

# Study of Change in Properties of ZnS (Organic Phase) Nanoparticles on Doping with Manganese and Yttrium Ions

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## Abstract:

Zinc sulphide (ZnS) is one of the primary semiconductors to be found and it has generally shown noteworthy crucial properties -- adaptability and a guarantee for novel assorted applications, including light-emitting diodes (LEDs), electroluminescence, infrared windows, sensors, lasers, and bio-device applications, and so on. Small particles have higher surface to volume proportion and subsequently have more available transporters for photoluminescence. In this paper, the work studied and discussed centers around the amalgamation of Zinc sulphide nanoparticles in natural stage. Doped ZnS nanoparticles are the most famous materials for research in semiconductor nanoparticles. Doped nanoparticles of semiconductor can yield high radiance. These outcomes proposed that doped semiconductor nanoparticles structure another class of glowing materials, with a wide scope of uses in for example presentations, sensors and lasers.

The more modest will be the size of quantum dots the higher the light discharge proficiency they could give. Accordingly it is sensible to expect that the orchestrated items in this paper, might actually be utilized in electroluminescent applications after doping. In this way, it very well may be seen that the substance properties of manganese particles are fundamentally the same as those of zinc particles. Accordingly doping manganese into ZnS semiconductor is truly great and improves the band edge discharge. X-Ray Diffraction was done to contemplate the construction of ZnS nanoparticles and the Photoluminescence estimations was done to examine the optical properties of prepared samples of ZnS,  $Zn_{1-x}Mn_xS$  and  $Zn_{0.94}Y_{0.06}S$ . In the later part of the study, particle size dispersion is performed to assess the size of the combined nanoparticles. Thus, stage moved ZnS nanoparticles were doped with different degrees of manganese and yttrium and impact of doping on the different qualities were examined. The photoluminescence component of ZnS nanoparticles doped with other metal particles is intricate. ZnS, which is a significant wide band hole semiconductor, has stood out attributable to its wide application including UV light radiating diodes, natural LEDs, proficient phosphors in level board show, photovoltaic gadgets and so on.

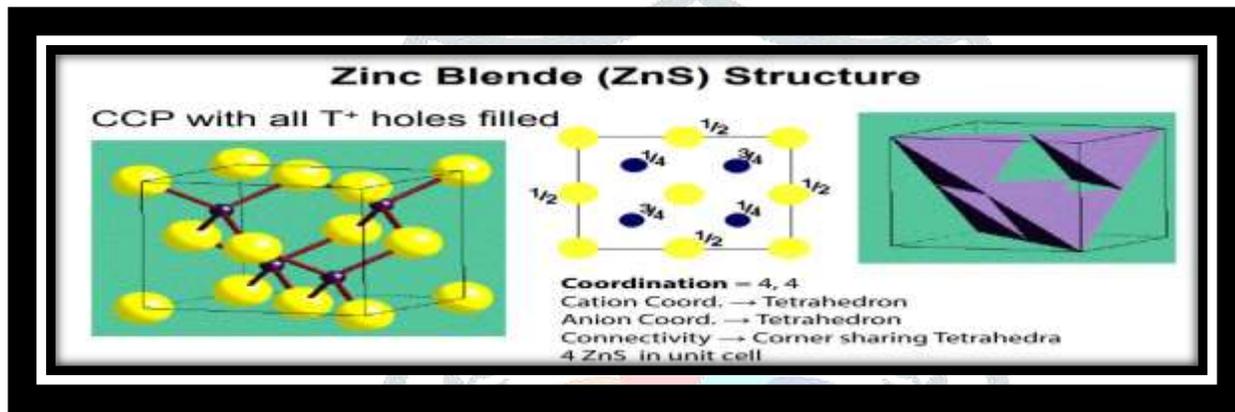
The investigation of molecule size examination shows the impact of doping on the normal size of the nanoparticles integrated. Doping with manganese and yttrium causes quantum confinement of the particles. The molecule size dissemination can be controlled by doping and the degree of doping is critical. Doping past a specific level expands the size of the particles. The ideal doping level of manganese acquired was 6% in extent

with 94% of Zinc. The  $Mn^{2+}$  particle, utilized as dopant in numerous glowing materials show a wide outflow top whose position relies emphatically upon the host cross section. Since an enormous bit of the particles in nanoparticles is situated on or close to the surface, the surface properties ought to have huge impact on their structural and optical properties.

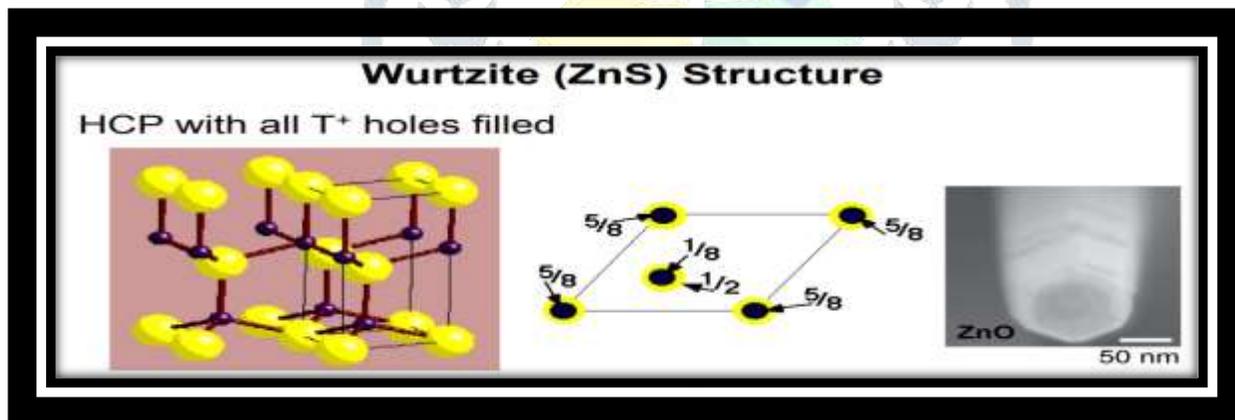
**Keywords :** Electroluminescence, Photoluminescence, Adaptability, Nanoparticles, Proficient, Semiconductor , X-Ray Diffraction, Estimations, , Photovoltaic , Doping, Glowing.

## 1 Introduction:

ZnS has two usually accessible allotropes --- Zinc Blende Structure ( Z B ) and another with a Wurtzite Structure ( W Z ). Zinc blende structure is the cubic structure and the Wurtzite is hexagonal as shown in the figure below :



Source : <https://www.chem.uci.edu/~lawm/10-21.pdf>



(Source : <https://www.chem.uci.edu/~lawm/10-21.pdf> [12])

ZnS has an enormous band-gap of roughly 3.72 eV for cubic zinc blende (ZB) and 3.77 eV for hexagonal Wurtzite ZnS and subsequently, it is more appropriate for obvious visually impaired bright --- light based gadgets like sensors/photo detectors[1]. The band design of a solid depicts scopes of energy levels that an electron is 'prohibited' or 'permitted' to have and it decides significant electronic and optical properties of that material.

The optical properties of nanocrystalline semiconductor have been concentrated widely in the previous years. These materials act uniquely in contrast to mass semiconductors[2]. With decline

in molecule size, the band construction of the semiconductor changes, the band hole increments and the edges of band split into discrete energy levels called Quantum-confinement zones. It is notable that the optical and electronic properties change significantly because of quantum confinement of the charge transporters inside the molecule. ZnS, which is a significant wide band hole semiconductor, has stood out inferable from its wide application including UV light producing diodes, natural LEDs, proficient phosphors in level board show, photovoltaic gadgets and so on[3]. The photoluminescence component of ZnS nanocrystals doped with other metal particles is intricate. Small particles have higher surface to volume proportion and subsequently have more available carriers for photoluminescence. The surface states are vital for the actual properties and optical properties of nanoparticles.

To use semiconductor nanostructures as building squares of utilitarian nanodevices, it is imperative to integrate the nanoparticles having assorted actual properties. This could be acknowledged through proper doping. Transition metal particles doped ZnS nanoparticles are the most well known materials for research in semiconductor nanocrystals. Doped nanocrystals of semiconductor can yield high luminescence[4]. These outcomes recommended that doped semiconductor nanocrystals structure another class of luminescence materials, with a wide scope of utilizations in for example presentations, sensors and lasers. With reducing molecule size a solid hybridization of the s-p conditions of the ZnS and the d conditions of the  $Mn^{2+}$  debasement should happen[5]. This hybridization brings about a quicker energy move between the ZnS host and  $Mn^{2+}$  impurity, yielding higher quantum productivity[6]. Impurity d-electron states go about as effective glowing places while communicating emphatically with s-p electronic conditions of the ZnS into which outside electronic excitation is ordinarily coordinated. The resulting move of electron and opening sets into the electronic level of the  $Mn^{2+}$  particle prompts the trademark yellow-orange emission.

## 2. Experimental Details :

### 2.1 Materials required :

Stearic Acid -  $C_{18}H_{36}O_2$  ; Zinc Nitrate -  $Zn(NO_3)_2$  ;

Chloroform -  $CHCl_3$  ; Manganese Chloride ( $MnCl_2$ ) ;

Yttrium Carbonate -  $Y_2(CO_3)_3$  ; Octadecane Thiol (ODT) -  $C_{18}H_{38}S$

### 2.2 Synthesis of Manganese and Yttrium doped ZnS Nanoparticles :

1) Firstly, for Manganese ions ( $Mn^{2+}$ ) doping , the corresponding aqueous salts of Mn and Zn were thoroughly blended in required weight proportions.  $10^{-3}$  M solution of  $MnCl_2$  in proportions of 2%, 4%, 6%, 8%, and 10% in weight are synthesized and mixed alongside Zinc Nitrate solutions  $\{Zn(NO_3)_2\}$ .

2) Secondly, for required doping with yttrium as impurity ,  $10^{-3}$  M yttrium carbonate solution  $\{Y_2(CO_3)_3\}$  was taken and dissolved in acidic distilled water and mixed in proportions of amount taken as 2% , 4% , 6% , 8%

& 10% and added with Zinc Nitrate solution  $Zn(NO_3)_2$  and the process is repeated to get the desired product as result.

Finally, we get  $Zn_{1-x}Mn_xS$  and ZnYS Nanocrystals in organic phase with Octadecane Thiol (ODT) as the capping agents and the samples thus prepared are ready to be used for further characterization techniques, in order to get the detailed investigation about the doping effect on properties especially optical property of ZnS nanoparticles.

### 3 Characterization using X-Ray Diffraction:

X-ray diffraction is presently a typical strategy for the investigation of gem structures and nuclear dividing. X-ray diffraction depends on helpful obstruction of monochromatic X-rays and a glasslike test[7]. These X-rays are created by a cathode ray tube, sifted to deliver monochromatic radiation, collimated to focus, and coordinated toward the sample. The connection of the X rays with the sample produces valuable obstruction (and a diffracted ray) when conditions fulfill Bragg's law  $n\lambda = 2d \sin\alpha$

where,  $n$  is a number,  $\lambda$  is the frequency of the X-rays,

$d$  is the interplanar dividing creating the diffraction and  $\alpha$  is the diffraction point.

In our present study, XRD pattern is obtained for  $Mn^{2+}$  doped ZnS nanoparticles and  $Y^{3+}$  doped ZnS nanoparticles, which are shown in fig 1 and 2 respectively. The X-Ray diffraction analysis of the coated filmed silicon substrates was done,  $Zn_{(1-x)}Mn_xS$  and ZnYS was performed on an XP device operating at 42 kV and a current of 32 mA. These patterns have been recorded within the range of  $40^\circ$  between upper and lower limit with a scan rate of  $2^\circ / \text{min}$ .

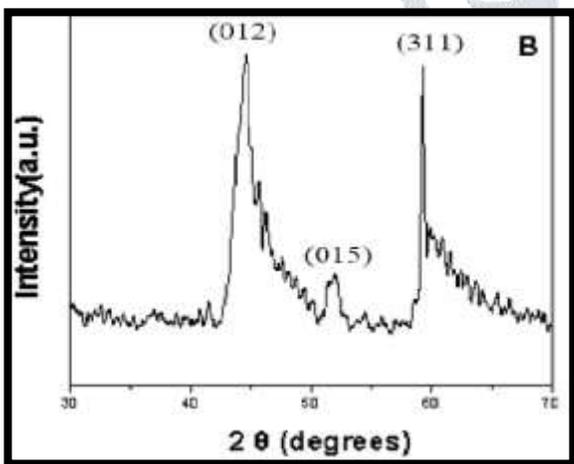


Fig. 1 XRD pattern for doped ZnMnS

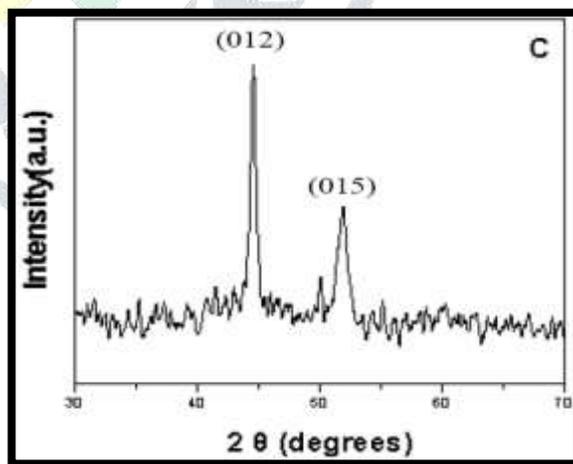


Fig. 2 XRD pattern for doped ZnYS

#### 4 Measurements using the technique of Photoluminescence measurement :

Photoluminescence is a typical technique used to portray the optoelectronic properties of semiconductors and different materials. Its guideline is straightforward: electrons are energized from the valence to the conduction band of the material by a laser with an energy larger than the band gap[8]. As an outcome, the photo-excited carriers unwind and afterward unexpectedly recombine with openings in the conduction band. On account of direct semiconductors, the abundance energy is radiated as light. By breaking down the range of the radiated light, it is feasible to gauge the material's reaction regarding power as a component of frequency[9]. The PL spectra obtained for different wavelengths for doped ZnYS is shown in the figure 3 ( wavelength = 330nm ) and figure 4 ( having wavelength = 465 nm )

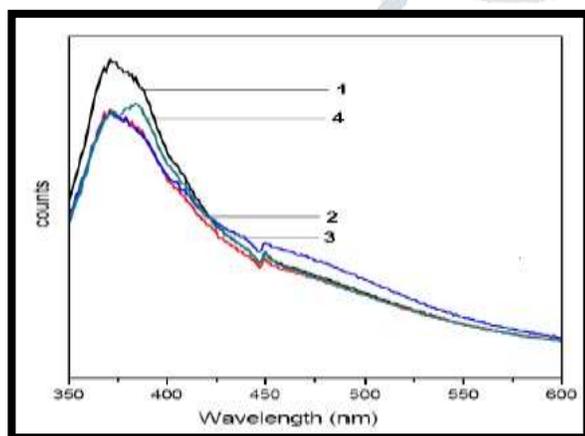


Fig. 3 PL spectra for ZnYS (330 nm)

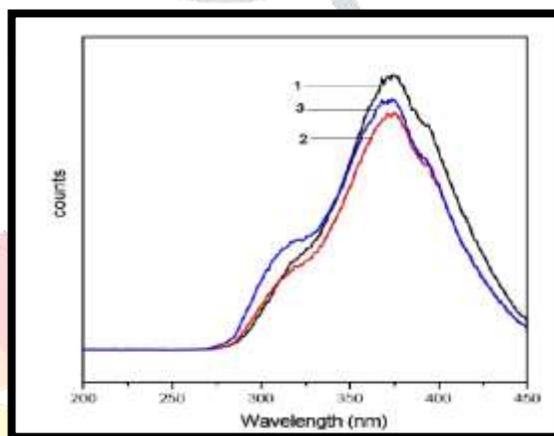


Fig. 4 PL spectra for ZnYS (465 nm)

#### 5. Results and Discussion :

##### 5.1 For XRD Analysis:

In the Fig.2 shown above for XRD Analysis of the data obtained in case of  $Zn_{(0.95)}Mn_{(0.05)}S$  nanoparticles blended in natural stage. The zinc blende stage continues up to 5% - Mn alloying with the ZnS nanoparticles . Subsequently, 5% Mn focus is by all accounts ideal for the homogenous development of alloyed having concentration  $Zn_{(1-x)}Mn_{(x)}S$  nanoparticles under encompassing conditions.

In the Fig.3 shown above for XRD Analysis of the data obtained in case of ZnYS nanoparticles combined in the proportion of Zn:Y being 94:6. The standard estimations of  $2\theta$  are  $44.255^\circ$  and  $51.867^\circ$  relating to (0,1,2) and (0,1,5) planes individually for a hexagonal design. The most noticeable pinnacles are acquired around  $44.58^\circ$  (0,1,2), more modest pinnacles are seen at  $52.15^\circ$  (0,1,5) grid planes of hexagonal ZnS.

The XRD designs don't show any huge change due to doping with manganese or yttrium into ZnS nanocrystals. The pinnacle acquired at  $59.15^\circ$  is because of zinc blende structure when doped with manganese. In any case,

this pinnacle isn't seen when doped with yttrium which is because of legitimate alloying of yttrium in the ZnS grid. The mean crystallite sizes  $D$  were resolved by the condition :

$$(D = 0.9 \lambda / \beta \cos \theta) \text{ ----- Scherer Condition,}$$

where  $\lambda$  is the X – beam frequency,  $\beta$  is the full width half greatest (FWHM)

and  $\theta$  is diffraction point.  $\lambda$  for  $\text{CuK}\alpha$  radiation is 1.54060 .

## 5.2 Discussion for Photoluminescence measurement results:

In the result obtained as figure 3 above, for photoluminescence spectra measurement of Octadecane Thiol (ODT) capped Zinc sulphide nanoparticles for the curve (1) ,  $\text{Zn}_{0.98}\text{Y}_{0.02}\text{S}$  nanoparticles for the curve no. (2), curve no. 3 corresponding to  $\text{Zn}_{0.94}\text{Y}_{0.06}\text{S}$  nanoparticles and curve no. 4 corresponding to  $\text{Zn}_{0.9}\text{Y}_{0.1}\text{S}$  nanoparticles at an excitation wavelength of 330 nm . Thus, for the graph discussed here we have plotted the photoluminescence emission spectra of pure ZnS and yttrium doped ZnS for the various known concentrations of yttrium, during the said process beam of wavelength 330nm is used. It exhibits multiple peaks for various. No significant variation is there in the photoemission found due to the doping with yttrium ( $\text{Y}^{3+}$ ). With the increase in  $\text{Y}^{3+}$  doping concentration the quenching of blue emission band is observed[13]. In the figure 4 shown above, photoluminescence emission spectrum of undoped ZnS and yttrium doped ZnS ( i.e. ZnYS ) having various concentrations of yttrium with an excitation wavelength of 465 nm and shows the peak emission for wavelength of 370 nm and the intensity of photo emission spectra is brilliantly seen.

## 6 Conclusion :

Doping manganese and yttrium ions into ZnS semiconductor is entirely good and improves the band edge emission spectra. The transition metal ions utilized here in this study as a dopant in numerous luminescent materials show an expansive emission top whose position relies unequivocally upon the host cross section[14]. The emission tone can change from green to dark red. Since an enormous part of the particles is situated on or close to the surface, the surface properties ought to have huge impact on their primary and optical properties. The more modest the size of quantum specks the higher the light emission effectiveness they could give. Consequently it is sensible to expect that the combined items in this work might actually be utilized in electroluminescent applications after doping.

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