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Improvement in the bandgap and photoluminescence behavior by Holmium (Ho) and Iron (Fe) co-doping in LaNiO_3 , synthesized using sol-gel route for novel sustainable energy applications

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Abstract

The effect of incorporating holmium and iron into LaNiO_3 (LNO) perovskites with compositions, $\text{LaNi}_{0.95}\text{Fe}_{0.05}\text{O}_3$ (LFNO), and $\text{La}_{0.95}\text{Ho}_{0.05}\text{Ni}_{0.95}\text{Fe}_{0.05}\text{O}_3$ (LHFNO), synthesized via the sol-gel method are examined. Structural and morphological properties are characterized by x-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM) show a progressive distorted rhombohedral phase formation for prepared samples with particle sizes ranging from 9 to 15 nm. Fourier Transform Infra-Red (FTIR) spectroscopy, UV-Vis DRS, Photoluminescence (PL) and XPS for its structural, morphological and spectroscopic modifications owing to doping. Structural studies confirm the formation of distorted rhombohedral phases with particle sizes ranging from 9 to 15 nm, increasing with doping and then co-doping. Surface morphology studies reveal agglomerated particles, while the elemental composition obtained from Energy dispersive x-ray spectroscopy (EDX). The elemental composition and the molecular bonding characteristics particularly metal-oxygen bonds of the octahedra are analyzed using EDX and FTIR spectroscopy. The optical band gap measured to be between 2.4eV and 3.3eV from UV-DRS measurements, decreasing with doping and further by co-doping. PL spectroscopy demonstrates the recombination kinetics of photogenerated electron-hole pairs significantly with dopants inclusion. Furthermore, XPS analysis clarifies the electronic energy levels and vacancies through valence states of La and Ni ions in both pure and doped samples. The results indicate an overlap between the La 3d and Ni 2p core level spectra due to spin-orbit coupling. Overall, Ho-Fe co-doping tailors the electronic and optical properties leading to an enhanced performance characteristics.

Keywords: LaNiO_3 , Sol-Gel method, XRD, PL and XPS

1. Introduction

Perovskite oxides, with the general chemical formula ABO_3 , represent a broad class of materials that exhibit a wide range of intriguing physical and chemical properties. In the perovskite structure, the A-site is typically occupied by rare-earth or alkaline-earth elements, while the B-site is filled by transition metal ions [1]. Due to this structural versatility, these materials display remarkable optical, magnetic, electrical and structural characteristics [2]. Consequently, perovskite oxides have attracted considerable interest for applications in catalysts, chemical sensors, solid oxide fuel cell electrodes, hydrogen storage system, optoelectronic devices and solar cells [3-6]. The exceptional performance of perovskite oxides largely attributed to several fundamental features, including a tunable band gap, flexible electronic structure, uniform morphology, nanoscale particle size, and the presence of lattice defects such as oxygen vacancies [7-10]. These characteristics provide researchers with

significant control over the functional properties of these materials, allowing them to be tailored for specific technological applications.

Furthermore, the properties of perovskite oxides can be effectively tuned through partial substitution of cations at the A-site, B-site, or simultaneously at both sites. Such substitutions can lead to modifications in the oxidation state of the B-site ions, formation of structural defects such as cation or oxygen vacancies, and lattice distortions [11, 12]. In certain cases, these substitutions may also induce the formation of secondary phases due to structural transformation [13]. These structural and electronic modifications play an important role in improving the electrical, catalytic, and optical performance of perovskite materials. Therefore, doping is widely regarded as an effective strategy for tuning the structural and electronic properties of perovskite oxides to achieve desired functional characteristics for specific applications.

Among the various perovskite oxides, lanthanum nickel oxide (LNO) has been extensively studied due to its diverse physical and chemical properties. LNO exhibits promising optical, electrical, and magnetic properties, making it suitable for a wide range of technological applications. Owing to its high electrical conductivity and structural stability, LNO has been employed in conductive thin films, electrocatalysis, solid oxide fuel cell electrodes, supercapacitors and photocatalytic system [14-17]. At room temperature, LNO generally crystallizes in a rhombohedral structure (space group R-3c) consisting of corner-sharing NiO_6 octahedra, where the A-site is occupied by La^{3+} ions. The material also exhibits strong hybridization between Ni 3d and O 2p orbitals, which significantly influences its electronic properties [16].

In addition, LNO shows considerable flexibility in accommodating cation substitutions, making it an ideal candidate for controlled doping to tailor its functional properties. Partial substitution of La^{3+} at the A-site or Ni^{3+} at the B-site enables modification of the lattice structure, electronic configuration, and oxygen stoichiometry. Such substitutions can enhance electrical conductivity, catalytic activity, and structural stability, thereby expanding the potential applications of LNO-based materials. LNO has been synthesized using several techniques, including high temperature solid state reaction, co-precipitation, liquid mixed technique, wet chemical methods, Pechini method, citrate sol-gel method, and other related approaches [18]. Among these techniques, the sol-gel combustion method has attracted considerable attention because of its low synthesis temperature, rapid reaction rate, high purity and one-step synthesis process [19].

In the present work, LNO samples are synthesized using the sol-gel combustion method. Three different compositions are prepared to investigate the effect of cationic substitution on the structural and functional properties of LNO. The first sample is pure LNO, which serves as the reference material. The second sample consists of LNO doped with 5% iron (Fe) at the B-site, while the third sample involves co-doping with 5% holmium (Ho) at the A-site along with 5% Fe at the B-site. This systematic approach enables a comparative analysis of the pure, singly doped, and co-doped LNO samples. Studies on Ho and Fe co-doping in LNO are relatively limited. Previous reports have shown that Ho doping in BFO (BiFeO_3) enhances its multiferroic properties while Fe plays a significant role in influencing the ferroelectric properties of perovskite materials [20]. Motivated by these findings, the present study focuses on the synthesis of pure, Fe doped and Ho-Fe co-doped LNO using the sol-gel auto-combustion method. The objective is to investigate the influence of Fe and Ho substitution on

the structural, morphological, and optical properties of LNO. The synthesized perovskite powders are characterized using XRD to identify their crystalline phases and FE-SEM to examine their surface morphology. Furthermore, UV-Visible diffuse reflectance spectroscopy is employed to estimate the optical band gap of the samples. Photoluminescence spectroscopy is used to study defect levels and charge carrier recombination behavior while XPS is performed to analyze the surface chemical composition, oxygen vacancies and to investigate the valence states of the constituent elements particularly La and Ni.

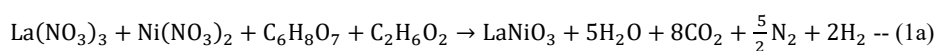
2. Materials and Methods

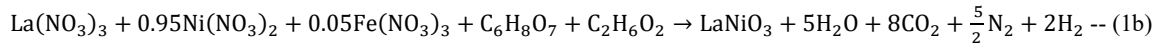
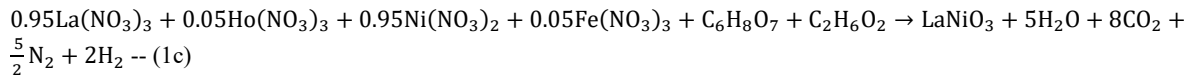
2.1 Synthesis of pure, doped and co-doped LNO

The samples are synthesized using high purity starting materials including lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Spectrochem, 99.9 %), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (sigma Aldrich, 99.99 %), holmium nitrate pentahydrate ($\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), (sigma Aldrich, 99.99 %) ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), (sigma Aldrich, 99.99 %) citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (Spectrochem, 99 %) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (Spectrochem, 99 %).

Pure LNO, Fe-doped LNO ($\text{LaNi}_{0.95}\text{Fe}_{0.05}\text{O}_3$) LNO, Ho-Fe co-doped LNO ($\text{La}_{0.95}\text{Ho}_{0.05}\text{Ni}_{0.95}\text{Fe}_{0.05}\text{O}_3$) are synthesized using the sol-gel auto-combustion method [21]. This method is a wet chemical technique that combines the advantages of the sol-gel process, which ensures compositional homogeneity, with a rapid exothermic self-propagating combustion reaction that produces high purity oxide powders. In this process, metal nitrates are mixed with an organic fuel to form a homogeneous sol, which subsequently transforms into a gel. Upon heating, the gel undergoes auto-ignition, producing a voluminous and fine oxide powder.

For the synthesis of pure LNO, stoichiometric amounts (equation 1a) of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are used as precursor materials. For the preparation of LFNO, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is additionally introduced as the Fe source. Similarly, for the synthesise of LHFNO, $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are used along with the required quantities of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (equation 1b and 1c). The calculated stoichiometric amounts of these precursor salts are dissolved in 100 ml of distilled water and thoroughly mixed using a magnetic stirrer to obtain a homogeneous solution. Subsequently, citric acid and ethylene glycol are added to the solution in a molar ratio 3:2 to facilitate the formation of a polymeric metal-cation network. The resulting solution is continuously stirred and heated at 100°C for approximately 5 hours, leading to the formation of a viscous gel precursor. The obtained gel is the subjected to auto combustion at an elevated temperature, resulting in the formation of a brown fluffy powder. The resulting powder is ground using a mortar and pestle and subsequently calcined at 750°C for 2 hours in air to promote phase formation. After calcination, the powder is pressed into pellets using a hydraulic press and then sintered at 850°C for 4 hours. Finally, the sintered pellets are ground again to obtain fine powder, which is then used for various characterization studies. The stoichiometric quantities of the reactants are calculated according to the following overall reaction [22]:





2.2 Characterization Techniques

The crystal structure, phase purity, and structural ordering of the pure and co-doped LNO samples are examined using XRD with a PANalytical X'Pert³ powder diffractometer. The measurements are carried out using Cu K-alpha radiation ($\lambda=1.5405 \text{ \AA}$) in continuous slow scan mode at a scanning rate of 0.013° per second within the 2θ range of $20^\circ - 80^\circ$. The surface morphology and elemental composition of the samples are investigated using FE-SEM coupled with EDX performed on a ZEISS Gemini 300 scanning electron microscope. FTIR is conducted using PerkinElmer spectrometer in the wavenumber range $3000 - 400 \text{ cm}^{-1}$ to analyze the vibrational modes and confirm the structural features of the synthesized samples. The optical absorption properties of the samples are studied using UV-Vis DRS with PerkinElmer Lambda 1050 S spectrophotometer, recorded in the wavelength range of $200-800 \text{ nm}$. The PL spectra of the prepared samples are measured using a Sophisticated Fluorescence Spectrometer (Edinburgh FLS1000) equipped with a xenon (Xe) lamp with an excitation wavelength of 450 nm , to investigate the electron-hole recombination behaviour of the material. XPS measurements are carried out using a Thermo Fisher Model K-Alpha spectrometer to analyze the surface chemical composition and valence states of the elements. The spectra are calibrated using the adventitious C 1s peak, at 285.52 eV as the reference. The electron energies are analysed using a hemispherical energy analyser with parallel detection capability.

3. Results and Discussions

3.1 X-ray diffraction (XRD)

Figure 1 shows the XRD patterns of pure LNO, LFNO, and LFHNO. The diffraction peaks are observed at 2θ values of 23.24° , 32.82° , 40.57° , 47.42° , 53.13° , 58.58° , 68.79° , and 78.58° , which corresponds to the (012), (110), (202), (024), (122), (030), (220), and (134) lattice planes. These peaks are consistent with the standard data from JCPDS No. 98-002-7388 for LNO, confirming the formation of a perovskite structure with a rhombohedral crystal system and R-3c space group [23]. The absence of additional impurity peaks indicates the formation of a predominantly single-phase perovskite oxide.

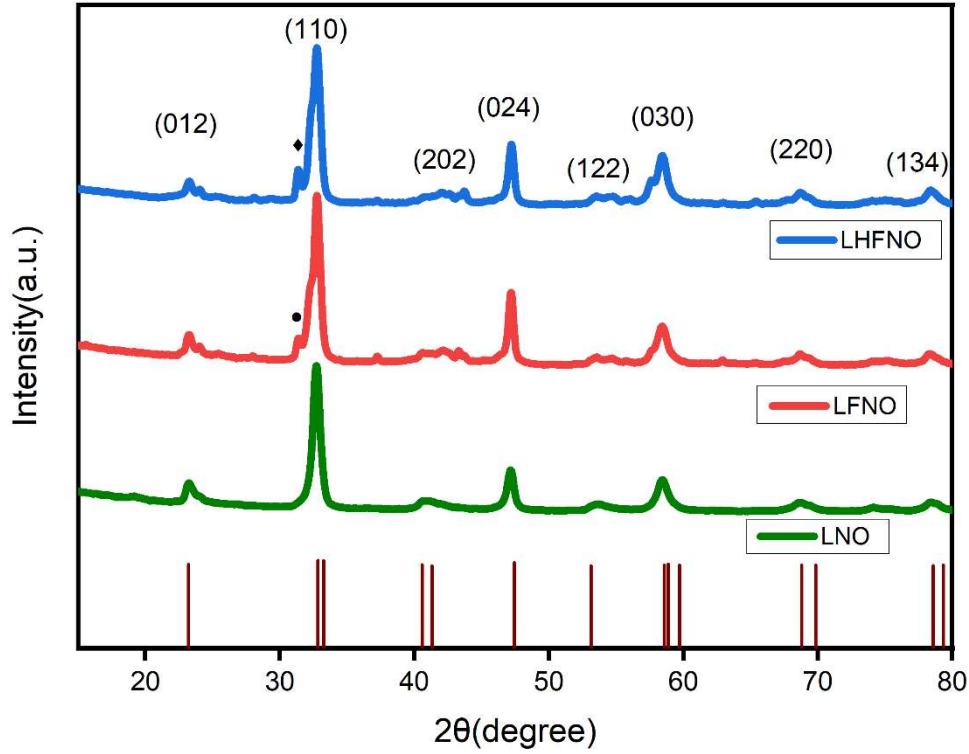


Figure 1. The JCPDS and XRD patterns of LNO, LFNO and LHFNO samples.

A closer examination of the diffraction angles (2θ) reveals that the most intense (110) peak appears at approximately 32.71° for pure LNO, slightly shift towards lower 2θ values upon Fe substitution. This shift may be associated with substitution of Ni^{3+} ions ($0.70 \text{ \AA}$) by smaller Fe^{3+} ions ($0.64 \text{ \AA}$) at the B-site, resulting in changes in the interplanar spacing according to Bragg's law (equation 2) [24].

$$n\lambda = 2d \sin\theta \dots\dots\dots (2)$$

Similarly, in Ho–Fe co-doped LNO, the peak further shifts toward lower diffraction angles due to the substitution of La^{3+} ions ($1.06 \text{ \AA}$) with smaller Ho^{3+} ions ($0.92 \text{ \AA}$) at the A-site. The systematic shift to the diffraction peaks toward lower 2θ values indicates lattice distortion caused by the incorporation of Fe^{3+} and Ho^{3+} ions into the LNO structure. These substitutions introduce structural strain while preserving the fundamental rhombohedral perovskite framework [24, 25]. The strain due to lower ionic radii modified the unit cell volume and the lattice constants which are given in table 1. Doping with Fe in B-site has increased the lattice parameters and thus the cell volume whereas co-doping with additional Ho in A-site, has made smaller unit cell. These results are reflected in the grain sizes as well, observed in the morphological analysis. [25, 26]

In addition to the primary reflections, weak peaks corresponding to secondary phases are also observed near the (110) peak in the doped samples (Figure 1). The minor reflections marked by • and ◆, correspond to LaFeO_3 and HoNiO_3 phases, respectively, which have also been reported in earlier studies [27, 28]. The appearance of these peaks suggests the formation of secondary phases during the doping process, likely due to ionic size mismatch and partial phase segregation. Although their intensities are significantly lower than those of the dominant LNO peaks, their presence indicates partial phase separation alongside the primary perovskite lattice.

Table 1. Lattice parameters and cell volume of LNO, LFNO and LHFNO

Samples	a (Å)	b (Å)	c (Å)	Cell Volume (Å ³)
LNO	5.459	5.459	13.143	339.279
LFNO	5.477	5.477	13.382	347.721
LHFNO	5.432	5.432	13.029	332.950

The average crystallite sizes of LNO and LFNO and LHFNO are calculated as 10.64 nm, 13.50 nm, and 14.39 nm respectively using Debye Scherrer's equation (3) [24].

$$D = k\lambda/\beta\cos\theta \dots\dots\dots (3)$$

where λ is the wavelength of the x-ray radiation (1.5409 Å), θ is the diffraction angle, D is average crystallite size assuming spherical particles, $k = 0.9$ is the shape factor, and β represents the full width at half maximum (FWHM) of the diffraction peak. A smaller value of β corresponds to a larger crystallite size. The increase in crystallite size upon B-site and A-site substitution due to the effective incorporation of dopant ions into the LNO lattice [29].

Lattice strain and crystalline imperfections arise due to distortions introduced during the doping process. The lattice strain ϵ can be estimated using the relation (4)

$$\epsilon = \beta_{hkl}/4\tan\theta \dots\dots\dots (4)$$

Since both crystallite size and lattice strain contribute to peak broadening and exhibit a Cauchy-type profile, the total peak broadening can be expressed as the sum of the size and strain induced contributions. This relationship (equations 5 and 6) is described by Williamson-Hall (W-H) method [29].

$$\beta_{hkl} = k\lambda/D\cos\theta + 4\epsilon\tan\theta \dots\dots\dots (5)$$

$$\beta_{hkl}\cos\theta = k\lambda/D + 4\epsilon\sin\theta \dots\dots\dots (6)$$

Figure 2 presents the W-H plots for LNO, LFNO and LHFNO samples. From the linear plot of $\beta\cos\theta$ versus $4\sin\theta$, the lattice strain values are obtained from the slope of the fitted line and are summarized in table 2. From the figure, doping with Fe has improved the perovskite ordering which with (Ho,Fe) co-doping, a distorted ordering is indicated with increasing size of the crystallites respectively due to strain broadening effect [29].

Table 2. Estimated crystallite size and strain values of LNO, LFNO and LHFNO

Samples	Crystalline Size D (nm)	Dislocation Density $1/D^2$ ($10^{15} m^{-2}$)	Lattice strain (ϵ)
LNO	10.64	8.83	0.00707
LFNO	13.49	5.49	0.00257
LHFNO	14.38	4.83	0.00725

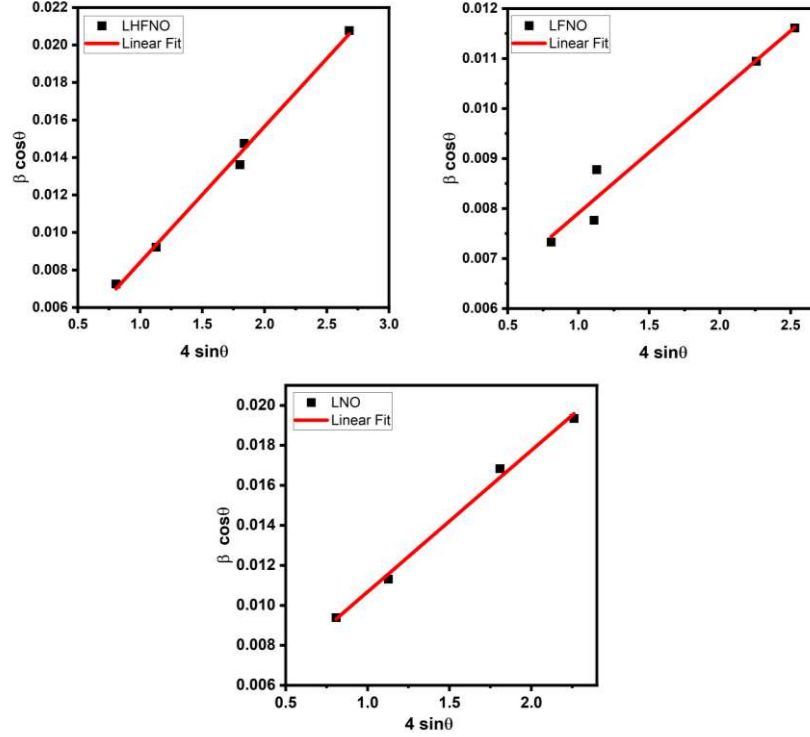


Figure 2. W-H Plot of LNO, LFNO and LHFNO

Another important parameter used to evaluate the structural stability of ABO_3 -type perovskites is the Goldschmidt tolerance factor (t), which is given by equation (7) [30, 31]:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \dots\dots\dots (7)$$

where r_A , r_B and r_O represent the ionic radii of the A-site cation, B-site cation, and Oxygen ion, respectively. For an ideal cubic perovskite structure, the tolerance factor is close to 1.0. The calculated tolerance factor for pure LNO is 0.88 indicating a deviation from ideal cubic structure and confirming the rhombohedral distortion. The tolerance factor values for LFNO and LHFNO are 0.887 and 0.883 respectively. The slight variation in the tolerance factor suggests structural distortions induced by the substitution of cations with different ionic radii [32].

3.2 FE-SEM and EDX Analysis

The SEM micrographs of LNO, LFNO, and LHFNO perovskites are presented in Figure 3. In general, the particles in all samples exhibit nearly spherical to sub-spherical morphologies with a noticeable tendency toward agglomeration. However, closer examination reveals significant differences in grain growth behavior and particle packing density among the samples. The average grain sizes calculated using *image J* software [22] are approximately 96 nm, 218 nm and 256 nm for pure LNO, LFNO and LHFNO samples respectively.

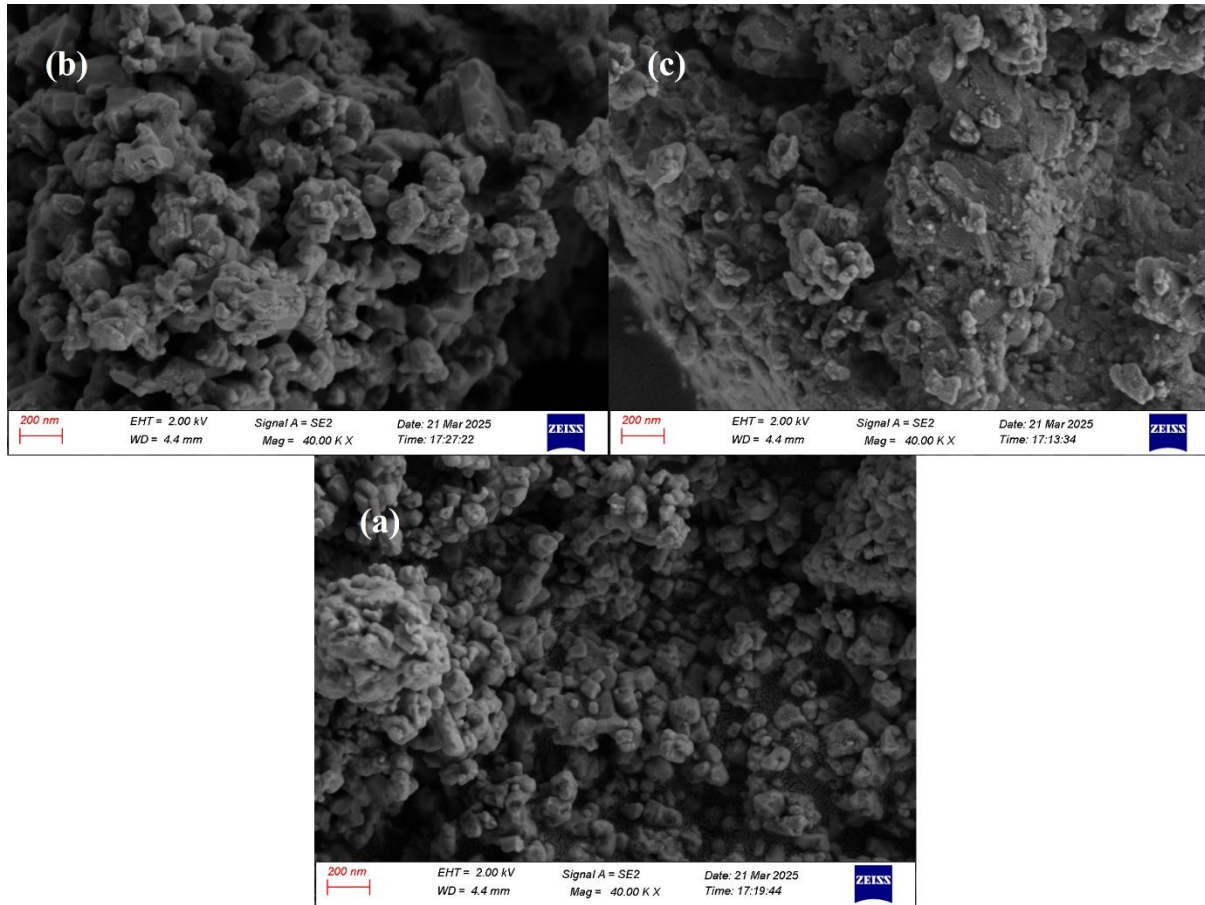


Figure 3. SEM micrographs of (a) LNO, (b) LFNO and (c) LHFNO

The pure LNO sample exhibits the smallest average grain size, whereas LFNO and LHFNO lead to progressively larger grains with a broader size distribution. Despite the increase in grain size, the doped samples still display significant agglomeration. For the pure LNO sample, SEM images reveal relatively small and irregular grains with noticeable intergranular voids. In LFNO sample, the grains become larger and exhibit more clearly defined boundaries compared to the pure LNO. The wider grain size distribution suggests that Fe substitution influences the crystal growth process and promotes grain coarsening.

The LHFNO exhibits the largest average grain size, and the morphology indicates the formation of larger crystallite domains through particle coalescence. The variation in grain sizes among the samples can be attributed to the presence of different dopant ions. Differences in ionic radii can alter bond lengths and bond angles within the lattice, leading to lattice distortion and structural disorder. These structural modifications influence grain growth behavior and may also induce grain misorientation. Furthermore, the incorporation of dopants can introduce lattice defects and dislocations, which may affect grain development and contribute to the observed microstructural variations.

Additionally, EDX spectroscopy is carried out at room temperature to determine the elemental composition of the samples. The EDX spectra of pure LNO, LFNO and LHFNO are presented in figure 4. In the spectrum of pure LNO (figure 4a), distinct peaks corresponding to La, Ni, and O are observed without any additional peaks, indicating high phase purity. In the doped samples (figures 4b and 4c), additional peaks corresponding to Ho and Fe are clearly visible,

confirming the successful incorporation of the dopant ions into the LNO lattice. The absence of impurity peaks further supports the phase purity of the synthesized materials.

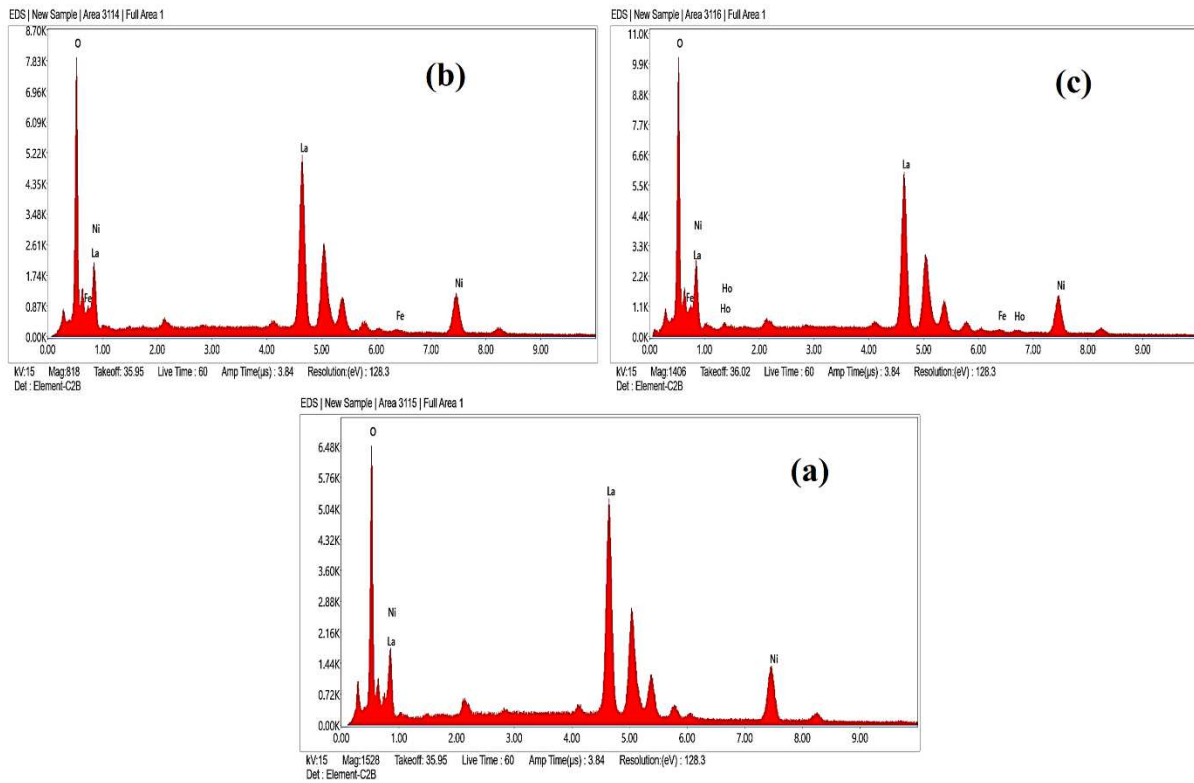


Figure 4. SEM EDX images of (a) LNO, (b) LFNO and (c) LHFNO

The elemental mapping results indicate a uniform distribution of the constituent elements across the samples, confirming their homogeneous chemical composition. A noticeable reduction in the intensity of the La peak in the Ho- and Fe-substituted samples further supports the successful substitution of La^{3+} and Ni^{3+} ions by Ho^{3+} and Fe^{3+} ions in the host lattice. The atomic weight percentages of constituent elements, listed in table 3, are in good agreement with the expected stoichiometric ratio, thereby validating the indented chemical composition of the synthesized samples.

Table 3. EDX results displaying the atomic weight percentages of LNO, LFNO and LHFNO

Samples	Grain Size (nm)	Atomic Weight %				
		La	Ni	O	Ho	Fe
LNO	96	31.1	23.6	45.3	-	-
LFNO	218	28.6	19.7	51.1	-	0.6
LHFNO	256	27.0	18.9	52.9	0.6	0.6

3.3 Fourier transform infrared Spectroscopy (FTIR)

FTIR spectroscopy is employed to identify the vibrational modes present and to confirm the chemical structure of the synthesized samples. The FTIR spectra of the synthesized LNO, LFNO, and LHFNO samples are presented in Figure 5 [24]. The high frequency vibration around 532 cm^{-1} is attributed to Ni-O stretching vibration in octahedral site [33].

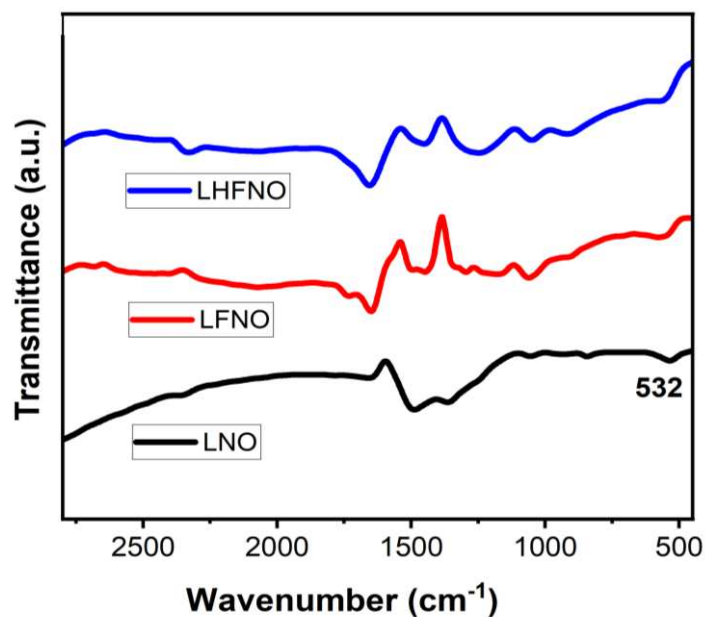


Figure 5. FTIR spectra of LNO, LFNO and LHFNO

From the figure a slight shift in the position of the bands upon doping is observed which suggests minor structural modifications caused by Ho and Fe substitution within the perovskite lattice while the overall LNO framework remains preserved. The occurrence of shoulder splitting may be assigned to the Jahn-Teller effect associated to Ni^{3+} which locally generate a deformation in the crystal lattice [33]. The peak broadening in the case of Ho and Fe doped samples can be attributed to the structural distortions and variations in the bond length which can be linked with the shoulder peaks appearing near the (110) plane of LNO. The bands appearing around 850 cm^{-1} can be assigned to nitrate anions and around 1500 cm^{-1} is stretching vibrations for carbon or similar residual components [2]. Overall, the FTIR results confirm the successful formation of the doped and co-doped perovskite phases. The presence of characteristic metal-oxygen vibrational bands verifies the formation of the perovskite lattice structure, while the slight shifts in absorption peaks after Fe and Ho substitution provide evidence for their effective incorporation into the crystal structure.

3.4 UV-visible diffuse reflectance spectroscopy

The optical properties of the synthesized materials are investigated using UV-Vis DRS. Figure 6(a) shows the DRS reflectance spectra of LNO, LFNO and LHFNO samples. Doped and co-doped samples exhibit a significant decrease in reflectance in the ultraviolet region, followed by a broad and gradually varying profile in the visible region. This absorption edge is attributed to the photoexcitation of electrons from the valence band (VB) to the conduction band (CB).

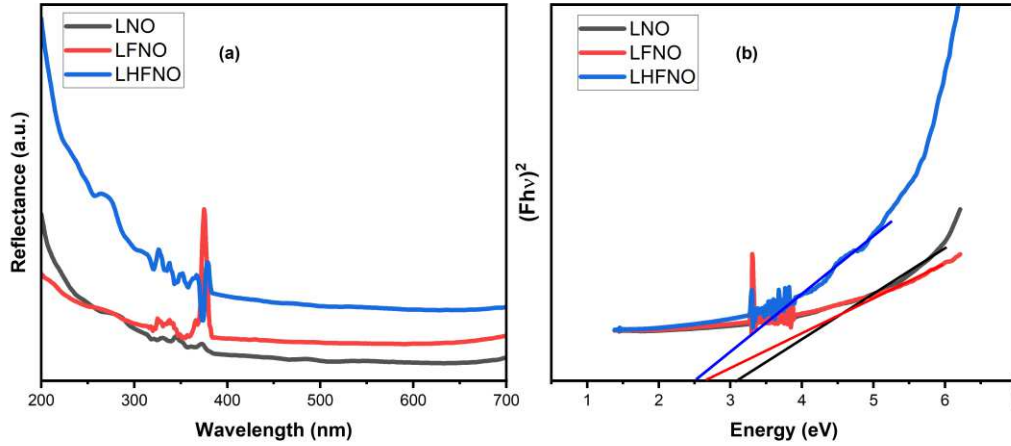


Figure 6. (a) UV DRS reflectance spectra and (b) Tauc's plot of LNO, LFNO and LHFNO

To estimate absorption coefficient from DRS data, the Kubelka-Munk (KM) function $F(R)$ is employed [34]. This function is related to the absorption coefficient (α) according to the following equation (8):

$$F(R_{\infty}) = \frac{(1-R)^2}{2R} \propto \frac{\alpha}{S} \dots\dots\dots (8)$$

Where R represents the reflectance, α is the absorption coefficient, and 's' is the scattering coefficient. The optical band gap (E_g) of the synthesized LNO, LFNO, and LHFNO samples is estimated using Tauc's relation given by equation (9):

$$[F(R)hv]^n = A(hv - E_g) \dots\dots\dots (9)$$

where h is Planck's constant, ν is the frequency of incident radiation, $h\nu$ represents the photon energy, E_g is the optical band gap energy and A is a constant. For direct allowed transition, the value of n is taken as 2 [26]. The optical band gap values are determined by plotting $(Fhv)^2$ versus photon energy ($h\nu$) and extrapolating the linear portion of the curve to intersect the energy axis, as shown in Figure 6(b).

The calculated band gap values are found to be 3.27eV for pure LNO, 2.75 eV for LFNO and 2.41 eV for LHFNO. The observed reduction in band gap with Fe and Ho substitution can be attributed several factors. One possible reason is the distortion of the metal-oxygen octahedral framework, caused by partial substitution at the A-site and B-site, which alters the metal-oxygen bond angles and modifies the electronic structure and adds more electronic energy levels. Another contributing factor is the formation of additional energy levels within the band structure, introduced by the dopant ion which create intermediate states between the CB and VB [23]. Additionally, the excitation of 3d orbital electrons of dopant ions (M^{3+} , where $M = \text{Fe}$ and Ho) into the CB of LNO may also influence the band gap energy. Other parameters such as variations in crystallite size and lattice distortion may further affect the optical band gap of the material [26]. In addition, the significant absorption in the 320-380 nm range can be attributed to ligand to metal charge transfer induced transitions which is from $\text{O } 2p \rightarrow \text{Ni}^{3+}$ [33].

Overall, the progressive decrease in the band gap from 3.27 eV (LNO) to 2.41 eV (LHFNO) confirms the successful tuning of the electronic band structure through Fe and Ho

incorporation. The observed band gap narrowing enhances visible-light absorption, indicating that the co-doped LNO perovskites could be promising candidate for photocatalytic and optoelectronic applications [26, 23].

3.5 Photoluminescence

PL is the emission of light from a material following the absorption of photons. When a material is photoexcited, an incident photon promotes an electron from the VB to the CB. The subsequent radiative recombination of the excited electron with a hole in the VB lead to the emission of light. PL spectroscopy is therefore a useful technique for studying the recombination mechanism and behavior of photo-generated electron-hole pairs. The intensity of the PL emission reflects the rate of radiative recombination of these charge carriers. A higher PL intensity generally indicates a higher recombination rate of excited carriers, whereas a lower intensity suggests more efficient charge separation and reduced recombination rate [35].

Figure 7 shows the PL spectra of pure LNO, LFNO, and LHFNO recorded at room temperature using an excitation wavelength of 450 nm. Several emission peaks are observed in the visible region with major peaks located at 495 nm, 527 nm, 557 nm, 591 nm, 621 nm and 654 nm. The emission around 495 nm is typically attributed to direct band-to-band radiative recombination between electrons in the CB and holes in the VB. The green emission region between 500 nm and 520 nm further confirms the presence of defect-related emission processes [21]. The peaks centred at 527 nm and 557 nm arise from shallow defect levels, including singly charged oxygen vacancies and self-activated centres generated due to local lattice distortions [36, 37].

The green emission near 572 nm is associated with recombination between a trapped hole at a doubly ionized oxygen vacancy and an electron located in a trap state close to the CB [38]. In the LHFNO, the orange-red emission peaks at 621 nm and 654 nm are attributed to characteristic of 4f-4f electronic transitions Ho^{3+} ions, specifically the transitions $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ respectively [39]. In contrast, the emission peaks observed at 621 nm and 654 nm in LFNO sample originate from Fe-related deep defect levels rather than rare-earth transitions. The substitution of Fe^{3+} ions for Ni^{3+} alters the charge balance in the perovskite lattice, which is typically compensated by the formation of additional oxygen vacancies and $^{3+}$ mixed valence states of $\text{Ni}^{2+}/\text{Ni}^{3+}$. These defects introduce deep acceptor levels within the band gap, facilitating radiative recombination through lower-energy defect states. Such observations are consistent with previous studies indicating that increased oxygen deficiency in perovskite oxides generates mid-gap defect states that contribute to visible-range radiative transitions [40, 41].

A noticeable increase in PL intensity is observed with doping, following the order LHFNO > LFNO > LNO. The enhanced PL intensity suggests an increased recombination rate of photogenerated electron-hole pairs. This increase in emission intensity with doping indicates reduced charge separation and enhanced recombination efficiency of photoexcited carriers, leading to a shorter carrier lifetime [42]. The pure LNO sample exhibits the lowest PL intensity, where the emission mainly governed by intrinsic oxygen-vacancy-related deep-level recombination. With Fe doping, the PL intensity increases significantly due to the formation of additional deep defect states, such as oxygen vacancies. The LHFNO shows the highest PL intensity, indicating the strongest defect-mediated recombination. Substituting La^{3+} with Ho^{3+} introduces additional lattice distortions, oxygen vacancies, which act as efficient radiative recombination centres. The incorporation of Ho^{3+} ions at the A-site causes distortion of the

LaO₁₂ coordination environment and introduces intermediate sub-bandgap states, thereby increasing probability of radiative recombination and resulting in the strongest PL emission among the samples [39].

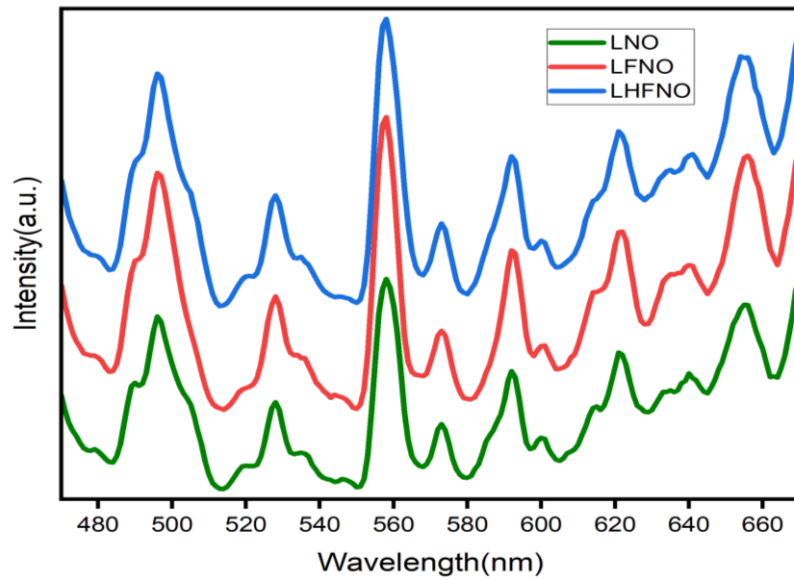


Figure 7. Photoluminescence spectra of LNO, LFNO and LHFNO

PL decay analysis provides further insight into the recombination dynamics of luminescent materials. Therefore, the room-temperature PL decay behavior of LNO, LFNO, and LHFNO samples is investigated in detail. Time-resolved PL measurements are carried out under 450 nm excitation, and the corresponding decay curves are shown in Figure 8.

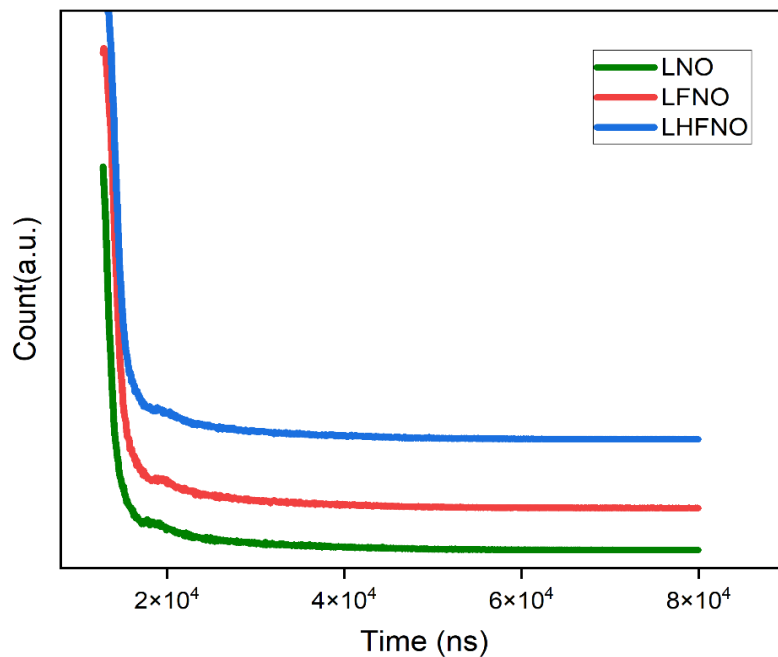


Figure 8. PL decay curves of LNO, LFNO and LHFNO

The luminescence decay profiles of all samples can be satisfactorily fitted using a first order exponential decay function given in equation (10) [39]:

$$I_t = A \exp\left(-\frac{t}{\tau}\right) \dots \dots \dots (10)$$

Where I_t is the PL intensity at time t , A is a pre-exponential constant, and τ represents the characteristic decay lifetime of the excited charge carriers. When $t = \tau$, the PL intensity decreases to $\frac{1}{e}$ of its initial value, indicating that τ corresponds to the time required for the excited carrier population to decay to approximately 36.8% of its starting value.

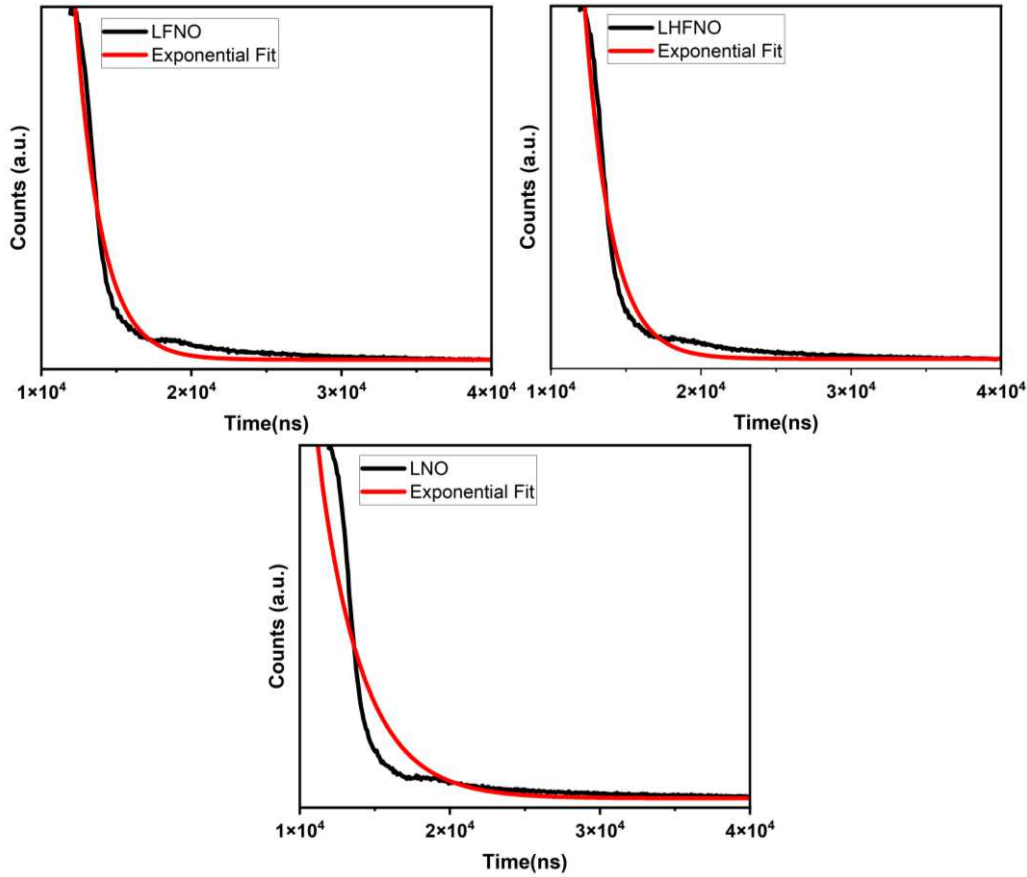


Figure 9. Decay plot with exponential decay fitting of LNO, LFNO and LHFNO

Figure 9 presents the single exponential fitting of PL decay curves. The calculated lifetimes for LNO, LFNO and LHFNO are 1.22 μ s, 1.62 μ s and 1.68 μ s respectively. The increase in lifetime observed in doped samples suggests the presence of defect levels within the conduction and valance bands. These defect states act as trapping centres that influence the recombination dynamics of charge carriers. Overall, the (Ho,Fe) codoped LNO promises improved optical behaviour comparatively.

3.6 X-ray Photoelectron Spectroscopy

XPS measurements are performed to analyze the chemical composition, defects and electronic structure of the synthesized samples. Figure 10 presents the XPS of the La 3d core levels for LNO, LFNO, and LHFNO samples recorded at room temperature. The La 3d spectra exhibit complex features with fine structures in addition to the characteristic spin orbit split peaks. The La 3d core level is split into components namely La 3d_{5/2} and La 3d_{3/2} which appears in the binding energy range of approximately 835 – 839 eV. The La 3d_{5/2} peak observed at around 835.23 eV is attributed to the La³⁺ oxidation state [43, 44].

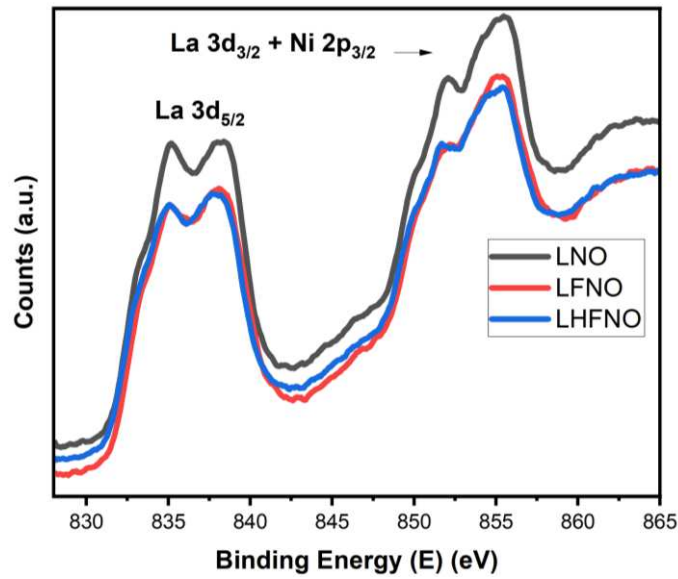


Figure 10. XPS La 3d of LNO, LFNO and LHFNO

Each La 3d peak further splits into a main peak and a satellite peak corresponding to different final state configuration. The main peak corresponds to the $3d^0 4f^0$ final state configuration, whereas the satellite peak corresponds to the $3d^0 4f^1 L$ configuration, where L represents a hole in the ligand orbital. The observed energy separation between the main and satellite peaks indicates strong La-O hybridization. The nature of these satellite peaks differs between metallic and insulating lanthanum compounds, resulting in variations in their BE positions relative to the main peak. In insulating compounds, the satellite peak originates from electron transfer from the ligand to the La 4f state, appearing at the higher BE side of the main peak [43].

The La $3d_{5/2}$ peak can be deconvoluted into two sub-peaks located at approximately 835.09 eV and 838.34 eV, the latter corresponding to a satellite peak, as illustrated in figure 11. The main peak exhibits a slight shift toward lower binding energy in the LFNO and LHFNO samples, which may be attributed to changes in the local electronic environment resulting from dopant incorporation. The BE region between 850 eV and 860 eV contains contributions from La $3d_{3/2}$ and Ni $2p_{3/2}$ states. Deconvolution of this region reveals three sub-peaks centered at 851.70 eV, 854.18 and 855.83 eV. The peak at 851.70 eV is assigned to La $3d_{3/2}$, while the peaks at 854.18 and 855.83 eV correspond to Ni^{2+} and Ni^{3+} oxidation states, respectively. The area and FWHM values of LNO, LFNO, and LHFNO samples are shown in table 4. The enhanced broadening in the Ho-Fe co-doped sample indicates increased structural disorder due to ionic size mismatch and dopant incorporation as can be seen in the XRD results. The variation in the integrated area of the La 3d components upon doping indicates the change in the surface La concentration which changes the electronic density and local coordination around La indicates the dopant incorporation influences the La-O bonding environment without altering the La^{3+} oxidation state [45].

Table 4. Deconvoluted results of La 3d displaying the BE, Area and FWHM of LNO, LFNO and LHFNO

Sample	Binding Energy	Area	FWHM
LNO	835.09	211935.8	3.79
	838.34	102484.8	2.24

	851.70	86108.1	2.68
	854.18	66568.0	2.08
	855.83	62608.4	1.82
LFNO	834.91	179893.8	3.65
	838.22	111302.1	2.53
	851.10	50638.0	2.23
	853.19	55481.0	2.45
	855.37	95749.2	2.59
LHFNO	834.76	181644.9	3.81
	838.08	102081.0	2.50
	851.24	67241.6	2.59
	853.73	62480.9	2.41
	855.57	64572.8	2.19

Figure 12 shows XPS of the Ni 2p core levels of LNO, LFNO, and LHFNO samples measured at room temperature. Analysis of the Ni 2p_{3/2} core level is complicated due to the partial overlap between the Ni 2p_{3/2} and La 3d_{3/2} peaks. The Ni 2p_{3/2} peak located at approximately 855.4 eV corresponds to the Ni³⁺ oxidation state, whereas the peak at around 852.08 eV is associated with Ni²⁺ state [43, 46]. The presence of satellite peak at the higher binding energy side of the main peak further confirms the existence of Ni²⁺ species in the samples. Because of the overlap with the La 3d_{3/2} peak, the Ni 2p_{3/2} region cannot be analysed independently without considering the La 3d_{3/2} spectra.

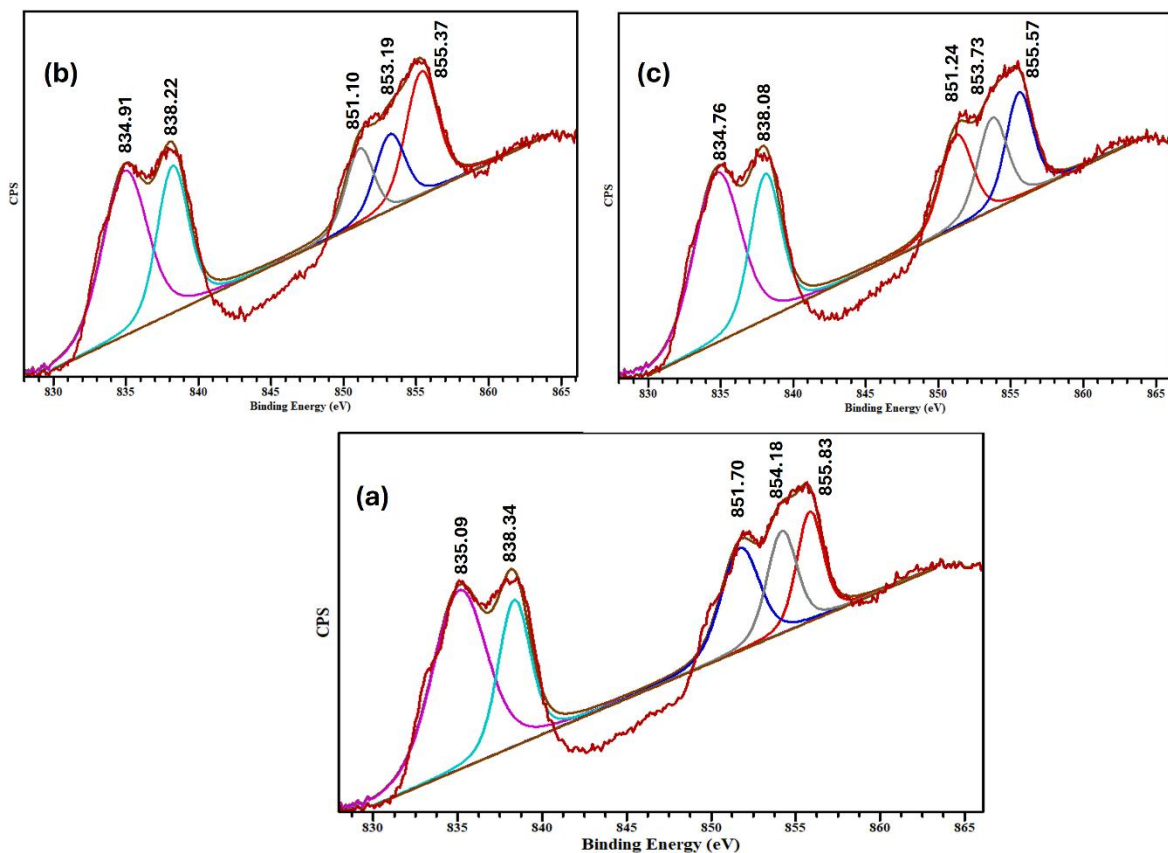


Figure 11. La 3d peak convolution of (a) LNO, (b) LFNO and (c) LHFNO

The Ni 2p_{3/2} peaks represent different chemical states of nickel within the lattice [43]. The intensity ratio of Ni²⁺/Ni³⁺ decreases upon Fe doping, which may be attributed to lattice stabilization resulting from the substitution of Ni with Fe³⁺ ions, which possess a stable oxidation state. This substitution likely reduces the concentration of oxygen vacancies. In contrast the Ni²⁺/Ni³⁺ intensity ratio increases in the LHFNO sample, which may be associated with increases lattice distortion leading to a higher concentration of oxygen vacancies. The Ni 2p_{1/2} peak is observed at approximately 872 eV.

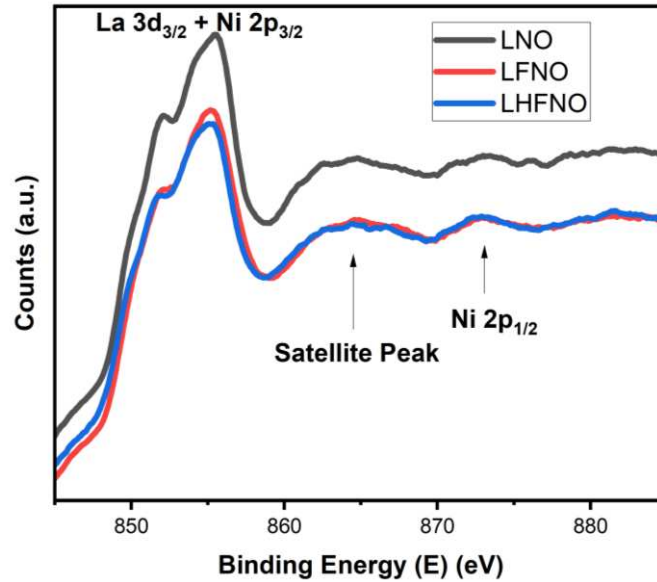


Figure 12. XPS spectra of Ni 2p of LNO, LFNO and LHFNO

Figure 13 shows XPS spectra of the O1s core levels for LNO, LFNO, and LHFNO samples. The O 1s peaks appear broad and asymmetric, indicating the presence of multiple oxygen species on the surface. Two main components are observed, the peak at approximately 528.5 eV corresponds to lattice oxygen, while the peak around 531 eV is attributed to oxygen vacancies or surface oxygen species [46].

The distinct separation in BE allows the lattice oxygen peak to serve as an indicator of the formation of the perovskite LNO structure containing trivalent Ni³⁺ ions. It is known that the rare-earth oxides are highly hygroscopic and can easily adsorb moisture when exposed to atmospheric conditions. The intensity of both O 1s components decreases with doping [43, 44]. From the above figures, evidently, co-doping both A and B sites of LNO has increased oxygen vacancies comparatively which is responsible for the decrease in the bandgap as well as increased recombination intensity in the PL spectra and thereby improving the optical properties of the samples.

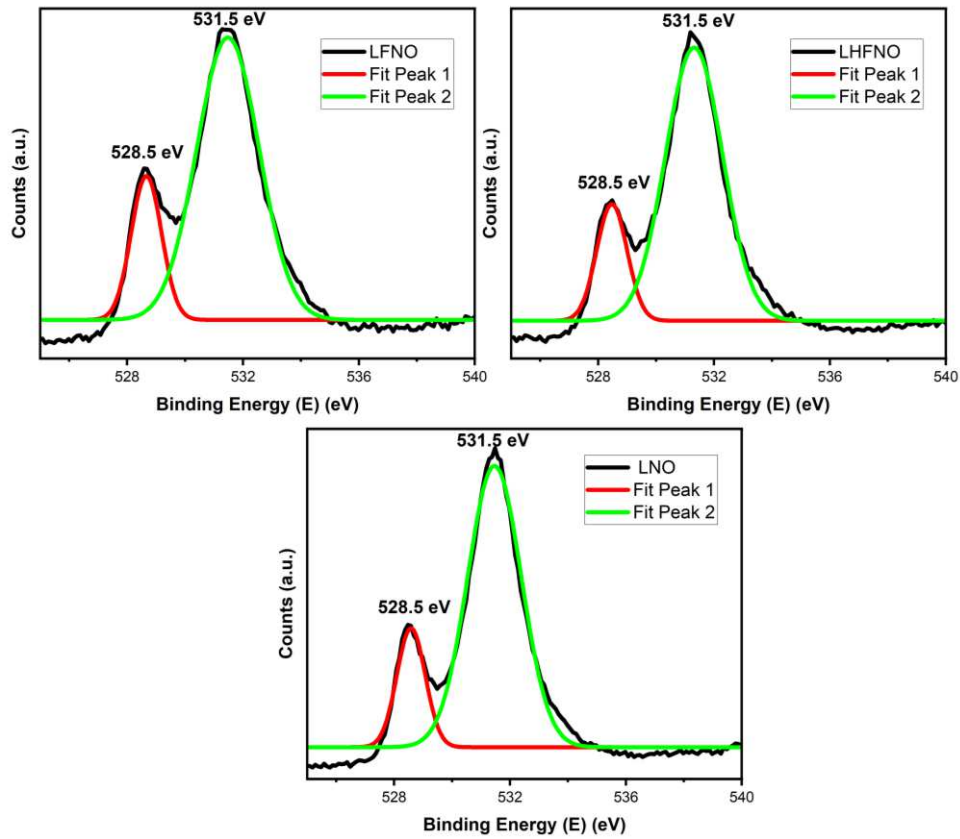


Figure 13. XPS spectra of O 1s of LNO, LFNO and LHFNO

Conclusions

In the present study, three samples of pure LNO, Fe doped LNO and Ho-Fe co-doped LNO are synthesized using the sol-gel auto-combustion method. The prepared powders are calcined at 750°C and sintering at 850°C. Structural analysis using XRD confirmed the formation of a distorted rhombohedral crystal structure with an R3c space group, with nanostructured crystallites. A shift of diffraction peaks toward lower angles is observed, which can be attributed to the difference in ionic radii of the dopant ions. Variations in lattice parameters, the c/a ratio and cell volume further indicate structural modifications induced by doping. FE-SEM images revealed nearly spherical particles with noticeable agglomeration. The observed variations in grain size attributed to differences in ionic radii, lattice distortion, and structural disorder introduced by the dopant ions which is consistent with the XRD results.

FTIR confirmed the presence of characteristic vibrational bonds. Shifts and changes in the spectra indicate modifications in molecular geometry resulting from Fe and Ho incorporation into the LNO lattice. The optical bandgap, determined using UV-DRS is found to vary from 3.1 eV to 2.5 eV, indicating stronger absorption in the visible region. The reduction in bandgap for LFNO and LHFNO compared to pure LNO is associated with lattice distortion, changes in octahedral coordination, the formation of oxygen vacancies and the introduction of defect levels between the VB and CB. PL spectra exhibited multiple emission peaks corresponding to band-to-band transitions and defect related states. The enhanced PL intensity observed in doped samples is attributed to reduced charge separation and increased recombination efficiency of photo-generated charge carriers. XPS analysis revealed characteristic La 3d_{5/2} and La 3d_{3/2} doublet peaks with partial overlap of the La 3d_{3/2} peak with the Ni 2p_{3/2} peaks due to spin-

orbit coupling. The spectra also confirmed the presence of nickel in mixed oxidation states, Ni^{2+} and Ni^{3+} . Overall, the results demonstrate that Ho-Fe co-doping significantly modifies the structural and optical properties of LNO due to more oxygen vacancies, recombination and spin-orbit coupling, resulting in reduced bandgap and increased photoluminescence, thus making the material better suitable for potential applications in photocatalytic and optoelectronic devices.

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Author statement

All the authors have equally contributed to writing, supervising, interpretation, editing, and reviewing the manuscript. Also the manuscript has been submitted with the consent of all authors.

CRedit authorship contribution statement

Meenakshi R Krishnan: Writing – original draft, interpretation, Validation, Methodology, Investigation. Roshima N S: Writing – original draft, interpretation, Validation, Methodology, Investigation. Jyotirmayee Satapathy: Review & editing, Validation, Methodology, and formal Analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of Interest

The authors declare no conflict of interest. Data availability Data will be made available on request.

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