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Influence of Precursors on Structural and Optical Properties of ZnO Nanopowders Synthesized in Hydrolysis medium

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Abstract : ZnO Nanopowders were synthesized with different precursors NaOH and KOH respectively. Influences of precursors on structural, morphological and optical properties of nanopowders were analyzed.Crystalline structure, size and lattice strain of nanopowders characterized using X Ray Diffraction (XRD). Morphology of nanopowders confirmed from Scanning Electron Microscopy (SEM) micrographs observed at different magnifications. Presence of functional groups were further confirmed from Fourier Transform Infrared (FTIR) spectra. Optical absorption and band gap of nanopowders calculated from UV-Vis optical absorption spectra. Luminescence behavior of nanopowders confirmed from emission peaks of photoluminescence (PL) spectra. Results reveal solutes play a vital role in optimizing properties of nanopowders. Sol-gel method used for synthesizing nanopowders provides opportunity for a variety of practical applications. As synthesized nanopowders can be utilized for fabrication of optoelectronic devices LED's, solar cells and photo detectors.
Keywords : Nanopowders; Solutes; SEM; XRD; ZnO;

Introduction

In recent times ZnO widely used in optoelectronic device applications due to its wide direct band gap, large exiton binding energy, Good transparency, high electron mobility, strong room temperature luminescence, high chemical stability, low cost ,flexibility in fabrication, Good absorption[1]. Due to its large band gap at room temperature it attractive for blue LEDs and lasers[2]. An exciton binding energy (60 meV) that is greater than the room temperature thermal energy (~26 meV) is a major advantage of ZnO over other materials, making it possible to create a low-threshold, exciton-polariton laser[3]. It has an internal piezoelectric field, suitable for surface acoustic wave applications, recently used to make piezoelectric nanogenerators[4]. As a multi functional oxide semiconductor, ZnO has attracted substantial interest for a wide range of applications including transparent conductors, UV Light emitting diodes, chemical and biochemical sensing ,field emitting devices, and host for dilute magnified semiconductors. To face ever challenging threats and often unseen enemies materials with unique properties are required. Researchers thought new ideas of miniaturization. The trend of miniaturization to the ultimate atomic scale has become more challenging. Various nanostructures of ZnO such as nanobelts, nanowires and nanoribbons with significant, optical, electrical, mechanical, piezoelectric features were existed which were not observed in the bulk materials. These nanostructures of ZnO possess high performance in novel optoelectronic device applications solar cells, light emitting diodes, photodiodes etc [5]. ZnO nanoparticles improve light extraction efficiency in nitride LEDs for use in solar cells due to its abundance and low cost, nontoxicity, high electron mobility, low crystallization temperature, large exciton binding energy (60 meV) and easy synthesis[6].

Various fabrication techniques have been established for the growth of ZnO Nanosructures .Aqueous solution growth, Electro chemical Deposition, evaporation-condensation, chemical vapor deposition, Vapor liquid solid growth, carbo thermal evaporation, flux growth and template based synthesis. Different researchers reported different Physical and chemical methods can be used to synthesize ZnO Nanoparticles. Various Physical methods like evaporation-condensation, Laser Ablation, Electric Arc Discharge, Chemical vapor deposition, Ball Milling-Annealing methods gas phase synthesis etc are limited due to their inability to obtain a uniform nano-sized particle. The chemical methods like Sono chemical method, Micro wave synthesis; Hydrothermal, Co-precipitation, Sol-gel, Wet chemical Method, combustion etc are more preferred[7].

The present work focuses on analyzing structural and optical properties of nanopowders synthesized by Sol-gel method. Sol gel method is preferred due to its better homogeneity, Less energy consumption, possibility of incorporating nanoparticles and organic materials into sol-gel-derived oxides, inexpensive equipment etc Several growth parameters including Ph ,temperature, time, concentration of reagent ,concentration of catalyzor , phase Transition sol-gel, Drying doping and co-doping the precursors influence on properties of nanoparticles. Various designs of ZnO nanostructures such as particles, wires, rods, spiral, helical, flower, tetrapod etc. can be obtained under different experimental conditions [8].

In the field of ZnO research the last decade was mainly concerned with optimization of different growth parameters and processing techniques. Thus currently research work related to production of high quality, reproducible ZnO nanoparticles for device application is the main focus. The objective of this research is to study the influence of solutes on structural and optical properties of pure and Transition metal ions doped ZnO nanoparticles. The purpose of this research is to utilize enhanced properties to drastically improve device performance of ZnO based optoelectronic devices.

Experimental Work

Materials

Zinc Nitrate, Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH), Distilled water were used as a starting materials. All chemical utilized were of AR grade they were brought and used without further purification.

Procedure

The zinc oxide (ZnO) nanoparticles were prepared by sol-gel method using zinc nitrate and sodium hydroxide as precursors. In this procedure aqueous solution of Zinc nitrate (0.4mol) was prepared with constant stirring of Zinc Nitrate in distilled water for 2 hours using magnetic stirrer. Aqueous solution of NaOH (0.8 mol) was also prepared in same way with constant stirring for 2 hours with magnetic stirrer. After complete dissolution of zinc nitrate, aqueous NaOH solution was added to Zinc Nitrate solution under constant stirring, drop by drop touching the walls of the vessel(for 15 mts).Resultant mixture so farmed vigorously stirred for 3 hours till white precipitate obtained within the solution. The precipitate obtained centrifuged and allowed to stay for 24 h at room temperature. During this time, OH^- and Cl^- ions were diffused through the medium and white gel-like precipitate of Zn $(OH)_2$ was formed. The remaining solution centrifuged for 10 min and the precipitate was removed. The obtained precipitate kept in an oven around 70ºC till the solution dries .During drying Zn $(OH)_2$ is completely converted to into ZnO. In the final step the particle was grinded to obtain powder[9].

In a similar process ZnO Nanopowder was synthesized using the solute KOH .The synthesized ZnO nanopowders labeled as

Sample 1: ZnO nano powder with NaOH

Sample 2: ZnO nano powder with KOH

Characterization

Characterization is performed to analyze properties of Nanopowders.XRD patterns of the samples were recorded using powder X-Ray Diffractometer (XRD-SMART lab)-Rigaku, JAPAN using secondary

monochromatic CuK_α radiation of wavelength λ = 0.1541 nm at 40 Kv/50mA in the scan range 2θ = 20 to 90°. Samples were supported on a glass slide. Structural properties including structure, crystalline size and lattice strain were determined from XRD pattern. Information about morphology of nanopowders was observed at different magnifications using Field Emission Scanning Electron Microscope (FESEM-SUPRA 55) - CARL ZEISS, GERMANY. Presence of functional groups resolved from FTIR spectra using FT-RAMAN Spectrophotometer 50-5000 cm-1 (BRUKER RFS).Optical absorption properties of nanopowders determined from Varian Cary 5E UV-VIS NIR. The spectra contains information about various absorption peaks existing in the Ultraviolet and visible region of spectra. The information about Luminescence emission peaks present in the UV and Visible region was resolved using spectrofluorometer (F-2500 FL Spectrophotometer, Hitachi).

Results and Discussions

X Ray Diffraction (XRD)

Figure 1.1 and 1.2 represent XRD patterns of nanopowders synthesized from NaOH and KOH respectively. Definite line broadening clearly indicates synthesized powders in the nanometer range. In Figure 1.1 the diffraction peaks observed at angles of 2θ = 31.940°, 34.612°, 36.433°, 47.692°.56.736°, 62.987° ,66.51°, 68.055° ,69.116°,72.656°,77.02°,81.41° and 89.667° correspond to lattice planes (100), (002), (101), (102), (110), (103), (200), (112) ,(201) ,(004), (202), (104) respectively. In Figure 1.2 diffraction peaks observed at different angles of 2θ=31.946° ,34.631°, 36.448°, 47.755° ,56.769° ,62.928° ,66.45° ,68.09° ,69.19° ,77.17° and 81.56° correspond to lattice planes (100),(002),(101),(102) (110),(103),(200),(112),(201),(004), (202),(104) respectively**.** Peaks show very good agreement with the reported values of the Joint Committee on Powder Diffraction Standards data (JCPDS 36-1451) and confirm the formation of hexagonal wurtzite zinc oxide[10]. No peaks corresponding to impurities were detected, which shows high purity of ZnO nanoparticles obtained. The sharp diffraction peaks indicate the good crystalline nature of nanopowders [11].

The crystallite size (D) of nanopowders calculated from Scherrer's formula $D= 0.9\ \lambda/\beta_{2\theta}\ \cos\theta$. The strain-induced broadening in powders due to crystal imperfection and distortion was calculated using the formula, $\varepsilon=\beta_{hkl}/\ 4\tan\theta$.(where k is a constant taken to be 0.94, λ is the wavelength of the X-ray used (λ=1.54Å),β is the full width at half maxima of the (002) peak of the X-ray diffraction pattern, and 2θ is the Bragg angle. It is also clear the peak width and crystallite size varies as 1/cosθ and strain varies as tanθ[12]. Crystalline size and lattice strain is found to be 38.39 nm and 0.006 nm for nanopowders synthesized using NaOH and 20.46 and 0.112 for nanopowders synthesized using KOH respectively. The variation in crystalline size and induced lattice strain is due to difference in reactivity because of change in atomic weight.

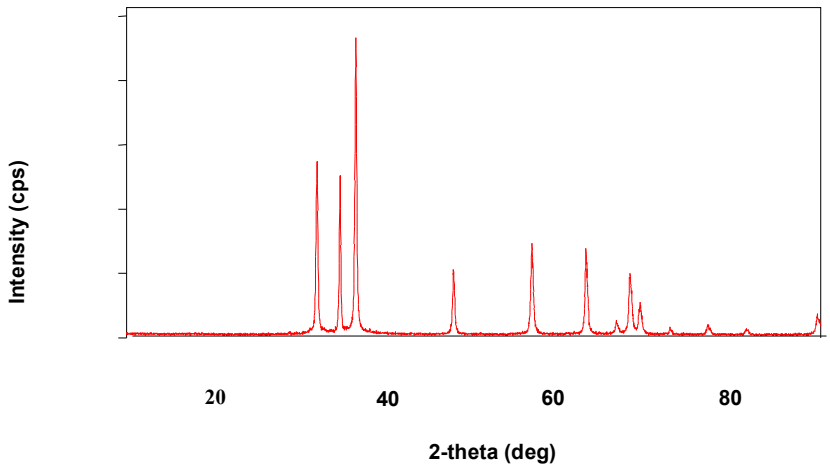

Figure 1.1: XRD spectra of ZnO Nanopowders synthesized from NaOH

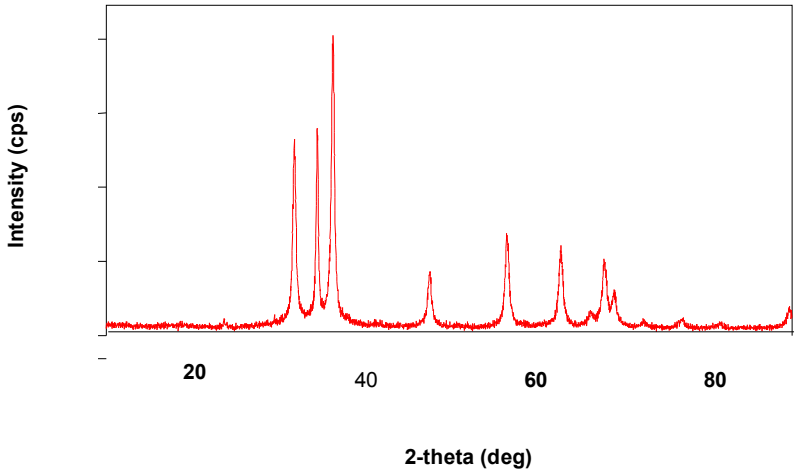

Figure 1.2: XRD spectra of ZnO Nanopowders synthesized from KOH

Scanning Electron Microscopy

Figure 2.1 and 2.2 represent SEM micrographs of ZnO Nanopowders observed at different magnifications. These pictures confirm the formation of nanopowders of ZnO.The morphology observed in the samples show fine grains of ZnO converted in to particles when observed at different magnifications[13]. The estimated particle size found to be varying between 30-50nm in the case of NaOH and 17 nm-25 nm the case of KOH.From spectra it was clear that particles possess irregular particle size distribution. Influence of KOH tends to cause the particle size to decrease, which can be attributed to more solubility of KOH.

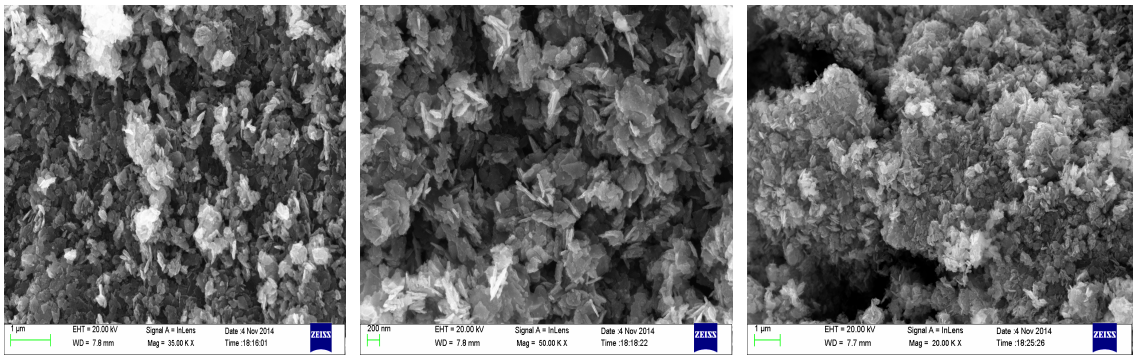

Figure 2.1: SEM images of ZnO Nanopowders synthesized using NaOH

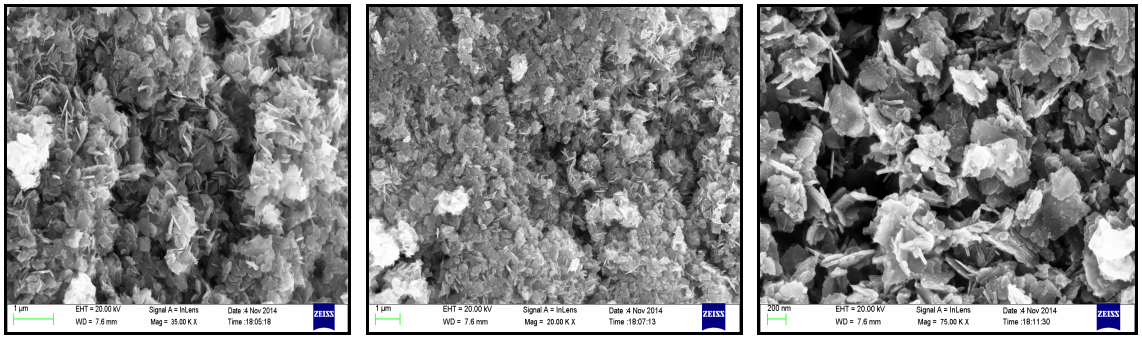

Figure 2.2: SEM spectra of ZnO Nanopowders synthesized using KOH

Fourier Transform Infrared (FTIR) Spectroscopy

Figure 3.1 and 3.2 represent FTIR spectra of ZnO Nanopowders synthesized using precursors NaOH and KOH respectively. Various modes of vibration are observed at different regions of FTIR spectra recorded in the range of 4000–500 cm−1. From FTIR spectra it is clear that modes of vibration observed near 4500 cm-1,1400 cm^{-1} and 930 cm^{-1} corresponds to stretching vibrations corresponding to O-H, C=O,C=C respectively[14]. The peaks observed at 469.761 cm-1 in figure 3.1 and 539.537 in figure 3.2 represent the presence of characteristic absorption peak of Zn-O. Structural properties of nanopowders were further confirmed from FTIR spectra.

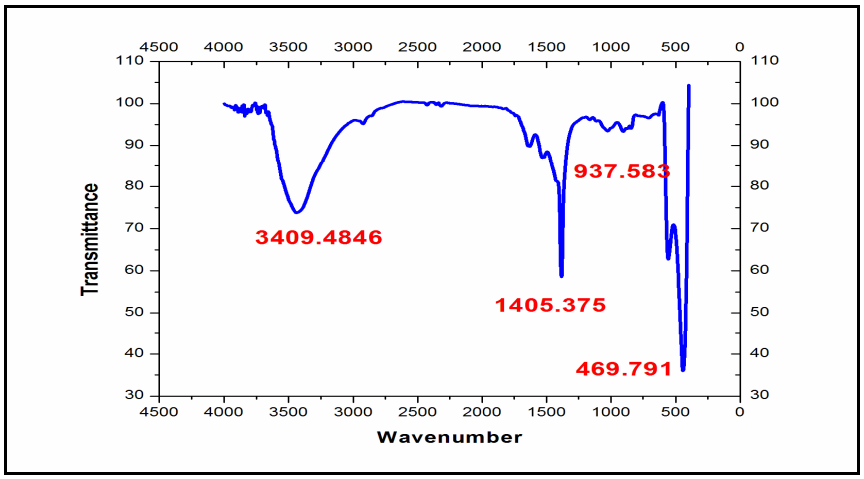

Figure 3.1: FTIR spectra of ZnO Nanopowders synthesized using NaOH

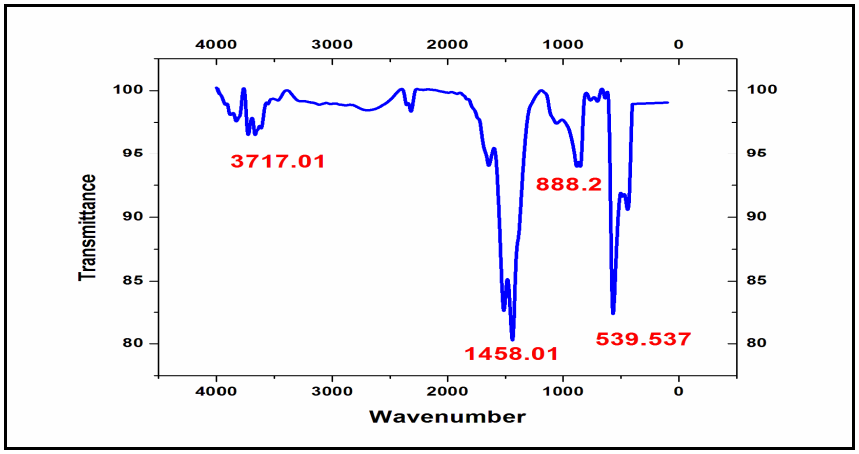

Figure 3.1: FTIR spectra of ZnO Nanopowders synthesized using KOH

UV-Visible Optical Absorption Spectra

Figure 4.1 and 4.2 represent optical absorption absorption spectra of ZnO nanopowders synthesized using NaOH and KOH respectively. The optical study was performed to evaluate the potentially useful optical qualities of the NPs. Both the samples exhibit strong absorption band maxima at 214 nm which shows significant blue shift corresponding to bulk ZnO observed at 388 nm. Synthesized nanopowders also show little absorbance in the visible region of absorption spectra[15]. The spectra show very small shift in the absorbance maximum with the use of solutes NaOH and KOH respectively. The shift might be associated with the broader nanoparticle distribution such that broader exciton absorbance.

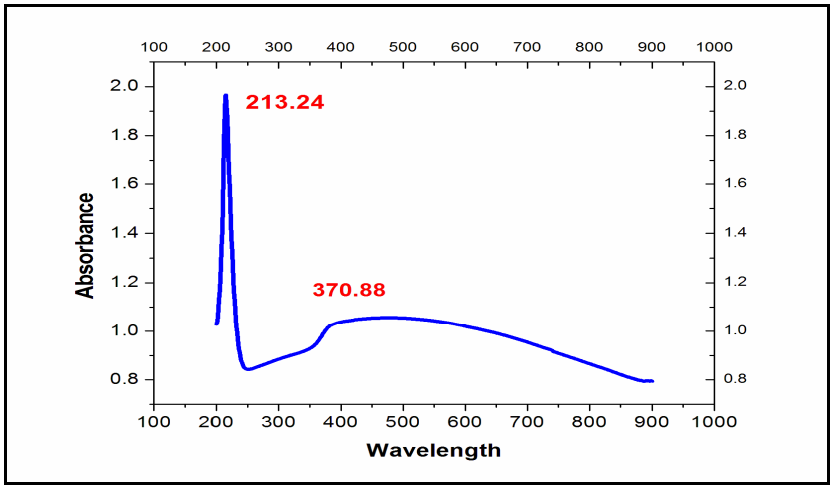

Figure 4.1: UV-Vis spectra of ZnO Nanopowders synthesized using NaOH

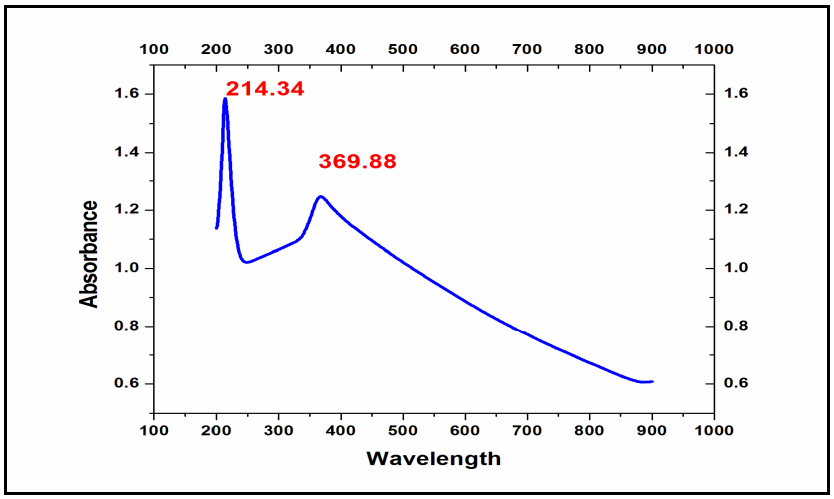

Figure 4.2: UV-Vis spectra of ZnO Nanopowders synthesized using KOH

Photo Luminescence (PL) Spectra

Figure 5.1 and 5.2 represent the PL Spectra of ZnO NPs synthesized using NaOH and KOH respectively. The PL spectra of ZnO nanopowder synthesized from NaOH comprises of broad luminescence peak covering entire visible region of PL spectra[16] .The luminescence peaks located at around 550 nm and 600 nm corresponds to yellow orange emission of PL spectra. These emissions were found to be extremely broad and this broadening may be due to phonon assisted by transition.PL spectra of ZnO nanopowder synthesized from KOH shows luminescence peak only in the UV region at 362.17 nm. Solutes influence PL which would further cause variation in the Luminescence properties of nanopowders[17].

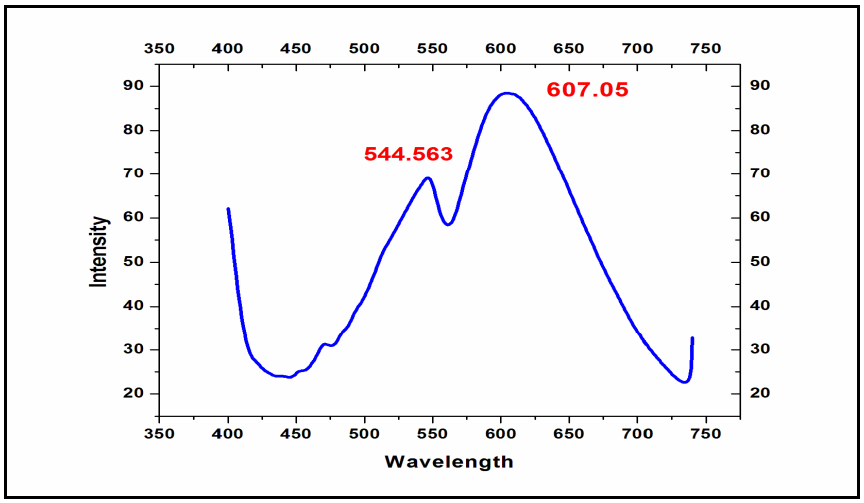

Figure 5.1: PL spectra of ZnO Nanopowders synthesized using NaOH

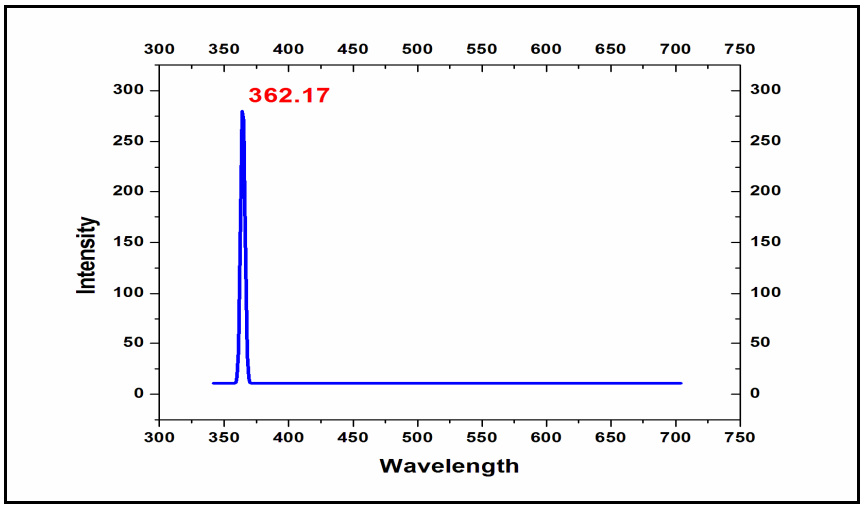

Figure 5.2: PL spectra of ZnO Nanopowders synthesized using KOH

Conclusion

In this paper successful synthesis of ZnO nanopowders with different precursors NaOH and KOH respectively by simple Sol-gel method was reported. Influence of precursors on crystalline structure, size, morphology, optical absorption and luminescence properties of nanopowders was explained in detail. XRD results showed obtained ZnO nanoparticles were composed of hexagonal wurtzite phase with very good crystallinity. Powders with less crystalline size obtained for nanopowders synthesized from KOH. Nanopowders with significant absorption in UV region and little absorbance in the visible region confirmed from optical absorption spectra. The luminescence peaks corresponds to yellow-orange emission in the case of Nanopowders with NaOH and significant UV emission revealed from PL spectra. Results reveal precursors play vital role in structural and optical properties of nanopowders. Nanopowders so formed using precursor KOH significant optical absorption and luminescence in UV region can be utilized in the fabrication of UV detectors. Powders synthesized using precursor NaOH can be utilized for fabrication of LED's due to presence of Luminescence peaks in the visible region of PL spectra.

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