

## INFLUENCE OF THE CAPPED POLYMER ON THE OPTICAL OF ZnS:Cu NANOCRYSTALLINE THIN FILMS

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**Abstract.** *The ZnS:Cu nanopowders were synthesized by the wet chemical method with Cu concentrations of 0.1, 0.15, 0.2, 0.3 and 0.4%. The microstructure of samples was investigated by the X-ray diffraction (XRD) measurement. The results show that the prepared samples belong to the Wurtzite structure with the average particle size of about 3–7 nm. The highest luminescence intensity of ZnS:Cu nanopowders corresponds to sample with Cu concentration of 0.2%. To investigate the effect of polyvinylalcohol (PVA) on the structure of ZnS:Cu, we have prepared the polyvinylalcohol (PVA)-capped ZnS:Cu thin films with a Cu concentration of 0.2% by dip-coating method. The PVA did not affect the microstructure of ZnS nanomaterials. The optical properties of samples were studied by measuring the absorption and the photoluminescence spectra in the wavelength range from 300 nm to 900 nm at room temperature. The value of direct band gap is about 3.8 eV. The dependence of the photoluminescence (PL) spectra of samples on the exciting power density, their time-resolved-luminescence spectra were also investigated.*

### I. INTRODUCTION

The ZnS nano material is a semiconducting material with direct and larger band gap. The direct band gap of ZnS is about 3.6 eV for bulk form and 3.98 eV for ZnS nano-form at 300 K [5] in the Wurtzite structure. The direct band gap of nano-materials may be controlled by doping, polymer coating and change of preparing conditions [1-4]. The doping of Cu has considerable influence to the optical properties of samples. However, the polymer has a role as the protected environment for ZnS nanoparticles. The optical properties of ZnS nanoparticles change considerably when diffusing them into polymer matrix with optimal concentration. These properties can be explained by the quantum confinement effect, the quantum size changed effect and the surface effect of polymer-capped nanoparticles [5,6].

In this paper, we present some results on the nanostructure and optical properties of the ZnS:Cu nanopowder with Cu concentrations of 0.1, 0.15, 0.2, 0.3 and 0.4%. In order to study the influence of polymer PVA (polyvinylalcohol) concentration on the optical ZnS:Cu nano-materials, we have synthesized the PVA capped ZnS:Cu nanocrystalline thin films with the constant Cu concentration of 0.2%, but different PVA concentration. In addition, the influence of Cu and PVA concentration to luminescence spectra, grain size and direct band gap of this film is also presented.

## II. EXPERIMENT

The ZnS:Cu nano-powder was prepared by the wet chemical method.  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  0.1 M,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  0.1 M and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  0.1 M were used as the initial solutions. For simplicity, we call them first, second, and third solution, respectively. The catalysis is  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  for first and second solutions in term of ratio 1:1. The water is the solvent for the third solution.

### II.1. The synthetic of the 0.1%, 0.15%, 0.2%, 0.3% and 0.4% Cu doped ZnS nano-powder (denoted as $B_1, B_2, B_3, B_4$ , and $B_5$ ) and the PVA doped ZnS nano-powder with Cu concentration of 0.2%

The first and second solution are mixed with appropriate ratio in order to create 0.1%, 0.15%, 0.2%, 0.3% and 0.4% Cu doped ZnS material. The pH has an important role in forming ZnS:Cu precipitates in this process. The third solution was added drop by drop to a reaction vessel. The ZnS:Cu precipitates were separated by centrifuge and drying at 80 °C.

In order to receive the PVA doped ZnS:Cu nano-powder with Cu concentration of 0.2% and the different PVA concentrations, the PVA amounts of 1 g, 2 g, 3 g and 4 g are dissolved in 100 ml of first and second mixed solutions with the constant Cu concentration of 0.2% . The mixed solution with PVA is heated at 80°C and then decreased to room temperature.

### II.2. The production of the PVA-capped 0.2% Cu doped ZnS nanocrystalline thin films

The first and second solutions with optimal concentration of 0.2 % Cu are mixed in the same way as above. Then PVA amounts of 1 g, 2 g, 3 g and 4 g are dissolved in 100 ml of first and second mixed solution. The PVA-capped Cu doped ZnS thin films are produced by the dip-coating method in the glass substrate.

Photoluminescence spectra at 300K of the samples are measured by the fluorescence spectrophotometer HP340-LP370 using a He-Cd laser source with the excitation wavelength of 325 nm. The ultraviolet absorption spectra of thin samples are measured by the spectrometer JASCO -V670. The X-ray diffraction patterns were recorded by the XD8 Advance Bukerding machine using the  $\text{CuK}_\alpha$  radiation of  $\lambda = 1.5406\text{\AA}$  and the particle size is measured by TEM The dependence of the photoluminescence spectra (PL) of samples on the exciting power density, their time-resolved-luminescence spectra are also investigated.

## III. RESULTS AND DISCUSSION

### III.1. The 0.1, 0.15, 0.2, 0.3 and 0.4% Cu doped ZnS nano-powder and the PVA doped ZnS nano-powder with Cu concentration of 0.2%

Fig. 1 shows the typical PL spectra of  $B_1, B_3$  and  $B_5$  nano-powders. It is clear that, the maximum position of PL peaks is about 500 nm and do not depend on the Cu doped concentration. However, the intensity of PL peaks changed with the Cu concentration. The optimal Cu concentration in ZnS:Cu nano materials is about 0.2%. For this concentration, the PL intensity of sample reaches to the highest.

Figure 2 shows the XRD patterns of B-ZnS:Cu, B-ZnS:Cu-PVA2 and B-ZnS:Cu-PVA4 powders. The positions of the peaks seem to be not changed in all samples. This means that the polymer PVA does not affect the crystal structure of the ZnS:Cu nanomaterials.

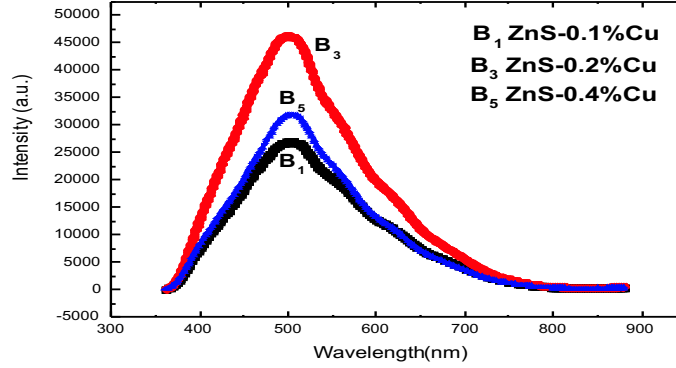


Fig. 1. The PL spectra of B1, B3 and B5 nano-powder

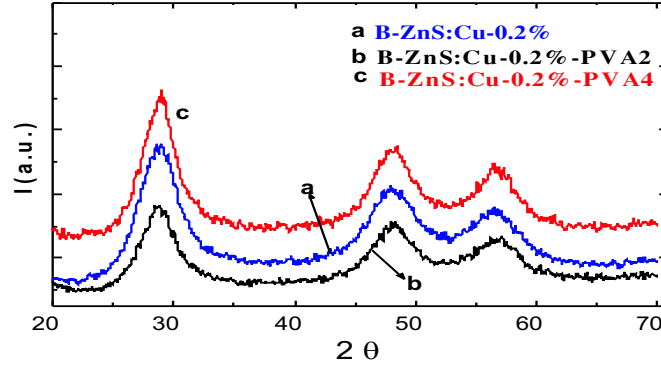


Fig. 2. The XRD spectra of, B-ZnS:Cu-PVA, B-ZnS:Cu and B-ZnS:Cu-PVA4 powder samples

Although the form of these patterns is very closed to the Sphalerite phase, but the peak positions are shifted in comparison with the Sphalerite phase. Thus, we think that ZnS:Cu nanoparticles present the Wurtzite phase with good crystallization. The positions, the widths as well as the intensities of XRD peaks are nearly the same for all samples. The average size of grains is about of 2.7 and 3.2 nm following the Scherrer formula as shown in Table 1.

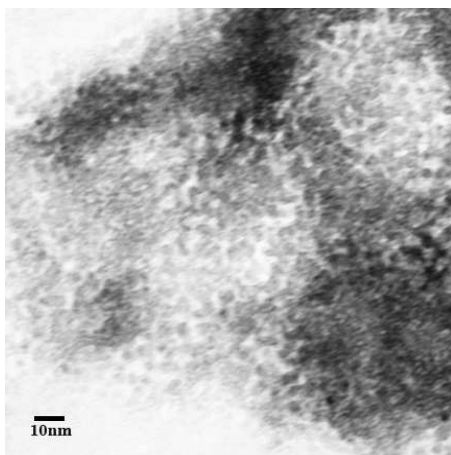
Table 1. The average size of grains

Samples	B-ZnS:Cu	B-ZnS:Cu-PVA2	B-ZnS:Cu-PVA4
$D$ (nm)	2.7	2.9	3.2

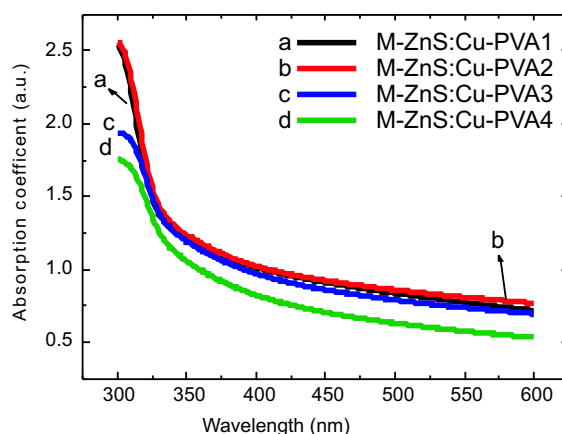
### III.2. The PVA-capped 0.2% Cu doped ZnS nanocrystalline thin films

As discussed above, the PVA does not affect the structure of ZnS:Cu nanomaterials. However, their PL intensity achieved maximum with the concentration of 0.2% Cu. Thus, we have made the PVA capped 0.2% Cu doped ZnS nanocrystalline thin films with different concentrations of PVA.

The morphology of the M-ZnS:Cu-PVA2 thin film was observed by TEM image in Fig. 3. The polymer grains are in sphere form which coated outside the ZnS:Mn nanoparticles. The average size of grains is smaller than 5 nm in the polymer PVA matrix. Thus, the calculated results by the Scherrer formular are in agreement with that of TEM image.



**Fig. 3.** TEM image of M-ZnS:Cu-PVA2 thin film



**Fig. 4.** The absorption spectra of the thin films with different polymer concentrations

Figure 4 presents the absorption spectra of the M-ZnS:Cu-PVA1, M-ZnS:Cu-PVA2, M-ZnS:Cu-PVA3 and M-ZnS:Cu-PVA4 thin films.

The absorption band of M-ZnS:Cu-PVA3 and M-ZnS:Cu-PVA4 thin films shifted towards the lower energy when the PVA increased. The relation between the absorption coefficient  $\alpha$  and the energy of photon can be calculated by the following equation [5, 6]:

$$\alpha = \frac{K(h\nu - E_g)^{n/2}}{h\nu}. \quad (1)$$

Here,  $K$  is constant,  $E_g$  is the direct band gap and  $n = 1$  for direct band gap.

From equation (1) and the absorption spectra in Fig. 4, we calculated the direct band gap of about 3.89 eV, 3.86 eV, 3.77 eV and 3.73 eV for the M-ZnS:Cu-PVA1, M-ZnS:Cu-PVA2, M-ZnS:Cu-PVA3 and M-ZnS:Cu-PVA4 thin films, respectively. These calculated results are given in Table 2. It is clear that the values of  $E_g$  decrease with increasing the PVA concentration. Nevertheless, these values of  $E_g$  are still larger than that of ZnS bulk samples (3.6 eV). If we assume the crystal is in sphere form, the crystallite radius  $r$  can

be determined by formula (see [5]):

$$\Delta E_g = E_g(\text{film}) - E_g(\text{bulk}) = \frac{h^2}{8\mu r^2} - \frac{1.8e^2}{\epsilon r} \quad (2)$$

Here,  $E_g(\text{bulk}) = 3.6$  (eV),  $\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$  with  $m_e^* = 0.34m_0$ ,  $m_h^* = 0.24m_0$ ,  $m_0$  is the mass of free electron. The calculated results of crystallite radius  $r$  for these thin films are given in Table 2.

The results show that the values of  $E_g$  decrease and the crystallite size increases when the PVA concentration increases. The results show that M-ZnS:Cu-PVA1 thin film gives the largest band gap and the smallest crystallite size with  $E_g = 3.89$  eV and  $r = 3.6$  nm.

**Table 2.** The direct band gap and the crystallite radius  $r$  of the thin films

Thin films	$E_g$ (eV)	$r$ (nm)
M-ZnS:Cu-PVA1	3.89	3.6
M-ZnS:Cu-PVA2	3.86	3.9
M-ZnS:Cu-PVA4	3.77	5.5
M-ZnS:Cu-PVA5	3.73	7.4

The above results can be explained as following: In the preparing process, the viscosity of solutions increases when the PVA concentration increases. Thus, the particle size increases due to the coalescence of particle crowd. From the preparing conditions, we see that ultrasonic ring frequency and time affect the particle size of samples and then affect  $E_g$  of samples.

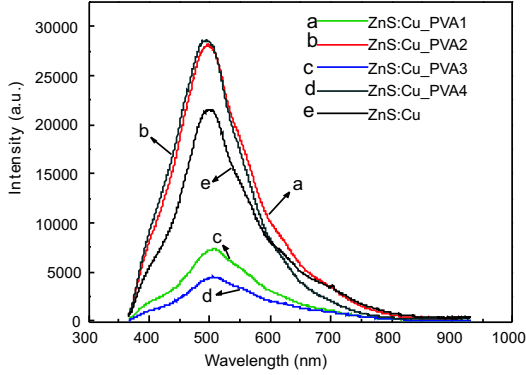
### III.3. The photoluminescence spectra, the luminescence dependence on the laser excitation power density, the time-resolved-luminescence spectra

Figure 5 presents the photoluminescence spectra of the thin films with different polymer concentration.

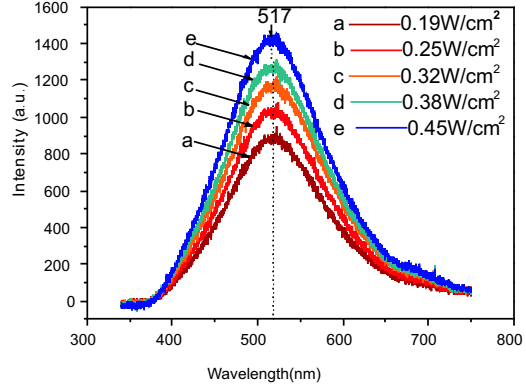
The maximum positions of PL peaks are about 500 nm and were not effected by PVA doped concentration. However, the intensity of PL peaks changed with the PVA concentration. The PL intensity of the M-ZnS:Cu-PVA1, M-ZnS:Cu-PVA2 samples are higher than that of other samples.

Figure 6 presents the PL spectra of the M-ZnS:Cu-PVA1 thin film with the exciting wavelength of 325nm and different exciting power densities. From these PL spectra, it can be seen that the maximum positions of the peak at 517 nm are not changed when the power density increases from  $0.19\text{W}/\text{cm}^2$  to  $0.45\text{W}/\text{cm}^2$ . However, their intensity was changed in the law  $I_{PL} = A(I_{EX})^n$  with  $n \approx 0.54$ .

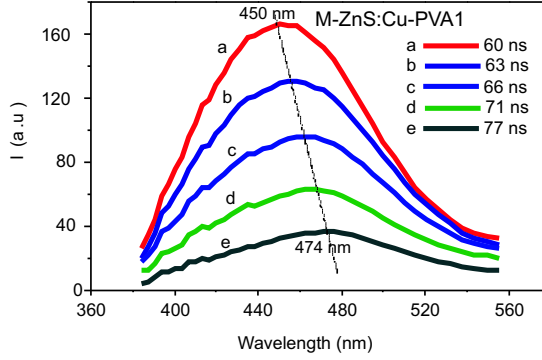
Figure 7 presents results of the time-resolved-luminescence spectra of the green band at 300 K with the exciting wavelength of 337 nm for M-ZnS:Cu-PVA1. It is clearly that the peaks of the band shift towards the lower energy and their intensity decreases about 5 times when the delay time increases from 60 ns to 77 ns. This is a typical characteristic of the donor-acceptor emission recombination.



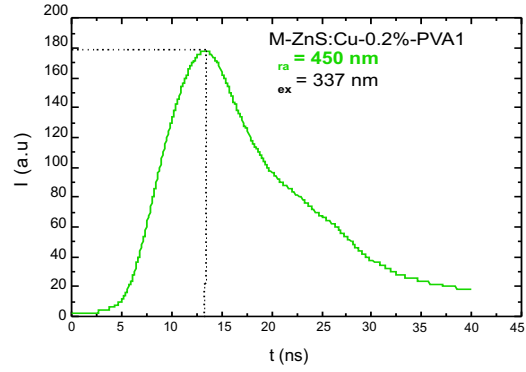
**Fig. 5.** The PL spectra of the thin films with different polymer concentrations



**Fig. 6.** The PL of the M-ZnS:Cu-PVA1 thin films at 300K with exciting wavelength of 325nm and power density  $0.32\text{W}/\text{cm}^2$



**Fig. 7.** The time-resolved-luminescence spectra and the fluorescence lifetime with the exciting wavelength of 325 nm for the M-ZnS:Cu-PVA1 thin film



**Fig. 8.** The decrease of photoluminescence at wavelength 450 nm at 300 K, the exciting wavelength of 337 nm for M-ZnS:Cu-PVA1 sample

Fig. 8 describes the PL decrease of M-ZnS:Cu-PVA1 thin film at the wavelength of 450 nm at 300K with the exciting wavelength of 337 nm. From the above plots, we calculated the luminescence lifetime of about 11 ns at the wavelength of 450 nm.

From the asymmetry of the time-resolved-photoluminescence spectrum as presented in Fig. 8 we suggest that the green luminescence band from 450 nm to 473 nm is the overlap of many photoluminescence lines due to the emission recombination of donor-acceptor pairs, where vacancies of  $\text{S}^{2-}$  and  $\text{Zn}^{2+}$  play as donor and acceptor centers, respectively.

#### IV. CONCLUSION

We have successfully prepared the M-ZnS:Cu-PVA1, M-ZnS:Cu-PVA2, M-ZnS:Cu-PVA3 and M-ZnS:Cu-PVA4 thin films by the wet chemical method and the dip-coating method on the glass substrate. The above obtained results allow us to conclude that

these thin films have good quality. The optical properties of ZnS nanoparticles change considerably when they are diffused into the polymer matrix.

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