

Spectroscopic and Antimicrobial Examine on LaNi_{1-x}Fe_xO₃ (x = 0.1 & 0.2) Nanoparticles Synthesized By Sol Gel Combustion Method



A. Sahana Fathima, S. Sharmila, V. Senthil Kumar

Abstract: Most of the perovskite materials exhibit an anti-bacterial effect, and due to their non-toxic nature they can be used in surgical tools. An attempt has been made to study the anti-bacterial activity and its spectroscopic analysis of Fe-doped Lanthanum Nickel Oxide nanoparticles prepared by sol-gel combustion method. The material exhibits cubic structure of LaNi_{1-x}Fe_xO₃ examined from XRD analysis. The optical absorbance, bandgap and the type of bonding have been identified using UV-VIS spectroscopic and FT-IR analysis. Antibacterial property of the synthesized material also studied using a gram positive bacteria (*Streptococcus pyogenes*) and gram negative bacteria (*Escherichia coli*).

Keywords: Lanthanum nickel oxide, Fe-doped, sol-gel combustion and anti-bacterial activity.

I. INTRODUCTION

Nanomaterials occupy an unavoidable place in the fast developing field of science and technology nowadays, especially in nanoelectronics and nano-medicine [1]. The properties of nanomaterials make them vital and advanced in many areas of human activity because of their unique size. The applications of nanoparticles also include catalysis, photonics, energy storage, fuel cells, sensing devices to nanomedicine [2]. At present microbial resistance to antibiotics has reached a critical level. In the last several years, nanosized metal oxide are used as an antimicrobial agents due to its nontoxic effects of mammalian cells [3]. After exploring various options to overcome the problem, nanosized metal oxide emerged as a promising material, due to its stability, lower toxicity and durability compared to other organic materials [4]. The growth and the antibacterial application of nanoparticle depends on the shape, morphology, size and the crystal defect of the particles. Actions of the antibacterial mechanism of the material includes production of ROS on the surface of these nanoparticles in the light causes oxidative stress in bacterial cells eventually leading to death of the cells [4].

Over a past two decades, both organic and inorganic perovskites materials focused in the field of fuel cells, batteries, super capacitor, solar cell and electrochemical sensing because of their chemical and physical properties including chemical stability, metal oxygen ionic conductivity, and high electrocatalytic activity [5]. In contemporary years, the design and synthesis of Perovskite nano materials have been studied widely by researchers due to their peculiar properties.

These materials exhibit attractive chemical and physical features like electrically active structure, electrical conductivity, chemical and thermal stability and super magnetic, dielectric, thermoelectric and photocatalytic properties [6]. Perovskite mixed oxides materials contains metal elements and non-metallic elements, LaNiO₃ perovskites oxides were widely investigated among the rare earth perovskites containing Ni³⁺ ions[7]. This material is considered extremely important among the perovskites due to their electronic, optical, catalytic properties etc.[8]. In this work, Fe-doped LaNiO₃ samples were prepared by sol gel combustion method and its spectroscopic and antibacterial property were analyzed.

II. MATERIALS AND METHOD

Fe doped LaNiO₃ nanoparticles were prepared by sol gel combustion method. Highly pure Lanthanum nitrate, Nickel Nitrate, Ferric Nitrate and Citric acid were used to prepare the material. pH value was monitored throughout the synthesis using Ammonia solution. All the precursors were taken in stoichiometric amount and dissolved in de-ionized water. For one hour at 60°C the solution was stirred continuously. Then it was placed in hot plate at 70°C to obtain gel. On further heating, it ignited and powder will be formed. Using muffle furnace the resultant sample was calcined at 650°C for 7 hrs and further utilized for characterization.

A. Material Characterization

The prepared LaNi_{1-x}Fe_xO₃ samples was unveiled to PANalytical X'pert PRO powder x-ray diffraction to understand the structure of the material. A functional group analysis was performed using FTIR spectroscopy (Model-MAGNA 550). Optical analysis was done using an ultra violet visible spectrometer. Anti-bacterial activity of the samples was determined by agar well diffusion method.

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III. RESULT AND DISCUSSION

B. Structural Analysis

The crystal structure and phase formation of Fe doped LaNiO₃ were identified using XRD pattern. Fig. 1 shows the XRD patterns of LaNi_{1-x}Fe_xO₃ (x= 0.1, 0.2) samples. XRD pattern evidently indicates that the crystalline nature of Fe doped LaNiO₃ nanoparticles, prefers the orientation (1 1 0) and exactly matches with JCPDS CARD no. 30-0710 and indexed in the cubic structure. All the diffracted peaks exhibit 2θ values corresponding to (1 0 0), (1 1 0), (1 1 1), (2 0 0) and (2 2 0) planes with most intense peak at 32.36°.

Few peaks were identified as impurities for 0.2 mole of Fe which have not seen in 0.1 mole of Fe, noted as * in Fig.1. The intensity of the peaks decreases with an increase in concentration of Fe content, due to the difference in electronic density or due to point defect [15] and Fe also has less ionic radii as compared to Ni as a result the intensity decreases and the peak broadened. The shifting of peaks occurs towards a lower angle because of the strain due to planar stress at large amount of doping [4]. The average

crystalline size of the obtained samples was calculated using Scherer’s formula. The calculated lattice parameter (a) of LaFe_{0.1}Ni_{0.9}O₃ (3.9117) and LaFe_{0.2}Ni_{0.8}O₃ (3.9915) gives an exact agreement with the theoretical value. The grain size of the sample decreases when increasing the concentration of the Fe content in the sample. Dopants are often added to materials to lower the grain size and also to reduce the particle size. Dislocation density increases with increase in concentration, the increase in dislocation density, and strain may occur due to the decrease in grain size.

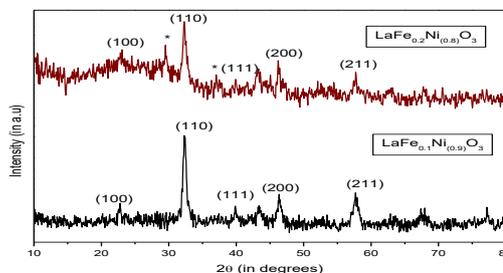


Fig.1 XRD Spectrum of Fe-doped LaNiO₃ nanoparticles

Table: 1 Structural parameters

Sample	Grain size (nm)	Lattice parameter (a)	Volume (m ³)	Strain ε (10 ⁻³ m)	Dislocation Density (10 ¹⁵ lines/m ²)
LaFe _{0.1} Ni _{0.9} O ₃	39.157	3.9117	59.8551	1.614	0.6521
LaFe _{0.2} Ni _{0.8} O ₃	37.905	3.9915	60.2155	1.825	0.6959

C. FT-IR Analysis

The FT-IR Spectra were recorded with wave number ranging from 400 – 4000 cm⁻¹ for Fe doped LaNiO₃ nanoparticles are shown in fig (2). The broad band observed at 3000-3400 cm⁻¹ is due to O-H stretching of citrates and water molecules adsorbed from atmosphere. The transmittance peak is absorbed from above 700 cm⁻¹ including 727, 839, 1361, 1500, 1506 cm⁻¹. The band 727 cm⁻¹ attributes to metal oxide (Ni-O) and peaks centered at ranges from 1350-1500 for La-Ni bonds[6]. Further the transmittance peak observed in the range of 1500 and 1361 cm⁻¹ suggests a monodentate coordination of the carboxylates to nickel. The FTIR spectra of the samples for different Fe concentration are identical.

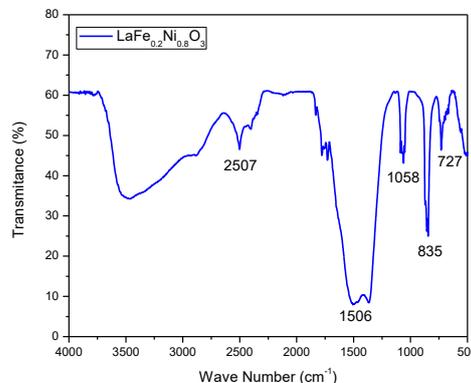
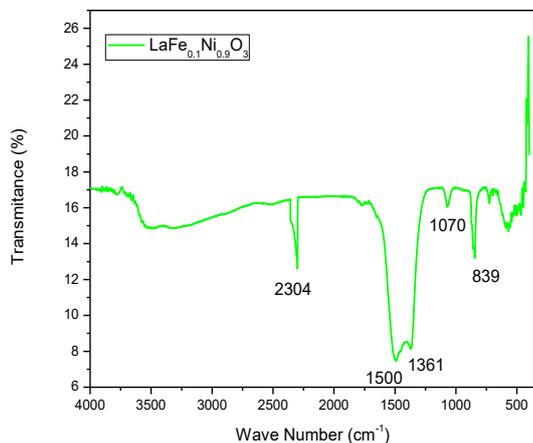


Fig.2 FTIR Spectrum Of LaFe_xNi_(1-x)O₃ nanoparticles at different Fe concentration



D. UV-VIS Analysis

Ultra-Visible Spectroscopy is a technique used to determine the optical properties of Nano sized particles. The absorption spectrum of Fe-doped LaNiO₃ nanopowders is shown in Fig 3. It indicates that LaFe_{0.2}Ni_{0.8}O₃ has higher absorbance than LaFe_{0.1}Ni_{0.9}O₃. This absorption spectrum reveals that absorption increases with an increase in the concentration of the dopant[9]. The band gap has been determined by plot a straight line in (hν) verses (αhν)² graph as shown in Fig 4. The band gap of LaFe_{0.2}Ni_{0.8}O₃ is 2.56 eV and for LaFe_{0.1}Ni_{0.9}O₃ is 2.36 eV. This result shows that while adding dopant the band gap increases.



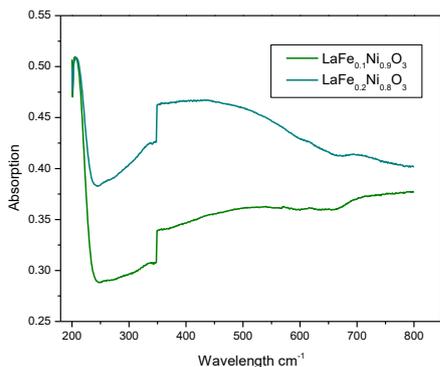


Fig 3 Absorbance spectra of $\text{LaFe}_x\text{Ni}_{(1-x)}\text{O}_3$ nanoparticles at different Fe concentration

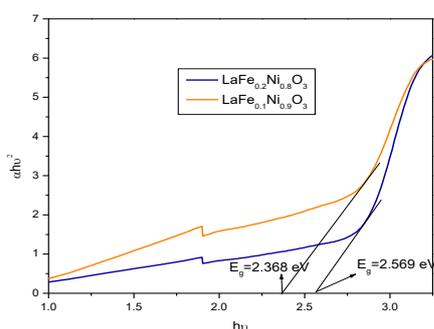


Fig 4 $h\nu$ vs $\alpha h\nu^2$ plot for $\text{LaFe}_x\text{Ni}_{(1-x)}\text{O}_3$ nanoparticles at different Fe concentration

E. Morphological Analysis

Samples were synthesized by sol gel citrate method was examined by Scanning electron microscope to study the surface morphology of the samples. The SEM pictures are shown in Fig (5a & b) for the prepared material. It is noticed that all the samples are homogenous[8]. Compared to fig 5A to 5B shows the obvious spherical shape with diameter less than micrometer. There is an improvement in morphology of the samples observed from the micrographs 5A-5B.

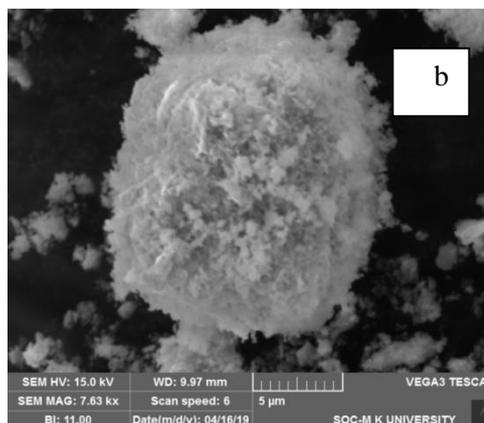


Fig 5(a-b) SEM images of Fe doped LaNiO_3 nanoparticles

F. Anti-Bacterial Analysis

The antibacterial activity of Fe doped Lanthanum Nickel Oxide nanoparticles were tested against Escherichia coli, Streptococcus pyogenes, using disc diffusion method. Fe doped Lanthanum Nickel Oxide nanoparticles were dispersed in appropriate concentration of 1 mg/ml with dimethylsulfoxide solution for this process. Then, using the micro-pipette the solution was impregnated to each sterile disc. To incubate, the discs were kept on culture swapped Mueller Hinton Agar medium using sterile force and allowed for 24 hr [15].

The antimicrobial activity of the $\text{LaFe}_x\text{Ni}_{(1-x)}\text{O}_3$ ($x=0.1,0.2$) samples was tested against the one gram negative and one gram positive bacteria and the results are revealed in fig (5). The zone of inhibition values were tabulated below for each strain. Fe (0.2) doped LaNiO_3 shows higher zone of inhibition for gram positive bacteria Streptococcus pyogenes than other samples. The activity shows that there is an interaction between the $\text{Fe}:\text{LaNiO}_3$ and bacterial cell membrane causing the death of bacteria due to induced toxicity. All the samples show a good death effect on microbes, and there is an increase in zone of inhibition area when the dopant concentration increases. $\text{LaFe}_{0.1}\text{Ni}_{0.9}\text{O}_3$ nanoparticle shows a very weak antibacterial activity in gram negative strains compared to all other tested samples. The comparison of antibacterial activity is shown in the fig (6). The test results show that $\text{Fe}:\text{LaNiO}_3$ nanoparticles were able to attach the membrane of pathogenic bacteria by electrostatic interactions that produces toxicity ions and damage cell membrane.

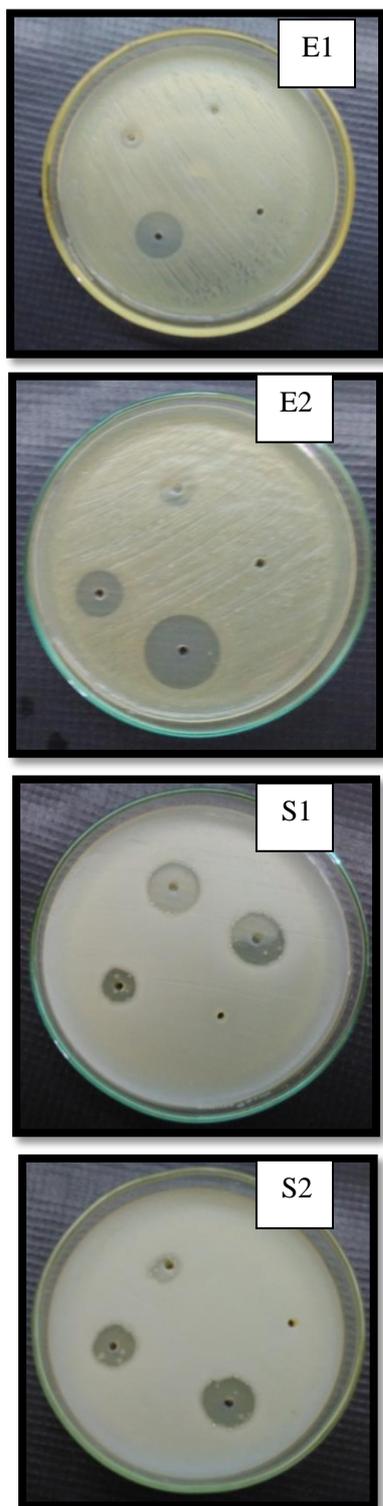


Fig 6 Anti-bacterial activity of $\text{LaFe}_x\text{Ni}_{(1-x)}\text{O}_3$ nanoparticles on Escherichia coli (E1, E2) Streptococcus pyogenes (S1,S2)

Table 3 Anti-bacterial activity of $\text{LaFe}_x\text{Ni}_{(1-x)}\text{O}_3$ nanoparticles on Escherichia coli (E1, E2) Streptococcus pyogenes (S1,S2)

Image	Sample	Zone of Inhibition (diameter in mm)		
		1.0mg/mL	0.5 mg/mL	0.25 mg/mL
E1	$\text{LaFe}_{0.1}\text{Ni}_{0.9}\text{O}_3$	15	11	11

E2	$\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$	20	15	12
S1	$\text{LaFe}_{0.1}\text{Ni}_{0.9}\text{O}_3$	30	20	18
S2	$\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$	32	27	16

IV. CONCLUSION

Fe-doped Lanthanum Nickel Oxide samples were prepared by using low cost and easy Sol-gel ignition method. The XRD pattern reveals the pattern of cubic structured LaNiO_3 with impurity free peaks and the grain size is also calculated. The functional group of the sample is also identified it shows La-Ni and La-O bands. UV-VIS analysis shows, a higher absorbance value for the $\text{LaFe}_{0.2}\text{Ni}_{0.8}\text{O}_3$ and the band gap of the material decreases with an increase in dopant concentration. Further antibacterial studies were done on different strains of the pathogens and an enhanced anti-bacterial property was observed due to the increased dopant concentration.

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