

## **Characterization of ZnO:Cu Nanoparticles by Photoluminescence Technique**

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### **ABSTRACT**

ZnO nanoparticles have recently been the focus of intense research in recent times due to some of their interesting properties such as blue shift of the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength, nonlinear optical effect etc. In the present work, ZnO nanoparticles were synthesized by thermal oxidation of ZnS nanoparticles. X-ray diffraction pattern of the ZnO nanoparticles were recorded and compared with the standard JCPDS values. From the JCPDS values, it was found that ZnO nanoparticles of present study are in cubic phase. The grain size of ZnO nanoparticles was calculated from Debye-Scherrer equation and was found to be approximately 19 nm. The PL spectra of the samples were recorded at room temperature with an excitation wavelength of 350 nm. The peak at 410 nm observed in the pristine ZnO samples of present study can be assigned to oxygen vacancies, i.e. to the recombination of electrons at the oxygen vacancy with holes at the valance band and that at 428 nm can be attributed to the transitions of electrons from the oxygen vacancy states to zinc vacancy states. The PL spectrum of ZnO doped with 1% Cu is similar to that of undoped samples. The PL spectrum of ZnO doped with 2% and 5% Cu exhibits peaks at 430 and 460 nm. The peak at 460 nm can be ascribed to the impurity level formed due to the incorporation of Cu<sup>2+</sup> in ZnO lattice. The emission spectra of samples doped with 5% Cu that the peak due to impurity level (460 nm) is less prominent compared to that doped with 2% Cu which may be ascribed to the quenching of emission line due to excess copper.

### **I. INTRODUCTION**

The II – VI semiconductors are typically wide band gap materials, serving as efficient light emitters. This makes them candidates to replace materials such as GaN in light emitting diodes [1-5]. Because of their uses in optoelectronic and semiconducting applications, II – VI semiconductors have recently been the focus of intense research in the area of nanomaterials. Blue shift of the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength, nonlinear optical effect is some of the interesting properties exhibited by these nanoparticles [6-8]. Particularly, semiconducting materials in the nanostructured form offers the possibility of possessing large optical nonlinear susceptibility and ultra fast response. They are very attractive for the realization of thermally stable and frequency selective lasers and photodetectors, whose performance have been found to be modulated drastically the shapes and sizes of nanocrystallites. ZnO is a direct band gap semiconductor with an energy gap of ~3.37 eV and a large exciton binding energy ~60 meV at room

temperature, which is 2.4 times effective than the effective thermal energy ( $K_{BT} = 25\text{meV}$ ) at room temperature and biexcitation energy is 15 meV [9-11]. These unique properties make ZnO a promising candidate for applications in optical and optoelectronic devices. In the present work, nanoparticles of ZnS are prepared through arrested precipitation method. Nanoparticles of ZnS are heated at  $850^{\circ}\text{C}$  to synthesize nanoparticles of ZnO. The structural and optical properties of nanoparticles of ZnO were characterized using X-ray diffraction (XRD) and Photoluminescence techniques. The ZnO nanoparticles were doped with copper using co precipitation method and the effect of doping in different concentrations on the emission spectra was discussed.

## **II. EXPERIMENTAL**

In the present work, zinc sulfide nanoparticles are prepared through wet chemical precipitation method in aqueous medium under ambient atmosphere. The reagents used for this study are zinc sulphate, Ethylenediaminetetra acetic acid (EDTA), the capping agent and sodium sulfide. 20 ml 0.5M zinc sulphate solution is measured into a 250 ml beaker. 5ml of 0.5M EDTA is then added and 10 ml of 1M sodium sulfide is finally added with continuous stirring to start the reaction. Distilled water is also added to make up 100ml of solution. The solution is centrifuged with water for five times and then with acetone to remove the byproducts, and traces of reactants, if any present. A white precipitate is formed, i.e, Zinc sulfide (ZnS). The as prepared zinc sulfide nanoparticles were heated at  $850^{\circ}\text{C}$  for 9 hours in a hot air furnace to obtain ZnO nanoparticles. The ZnO nanoparticles were doped with Cu at 1%, 2% and 5% Cu by taking appropriate amounts of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$ . X-ray diffraction patterns of the nanoparticles of zinc oxide were recorded using a PANalytical 3 kW X'pert PRO X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ) source over the diffraction angle,  $2\theta$ , between  $10^{\circ}$  and  $80^{\circ}$ . In the present study, UV-visible spectrophotometer UV-SHIMADZU 2401 PC is used to record the absorption spectra of the nanoparticles of ZnO in the wavelength range from 200 to 900 nm. The samples are dispersed in ethanol to record absorption spectra. The room temperature photoluminescence (PL) spectra of the samples were recorded using Perkin Elmer Fluorescence Spectrophotometer model LS 45(L2250106). The xenon lamp is used as an excitation source and excitation wavelength is 350 nm.

## **III. RESULTS AND DISCUSSION**

### **X-ray diffraction studies**

The XRD pattern of nanoparticles of ZnO of present study is shown in the figure 1. The figure shows three diffraction peaks at  $2\theta$  values of 31.2, 34.1, 35.9, 47.1, 56.3, 62.5, 67.2 and  $68.7^{\circ}$  corresponding to d values of 2.863, 2.626, 2.498, 1.927, 1.632, 1.484, 1.398 and  $1.369\text{\AA}$  respectively. The peaks are identified to originate from (100), (002), (101), (102), (110), (103), (112) and (201) planes of the cubic phase of ZnO (JCPDS Card No. 80-0075). The grain size of ZnO nanoparticles of present study were calculated using Debye-Scherrer equation [12] and is found to be approximately 19 nm.

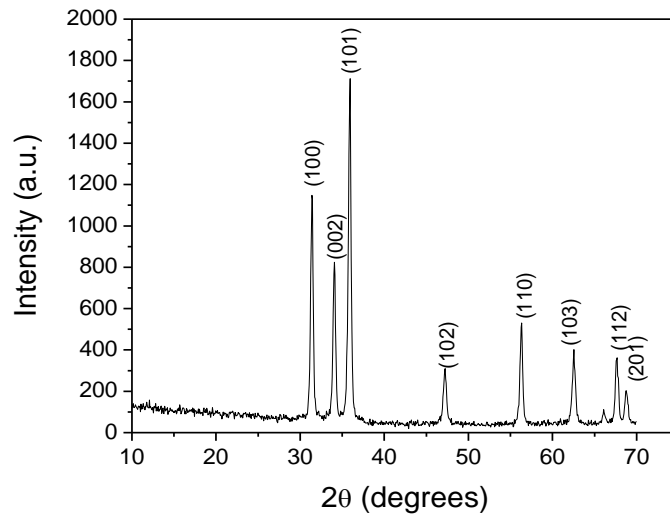


Fig1. X ray diffraction pattern of ZnO nanoparticles

### UV-Visible absorption studies

UV-Visible absorption spectrum of nanoparticles of ZnO of present study is shown in figure 2. From the figure it is observed that the absorption edge at  $\sim 257$  nm is blue shifted compared to bulk ZnO. The absorption can be attributed to the excitonic transition between  $1s_e-1p_h$  energy levels of ZnO. The band gap of ZnO calculated by extrapolating straight portion of the  $(ah\nu)^2$  vs  $h\nu$  plot is found to be  $\sim 4.58$  eV. It is reported that bulk ZnO has a band gap of 3.37 eV [13]. The band gap of nanoparticles is found to be increased due to quantum confinement effect. Nanoparticles exhibit quantum confinement effects when their grain sizes are comparable with the bulk Bohr exciton radius. Bulk Bohr exciton radius of ZnO is about 1 nm. The bandgap of nanoparticles of ZnO of present study showed considerable blue shift even though they have large grain sizes ( $\sim 20$  nm). This contradiction can be explained by the assumption that the real volume accessible for the exciton is smaller than the actual geometric size of the crystallites. There may be two reasons for the reduction of real volume accessible for the exciton. (1) The defects or dislocations in the crystal may cause different crystalline domains inside the particle causing additional spatial confinement or (2) the existence of a potential barrier at the surface which extends to the inner part of the particles causing additional confinement.

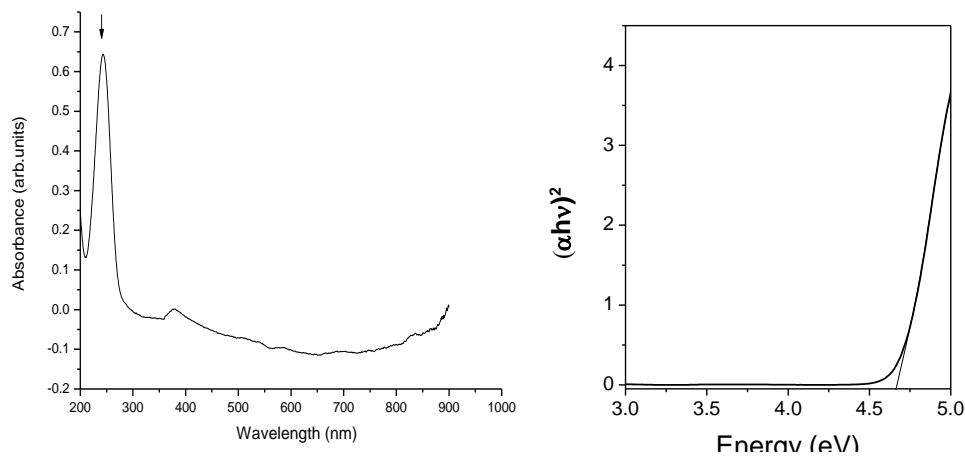
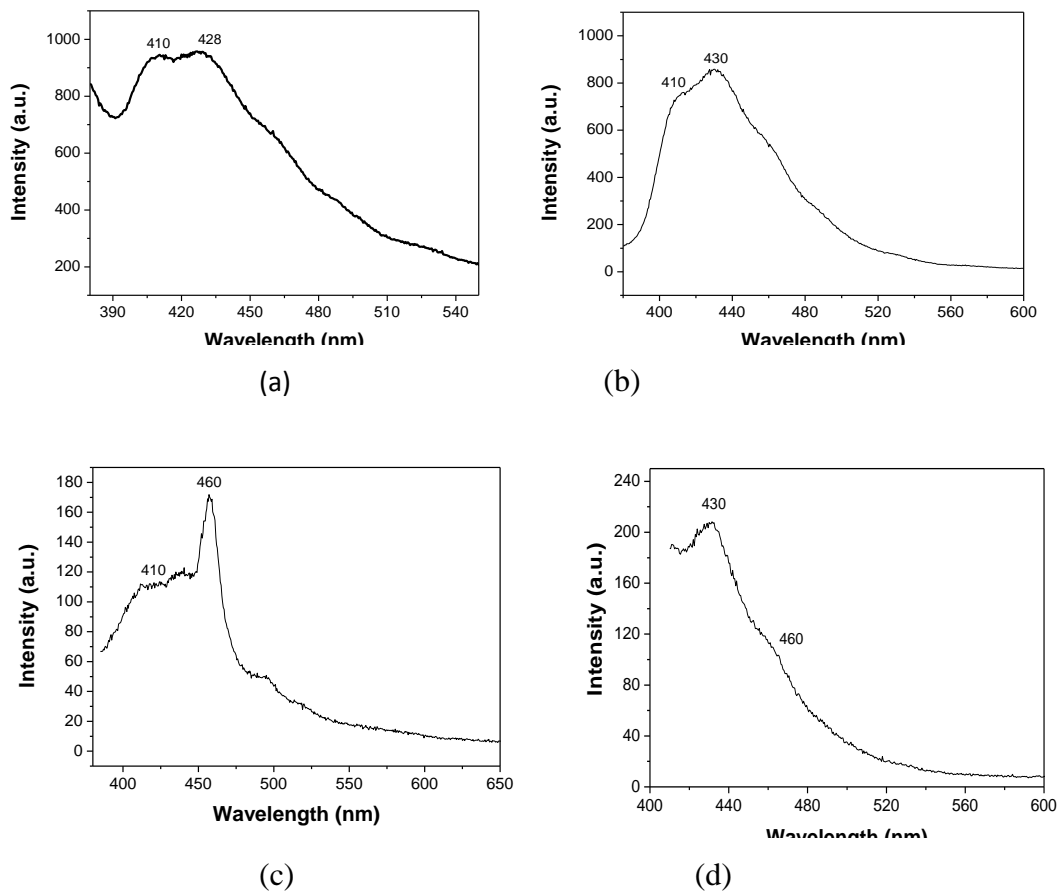


Fig 2. UV-Visible absorption spectrum and plot of  $(\alpha h\nu)^2$  vs  $h\nu$  for ZnO nanoparticles

### Photoluminescence studies

The room temperature PL emission spectrum of nanoparticles of ZnO of present study is shown in the figure 3 (a). The spectrum exhibits two broad peaks around 410 and 428 nm. As the energies corresponding to these peaks are less than the band gap of ZnO, the probability of even the higher energy band (410 nm) to be due to band edge emission can be ruled out and both the bands may be ascribed to transitions between discrete energy levels such as shallow trap, deep trap and surface state in the forbidden gap. Both Schottky and Frenkel defects exist in all solids. But there is always a tendency for one type of the defects to be dominant since the formation energies of these two defects are unequal. It is known that Schottky defects are dominant in cubic ZnO. The peak at 410 nm observed in the present study can be assigned to oxygen vacancies, i.e. to the recombination of electrons at the oxygen vacancy with holes at the valance band. The peak observed at 428 nm for the present sample can be attributed to the transitions of electrons from the oxygen vacancy states to zinc vacancy state [14]. The photoluminescence spectrum of ZnO nanoparticles doped with Cu at 1%, 2% and 5% are shown in the figures 3(b), (c) and (d) respectively. The PL spectrum of ZnO doped with 1% Cu exhibits peaks at 410 and 428 nm. The peaks at 410 and 428 nm were similar to that of undoped samples. The PL spectrum of ZnO doped with 2% and 5% Cu exhibits peaks at 430 and 460 nm. The peak at 460 nm can be ascribed to the impurity level formed due to the incorporation of  $\text{Cu}^{2+}$  in ZnO lattice. It can be observed from the emission spectra of samples doped with 5% Cu that the peak due to impurity level (460 nm) is less prominent compared to that doped with 2% Cu. It may be ascribed to the quenching of emission line due to excess copper.



**Fig 3. Photoluminescence emission spectrum of nanoparticles of ZnO (a) undoped, (b) doped with 1% copper (c) doped with 2% copper and (d) doped with 5% copper**

#### IV. CONCLUSION

In the present work, ZnO nanoparticles were synthesized by thermal oxidation of ZnS nanoparticles prepared by arrested precipitation technique. X-ray diffraction pattern of the ZnS and ZnO nanoparticles were recorded and compared with the standard JCPDS values. From the JCPDS values, it was found that the ZnS and ZnO nanoparticles of present study are in cubic phase. The grain size of ZnO nanoparticles was calculated from Debye-Scherrer equation and was found to be approximately 19 nm. The PL spectra of the samples were recorded at room temperature with an excitation wavelength of 350 nm. The peak at 410 nm observed in the pristine ZnO samples of present study can be assigned to oxygen vacancies, i.e. to the recombination of electrons at the oxygen vacancy with holes at the valence band and that at 428 nm can be attributed to the transitions of electrons from the oxygen vacancy states to zinc vacancy states. The PL spectrum of ZnO doped with 1% Cu is similar to that of undoped samples. The PL spectrum of ZnO doped with 2% and 5% Cu exhibits peaks at 430 and 460 nm. The peak at 460 nm can be ascribed to the impurity level formed due to the incorporation of  $\text{Cu}^{2+}$  in ZnO lattice. The emission spectra of samples doped with 5% Cu that the peak due to

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## REFERENCES

- [1.] J. Wang, T. Miki, A. Omino, K. S. Park, M. Isshiki: J. Cryst. Growth 221, 393 (2000)
- [2.] M. K. Lee, M. Y. Yeh, S. J. Guo, H. D. Huang: J. Appl. Phys. 75, 7821 (1994)
- [3.] A. Toda, T. Margalith, D. Imanishi, K. Yanashima, A. Ishibashi: Electron. Lett. 31, 1921 (1995)
- [4.] A. Cho: J. Vac. Sci. Tech. 8, S31 (1971) 16.70 C. T. Foxon: J. Cryst. Growth 251, 130 (2003)
- [5.] J. Wang, A. Omino, M. Isshiki: J. Cryst. Growth 229, 69 (2001)
- [6.] J. B. Baxter and E. S. Aydil, Appl. Phys. Lett. 86, 53114 (2005).
- [7.] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science 292, 1897 (2001).
- [8.] J. Song, J. Zhou, and Z. L. Wang, Nano Lett. 6, 1656 (2006).
- [9.] Z. L. Wang, Annu. Rev. Phys. Chem. 55, 159 (2004).
- [10.] J. Sawai, H. Igarashi, A. Hashimoto, T. Kokugan, and M. Shimizu, J. Chem. Eng. Japan 29, 556 (1996).
- [11.] S. C. Minne, S. R. Manalis, and C. F. Quate, Appl. Phys. Lett. 67, 3918 (1999)
- [12.] B D Cullity, Elements of X-ray diffraction, II Edition, (1978) Addison – Wesley Publishing Company, Massachusetts.
- [14.] S Wageh, Z S Ling and X Rong, J. Cryst. Growth **255** (2003) 332.
- [15.] R Raji and K G Gopchandran, Mat.Res.Exp. **4** (2017) 52.
- [16.]