

**EFFECT THIOLGLYCOLIC ACID (C₂H₄O₂S) AS CAPPING
AGENT ON ZNS:MN SEMICONDUCTOR
NANOCRYSTALS :SYNTHESIS AND OPTICAL AND
STRUCTURAL CHARACTERIZATION**

A. Rahdar*

Abstract

In this paper, we report structural and optical properties of Mn doped ZnS nanoparticles, having average size 2.44–1.60 nm have been synthesized by co-precipitation method using Thioglycolic Acid as external capping agent. Zinc blende crystal structure ZnS:Mn nanoparticles has been confirmed by the X-ray diffraction studies. Absorption spectra have been obtained using UV-Vis spectrophotometer to find the optical direct band gap. The obtained values have been founded to being range 3.80-4.39 eV. We also found that optical band gap (E_g) increases with the increase in molar concentration of doping agent. This behavior is related to size quantization effect due to the small size of the particles.

Keywords: ZnS:Mn, Chemical co-precipitation, Thioglycolic Acid ,Capping agent, Optical band gap.

* Department of Physics, Faculty of Science, University of Zabol, Zabol, Iran.

1. Introduction

In the last decade many efforts have been dedicated to synthesis and study the physicochemical characterization of nanometer-scale semiconductors. Interest in semiconductor nanoparticles is justified by the fact that fundamental physical and chemical properties of them can be very different from those of the bulk materials. Their reduced dimensions enable one to reduce the size of electronic circuitry. They are expected to have higher quantum efficiencies due to increased oscillator strengths as a result of quantum confinement. A threshold for the occurrence of quantum effects is given by the value for the Bohr radius of exciton (aB) in the bulk material [1]. The band gap of particle can be tuned by changing the size of nanocrystals below aB . Thus, one observes an increase in the band gap of semiconductor with a decrease in particle size. Moreover, as the particles become smaller a higher surface-to-volume ratio is obtained leading to a rapid increase in surface states, thus, reducing the band gap emission (excitonic emission) via nonradiative recombination in surface traps and affecting the chemical reaction dynamics. Wide band gap semiconductor nanocrystals containing a great number of defects, surface states or doped with optically active luminescence centers have created new opportunities for optical studies and development of applications.

As a representative of wide band gap semiconductor nanocrystals, ZnS has been synthesized by different methods [2-7]. The excitonic Bohr radius of ZnS is $ZnS = 2.5 \text{ nm}$ [8]. ZnS can have two different crystal structures (zinc blende and wurtzite), both of which have the same band gap energy (3.68 eV) and the direct band structure. In optoelectronics, it is used as light emitting diode, reflector, dielectric filter and window material [7]. Research on nanocrystals of ZnS containing Mn, Fe, Ni and Cu has been in full swing as the solubility limit for these transition metals in II-VI host lattice is high [8,10]. Nevertheless the theoretical and experimental researches on Mn doped ZnS are still limited.

Considering the above discussion, in the present paper, we tried to find the structural and optical properties of ZnS:Mn nanoparticles with different molar $MnCl_2$ as doping agent and Thioglycolic Acid as capping agent. Our main purpose is to study the effect of Mn doping on structural and optical properties of ZnS:Mn nanoparticles synthesized by co-precipitation method.

Experimental procedure

Material

Zinc chloride (ZnCl_2), sodium sulfide (Na_2S) and (MnCl_2) as starting materials, Thioglycolic Acid as a capping agent for control particles size and double-distilled water as dispersing solvent were used to prepare ZnS:Mn nanoparticles.

Preparation of ZnS:Mn nanoparticles by co-precipitation method

The ZnS:Mn nanoparticles were prepared by the chemical co-precipitation method as follows. First, ZnCl_2 was dissolved in double-distilled water with 0.1 molar concentrations and then obtained molar solution was stirred for 20 min at room temperature to achieve complete dissolution. Sodium sulfide and MnCl_2 was also dissolved in double-distilled water separately as per molar concentration. Afterwards, first Na_2S solution was added drop by drop to the ZnCl_2 solution. Next the MnCl_2 solution with desired molar concentration was added to this solution. Then, an appropriate amount of Thioglycolic Acid (0.2 M) was added to the reaction medium to control the particle size of ZnS:Mn. The resulting solution was stirred continuously for 4 hours. In the final step, the white obtained precipitate was filtered and dried at room temperature to remove both water and organic capping and other byproducts formed during the reaction process. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle.

It is necessary to mention that different sample of nanoparticles has been obtained by changing the molar concentration of doping agent namely ZnS:Mn (a), ZnS:Mn (b), ZnS:Mn (c) as the amount of molar concentration of doping agent used in the preparation is 1 M, 2 M, 3 M respectively.

Results and discussion

Structural Characterization

The XRD patterns for of ZnS:Mn nanoparticles were recorded by Bruker system using Cu K_α radiation ($\lambda=0.154056$ nm) with 2θ ranging $20-70^\circ$ And with different amounts of doping agent (MnCl_2) are shown in Fig. 1.

Three different peaks are obtained at 2θ values of 29.55° , 48.81° and 57.79° for ZnS:Mn(A) nanoparticles. This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes, respectively. The lattice parameter has been computed as 6.30 \AA , which is close to the standard value (5.42 \AA). It is also seen from the Fig 1 that peaks are broadened. A careful observation of the figure reveals that the broadening occurs by increasing Molar concentration of doping agent. [17].

The peak broadening at lower angle is more meaningful for the calculation of particle size. The mean crystallite size (D) of nanoparticles was also estimated using the Scherrer formula (Scherrer 1918) using (111) reflection from the XRD pattern as follows:

$$D = \frac{0.9\lambda}{B\cos\theta}, \quad (1)$$

Where λ , B, and θ are the X-ray wavelength of the radiation used ($K_{\alpha}(\text{Cu}) = 0.154056 \text{ nm}$), the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle, respectively.

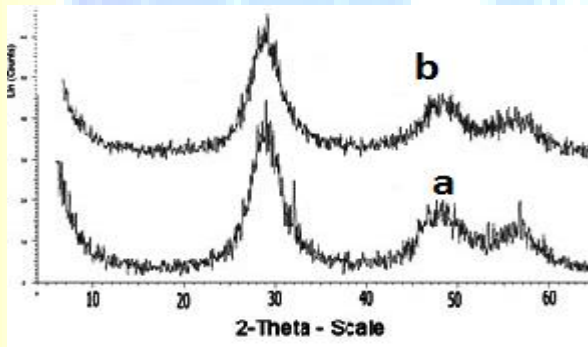


Fig. 1. XRD patterns of ZnS:Mn nanoparticles with different of Percent of impurity(doping agent).

The values of mean crystallite size obtained from XRD for different doping agent are listed in Table 1. It is clear that the crystallite size increases (2.44–1.60 nm) by decreasing the molar of doping agent.

Optical Characterization

The optical absorption spectra of nanoparticles were measured using a USB-2000 UV-Vis spectrophotometer. The absorption spectra of the different samples are shown in Fig. 2. The absorption edge is observed in the range of 320–280 nm, which is blue shifted compared to bulk ZnS.

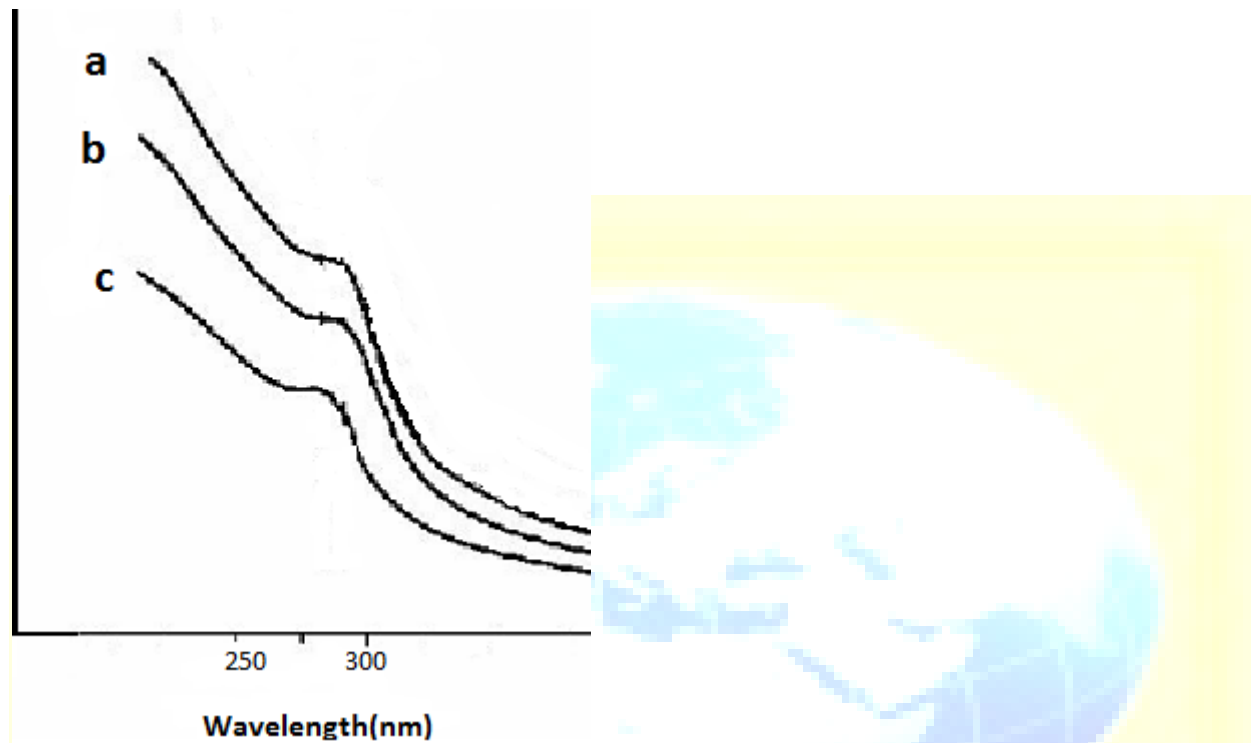


Fig. 2. Absorption spectra of different samples of ZnS:Mn nanoparticles.

As the Mn concentration increases, the absorption edge shifts to lower wavelength side and intensity also increases with increasing Mn concentration compared to undoped ZnS. This blue shift of the absorption edges for different sized nanocrystals is related to the size decrease of particles and is attributed to the quantum confinement limit reaching of nanoparticles. The quantum confinement effect is expected for semiconducting nanoparticles, and the absorption edge will be shifted to a higher energy when the particle size decreases [6,9]. The obtained optical band gap values for different samples are shown in Table 1.

Table 1. Mean crystallite size and optical band gap variation of ZnS: Mn nanoparticles with different concentration of doping agent(*Percent of impurity*).

Sample	Molar concentration of Capping agent	Percent of impurity (doping agent)	Mean Mnystallite size (nm)	Optical band gap E_g (eV)
ZnS:Mn(a)	0.2	1	2.44	3.80
ZnS:Mn(b)		2	2.29	4.10
ZnS:Mn(c)		3	2.10	4.25

It is necessary to mention that the optical band gap values of the ZnS:Mn nanoparticles were determined by Tauc's relation [11,12]:

$$ah\nu = \alpha_0(h\nu - E_g)^{1/2} \quad (2)$$

Where $h\nu$, α_0 and E_g are photon energy, a constant and optical band gap of the nanoparticles, respectively. Absorption coefficient (α) of the powders at different wavelengths can be calculated from the absorption spectra. Finally, the values of E_g were determined by extrapolations of the linear regions of the plot of $(ah\nu)^2$ versus $h\nu$. As seen in Table 1, the values of optical band gap ' E_g ' increases with the increase in molar concentration doping agent and therefore decrease particles size that as mentioned earlier is due to quantum confinement effect.

These semiconductor nanocrystals were then subjected to transmission electron microscopy (TEM, JEOL JEM3010) for characterization. Figure 3 shows TEM image of ZnS:Mn Semiconductor nanocrystals.

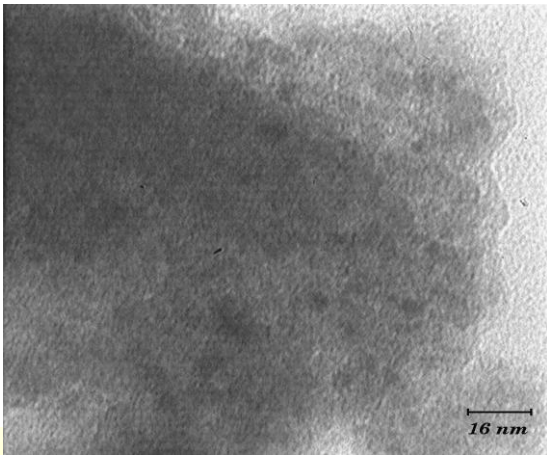


Figure 3. TEM image of ZnS:Mn(a) Semiconductor nanocrystals.

The ZnS:Mn powder was highly soluble in water and was subjected to PI (Perkin-Elmer) spectroscopy in aqueous solution. Figure 4 shows the PI spectrums obtained by exciting at 284 nm.

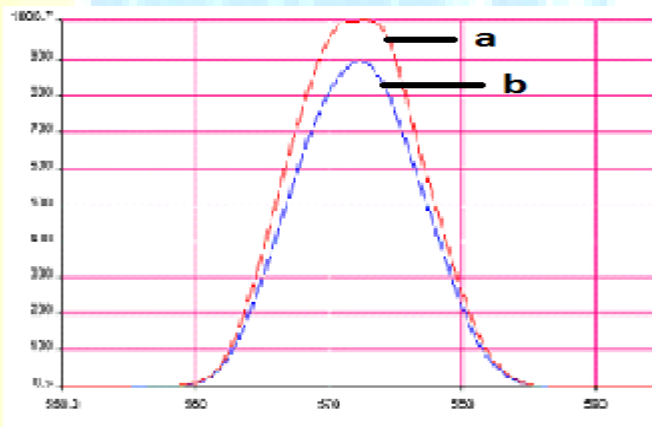


Figure 4. PI spectrums of ZnS:Mn(a) and ZnS:Mn(b) nanocrystals .

Despite the interference of light used for excitation, a PI band is clearly visible with a peak at 573 nm. The large Stokes shift is attributed to the $4T_1 \rightarrow 6A_1$ transition of the Mn doping agent. In the other word, The peak at 573 nm arises due to the excitation and subsequent de-excitation of Mn^{2+} ions, Similar results are shown by Kim et al (2008).

Conclusions

It is possible to produce different size ZnS:Mn nanoparticles using a simple chemical method with using different molar concentration of doping agent. XRD and Optical band gap data have been obtained to confirm nano-size of these materials. It is also observed that the particle size depends on molar concentration of doping agent. A decrease in formation rate of nanoparticles gives rise to a larger final particle size for all the studied synthesis conditions. Chemical reaction rate affects both nucleation and growth process. It has been shown that nucleation and growth take place simultaneously when the chemical reaction is slow. Besides, it can conclude that a slow chemical reaction rate is associated with a more important ripening contribution to the growth. As the particle size depends on the molar concentration of doping agent, a decrease in the size of particle is observed with the increase of molar concentration of doping agent. The mean crystallite size range of particles was between 1.5 and 2.45 nm, depending on molar concentration of doping agent. The optical band gap values of ZnS:Mn nanoparticles have changed from 3.82 to 4.42 eV by increasing the molar concentration of doping agent. These values exhibit a blue shift in E_g which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles.

Considering these results, the chemical co-precipitation method using Thioglycolic Acid as a capping agent is very efficient for the preparation of ZnS:Mn nanoparticles in order to control the particle size and also for modern optoelectronic technology and other industrial applications.

Acknowledgement

The authors would like to thank Dr. M. Ali-Ahmad, Mrs.M.Asudeh, Mr.H.Rahdar and Mrs. Heidari Mokarrar for their support and assistance with this project.

References

- H.C. Warad, S.C. Ghosh, B. Hemtanon, C. Thanachayanont and J. Dutta: Sci. Tech. Adv. Materials 6 (2005) 296-301.
- A.R. Mirhabibi, M. Rabiee, R. Aghababazadeh, F. Moztaarzadeh and S. Herasaki: Pigment & Resin Technology 32(3) (2003) 358-363.
- D. Mohanta, S.S. Nath, N.C. Mishra and A. Choudhury: Bull. Mater. Sci. 26 (3) (2003)289-294.
- F. Huang and J.F. Banfield: J. Am. Chem. Soc. 127 (2005) 4523-4529.
- N. Arul Dhas, A. Zaban and A. Gedanken: Chem. Mater. 11 (1999)806-813.
- W. Chen, Z. Wang, Z. Lin and L. Lin: J. Appl. Phys. 82 (1997)3111-3115.
- Y. Nakaoka and Y. Nosaka: Langmuir 13 (1997) 708-713.
- M. Motlan, G. Zhu, K. Drozdowics-Tomsia, K. McBean, M.R. Phillips and E.M. Goldys: Optical Materials 29 (2007) 1579-1583. Journal of Nano Research Vol. 9 131
- J. Cizeron and M. P. Pileni: J. Phys. Chem. B 101 (1997)8887-8891.
- P. Calandra, A. Longo and V.T. Liveri: J. Phys. Chem. B 107 (2003) 25-30.
- P. Calandra, A. Longo and V. Turco Liveri: Colloid Polym. Sci. 279 (2001)1112-17.
- H. Zhang, B. Gilbert, F. Huang and J.F. Banfield: #ature 424 (2003) 1025.
- J.H. Yu, J. Joo, H.M. Park, S.I. Baik, Y. W. Kim, S.C. Kim and T. Hyeon: J. Am.