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Studies on Structural And Optical Properties of Al Doped Zno Nanopowders

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Abstract: *Nanopowders synthesized by using sol-gel technique can be used in optoelectronic applications such as optical sensors and light emitters. In this communication Pure Zinc Oxide and Al doped ZnO Nanopowders (AZO) were synthesized and characertization was performed by using electron microscopy and Photoluminescence (PL).The influence of Al doping on structural, morphological and optical properties of ZnO Nanopowders were investigated. The structural properties reveals hexagonal wurtzite structure and with no impurity phase. The morphology of nanopowders was confirmed from Scanning Electron Microscopy. The Functional groups identified from FTIR spectra. Optical absorption and Luminescence emission properties were analyzed from spectra UV-Visible and Photo Luminescence Characterization Techniques.*
Key Words*: ZnO Nanoparticles, Sol – Gel, Luminescence, SEM, Photo Luminescence.*

I. Introduction

Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of < 100 nm can be considered a nanoparticle. Zinc oxide (ZnO) is recognised as a potential II–VI photonic semiconductor materials owing to its wide band gap (~3.37 eV) and high exciton binding energy (~60 meV) [1]. It possesses considerable potential for applications in optoelectronic devices such as UV lasers, gas and bio sensors. Nanostructuring and/or wavelength-scale ordered patterning of ZnO should assist the tuning of optoelectronic properties even more usefully. The last few years have witnessed tremendous efforts on understanding the physical and optical properties of ZnO with particular attention on fabrication and device applications [2]. Many fabrication methodologies and top–down approaches have been applied to obtain high quality nano/microstructured ZnO thin films [3,4]. It is also well established that ZnO optoelectronic properties strongly vary depending on the fabrication and it is highly desirable to fabricate high quality devices at low cost. Recently, we explored an economical way of fabrication for high quality semiconductor photonic structures from self-assembly templating followed by electrochemical deposition [5].G.Vijaya prasanth et.al., [6] investigated on structural,optical and magnetic properties of Ni doped ZnO Nanostructures by Co precipitation method. Sethuraman Gayathri1 et. al., [7] reported on variation in the structural and optical properties due to the doping with Ag . Wasi khan et.al., characterized [8] Undoped and Al-doped ZnO (AZO) nanoparticles (NPs) have been successfully synthesized by the simple sol-gel method. The NPs have been characterized by a number of techniques as x-ray diffraction (XRD), UV-visible spectroscopy and scanning electron microscopy (SEM) at room temperature for 0%, 0.5%, 1% and 2% of Al concentration. G. Vijaya Prakash et.al.,[9]Zinc oxide (ZnO) is recognised as a potential II–VI photonic semiconductor and wavelength-scale ordered patterning of such material helps favourably in tailoring the photonic properties. G. Amin et.al., [10] proposed the influence of the pH value, precursor concentration (C), growth time and temperature on the morphology of zinc oxide (ZnO) nanostructures. Sankara Reddy B.et.al.,[11]synthesized that undoped ZnO and 5 mol% of Ag, 5 mol% of Co individually doped and co-doped (Ag, Co) ZnO nanopowders were synthesized , studied different properties and antibacterial activity were studied. Crystal structure and grain size were characterized by X-ray diffractometer and reveals that all synthesized ZnO samples were hexagonal structure and the sizes of ZnO nanoparticles were 23 nm, 20 nm, 17 nm, and 25 nm for undoped ZnO, 5 mol% of Co doped, 5 mol% of Ag doped and co-doped (Ag, Co) ZnO nanoparticles respectively. FESEM, TEM characterizations were used to determine the morphology and size of the ZnO nanoparticles. EDAX spectrum indicates that the successful dopants of Ag, Co peaks in the ZnO lattice and which indicates the purity of the samples. B. Sudheer Kumar et.al.,[12] proposed ZnO nanoparticles have been synthesized by SOL-GEL process from zinc nitrate. The powder was characterized by X-ray diffraction, scanning electron transmission. N.V.S.Venugopal et.al.,[13] synthesized and characterized the penetration power of nano pesticides is more and control different diseases. Here in this communication we reported a novel nano mancozeb formulation using polypropyleneglycol as encapsulating agent. The size distribution of nano mancozeb is obtained at 40-80 nm. The bio activity nature of nano formulated mancozeb is many times more when compared to the commercial mancozeb.

II. Experimental

2.1 Materials

Zinc Nitrate Zn $(NO_3)_2$, Sodium hydroxide (NaOH), Aluminum Nitrate Al $(NO_3)_3$ and Ethanol. The reagents used are of Analytical grade and they were used without further purification.

2.2 Experimental Procedure

2.2(a): Preparation of ZnO Nanoparticles

To prepare pure ZnO Nanoparticles aqueous ethanol solution of Zinc Nitrate (0.2 M) was prepared by dissolving Zinc Nitrate under constant stirring for one hour. Aqueous Ethanol solution of Sodium Hydroxide was also prepared in the same way with constant stirring for one hour. After complete dissolution of Zinc Nitrate, aqueous solution of sodium hydroxide was added to Zinc Nitrate solution.

2.2(b): Preparation of Zinc Solution:

The alkali solution of zinc was prepared by dissolving zinc nitrate [Zn $(NO_3)2 \cdot 6H_2O$] and KOH in distilled water to form a 100 ml solution [Zn^{2+} =0.5M, OH^- =1.0 M]. Under constant stirring, the reaction solution was heated to 50^oC temperature and keeping the PH-8. (Polyvinylpyrrollidone) PVP was used as capping agent. After few hours of reaction, the white precipitate so obtained is deposited in to the bottom of the flask was collected and washed it. Finally, the precipitate was centrifuged and dried at room temperature for 30 hours. The samples were stored at room temperature to determine properties of Nanopowder

III. Characterization

The structural properties of nanopowders including crystal structure, phase impurity were analyzed from X Ray Diffraction (XRD) spectra. The morphology of Nanopowders were evaluated from micrographs taken from Scanning Electron Microscopy (SEM).Structural properties of Nanopowders were further Analyzed using Fourier Transform Infra Red (FTIR) Spectra. Optical Properties were recorded from UV-Visible optical absorption spectra and Photo Luminescence Spectra

IV. Results And Discussions

4.1. X Ray Diffraction (XRD)

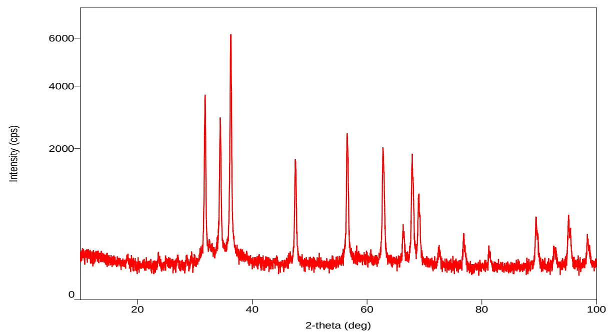


Figure 1.1: XRD Spectra of Pure ZnO Nanoparticle

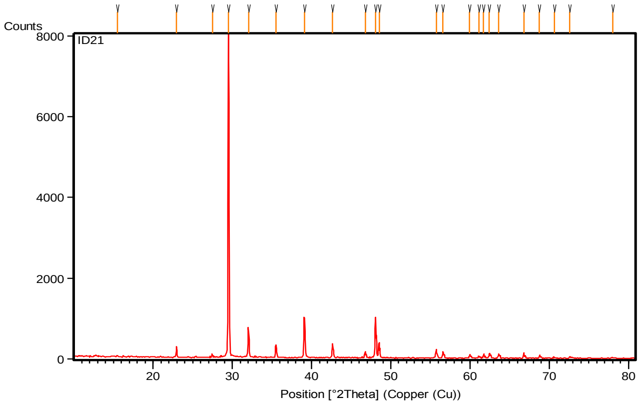


Figure 1.2: XRD Spectra of Al doped ZnO Nanoparticle

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).The structural properties including crystalline size, lattice strain, chemical composition and crystalline orientation can be obtained from XRD spectra. Figure 1.1 and 1.2 represent XRD Spectra of Pure and Al doped ZnO Definite line broadening clearly indicates the synthesized powders were in nanoscale. In Figure 1.1 , diffraction peaks are at 31.774°, 34.400°, 36.248° ,47.499° ,56.724° ,62.771° ,66.290° ,67.866°,69.019°,72.56°,76.85°,81.259°,89.470°,92.63°,95.147° and 93.487° respectively. In Figure 1.2 ,the diffraction peaks are at 15.5053° ,22.97°,27.47° ,29.54° ,32.05° ,39.11° ,42.67° ,46.78° ,48.08° ,48.53° ,55.72°,56.56°,59.95°,61.12°,62.42° and 63.31° respectively. The peaks observed in spectra closely correspond to the hexagonal wurtzite structure of ZnO (JCPDF 36-1451). The average crystallite size of the obtained particles was measured from the broadening of the diffraction peaks and application of the Scherer formula.

$$D = \frac{k\lambda}{\beta \, Cos\theta} \qquad \text{-----} \quad (1)$$

Where K is the constant with value 0.94, λ is the wavelength of X Ray source, β is the full width at half maximum of the diffraction peak, and θ is the Bragg's angle corresponding to the maximum intensity peak in XRD pattern.
The strain-induced broadening in powders due to crystal imperfection and distortion was calculated using the formula,

$$\varepsilon = \frac{\beta hkl}{4 \, Tan\theta} \qquad \text{---------} \quad (2)$$

The average crystalline size and corresponding lattice strain calculated is found to be 36.448 nm and 0.0029 for pure ZnO and 62.83 nm and its corresponding lattice strain is 0.0023 in the case of Al doped ZnO. The average crystalline size estimated is observed to be increased due to incorporation of Al in the Lattice of ZnO. So the Al doping resulted in the Increase in crystalline quality

4.2.Scanning Electron Microscopy (SEM)

SEM is High-resolution Microscope which provides detailed surface data of solid samples. Including topographical, morphological and compositional information. Figure 2.1 and Figure 2.2 represent high resolution SEM images of Pure and AZO Nanopowders observed at different magnifications.The images clearly represent formation of Nanoparticles.SEM Micrographs clearly indicate Pure ZnO Nanoparticles are nearly spherical like structures and Aluminium doped ZnO Nanopowders show nanoflakes changed to nanobar when observed at different magnifications. The SEM images represent agglomerations of particles are much less in this method of preparation. Fig:2.1 describes the SEM Pictures of Pure ZnO nanoparticles and Fig: 2.2 gives the SEM Pictures of Al Doped Pure ZnO nanoparticles

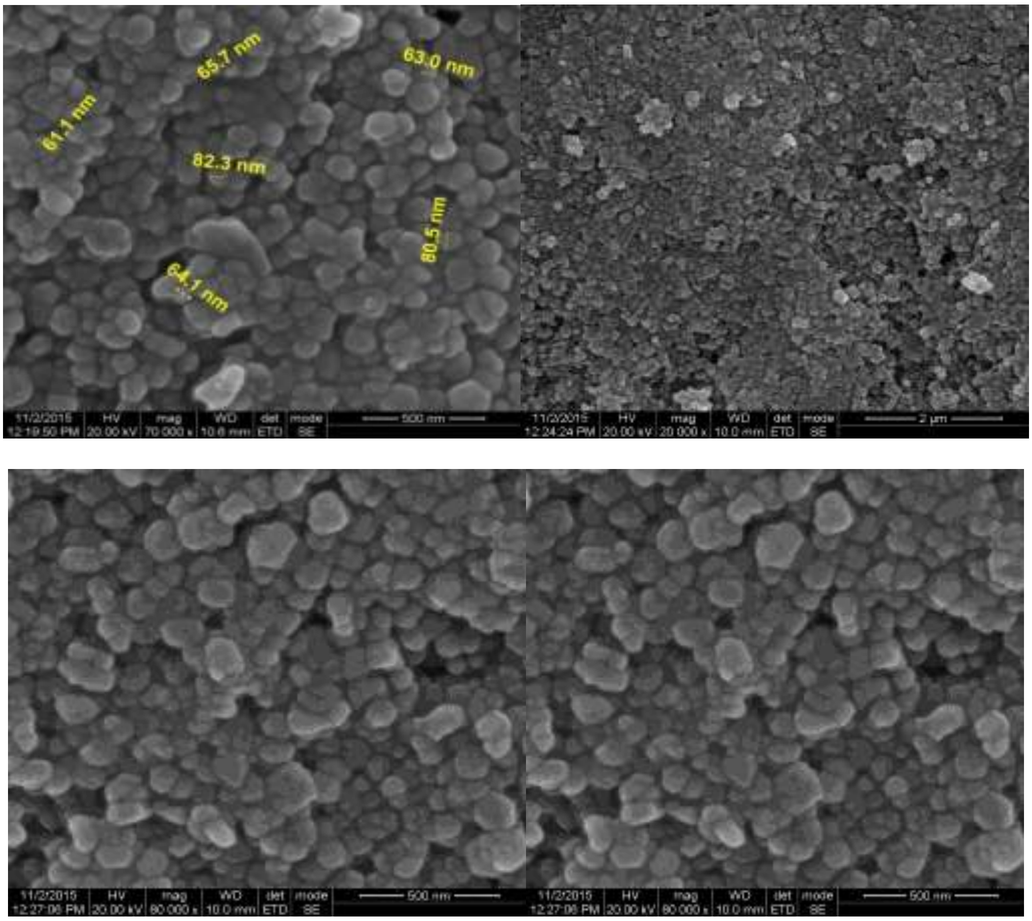
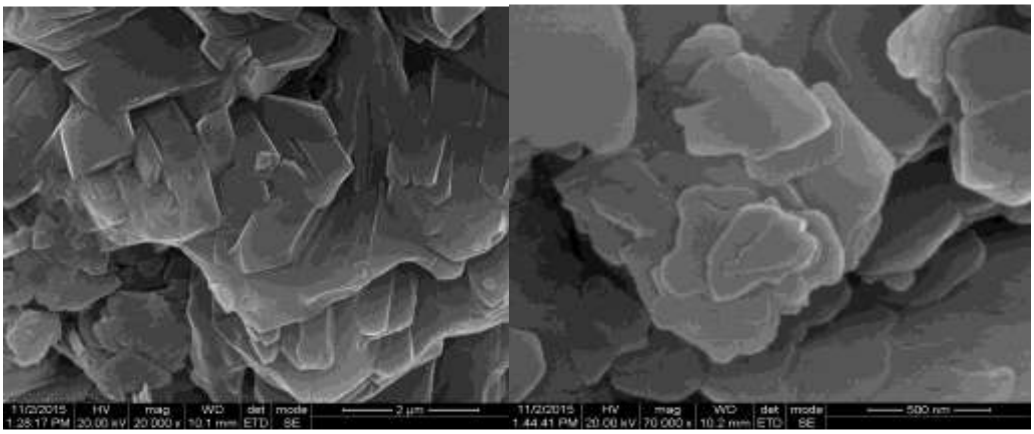


Figure 2.1:SEM Pictures of Pure ZnO nanoparticles



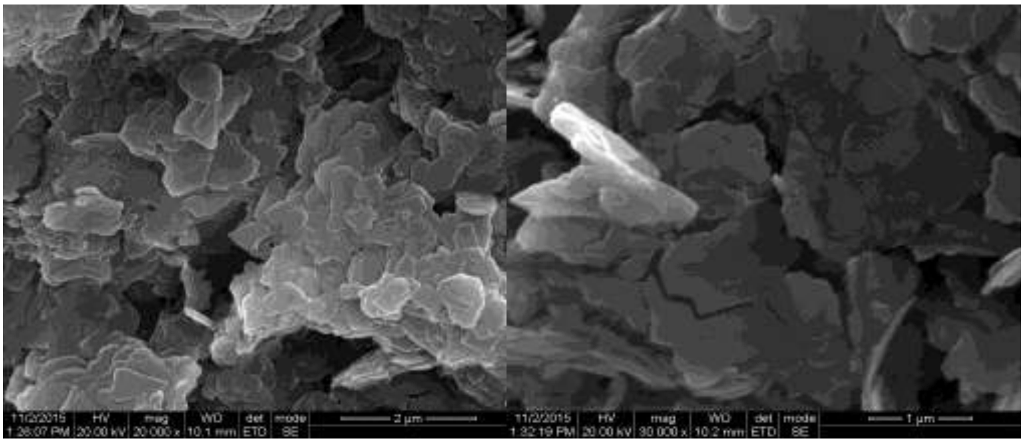


Figure 2.2 :SEM Pictures of Al Doped Pure ZnO nanoparticles

4.3. Fourier Transform Infrared (FTIR) Spectroscopy.

FTIR is a sensitive technique useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range. The formation of Wurtzite structure in ZnO Was further supported by this spectrum. Figure 3.1 and Figure 3.2 represent FTIR spectra of Pure and Al doped ZnO Nanopowder synthesized using Sol-gel process. Absorption bands were observed in spectra around 4000-500 cm^{-1}. Analysis of spectra was done based on the results of Nanoparticles published in the literature. In the spectra of Pure and Doped ZnO the peaks observed in the Range. The broad band around 3600 cm-1 corresponds to chemically bonded hydroxyl groups. The absorption bands near 2400 cm-1 corresponds to C-H .The stretching mode of vibration bands due to C=O observed between 1600-1400 cm-1.In Figure 3.1 Below 700 cm-1 the single broad peak around 470 cm-1 is observed which corresponds to stretching mode of Zn-O and in Figure 3.2 three peaks around 831.408 ,581.704,389.826 associated with the vibrations of metal–oxygen, aluminum–oxygen and metal–oxygen–aluminum . So the doped samples show the three peaks around 500 to 900 cm−1 that is assigned to the formation of metal aluminates. The results were shown in the fig: 3.1 and 3.2.

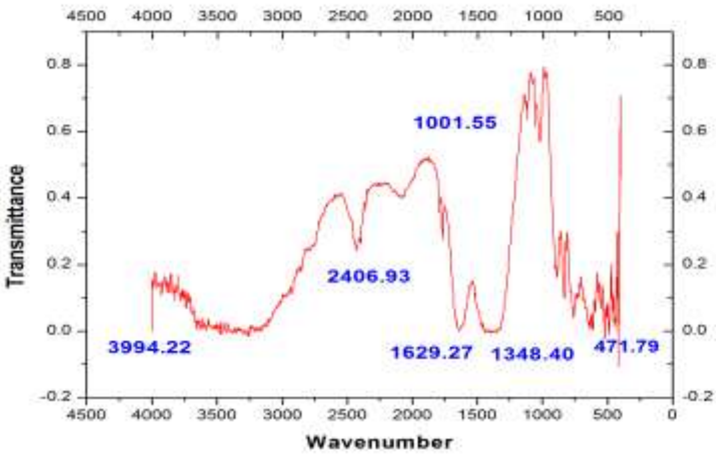


Figure 3.1: FTIR spectra of Pure ZnO Nanopowder

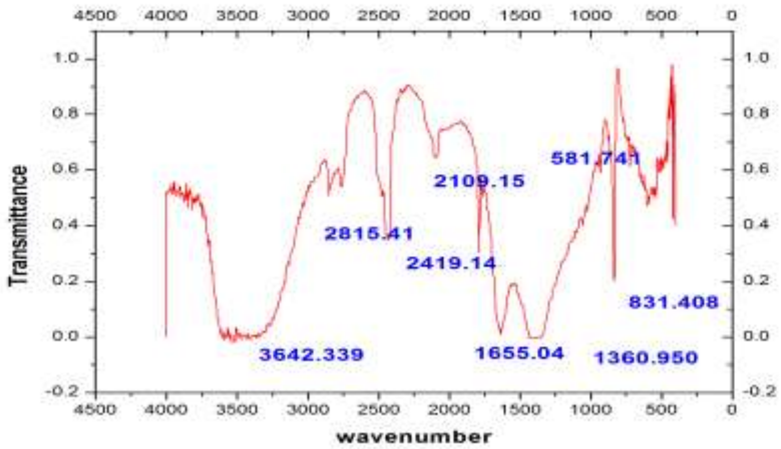


Figure 3.1: FTIR spectra of Al doped ZnO Nanopowder

4.4 UV-Visible Optical Absorption

UV-Vis spectroscopy is used in the semiconductor industry to determine optical properties of Nanopowders.UV/Vis spectroscopy determine the concentration of the absorber in a solution. The optical absorption spectra of nanopowders were obtained by suspending them in distilled water for a long time at room temperature. Various absorption peaks were observed in spectra due to the relatively large binding energy of the exciton (60 mV).The pure and AZO nanopowders show optical absorption peak around 236 nm and samples possess good absorption below 400 nm. From spectra it is clear that AZO Nanopowder absorb strongly at 300 nm it is due to presence of tiny small peak in Pure ZnO compared to AZO Nanopowder.

The optical band gap of ZnO Nanopowder is calculated using the Tauc relation

$$\alpha = \frac{A(h\upsilon - Eg)}{h\upsilon} \qquad \text{-------- (3)}$$

Where, α is the absorption coefficient, B is a constant, hν is the energy of incident photons and exponents n whose value depends upon the type the transition which may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The Energy gap value of Nanopowder obtained from Tauc relation is found to be 3.6eV in the case of pure ZnO and 3.9 eV in the case of Al doped ZnO Nanoparticles which is higher than the value of bulk ZnO. The results were shown in the fig: 4.1 and 4.2.

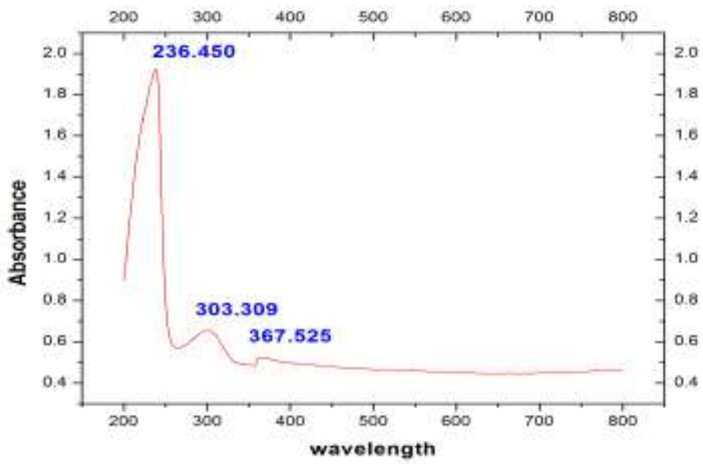


Figure 4.1: Optical absorption spectra of Pure ZnO Nanopowder

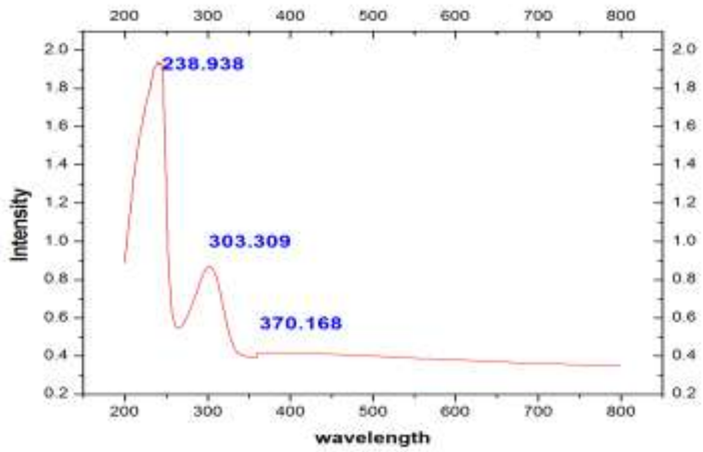


Figure 4.2: Optical absorption spectra of Al doped ZnO Nanopowder

4.5 Photo Luminescence (PL) Spectroscopy

Photoluminescence is a contact less non destructive method which is widely used to study luminescence properties of nanopowders. Figure 5.1 and Figure 5.2 represent PL spectra of pure and Al doped ZnO Nanopowders synthesized using Sol-gel process. The spectra represent characteristic intensity peaks in the UV and visible region. From spectra it is clear that pure ZnO particles exhibit absorption peak at 360.423 in the UV Region and Broad blue emission peaks around 412.977 nm, 439.254 nm, 492.96 nm and green emission peaks at 466 nm in the visible region. The spectra of Al doped ZnO exhibits broad peak around 400 nm which reveals significant blue emission peak in the visible region .From Spectra it is clear the emission properties of ZnO will be improved by doping with transition metal ion Al. The results were shown in the fig: 5.1 and 5.2.

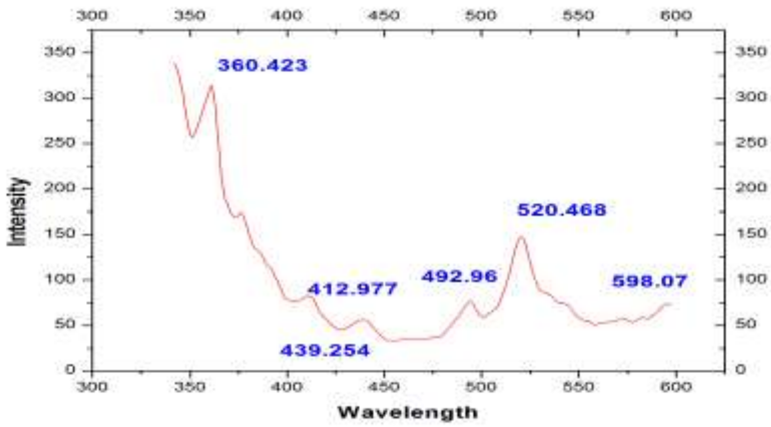


Figure 5.1: PL spectra of Pure ZnO Nanoparticles

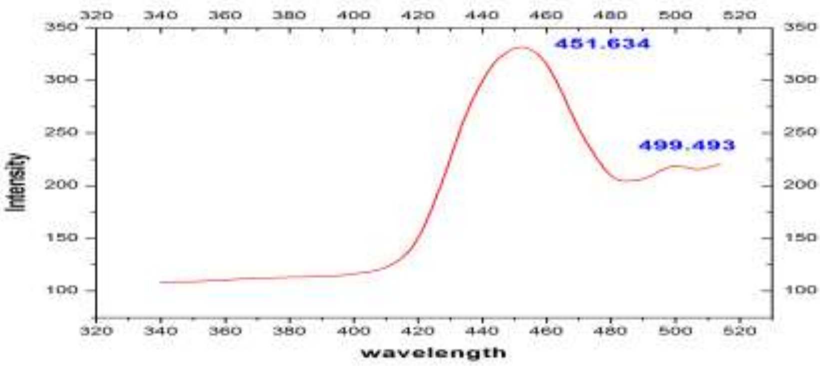


Figure 5.2: PL spectra of Al doped ZnO Nanopowder

V. Conclusion

Pure and Al doped ZnO Nanopowders were synthesized by simple, inexpensive and low cost, Sol-gel Process. The Structural, Morphological and Optical properties of Nanopowders were analyzed by performing XRD, SEM, FTIR, UV-Visible and PL Characterizations. XRD measurements showed that the synthesized nanopowders are crystalline with Hexagonal Wurtzite phase. The average crystalline size of Nanopowders is found to be 36.448 nm and 62.83 nm in the case of pure and Al doped ZnO. The morphology strongly influenced by Doping with Aluminum. The formation of Wurtzite structure in ZnO was further confirmed from FTIR Spectra. The Energy band gap value of nanoparticles obtained is found to be increased by doping with Al. The increase in the light output intensity could be attributed to increase in the Light tramnsmittance.PL studies indicate synthesized nanoparticles are suitable for optoelectronic device applications. These AZO nanoparticles were suitable for LEDs.

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