STRUCTURAL AND OPTICAL PROPERTIES OF CU^{2+} DOPED ZnS NANOPARTICLES FOR PHOTOLUMINESCENCE APPLICATION

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Abstract - ZnS and Cu doped ZnS nanoparticles were prepared using chemical co-precipitation method. The structural and optical properties were analyzed for different Cu^{2+} doping ratio (0.02M, 0.04M, 0.06M) using XRD, UV Visible spectroscopy, Photoluminescence spectra and FTIR study. The XRD pattern confirms Zinc blende structure with average crystallite size by 1.5 nm to 2.9 nm. The calculated band gap is in the ratio of 4.5 eV to 4.7 eV & band gap changes as the doping ratio of Cu^{2+} increases from 0.02M to 0.06M. Photoluminescence study of ZnS and Cu^{2+} doped ZnS exhibits blue and green emission peaks. FTIR spectral study confirms the presence of Cu^{2+} doped ZnS nanoparticles.

Keywords: Band gap, Optical properties, Cu^{2+}, ZnS.

1. INTRODUCTION

Synthesis of materials under nanoscale gains considerable attention among the recent day researchers. The Nano dimensional compound semiconductors are most preferred system for the past two decades due to their versatility, easy to synthesize and high valuable physical and chemical properties (Alivisatos 1996, Brus 1986). By controlling and maneuvering the materials under Nano regime are opened new pathways for the development of device technologies. Compared to group III-V, group II-IV, group I-III-V and group IV based semiconductors group II-VI elements based semiconductors have appreciable properties. Based on the literature survey, in group II-VI elements based semiconductors, zinc and cadmium related chalcogenides have vital role in many environmental and industrial based applications (Murray et al 1993). Besides, doped II-VI semiconductors attain maximum scientific attention due to their enhanced physical and chemical properties.The main reason semiconductor materials are so useful is that the behavior of a semiconductor can be easily manipulated by the addition of impurities, known as doping. Semiconductor conductivity can be controlled by introduction of an electric or magnetic field, by exposure to light or heat, or by mechanical deformation of a doped mono crystalline grid; thus, semiconductors can make excellent sensors. Current conduction in a semiconductor occurs via mobile or "free" electrons and holes, collectively known as charge carriers. Doping a semiconductor such as silicon with a small amount of impurity atoms, such as phosphorus or boron, greatly increases the number of free electrons or holes within the semiconductor.Doped semiconductors are semiconductors which contain impurities, foreign atoms which are incorporated into the crystal structure of the semiconductor. These impurities can either be unintentional due to lack of control during the growth of the semiconductor or they can be added on purpose to provide free carriers in the semiconductor.

2. LITERATURE REVIEW

W.Q.Peng et al (2005) prepared ZnS doped with Cu a facile wet chemical method, with the copper concentration varying from 0 to 2 mol%. The PL spectrum of the undoped ZnS nanoparticles was deconvoluted into two blue luminescence peaks (centered at 411 nm and 455 nm, respectively) were reported. But for the doped samples, a third peak at about 500 nm was also identified.

S.Sambasivamet al(2008) prepared Nanoparticles of $Zn_1-xCuxS$ with Cu concentrations of x = 0.0, 0.1, 0.2, 0.3 and 0.4 prepared by a co-precipitation reaction method from homogeneous solutions of zinc and copper salts. Both the ZnS and ZnS:Cu nanoparticles excited at about 370 nm exhibits a broad green emission band peaking around 491 nm, which confirms the characteristic feature of Zn2+ as well as Cu2+ ions as luminescent centers in the lattice. The TEM micrographs showed spherical morphology for ZnS nanocrystals and the average size of the particles was estimated to be around 8.5 nm.

G.Murugadoss et al (2009) prepared ZnS nanoparticles with Mn^{2+} doping (0.5-20%) by chemical precipitation method. The structure of the nanoparticles has been analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and UV–vis spectrometer. The size of the particles is found to be 3–5 nm range. Photoluminescence spectra were recorded for undoped ZnS nanoparticles using an excitation wavelength of 320 nm, exhibiting an emission peak centered at around 445 nm.

Anoop Chandran et al (2010) prepared ZnS nanoparticles by hydrothermal method. Average crystallite size was calculated from XRD pattern. The size of ZnS nanoparticles was 20.036 nm. Tem images were taking to determine the grain size and shape. Bandgap energy of the material was calculated from the UV –Vis absorption spectrum of the sample.

M.Kuppayee et al (2011) have prepared ZnS doped with Cu^{2+} nanoparticles by chemical co precipitation method with Tri-n- octylphosphine oxide and sodium hexa meta phosphate. The size of the nanoparticles were found to be 4-6nm range. The synthesized particles were analyzed using X-Ray diffraction (XRD), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), UV-visible spectrometer, photoluminescence (PL) and thermos gravimetric- differential scanning calorimetry (TG-DTA).

Khalid T. Al- Rasoul et al (2013) prepared ZnS nanoparticles doped with Ni and Cu with different ratios from a mixture of zinc acetate nickel chloride and copper chloride with sodium sulphide in aqueous solution. The X-ray diffraction patterns showed the typical inter planer spacer corresponding to the cubic phase. Crystallographic studies show the zinc blend crystals varies average crystallite size approximated 4.27 and 4.56 nm for ZnS: Cu and ZnS: Ni respectively, which is almost similar to the average particle size calculated from effective mass approximation .UV-Vis spectrophotometer measurements blue shift for both doping elements.

3.   MATERIALS AND METHODS

A.R. grade zinc acetate di hydrate $(Zn(CH_3COO)_2.2H_2O)$, copper Chloride di hydrate $(CuCl_2.2H_2O)$, sodium sulphide (Na_2S), Sodium hexa meta phosphate, were procured commercially and were used without further purification. De ionized water was used as a solvent for the experiment.First a desired molar proportion say 0.4 mole zinc acetate di hydrate was weighed and dissolved in 50 ml of de ionized water. Then 1g of sodium hexa meta phosphate was added to the solution and solution was continuously stirred for about ½ hour. Likewise an equal molar proportion of sodium sulphide was weighed and dissolved in 50 ml of deionized water and was stirred vigorously at a constant speed to get a homogenous solution of Na_2S.

Then Na_2S solution was taken in a burette and the zinc acetate solution was taken in the beaker and placed over the magnetic stirrer and temperature was put at 80° C, the Na_2S solution was added drop wise to the zinc acetate solution at constant stirring for about two hours. The solution was cooled to room temperature. The prepared solution was wrapped with an aluminium foil and the solution was kept undisturbed for about 24 hours so that the Nano particles get deposited at the bottom of the beaker.

The overflow solution was drained off and the precipitate was cleaned using ethanol to remove the water insoluble impurities. Then the precipitate is repeatedly cleaned 3 times by de-ionized water and finally the precipitate was filtered using whattmann filter paper. The obtained precipitate was dried using a hot air oven at 200^oC for 2 hours. The obtained dried samples were grinded with mortar and pestle to get a fine powder. Thus pure form of ZnS Nano particles was obtained.200^oC for 2 hours. The obtained dried

samples were grinded with mortar and pestle to get a fine powder. Thus pure form of ZnS Nano particles was obtained.For the doping of the copper, the same procedure was followed.

A solution of zinc acetate and sodium hexa meta phosphate was taken and the various concentration of the dopants namely 0.02 mole, 0.04 mole, 0.06 mole of copper chloride di hydrate were weighed and added to the homogeneous solution and stirred vigorously at constant speed. Then same work procedure as discussed earlier were carried out to get the copper doped ZnS nano particles.

4. RESULTS AND DISCUSSION

4.1 XRD ANALYSIS
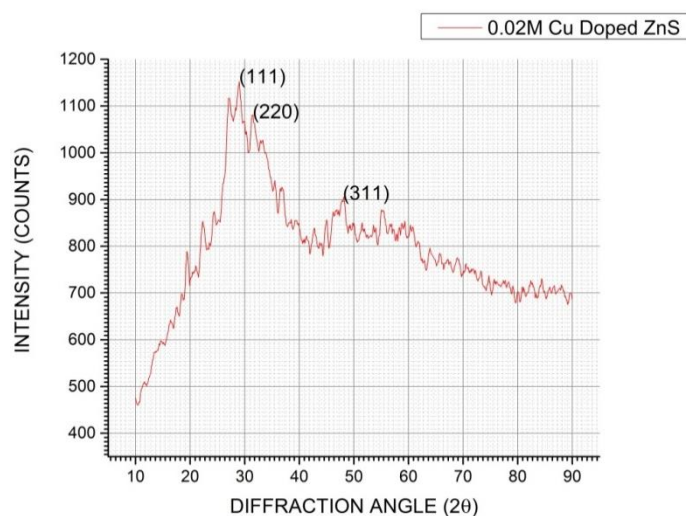
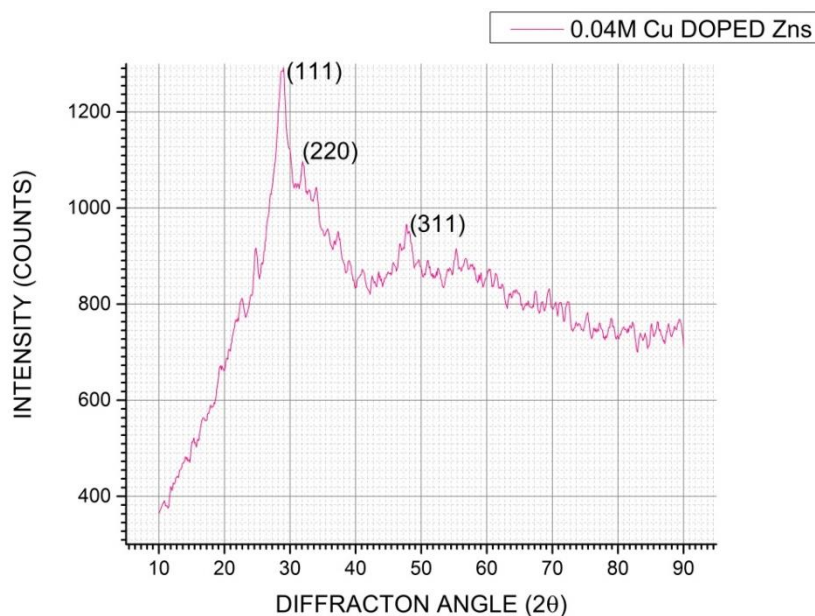Figure 4.1.1-XRD diffraction spectrum of 0.02m Cu^{2+} ZnS

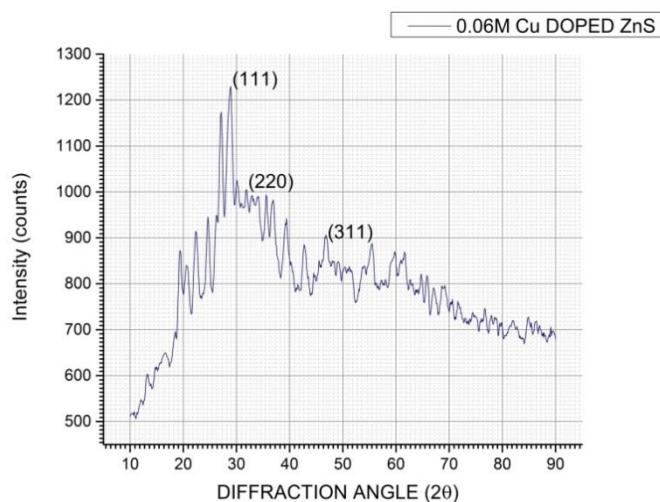Figure 4.1.2-XRD diffraction spectrum of 0.04m Cu^{2+} ZnS

Figure 4.1.3-XRD diffraction spectrum of 0.06m Cu^{2+} ZnS

S.No	Sample	2θ (Degrees)	FWHM	D X 10^{-10}	Miller indices	Crystalline size x10^{-9}	Lattice parameter x10^{-10}
1	0.02M Cu^{2+} ZnS	28.9550	4.21000	3.08120	(111)	1.95080	5.33697
2	0.02M Cu^{2+} ZnS	33.500	3.8000	2.67283	(220)	2.1853	7.556
3	0.02M Cu^{2+} ZnS	47.6541	3.04170	1.90679	(311)	2.8583	6.3241
4	0.04M Cu^{2+} ZnS	28.200	3,96	3.16196	(111)	2.0702	4.7966
5	0.04M Cu^{2+} ZnS	32.300	4.5600	2.76934	(220)	1.815	5.53868
6	0.04M Cu^{2+} ZnS	47.43000	2.94000	1.91528	(311)	2.95	6.3522
7	0.06M Cu^{2+} ZnS	28.000	5.7600	3.18409	(111)	1.4228	5.515005

Table 4.1 Shows that different parameters for Cu^{2+} doped ZnS nanoparticles

The X-ray diffraction patterns of the powdered nano particles were recorded using XRD-1008 diffractometer with Cu-Kα radiation (1.5418 A˚). The XRD patterns of ZnS and ZnS:Cu show very broad diffraction peaks that are the characteristic peak of the nano sized particles.For all samples of ZnS doped with Cu $^{2+}$ ions , strong absorption peaks were observed at 2θ = 28˚, 32˚ , 47˚ corresponding to the lattice planes of (111), (220) and (311) and they were well matched with the zinc blende cubical structure (JCPDS CARD NO. 05-0566).

No diffraction peaks were observed due to the copper impurities and this shows that the copper are dispersed in the zinc matrix.

The crystalline sizes of the particles were calculated using the Debye-Scherer formula as given below

$$D = \frac{k\lambda}{\beta \cos\theta} \text{ ------------- 4.1}$$

Where,

D – crystalline size

K – constant(0.9)

λ – wavelength of the X-ray (1.5418 A˚)

β – full width half maximum (radian)

θ – diffraction angle (degree)

The size of the Cu doped with ZnS nanoparticles ranges from 1.4 nm to 2.9 nm. This shows that the addition of the surfactant has effectively reduced the size of the nanoparticles thus controlled the nucleation process.

The lattice parameters of the obtained particles were calculated using the formula

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \text{ ---------------- 4.1.1}$$

d – interplanar distance

h,k,l – miller indices

a – lattice constant.

The lattice constant of the ZnS calculated ranged from 4.7966 A˚ to 7.556 A˚ which were evident for the Face centered Cubic (FCC) Zinc Blende structure of the ZnS nano particles.
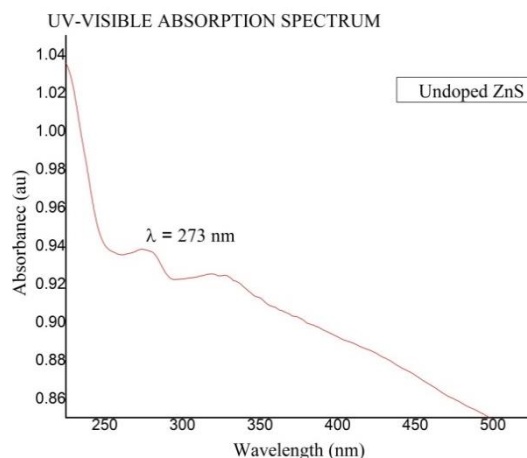
4.2. UV-VISIBLE ABSORPTION SPECTRA ANALYSIS

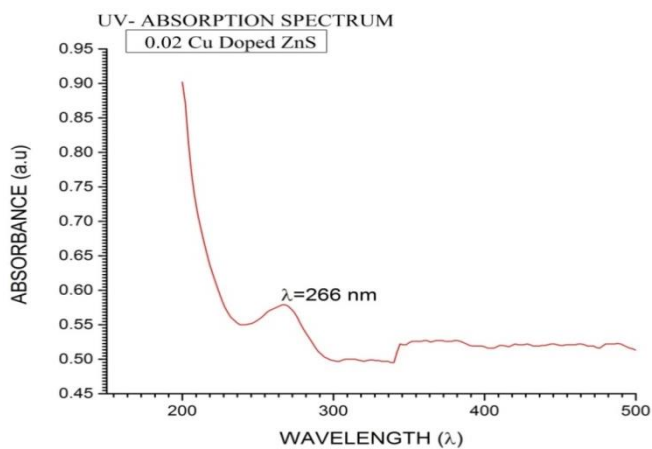Figure 4.2.1 UV-visible of undoped ZnS
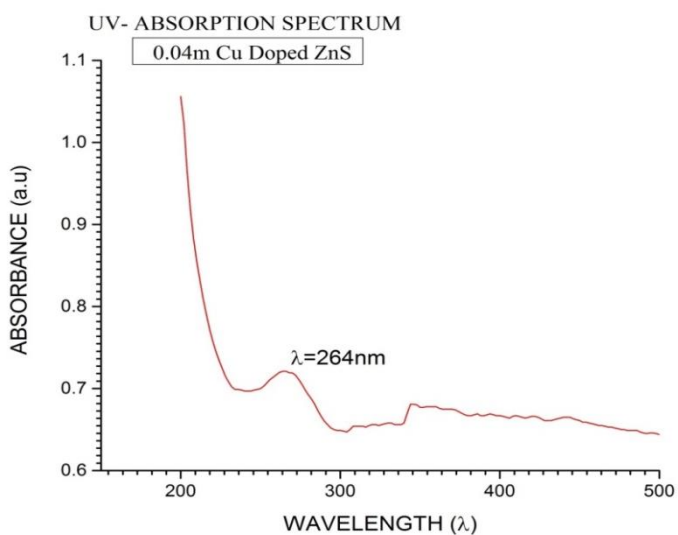
Figure 4.2.2-UV-visible spectrum of 0.02M Cu^{2+} ZnS

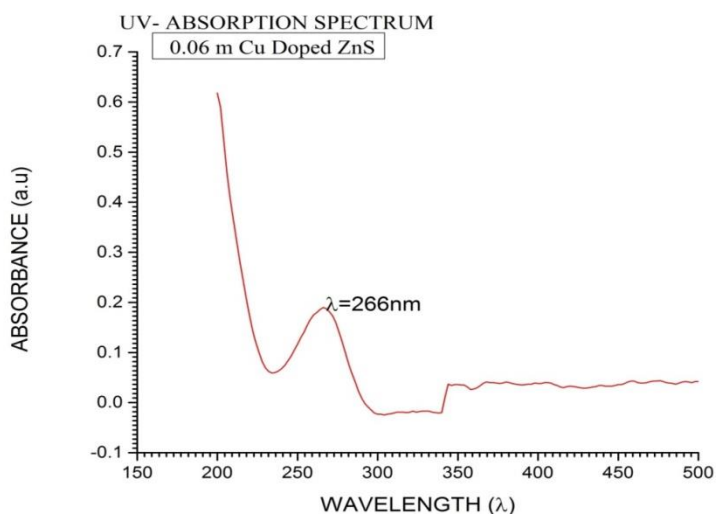Figure 4.2.3-UV-visible spectrum of 0.04M Cu^{2+} ZnS

Figure 4.2.4-UV-visible spectrum of 0.06M Cu^{2+} ZnS

The absorption UV visible spectrum of the undoped and Cu doped ZnS nano particles were studied using UV-1700 series at room temperature. The absorption behaviour of the undoped ZnS and copper doped ZnS dispersed in Ethanol were studied. The strong peaks of sodium hexa meta Phosphate encapsulated undoped ZnS were observed at 273.04nm and that of the cu^{2+} doped ZnS were observed at 264 nm and 266 nm that were associated with the first exitonic state of the $ZnS:Cu^{2+}$ and the narrow shape of the peaks are evident for the size of the particles.

Comparing the doped and undoped ZnS the copper doped ZnS are strongly blue shifted. This may be due to the presence of the Na^+ ions in the surfactant. The energy gap of the particles were found using the Plank's quantum formula

$E = h\nu$------------------ 4.2

Where

E – Energy gap (eV)

h – Plank's constant(6.626×10^{-34} Js)

$\nu = \dfrac{c}{\lambda}$-------------------- 4.2.1

ν – frequency of light (Hz)

c – velocity of light (3×10^8 m/s)

λ – wavelength of light (m)

The bandgap of the undoped ZnS was calculated as 4.550 eV and that of the doped ZnS were 4.668 eV for 0.02M, 4.7059eV for 0.04M of Cu and 4.668 eV for 0.06M of Cu.It was observed that the peak absorption of the copper doped ZnS particles were in the UV region.

4.3. PHOTO LUMINESCENCE

The room temperature Photo Luminescence spectra of different concentrations of Cu^{2+} doped ZnS nanoparticles were studied.
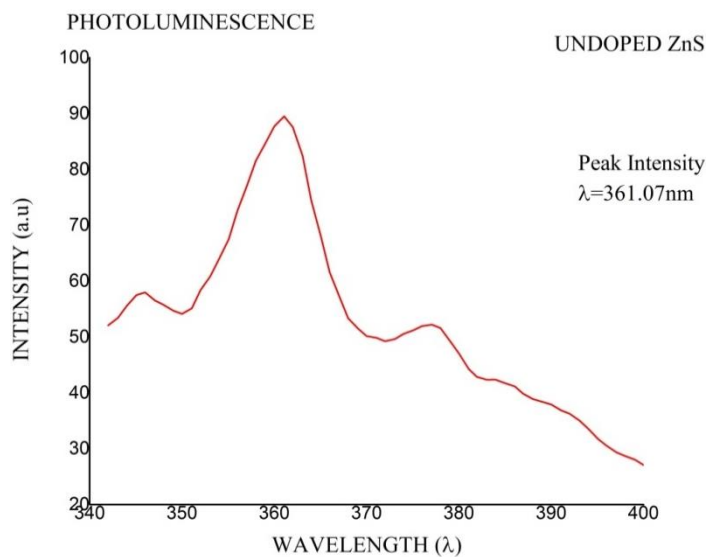

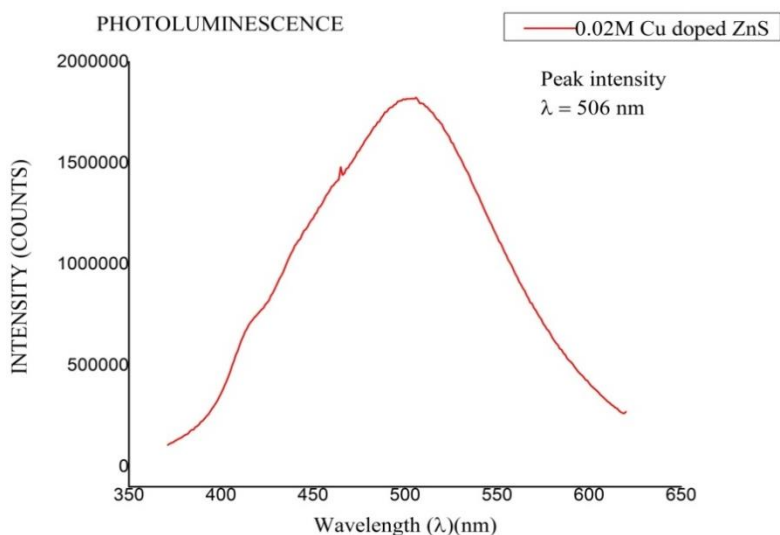Figure 4.3.1 Photoluminescence of undoped ZnS

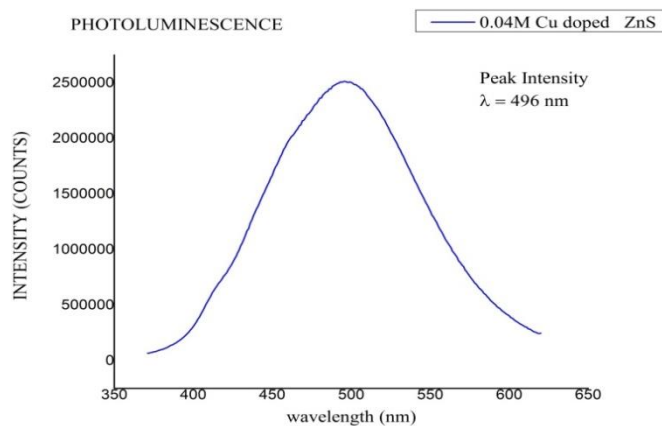Figure 4.3.2 Photoluminescence of 0.02M Cu doped ZnS

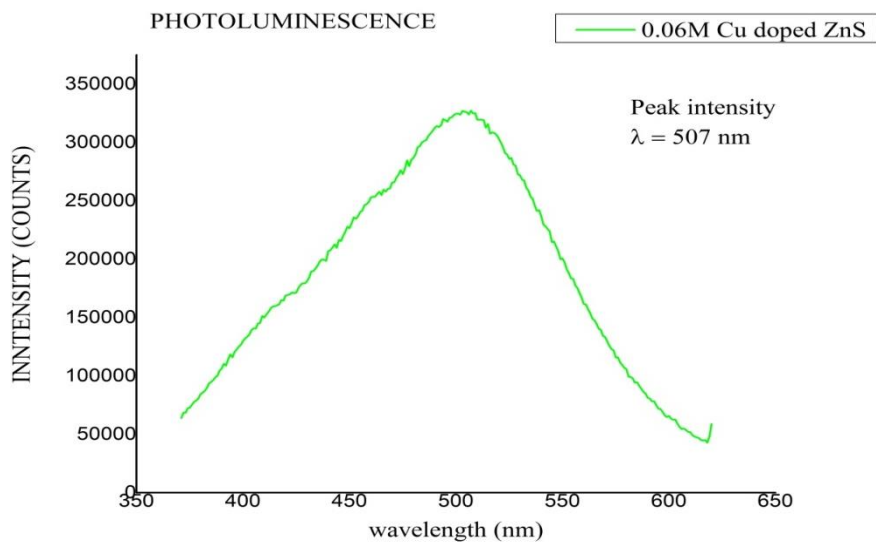Figure 4.3.3 Photoluminescence of 0.04M Cu doped ZnS

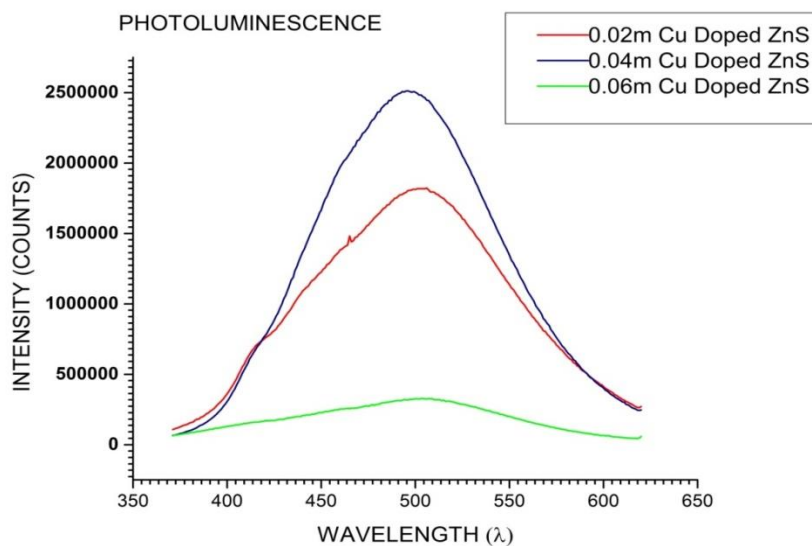Figure 4.3.4 Photoluminescence of 0.06M doped ZnS

Figure 4.3.5 Photoluminescence of Various Concentrations of Cu^{2+} Doped ZnS

The peak intensity of the undoped ZnS was observed at 361.07 nm which were very much less than that of the doped sample. By addition of the Cu^{2+} ions more defects were introduced. This might be the reason behind the peaks that appeared in the longer wavelength side. Comparing the two spectra the Cu^{2+} doped ZnS spectra was more red shifted from that of the undoped ZnS.The spectra showed a broad emission spectrum around 400-600nm. It was in agreement with the earlier results in ZnS:Cu^{2+} nano particles.Three emission peaks (506nm, 496nm, 507nm) were observed in the bluish green region that arises from the combination between the shallow donor level and t_2 level of $cu^{2+.}$ With an increase in the concentration (0.04-0.06) the green light position is symmetrically displaced and shifted towards the longer wavelength region (from 496nm to 507nm), but the intensity of ZnS:Cu is decreased by higher concentration of Cu^{2+}.The figure shows the intensity of the various concentrations of Cu^{2+} doped ZnS. It showed that the optimum concentration of doping for enhanced PL emission was at 0.04M.

Hence we can conclude that from increasing the concentration of Cu^{2+} from 0.02M to 0.04m there was a blue shift and increase in the intensity, but on further increasing the concentration a symmetric red shift was observed but the intensity was drastically decreased.

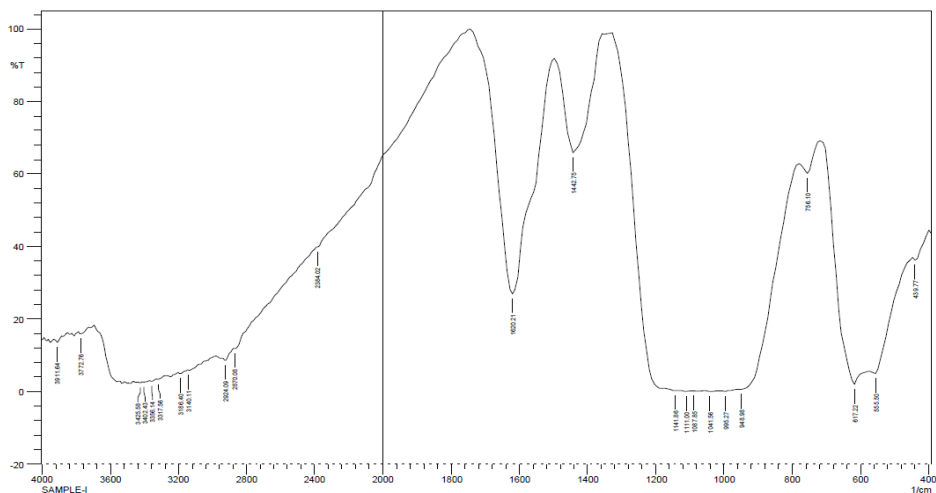## 4.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Figure 4.4.1 FTIR spectroscopy of Cu^{2+} doped ZnS

The FTIR spectra of the undoped and Cu^{2+} doped ZnS were recorded in the range from 4000 cm^{-1} to 400 cm^{-1} using shimadzu spectrometer in the transmission mode.The peaks appearing around 1110 cm^{-1} and 618 cm^{-1} are due to vibrations of the ZnS particles. Thus these vibrations confirm the presence of the host materials in the sample. The other vibrations around 2924 cm^{-1}, 2364 cm^{-1}, 1635 cm^{-1} were due to the micro crystalline formation of the sample. The peak vibrations at 555 might be due to the sulphur oxygen interaction. The vibration around 3425 cm^{-1} was due to the O-H stretching vibration and at 2384 was additional band vibration. The vibrations at 1041 cm-1, 995 cm-1 were due to the asymmetric stretching vibration of the molecules.

5. CONCLUSION

ZnS and Cu^{2+} doped ZnS nanoparticles were synthesized successfully by chemical co-precipitation method. The detailed characterization of the nanoparticles was carried out using X-Ray Diffraction (XRD), UV-Visible spectroscopy, Photoluminescence spectroscopy and FTIR Spectroscopy.

The X-ray diffraction (XRD) patterns of the SHMP encapsulated ZnS exhibited zinc Blende structure. The size of the nano particles ranged from 1.5 nm to 2.9 nm. From the optical studies the bandgap of the undoped ZnS was about 4.550 eV and that of the cu^{2+} doped were calculated as 4.668 eV for 0.02M, 4.7059 eV for 0.04M and 4,668 eV for 0.06M concentrations. This also indicated that the doped samples peaks were blue shifted when compared with the undoped nanoparticles. This shift is due to the decrease in the particle size of the samples.The photoluminescence of the samples shows maximum emission at 506nm, 496nm and 507nm for 0.02M, 0.04M and 0.06M for various concentrations of copper respectively which where the wavelengths corresponding to the bluish green region. The maximum of emission for that of the undoped ZnS was observed at 361.07nm. A red shift is observed for the cu^{2+} doped ZnS to that of the undoped samples. The optimum concentration of the Cu^{2+} for the enhanced photoluminescence was determined as 0.04M. The vibrational peaks acquired from the Fourier Transform Infrared Spectroscopy studies confirmed the presence of ZnS and the nano crystalline structure of all the samples.The ZnS due to its wide bandgap region has a profound application in the semiconductor industries in the fabrication and manufacture of Field emitters, Field Effect Transistors (FETs), p-type conductors, catalysers, UV-light sensors, chemical sensors (including gas sensors), bio sensors and nanogenerators.

Zinc sulphide which is an excellent photoluminescence material when doped with Cu^{2+} gives a bluish green colour and a long time glow in the dark. When doped with other material such as Manganese gives reddish orange glow and when doped with silver gives bright blue. ZnS as it transmits light from visible wavelengths to just over 12 micrometres it can be used as an infrared optical material.

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