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Structural and Optical Investigation of Al Doped ZnO Nanoparticles Synthesized by Sol-gel Process

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Abstract

Background/Objectives: Nanoparticles possess unique properties due large surface to volume ratio and quantum confinement effect. ZnO is suitable for laser diodes, LEDs and Photodetectors due to wide direct band gap, high melting point, high thermal conductivity etc. **Methods/Statistical analysis:** Pure Zinc oxide and Al doped ZnO Nanopowders are fabricated by Sol-gel method. Influence of Al doping on structural and optical properties of Nanopowders were analyzed by X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible optical absorption (UV-Vis) and Photoluminescence (PL) Characterizations. Sol-gel method is preferred due to its simplicity, low Cost and Environment friendly. Structural properties including crystalline size, Lattice strain were obtained from XRD. Morphology of Nanopowders confirmed from SEM micrographs observed at different magnifications. Presence of functional groups obtained from FTIR spectra. Band gap is determined from UV-Visible optical absorption spectroscopy. Luminescence emissions were confirmed from PL characterizations. **Findings:** The average crystalline size of Nanopowders is found to be 36.448 nm and 62.83 nm for pure ZnO and Al doped ZnO nanopowders respectively. The morphology strongly influenced by doping with Aluminum. Structural properties of nanoparticles again proved from FTIR Spectra. The energy band gap value of Nanoparticles obtained is found to be decreased by doping with Al. The increase in the light output intensity could be attributed to increase in the Light transmittance. **Application/Improvements:** The synthesized Nanopowders can be used in the fabrication of ZnO Nanorods, Nanowires which is an attractive potential application in the Light emitting devices, UV Photodetectors.

Keywords: Nanoparticles, Scanning Electron Microscopy, UV-Visible Optical Absorption, X-Ray Diffraction, Zinc Oxide

1. Introduction

Nanoparticles are current interest for electronic and optoelectronic devise applications[1]. Transparent oxide semiconductors are widely studied due to superior conductivity, optical transparency. Metal oxides exhibit unique physical and chemical properties due to benefits of high density of corner or edge surface sites, control particle sizes, surface faceting, high stability and crystallographic quality[4]. Metal oxides can adopt structural geometries of metallic, semiconductor or insulator character[5].They have found various advanced applications in chemistry, physics and material science such as gas sensing, fuel cells, photo catalyst, optics, magnetic electric, multiferroic etc[6]. Examples of various metal oxide nanoparticles are iron-oxide, tin oxide, aluminum oxide, magnesium oxide, tungsten oxide, vanadium oxide, rhenium oxide, molybdenum oxide, zirconium, rhenium oxide, yttrium oxide, europium oxide and so on[7].

Scientific development in materials technology over last few years realizes the usage of wide-band gap semiconductors for various optoelectronic device applications. The semiconductor ZnO is an attractive material in the research community due to its wide direct band gap (Eg -3.3 eV at 300 K), large exiton binding energy (60 MeV), large piezo electric constants, large non

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linear optical coefficients and high thermal conductivity. ZnO also possess unique piezoelectric, pyroelectric and multiple properties. Zinc oxide nanoparticles suitable for wide range of applications e.g., gas sensor, chemical sensor, storage, optical and electrical devices, solar cells, and drug-delivery[9]. Nanoparticles of metal oxides comprising zinc elements, particularly those that contain two or more metals at least one of which is zinc, offer a unique and surprising way to provide such long lasting superior protection[10].

Many researchers reported crystalline size, band gap and optical absorption and emission properties of ZnO improved by introducing dopants in to ZnO lattice. The transition metals (Al, Cu, Ni, Ag, Co) doped ZnO show better properties, as these metals have ionic radius nearly similar to ZnO[11]. Al^{3+} has been the most used dopant element due to its small ionic radius and low material cost. Al doped ZnO nanopowders possess room Temperature Ferromagnetism. Al doped ZnO nanopowders are also used in transparent conductive pates due to its optical conductivity and transparency in visible region. The substitution of Zn^{2+} ions with Al^{3+} in ZnO lattice improves the electrical conductivity through the increase of charge carriers where it is reported that the electron concentration increases from 1016 to 1021/ cm−3[16].

As ZnO possess wide range of applications, various fabrication methods such as Ball Milling, Hydrothermal, Coprecipitation, Spray pyrolysis, Solution combustion, Microwave method, Sol-gel, Vapor deposition etc were employed to fabricate various ZnO Nanostructures[13]. In this paper ZnO and Al doped ZnO Nanopowders were fabricated by Sol gel method due to its simple, inexpensive and low temperature sintering capability[14]. The influence of Al dopant properties of ZnO were analyzed by performing various spectroscopic Investigations using XRD, SEM, FTIR, UV-Visible and PL characterizations[15].

2. Experimental Procedure

2.1 Synthesis of Al Doped ZnO Nanopowders

Zinc Nitrate, Sodium Hydroxide, Aluminum Nitrate are utilized for preparation of Al doped ZnO Nanopowders. The chemicals brought were of analytical Grade and used without further purification. Aqueous ethanol solution of Zinc Nitrate (0.2M) prepared by dissolving Zinc Nitrate under constant stirring for one hour using magnetic stirrer. Aqueous ethanol solution of Sodium Hydroxide obtained with similar process with constant stirring for one hour using magnetic stirrer. Aqueous solution of Sodium hydroxide was mixed with Zinc Nitrate solution after complete dissolution of solutes. The beaker sealed and allowed to stay for 10 hours and further supernatant solution separated carefully and centrifuged for 10 min and the precipitate obtained was removed. Thus remaining solution washed with distilled water and ethanol to separate impurities attached with nanoparticles. The solution so formed kept in an oven around 70°C till precipitate dries and finally grinded with hand to obtain powder[16].

To synthesize Al doped ZnO Nanoparticles the aqueous solution of Aluminum nitrate prepared and added to Zinc Nitrate solution before NaOH solution and similar process is repeated to obtain al doped ZnO Nanopowders.

3. Characterization

The structural properties of nanopowders including crystalline size and lattice strain determined from X Ray Diffraction (XRD) spectra. Morphology of nanopowders viewed 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

4. Results and Discussions

4.1 X-Ray Diffraction (XRD)

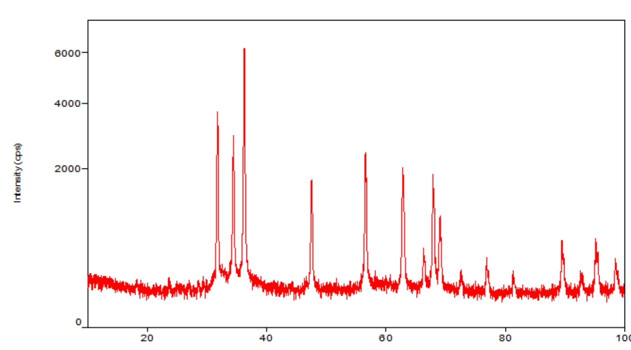

Figure 1. XRD spectra of ZnO Nanopowders.

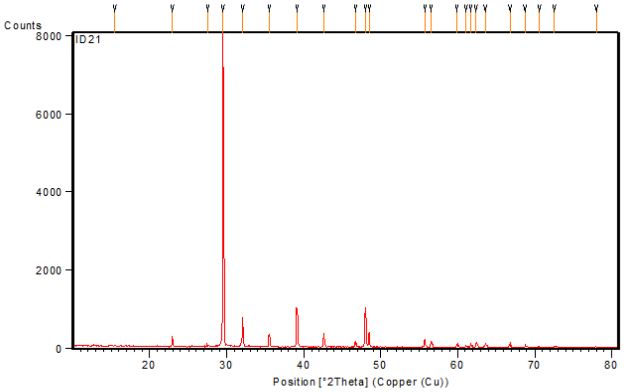

Figure 2. XRD spectra of Al doped ZnO Nanopowders.

The structural properties of nanoparticles including crystalline size, lattice strain, chemical composition and crystalline orientation can be obtained from XRD spectra. Figure 1 and 2 represent XRD Spectra of ZnO and AZO nanopowders. From spectra line broadening clearly indicates synthesized powders in nanoscale. In figure 1 diffraction peaks 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 2, diffraction peaks 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 confirm the formation of hexagonal wurtzite structure of ZnO (JCPDF 36-1451). The average crystallite size of nanopowders obtained using Scherrer's formula[17].

$$D = \frac{k\lambda}{\beta \, Cos\theta} \tag{1}$$

Where K is the constant with value 0.94, λ represents wavelength of X Ray source, β is FWHM of the diffraction peak and θ is the Bragg's angle.

The strain-induced broadening in powders calculated from the formula,

$$\varepsilon = \frac{\beta hkl}{4 \, Tan\theta} \tag{2}$$

The average crystalline size and lattice strain calculated is found to be 36.448 nm and 0.0029 for pure ZnO and 62.83 nm and 0.0023 for AZO nnaopowders. 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 3 and Figure 4 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 viewed at different magnifications. From spectra it is also clear that agglomerations of particles are much less by this method of preparation[18].

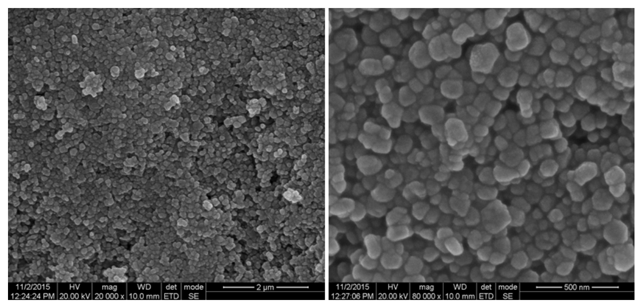

Figure 3. SEM micrographs of ZnO Nanoparticles.

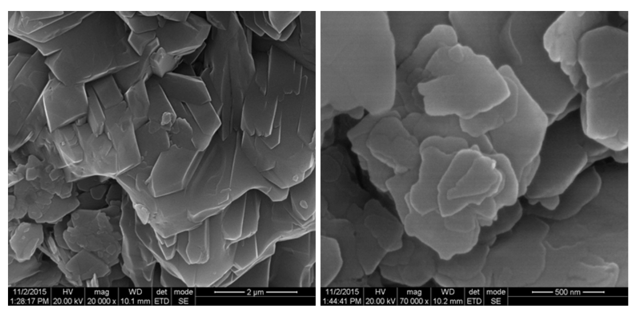

Figure 4. SEM micrographs of Al doped ZnO Nanoparticles.

4.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra used to analyze presence of functional groups in molecules. Presence of dopants was further supported by this spectrum. Figure 5 and Figure 6 represent FTIR spectra of ZnO and AZO Nanoparticles. Spectra consist of various absorption bands around 4000-500cm^{-1}. Analysis of spectra was done based on the results of nanoparticles published in the literature. 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 the single broad peak around 470 cm-1 corresponds to stretching mode of Zn-O. In Figure 3.2 three peaks around 831.408 cm^{-1}, 581.704cm^{-1} and 389.826cm^{-1} attributed to presence of Al in ZnO lattice.

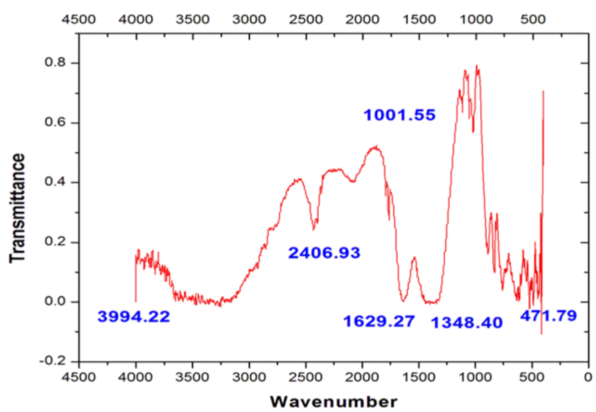

Figure 5. FTIR spectra of ZnO Nanopowders.

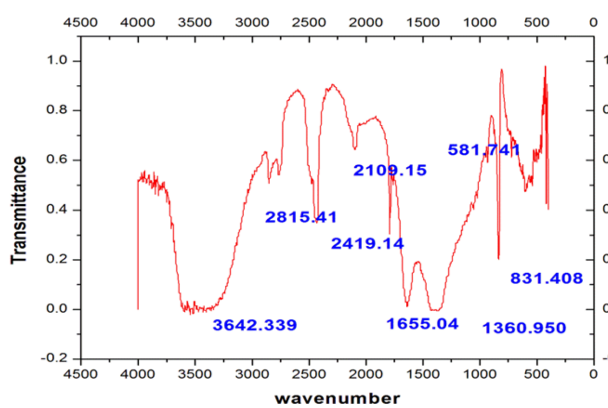

Figure 6. FTIR spectra of Al doped ZnO Nanopowders.

4.4 UV-Visible Optical Absorption

UV-V is spectroscopy is used in the semiconductor industry to determine optical properties of nanopowders. UV-Vis spectroscopy determines the concentration of the absorber in a solution. Absorption spectrum is formed by suspending nanopowders 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 Nanoparticles absorb strongly at 300 nm it is due to presence of tiny small peak in Pure ZnO compared to AZO Nanoparticles[17].

Optical band gap of nanopowders determined with the help of Tauc relation

$$\alpha = \frac{A(hv - Eg)}{hv} \tag{3}$$

Where, α represents absorption coefficient, B is a constant, hν is photon energy. Band gap value is found to be 3.6eV for pure ZnO and 3.5 eV for AZO Nanoparticles. It is also clear that band gap determined is higher than the value of bulk ZnO[19].

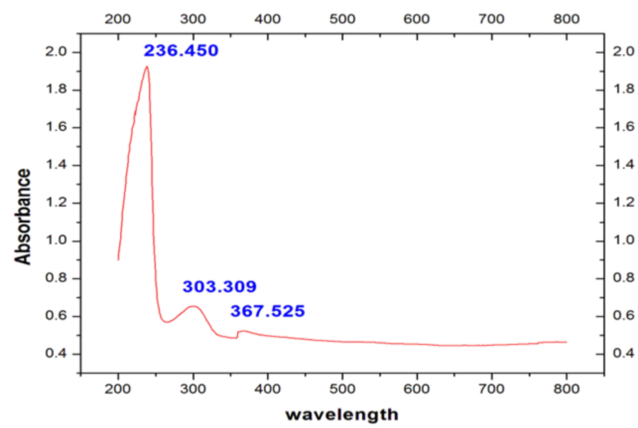

Figure 7. UV-Vis optical absorption spectra of Pure ZnO Nanopowders.

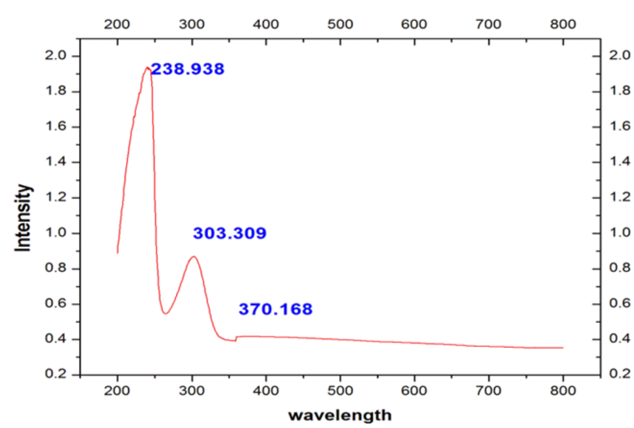

Figure 8. Optical absorption spectra of Al doped ZnO Nanopowders.

4.5 Photo Luminescence (PL) Spectroscopy

Photoluminescence is a contact less non destructive method which is widely used to study luminescence properties of nanopowders. PL spectra of ZnO and AZO nanopowders represented in Figure 9 and Figure 10 respectively. 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, 492.96nm and emission peaks near 466 nm corresponding to green luminescence in visible region. The spectra of Al doped ZnO exhibits broad peak around 400 nm (blue luminescence) in visible region of PL spectra. From Spectra it is clear the emission properties of ZnO can be modified by introducing Al in to ZnO lattice.

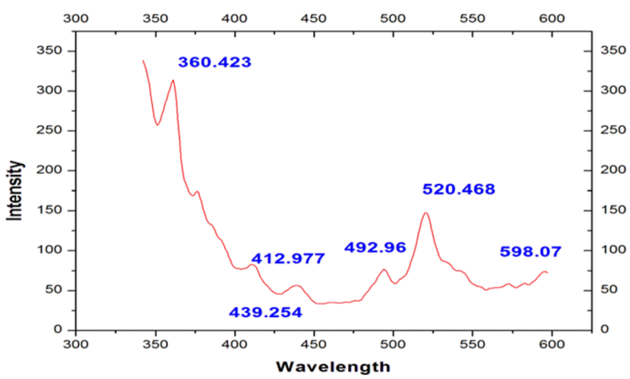

Figure 9. PL spectra of Pure ZnO Nanopowders.

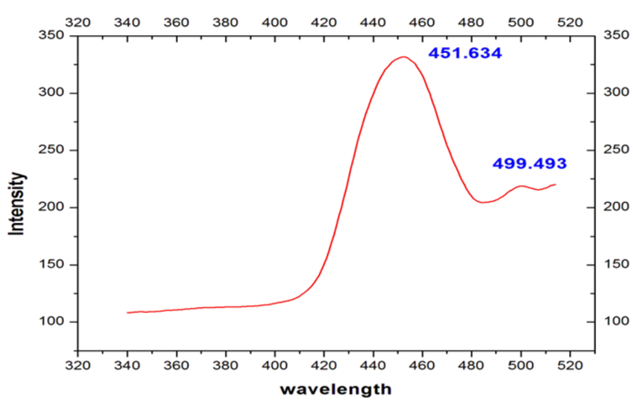

Figure 10. PL spectra of Al doped ZnO Nanoparticles.

5. Conclusion

Nanopowders of pure and AZO have been successfully fabricated by simple, inexpensive and environmental friendly Sol-gel method. Properties were obtained by performing characterizations using XRD, SEM, FTIR, UV-Visible and PL techniques. 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 corresponding to pure and AZO nanopowders. Morphology strongly influenced by Doping with Aluminum. Structural properties further confirmed from FTIR Spectra. Energy band gap value of Nanoparticles obtained is found to be decreased by doping with Al. The increase in the light output intensity could be attributed to increase in the Light transmittance. PL studies indicate synthesized nanoparticles are suitable for optoelectronic device applications. These AZO Nanoparticles were suitable for LEDs and UV Photodetectors.

6. References

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