

Synthesis, Structural and Antibacterial Activity of Aluminium and Nickel Doped ZnO Nanoparticles by Sol-gel Method

Abstract

Nickel and aluminium doped zinc oxide (ZnO) nanoparticles were synthesized by sol-gel method and their structural, morphological, and antibacterial activity were studied. X-Ray Diffraction (XRD) studies reveals that all synthesized ZnO nanoparticles have hexagonal wurtzite structure and Al doping decreases the crystallite size. Scanning Electron Microscopic (SEM) investigation reveals that the surface morphology of zinc oxide nanoparticles is significantly modified by doping with Ni and Al. Energy Dispersive analysis of X-ray spectroscopy (EDX) indicates that the dopants Ni and Al are successfully incorporated in the ZnO nanoparticles. Fourier transform infrared spectra (FTIR) were recorded to analyse the effect of Ni and Al doping on the vibrational frequencies of zinc oxide nanoparticles. The antibacterial activities of ZnO nanoparticles, Al doped ZnO nanoparticles and Ni doped ZnO nanoparticles were examined using the disc diffusion method against four pathogenic bacteria.

Keywords : Dopant , Nanoparticle , SEM , Sol-gel process , XRD ,Zinc oxide

1. Introduction

Nano structured materials have a larger percentage of atoms at their surface which lead to high surface reactivity. Thus, nanomaterials have witnessed recently significant importance in the basic and applied sciences as well as in bio nanotechnology [1]. Most preferentially, among different metal oxide nanoparticles, ZnO nanoparticles have their own importance due to their vast area of applications, for example, gas sensor, biosensor, cosmetics, storage, optical devices, solar cells, and drug-delivery [2]. In the Earth crust ZnO is present as zincite mineral but mostly ZnO used for commercial purposes is produced synthetically. ZnO is often called II-VI semiconductor in materials science because zinc and oxygen belong to the 2nd and 6th groups of the periodic table [3]. Zinc oxide, a direct wide bandgap (3.4 eV) n-type semiconductor, has a stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm and composed of a number of alternating planes with tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis. It has attracted intensive research effort for its unique properties and versatile applications [4]. The lack of a center of symmetry in wurtzite, combined with strong electromechanical coupling, results in pronounced piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensor [5]. Nanostructure zinc oxide is a promising material for chemical gas sensors because of its large surface-to-volume ratio, which improves its response. ZnO gas sensors have

been recently studied extensively due to the simplicity of its preparation [6]. Among a variety of semiconducting materials, zinc oxide is rich in nanostructures and it has the capability to produce into a variety of morphologies of nanowires [7].

Among the various methods of synthesis, there are the hydrothermal method, electrochemical depositions, sol-gel method, chemical vapor deposition, thermal decomposition, micro emulsion and combustion method [8]. As an alternative approach, the electrochemical route is of considerable interest because of a possibly precise particle size control achieved by adjusting current density or applied potential [9]. ZnO nano powders doped with different ions such as Al, In, Ga, etc. have improved electrical, optical, and catalytic properties. Among these, Aluminium doped ZnO nanopowders are both conductive and transparent in the visible region and thus can be utilized in transparent conductive pastes. The sol-gel process had attracted considerable attention because of its simplicity, acceptable costs and the crystalline quality of the ZnO prepared by that process [10]. Zinc aluminate spinel ($ZnAl_2O_4$) is one of the metal oxide semiconductors suitable for use in photoelectronic devices. ZnAlO is wide band gap semiconductor ($E_g \sim 3.8$ eV). The ZnO presents a great interest for the scientific Community due to its applications in different fields: electronics, opto-electronics, dielectrics, and sensing materials, as a photocatalyst and as an antimicrobial agent [11]. It is a significant task to prepare Ni, Al, co-doped zinc oxide nanoparticles with better optical, electrical and

ferromagnetic behavior for potential applications in magneto electronic and optoelectronic devices [12].

Nanoscale particles have emerged as novel microbial agents owing to the high surface area to volume ratio, which is coming up as the current interest in the researchers due to the growing microbial resistances against metal ions, antibiotics and the development of resistant strains [13]. ZnO exhibits significant antimicrobial activities when particle size is reduced to the nanometer range, then nano-sized ZnO can interact with bacterial surface and/or with the bacterial core where it enters inside the cell, and subsequently exhibits distinct bactericidal mechanisms [14].

Zinc oxide nanoparticles are known to be one of the multifunctional inorganic nanoparticles with effective antibacterial activity. Antibacterial and antifungal activities of ZnO nanoparticles are observed even at very lower concentrations and also the antifungal activity does not affect soil fertility compared to the conventional antifungal agents.

ZnO nanoparticles showed complete inhibition of *E. coli* growth at concentrations, whereas growth of *S. aureus* was completely inhibited for parallel experiments using flow cytometry based assays clearly demonstrated that growth inhibitory properties of ZnO nanoparticles were accompanied by a corresponding loss of cell viability [15]. The aim of this study is to synthesize ZnO nanoparticles doped with nickel and aluminum by sol-gel method and to study the effect of doping on the structural and morphological properties.

ZnO nanoparticle exhibit significant antimicrobial activities. In this study we considered the antibacterial activity of Ni and Al doped ZnO nanoparticles

2. Materials and Methods

2.1. Materials

Zinc acetate, Nickel chloride hexahydrate, Aluminium nitrate and methanol. All the chemicals were of analytical grade and were purchased from Merck AG (Darmstadt, Germany).

2.2. Preparation of ZnO nanoparticles

Zinc oxide nanoparticles were synthesized by sol-gel method using zinc acetate and methanol as precursors. 16 g of

zinc acetate was dissolved in 112 ml of methanol. After 10 minutes of magnetic stirring at room temperature the resultant solution was subjected to gelation at 80°C with constant stirring for 5 hours, from which the zinc oxide nanoparticles in the form of powder was obtained. The resultant powder was annealed at 450°C for 6 hours.

To prepare nickel doped ZnO nanoparticles, 16 g of zinc acetate was dissolved in 112 ml of methanol. After 10 minutes of magnetic stirring at room temperature, 2.8 g of nickel chloride hexahydrate was added. After an additional 15 minutes of magnetic stirring the resultant solution was subjected to gelation at 80°C with constant stirring for 5 hours. The resultant powder was annealed at 450°C for 6 hours.

Aluminium doped ZnO nanoparticle was synthesized by the addition of 2.5 g of Aluminium nitrate instead of nickel chloride in the above procedure.

2.3. Product characterization

The powder x-ray diffraction (XRD) was performed using automated x-ray diffractometer (X-PERTPRO Philips system) operating CuK_α at wavelength 1.54056 Å. The average crystallite size (D) has been calculated using Scherrer's relation $D = K\lambda/\beta\cos\theta$, where the constant K is taken to be 0.94, λ is the wavelength of x-ray used and β the full width of half maximum (FWHM). The morphology of the zinc oxide samples are characterized by scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX) to analyse the elemental composition of the synthesized materials. The FTIR spectra was recorded using a SHIMADZU instrument. Antimicrobial activities of the samples are determined by well diffusion method. Four pathogenic bacterial strains namely *Escherichia coli*, *Klebsiella pneumonia*, *Bacillus cereus* and *Staphylococcus aureus* are used in this investigation.

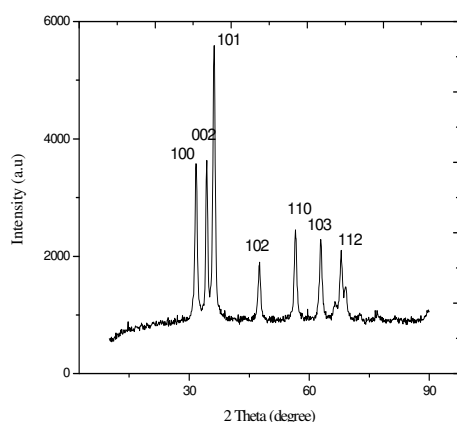
3. Results and discussion

3.1. X-ray diffraction analysis

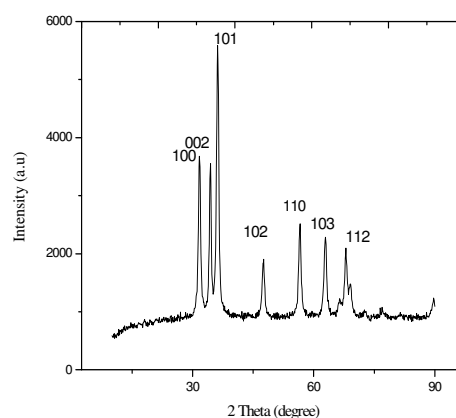
X-ray diffraction patterns of the synthesized ZnO nanoparticles are shown in Fig. 1. All the peaks are indexed and found to be well matched to wurtzite structure of ZnO having hexagonal phase, which is in good

agreement with the standard JCPDS (Card No. 36-1451). Based on the Scherrer equation the average crystallite size of the nanoparticles are observed as 18 nm, 17 nm and 11 nm for undoped , Ni doped and Al doped ZnO nanoparticles respectively. The peaks were identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. It was observed that doping with Al decreases the

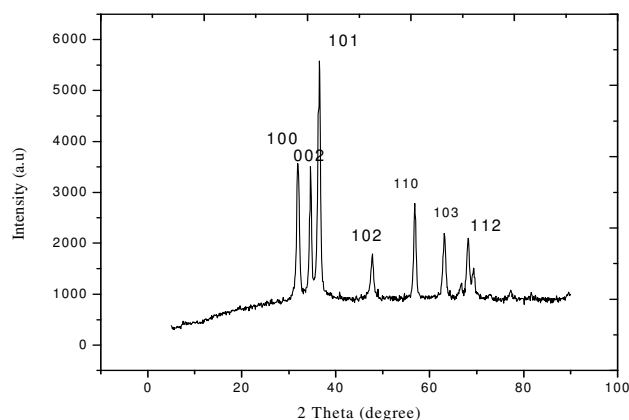
particle size of the ZnO nanoparticles. The intensity of XRD peaks of Al doped ZnO nanoparticle decreased when compared to that of undoped ZnO nanoparticle. Also the centre of all diffracted peaks of Al doped ZnO has a slight shift towards higher value of 2θ compared to that of ZnO. This result is in good agreement with the report of vadivel et.al.,(2015) [16].



(a)



(b)



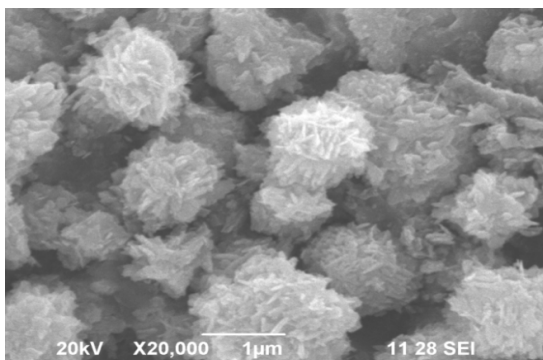
(c)

Fig. 1 : XRD patterns of (a) Undoped , (b) Ni doped and (c) Al doped ZnO

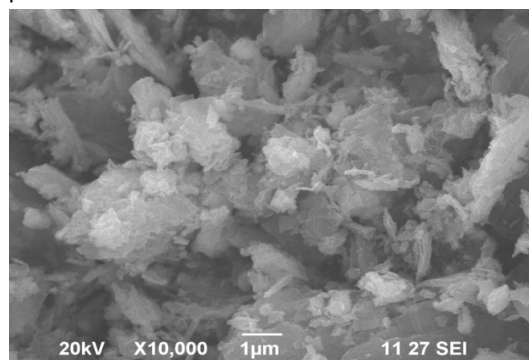
3.2. Scanning electron microscopy

Scanning electron microscopy (SEM) was employed to analyse the morphology and the growth features of prepared nanoparticles. Fig. 2(a), 2(b) and 2(c) show the SEM images of undoped ZnO, Ni doped ZnO and Al doped zinc oxide nanoparticles respectively. The undoped ZnO nanoparticles have flower-like

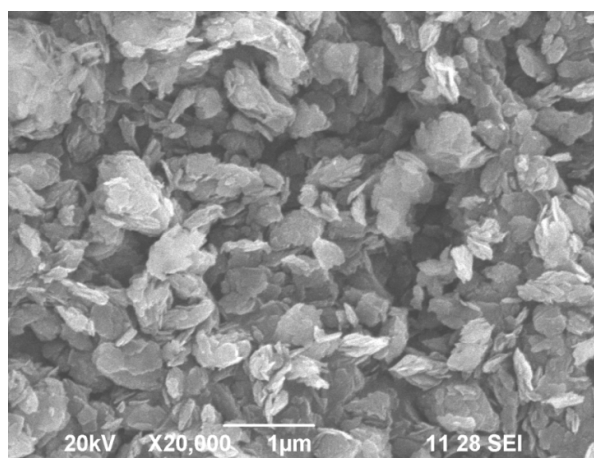
shape. From SEM micrographs, a non-uniform distribution of particles is observed. It consists of either several single particle or a cluster of particles. The morphology of Ni and Al doped ZnO nanoparticles completely varies from that of undoped ZnO nanoparticles. This may be attributed to the effect of doping in ZnO nanoparticles.



(a)



(b)



(c)

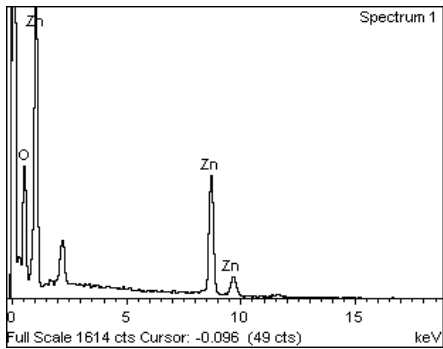
Fig. 2: SEM image of (a) Undoped ZnO (b) Ni doped ZnO (c) Al doped ZnO nanoparticles

3.3. Energy dispersive x-ray diffraction spectroscopy

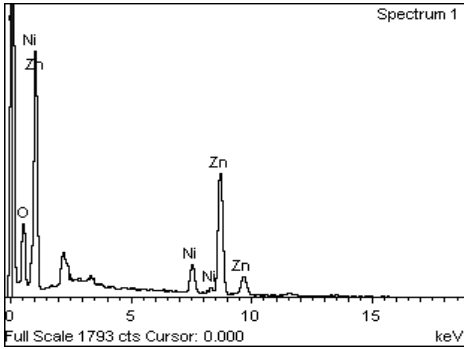
The elemental composition of the undoped ZnO, Ni doped ZnO and Al doped ZnO nanoparticles are carried out by EDX spectrum. Fig: 3(a) shows the EDX spectrum of undoped ZnO nanoparticles. The strong peaks observed in the spectrum are related to Zinc and oxygen. The prepared undoped ZnO nanoparticles have atomic percentage of 27.75

of Zinc and 72.25 of oxygen. This confirmed the formation of ZnO nanoparticles. The EDX spectrum of Nickel doped ZnO nanoparticle is shown in fig: 3(b). It shows the atomic percentage of 39.61 of Zinc, 55.81 of oxygen and 4.58 of Nickel. This confirmed the doping of Ni ion into the ZnO lattice. Fig: 3(c) shows the EDX spectrum of aluminium doped ZnO nanoparticles. It was found that Al-doped zinc

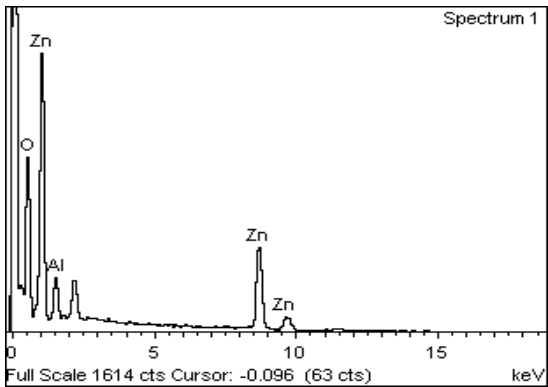
oxide nanoparticles have atomic percentage of 17.73 of Zinc, 75.27 of oxygen and 7 of aluminium. This clearly confirms the doping of Al into the ZnO lattice.



(a)



(b)



(c)

Fig 3: EDX Spectrum of (a) Undoped ZnO (b) Ni-doped ZnO (c) Al doped ZnO

Table 1 : The atomic content of the nanoparticles obtained from the EDX measurements.

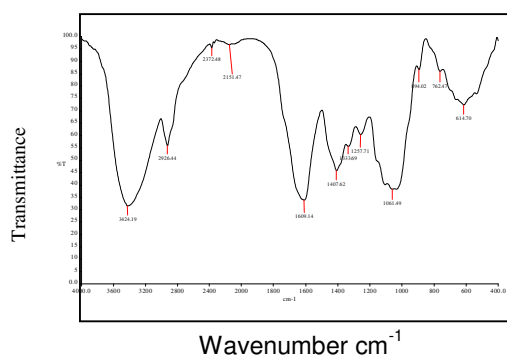
Type of nanoparticles	EDX results
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	Oxygen (at%)	Nickel (at%)	Aluminium (at%)	Zinc (at%)
Undoped ZnO	72.25	-	-	27.75
Ni doped ZnO	55.81	4.58	-	39.61
Al doped ZnO	75.27	-	7	17.73

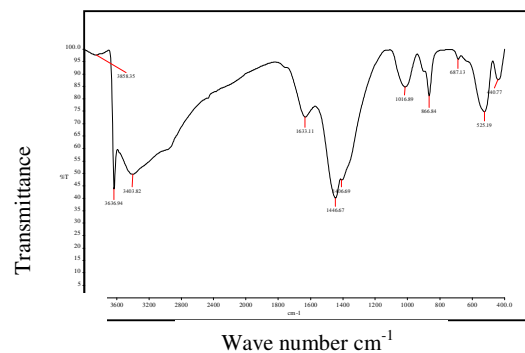
3.4. FTIR measurements

Fig. 4(a), 4(b) and 4(c) illustrates the FTIR spectra of undoped, Ni doped and Al doped ZnO nanoparticles respectively in the range of 400-4000 cm^{-1} . FTIR spectra of the synthesized nanoparticles show a significant spectroscopic band at around 500 cm^{-1} , which is the characteristic band of ZnO. The strong O-H band **was observed** in the range of 3400-

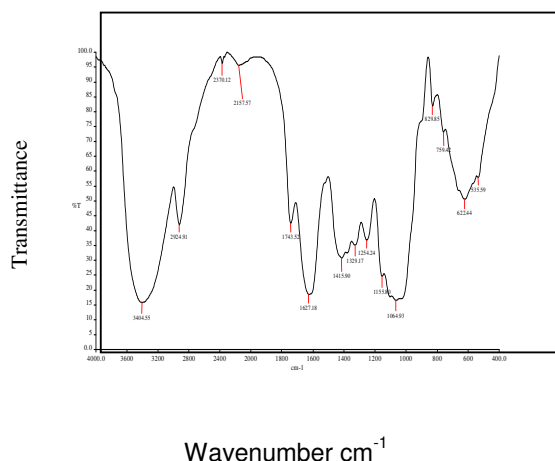
3650 cm^{-1} in all the FTIR spectra. The bands at 1600-1650 cm^{-1} in all the samples are due to the carbonyl groups of the carboxylate ions which might remain adsorbed on the nanoparticles. Inclusion of Ni and Al ions in the ZnO lattice in Ni doped and Al doped ZnO nanoparticle was confirmed by the emergence of the bands at 1063.93 cm^{-1} [Fig. 4(b)] and 525.19 cm^{-1} [Fig. 4(c)].



(a)



(b)



Wavenumber cm^{-1}

(c)

Fig. 4 : FTIR spectrum of (a) Undoped ZnO (b) Ni doped ZnO (c) Al doped ZnO nanoparticles

3.5. Antibacterial activity

Antibacterial activities of undoped ZnO , Ni doped ZnO and Al doped ZnO nanoparticles are examined using the disc diffusion method. Antibacterial activities are studied against four pathogenic bacteria (Eschericia Coli, Klebsiella Pneumoniae, Bacillus Cereus, and Staphylococcus aureus). The ranges of bacterial strains for undoped and doped ZnO nanoparticles are shown in the Table 2.

The undoped ZnO nanoparticles was found to be moderately active against all the four bacteria. However when doped with Aluminium

and Nickel the activity was found to be increasing as shown by the inhibition zone . Ni doped ZnO nanoparticle was found to be only active against Kiebsiella Pneumoniae and Staphylococcus Aureus. The inhibition zone increased from 8 to 12 in both cases. But Al doped ZnO nanoparticle was found to be more active against all the four bacteria as shown by the inhibition zone in Table :2. Compared to undoped sample the inhibition zone increased from 9 to 13 for Escheichia Coli and from 8 to 12 for all the other three bacteria. Fig. 5 shows the antibacterial activity of nanoparicles against the four bacteria.

Table 2 : Various ranges of bacterial strains for undoped and doped ZnO nanoparticles

S. No	Name of Bacteria	Inhibition zone for samples		
		Undoped ZnO A	Ni doped ZnO B	Al doped ZnO C
1	Escherichia Coli	9	7	13
2	Klebsiella Pneumoniae	8	12	12
3	Bacillus Cereus	8	8	12
4	Staphylococcus Aureus	8	12	12

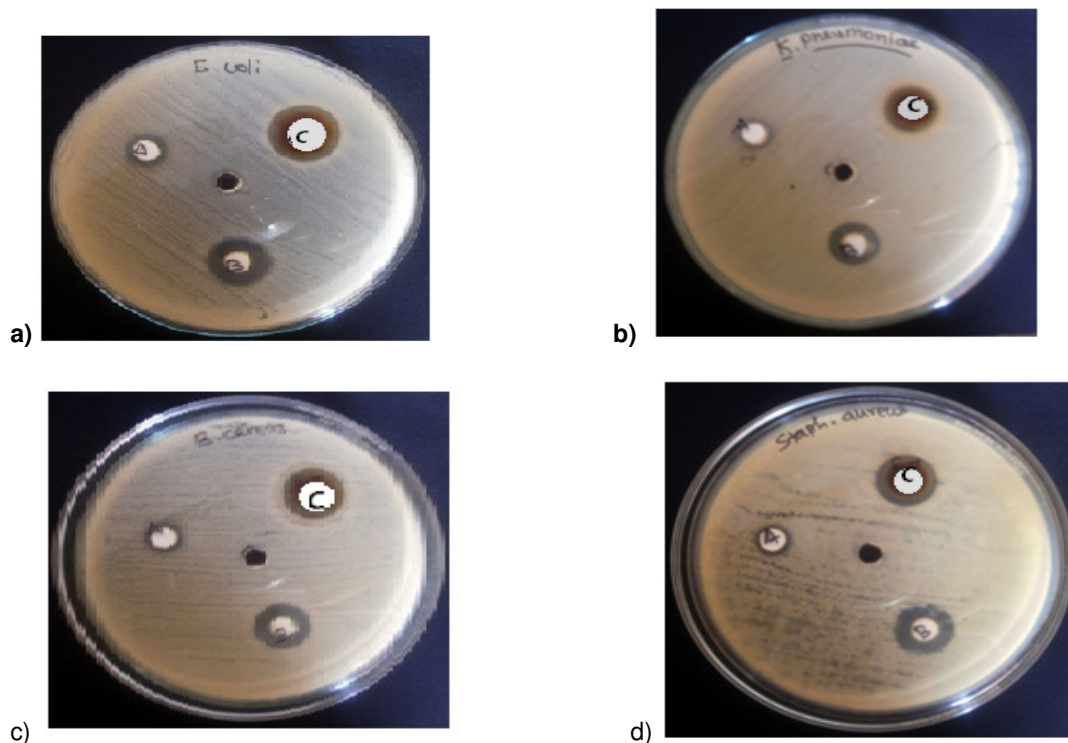


Fig. 5 : (a) Antibacterial activity against E-coli (b) Antibacterial activity against KlebsiellaPneumonia (c) Antibacterial activity against bacillus cereus (d) Antibacterial activity against Staphylococcus aureus.

4. Conclusion

Zinc oxide , Ni doped ZnO and Al doped ZnO nanoparticles **are** prepared by sol-gel method and the prepared nanoparticles **are** characterized by XRD, SEM, EDX & FTIR.

The crystallite size of the prepared nanoparticles determined by Debye-sherrers equation was found to be in the nanometer range and **showed** preferred growth orientation along (101) plane. All the nanoparticles **are found to have** wurtzite structure. **Doping with Al** decreases the particle size . The surface morphology of the ZnO , Ni doped ZnO and Al

doped ZnO nanoparticles characterized by SEM analysis suggested different morphological structures. Chemical purity and

stoichiometry of the samples **are** investigated by EDAX Spectroscopy . FTIR spectral studies showed the characteristic bands of ZnO nanoparticles .

Antibacterial activity studies **are** carried out by Disc diffusion method and it **was** found that the aluminium doped zinc oxide **nanoparticle was** more active against all pathogenic bacteria .

Hence it can be used for medicinal applications.

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