Additionally, the ionic size mismatch caused by the introduction of Li^+ ions that causes lattice deformation improves conductivity and promotes charge transport.



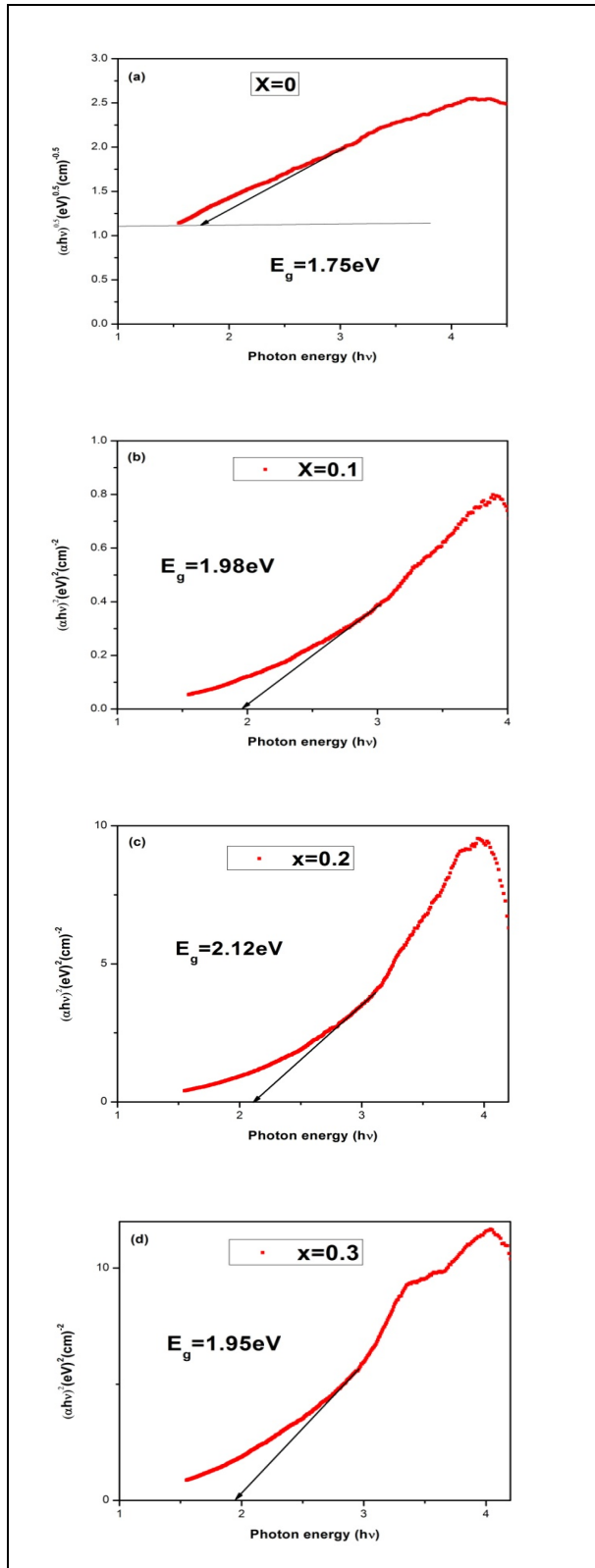


Fig. 9: Indirect band gap of Ni_{1-x}Li_xFe₂O₄ annealed at 750°C

An indirect band gap is a characteristic of certain semiconductors where the lowest energy level of the conduction band and the highest energy level of the valence band occur at different momentum values in the

electronic band structure. This means that an electron transitioning between these bands must also interact with a phonon (a vibration in the crystal lattice) to conserve momentum. In Fig. 9, the displayed graphs illustrate the variation in indirect band gap energy of lithium-doped nickel ferrite as a function of lithium content ($x = 0.1, 0.2$, and 0.3). These plots, constructed using the Tauc plot method, show photon energy ($h\nu$) in eV on the horizontal axis and $(\alpha h\nu)^{1/2}$, related to the absorption coefficient α , on the vertical axis. The E_g value is obtained from the x-intercept of the curve's extended linear portion. It starts at 1.7 eV for $x=0$ in Fig. 9 (a), drops to 1.53 eV at $x=0.1$ in Fig. 9 (b), increases to 1.79 eV at $x=0.2$ in Fig. 9 (c), and slightly decreases to 1.6 eV at $x=0.3$ in Fig. 9 (d). Lithium incorporation into nickel ferrite alters the material's electronic structure and crystal lattice, impacting its energy band configuration. The E_g increase at $x=0.2$ in Fig. 9 (c) suggests that moderate doping enhances semiconducting properties by modifying the electronic density of states. The subsequent decrease at $x=0.3$ in Fig. 9 (d) may be attributed to structural distortions or increased defect states from excessive doping. Lithium-doped nickel ferrites with tunable band gaps have shown dependence on the Bras model (Eqn 4) (Parray *et al.* 2024).

$$E_g = E_g^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2er^2} \left(\frac{1}{me} + \frac{1}{mh} \right) - \frac{18e^2}{4\pi\epsilon_0\epsilon_r} \quad \dots (4)$$

The band gap influences the material's ability to absorb photons and generate electron-hole pairs. The observed band gap energies (1.53–1.79 eV) align well with the visible light spectrum, enabling efficient light absorption.

4.5 Photoluminescence(PL) Spectroscopy Measurement

The photoluminescence spectra of lithium-doped nickel ferrite (Fig. 10) for doping concentrations of $x=0, 0.1, 0.2$, and 0.3 , reveal the optical emission properties of the material, which are highly relevant for its potential applications in hydroelectric cells.

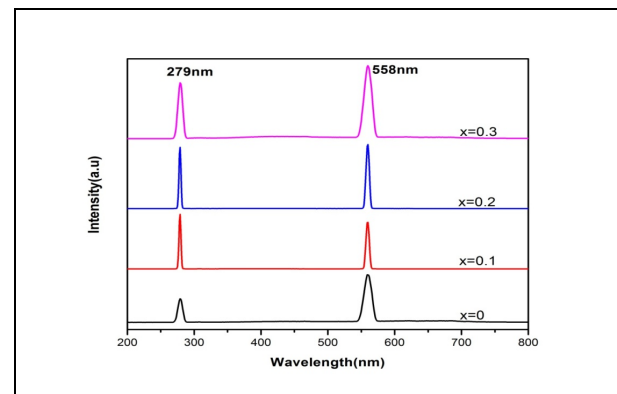


Fig. 10: PL spectra of the li-substituted nickel ferrite sample annealed at 750°C

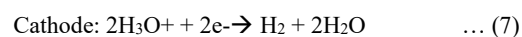
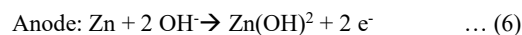
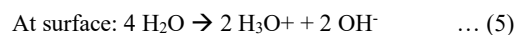
The spectra demonstrate two prominent emission peaks at approximately 279 nm (UV region) and 558 nm (visible area), with variations in intensity across different doping levels. The emission at 279 nm corresponds to electronic transitions involving charge transfer or recombination processes in the ferrite matrix, influenced by lithium doping (Das *et al.* 2020). The peak at 558 nm in the visible region is associated with surface states or defects introduced by doping, which can enhance charge separation and transfer efficiency. The intensity of the emission peaks increases with higher lithium doping concentrations, with $x=0.3$ exhibiting the most significant enhancement. This indicates improved optical activity due to the incorporation of lithium ions, which modify the electronic band structure and reduce non-radiative recombination (Nishant *et al.* 2020). Lithium doping introduces oxygen vacancies and structural defects, which contribute to enhanced photoluminescence by increasing the density of radiative recombination centers (Rakesh *et al.* 2021). Enhanced UV absorption can catalyze the dissociation of water molecules into hydrogen and oxygen, improving cell performance (Das *et al.* 2020). The peak at 558 nm signifies potential applications under solar illumination, as visible light absorption enhances the material's usability for photocatalytic reactions in hydroelectric cells. Lithium doping ensures higher light utilization efficiency (Rakesh *et al.* 2021). Lithium doping at $x=0.3$ appears to optimize both UV and visible light emission, aligning well with the requirements for hydroelectric cells. Excessive doping, however, may lead to aggregation effects or excessive defects, reducing efficiency (Nishant *et al.* 2020). The photoluminescence characteristics of lithium-doped nickel ferrite suggest that the material is suited for hydroelectric cells. Enhanced optical properties resulting from lithium doping improve charge transfer and water dissociation, essential for electricity generation through hydroelectric mechanisms. Lattice defects (such as oxygen vacancies, interstitials, etc.) may be responsible for the peak seen at shorter wavelengths (around 560 nm), which function as unsaturated or dangling bonds in ionic oxides.

5. MECHANISM OF HYDROELECTRIC CELLS (HEC) AS GREEN ENERGY

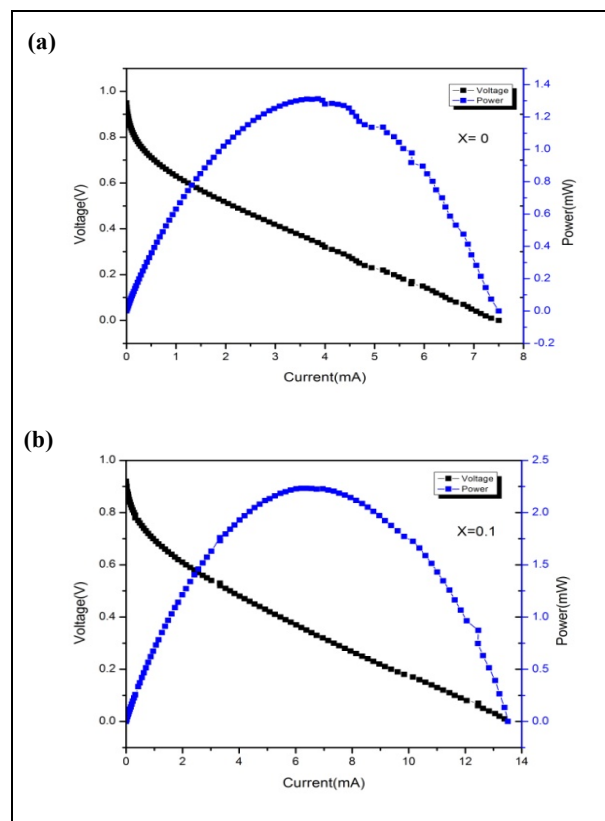
Hydroelectric cells generate electrical energy by utilizing the reaction of water with specific metal oxides and ferrites. Nickel ferrite has shown promising electrochemical properties, and lithium doping further enhances its performance in energy conversion applications. Water molecules divide heterolytically into H^+ and OH^- ions as a result of the electrostatic interaction between the dipolar water molecule and the surface dangling bonds. On the HEC surface, this creates a monolayer of chemisorbed OH^- ions, on top of which

hydrogen bonds to produce several layers of water molecules. The hydronium ion, or H_3O^+ , is formed when the H^+ ion joins with another water molecule since it cannot exist alone. The water splitting process at the surface is continued by these hydronium ions, which generate an electric field inside the nanopore causing physidissociation (Shukla *et al.* 2024). The anode (zinc electrode), where zinc undergoes oxidation and at once forms zinc hydroxide (OH^- ions flow). Further, careful material selection and surface optimization preserve the zinc electrode's efficacy over time. During operation, a homogenous and stable layer of zinc hydroxide is formed, which helps passivate the surface and minimize self-degradation and corrosion. Effective ion transport is made possible by the electrode's mesoporous shape, which reduces localized stress and increases stability over repeated cycles. Through an external circuit, the electrons travel to the cathode, which is an inert silver electrode, where they are absorbed by hydronium ions and converted to water and hydrogen gas.

(Kotnala *et al.* 2022). The electrochemical reactions are summarized in equations (5-7).



5.1 V-I Characteristics



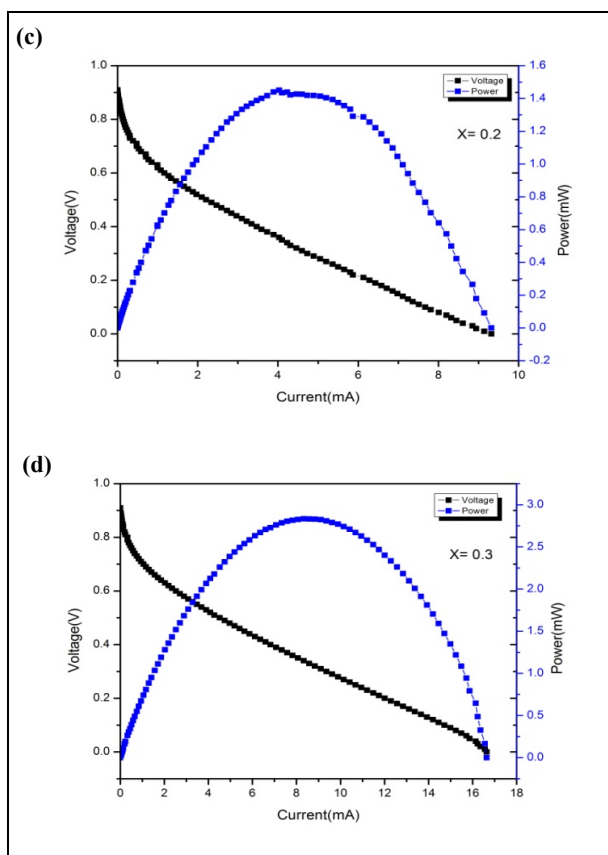


Fig. 11: V-I polarization plot of lithium substituted nickel ferrite HEC annealed at 750°C

The voltage-current (V-I) characteristics of lithium-doped nickel ferrite with varying lithium concentrations were determined to study its efficiency in hydroelectric cell applications. The graph in Fig. 11 depicts the Voltage-Current (V-I) and Power-Current (P-I) relationships for lithium-doped nickel ferrite at a doping concentration of $x=0$. It shows how voltage (volts) and power (milliwatts) change with current (milliamps). The black line representing voltage vs. current initially exhibits a linear increase, suggesting ohmic behavior at low currents. As the current increases, the voltage plateaus and eventually decreases, indicating non-linear electrical characteristics typical of ferrites. The blue line illustrating power vs. current demonstrates a quadratic rise initially, reaching its peak at about 7.5 mA before declining. This pattern aligns with the voltage drop and is characteristic of ferrite materials, which display semiconductor-like properties combining resistive and inductive elements. Electron hopping between Fe_2^+ and Fe^{3+} ions in the spinel lattice's octahedral sites is often attributed to its conduction mechanisms. The maximum power output (~ 1.4 mW at ~ 7.5 mA, Table 2) is crucial for energy harvesting or electronic device applications, determining the optimal operating point, which can guide future optimization efforts in areas such as doping concentration, grain size, and sintering temperature. For $x=0.1$, the voltage increases linearly at lower currents, showing ohmic behavior (Kumar *et al.* 2024; Badola *et al.* 2023).

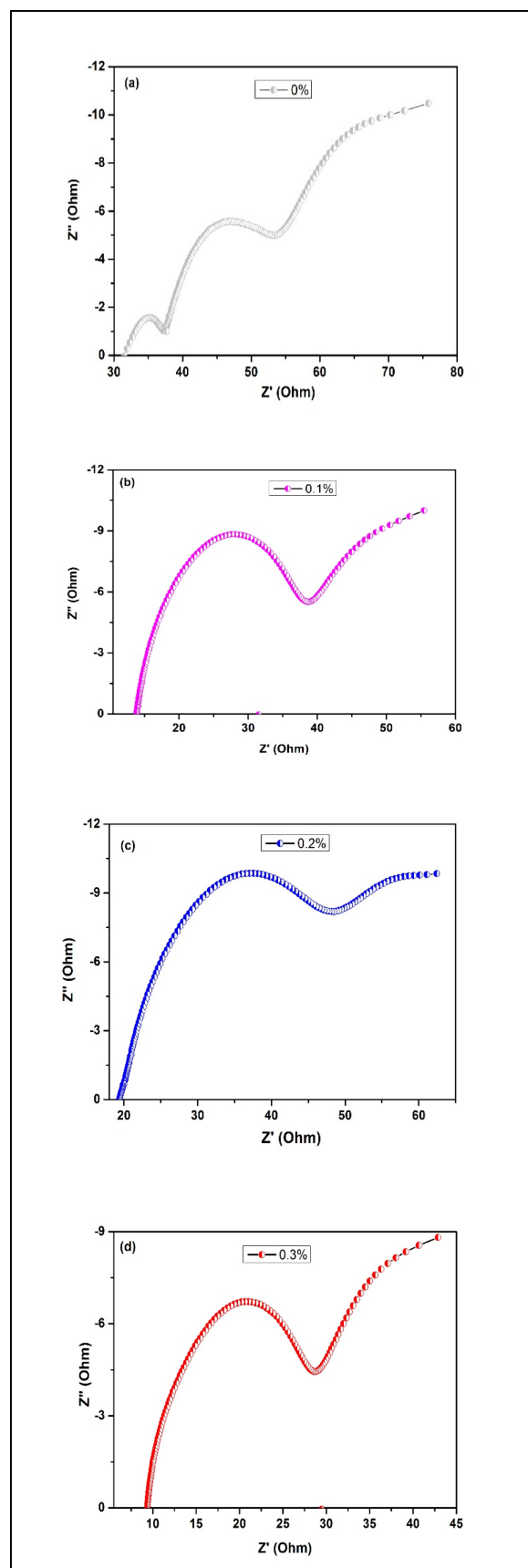


Fig. 12: Nyquist plot of lithium substituted nickel ferrite hydroelectric cells annealed at 750°C

The power curve peaks at a specific current, suggesting an optimal operating point, with a maximum power of approximately 2.2 mW. For $x=0.2$, the voltage behavior resembles that of $x=0.1$ but with a lower peak voltage and a steeper drop at higher currents. The maximum power output is about 1.6 mW (Table 2), lower than $x=0.1$. For $x=0.3$, the voltage rises more sharply at lower currents and maintains higher values before dropping off. The saturation effect is more pronounced at higher currents. The peak power output is approximately 3 mW, the highest among the three samples. All samples show a non-linear increase in voltage with current, transitioning from an ohmic regime to a saturation regime. $x=0.3$ exhibits the highest power output, followed by $x=0.1$ and $x=0.2$. This indicates an optimal doping level at $x=0.3$, where carrier mobility and structural stability are maximized. The observed trends align with the crystallite size and strain analysis. For $x=0.3$, the larger crystallite size and reduced strain likely enhance electrical properties, reducing defect-induced scattering (Kotnala *et al.* 2022). The results suggest that the ideal lithium doping level to maximize conductivity is $x = 0.3$ at nanoscale. Further doping may result in excessive vacancies and aggregation beyond this concentration, which could have a detrimental effect on conductivity. Changes in defect density due to doping levels influence recombination rates and mobility, affecting power output.

5.2 Impedance Analysis

The Nyquist plots displayed in Fig.12 illustrate the impedance properties of lithium-doped nickel ferrite at various doping levels. These graphs depict the connection between the real (Z') and imaginary (Z'') components of impedance. Such impedance analyses are crucial for comprehending the electrical characteristics of the material, particularly in hydroelectric cell

applications, where the material's capacity to facilitate ionic and electronic charge movement directly influences the cell's performance and energy output. For undoped nickel ferrite ($x = 0$), the Nyquist plot exhibits a semicircular arc at lower frequencies, indicative of bulk resistance and grain boundary effects. The comparatively high impedance suggests limited conductivity, which could impede the ion transfer necessary for efficient hydroelectric cell operation.

Table 2. Current, voltage and power generated by pellets of $\text{Ni}_{1-x}\text{Li}_x\text{Fe}_2\text{O}_4$ samples

Sample (x)	Open Cell Voltage (V)	Short Circuit Current(mA)	Offload output power (mW)	Peak Power (mW)
X=0	0.94	7.5	7.05	1.4
X=0.1	0.91	13.51	12.29	2.2
X=0.2	0.90	9.32	8.388	1.6
X=0.3	0.90	16.64	14.98	3

With lithium doping ($x = 0.1$), the Nyquist plot (Fig. 12 (b)) shows a decreased arc radius, implying enhanced conductivity. This lithium addition improves charge transport by reducing grain boundary resistance, which is vital for maximizing hydroelectric cell efficiency. Such improvement could lead to better ion exchange and water dissociation, essential processes in hydroelectric cells (Kashyap *et al.* 2024). At doping ($x = 0.2$) (Fig. 12 (c)), a further decrease in impedance is observed, as evidenced by the smaller semicircular arc. The improved conductivity results from lithium ions being incorporated into the nickel ferrite crystal structure, enhancing the material's charge transfer capabilities. This doping concentration appears to optimize electronic pathways and lower impedance, benefiting hydroelectric cell applications by improving ion flow and water dissociation efficiency (Kumar *et al.* 2022). For the

doping level ($x = 0.3$) (Fig. 12 (d)), the semicircular arc in the plot reflects the material's resistive and capacitive behavior. A notable reduction in arc radius compared to lower doping concentrations indicates a significant improvement in conductivity. Similar comparable values are also reported by other research groups that have used monovalent elements like lithium, sodium and silver. (Vivek *et al.* 2024; Saini *et al.* 2022a).

6. CONCLUSION

The influence of Li^+ substitution on the properties of NiFe_2O_4 nano ferrites has been studied. The XRD studies confirmed that the ferrite materials' average crystallite size decreased from 47 to 40 nm with an increase in the molar content of Li^+ ($x = 0.1, 0.2$, and 0.3). The SEM micrographs confirmed that the grain size decreased from 0.215 to 0.138 μm . A higher specific surface area and more active sites for ion interaction and water adsorption result from the decrease in crystallite and grain size with increased Li^+ concentration. By facilitating charge transfer at the electrode–electrolyte contact, this increased surface reactivity raises the current output of the hydroelectric cells. The presence of defects and oxygen vacancies required for water splitting is confirmed by the wide and intense PL spectrum of the Li^+ -substituted ferrite materials, which range from 279 to 558 nm. The energy band gap is found in the range of 2.06 eV to 2.12 eV. The impedance of Li^+ -substituted ferrite is significantly lower than that of pure NiFe_2O_4 , according to impedance spectroscopy. The pronounced defective states in the Li^+ -substituted Ni-ferrites were mostly responsible for the greater offload currents for the hydroelectric cell made with the Li^+ -substituted nickel ferrite compared to the virgin sample, as seen by the V–I polarization plots. With a 17-mA current output, the Li^+ -fabricated hydroelectric cell with the molar content $x = 0.3$ of lithium showed the maximum value of current.

Impedance analysis reveals the ionic and electronic charge movement that influences the hydroelectric cell performance and green energy output.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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