

Structural, optical band gap and photoluminescence studies of chemically capped (ZnS, ZnS:Mn) nanophosphors

K. S. RATHORE*, Y. JANU^a, DEEPIKA, K. SHARMA, N. S. SAXENA

Semi-conductor and Polymer Science Laboratory, 5-6, Vigyan Bhawan, Department of Physics, University of Rajasthan, Jaipur-302004 (India), Ph./Fax: +91-141-2704056

^a*Radiation and Solar Devices group, Defence Laboratory, Jodhpur, Rajasthan-342011*

A wet chemical precipitation method is optimized for the synthesis of ZnS and ZnS:Mn nanocrystals. The nanoparticles were stabilized by capping with EDTA. XRD studies shows the phase singularity of ZnS and ZnS:Mn having zinc blende (cubic) structure. XRD line broadening indicate the average crystalline size of undoped is 2.8 nm and for doped ZnS, it is 3 nm. The effect of change in stoichiometry and doping with Mn²⁺ on the optical band gap and the photoluminescence properties of ZnS nanophosphors have been investigated. Sulphur vacancies (V_s) related emission peak maxima 425 nm has been dominated in undoped ZnS nanoparticles. Emission characteristic of ZnS nano phosphors has been changed with Mn²⁺ activation due to ⁴T₁-⁶A₁ transition of Mn²⁺ in ZnS matrix.

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1. Introduction

Nanocrystalline semiconductors have been extensively studied in recent years [1–4], owing to their novel physical properties, as well as their wide range of potential applications. They are good candidates for application to electro-optic devices due to their reduced size, enabling a reduction in the size of the electronic circuitry. Moreover, it is also possible to tune their properties to suit a specific application by merely changing their size [5]. Efficiently luminescing nanocrystalline semiconductors of type A^{II}B^{VI}, where A = Zn, Cd, Pb etc and B = S, Se etc., have formed an important class of luminescent materials [6] and attracted much attention not only due to their unique properties but also possible applications to novel photonic devices [7] and optoelectronic devices [8]. The nanocrystal based emitters can be used for many purposes such as optical switches, sensors, electroluminescence devices [9], biomedical tags [10], etc. Keeping these things in mind, research on the optical properties of transition metal-doped semiconductors has emerged as an interesting field. Among the semiconductors of interest is zinc sulfide (ZnS). ZnS is an important opto-electronic device material that is used in the violet and blue regions, owing to its wide band gap [11]. Doping ZnS nanoparticles with Mn²⁺ (ZnS:Mn) is attractive due to its high fluorescence quantum efficiencies. The impurity states of doped compound semiconductors play a special role in affecting the electronic energy structures and transition probabilities [12]. In 1994, Bhargava et al. [1] reported that Mn-doped nanocrystalline semiconductors yield both high

luminescent efficiencies and lifetime shortening. They showed that ZnS:Mn nanocrystals could exhibit orange luminescence with high fluorescence quantum efficiency (approximately 18%) under the interband excitation of the host crystal by UV light. The luminescent time decay was also found to decrease with decreasing particle size. These spectacular results suggest that nanocrystalline ZnS:Mn systems may form a new class of luminescent material with applications to displays, lighting and lasers [3]. In line with these applications, it is important to establish the optical absorption characteristics together with the photoluminescence characteristics of nanocrystalline ZnS:Mn.

In this paper we have reported the optical properties and photoluminescence characteristics of ZnS and Mn doped ZnS nanoparticles synthesized via chemical method using Ethylene Diamine Tetra Acetic acid (EDTA) as capping agent.

2. Experimental

2.1 Synthesis

Nanoparticles of ZnS and ZnS:Mn have been prepared by chemical precipitation method. All the chemicals were of analytical grade and were used without further purification.

Nanoparticles of ZnS were prepared at 300 K by dropping simultaneously 50 ml of 1M solution of ZnSO₄ and 50 ml of 1M solution of Na₂S into 200 ml of distilled water containing 50 ml of 0.1M solution of EDTA, which

was vigorously stirred using a magnetic stirrer. The high insolubility of ZnS formed out of the chemical reaction caused the formation of a number of new nuclei while preventing the growth of already existing ones, thus limiting the particle size.

ZnS:Mn nanoparticles were prepared at 300 K by dropping simultaneously 50 ml of 0.9M solution of ZnSO₄, 50 ml of 1M solution of Na₂S and 50 ml of 0.1M solution of MnSO₄ into 200 ml of distilled water containing 50 ml of 0.1M solution of EDTA and were stirred using a magnetic stirrer. The role of EDTA was to stabilize the particle against aggregation which may lead to an increase in the particle size. The precipitate was separated from the reaction mixture and was dried at room temperature. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle.

2.2 Characterization

The diffraction patterns of the samples have been studied by X-ray diffraction pattern recorded on an X-ray diffractometer (Philips X'pert) in the 2θ range 20–60° with the scan rate of 3°/min using Cu K α radiation of wavelength $\lambda = 0.15406$ nm. UV–Vis spectrophotometric measurements were performed by using a spectrophotometer (Ocean Optics USB 2000). The photoluminescence (PL) emission spectra of nanocrystalline ZnS and ZnS:Mn samples at 300 K have been recorded by using spectrofluorometer, JASCO FP-6500.

3. Results and discussion

3.1 XRD measurements

The nanostructure of the ZnS and ZnS:Mn nanoparticles have been studied at room temperature by using X-ray diffraction pattern. Fig. 1 shows the XRD patterns of ZnS and ZnS:Mn nanoacrytals.

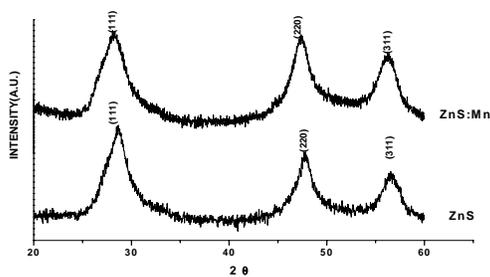


Fig. 1. XRD patterns of ZnS and ZnS:Mn nanoacrytals.

The obtained peak positions correspond to Zinc blende type patterns for both the samples. Mn²⁺ alloying into ZnS did not create any phase change. The observed broad peaks corresponds to the Bragg angle for the (111), (220) and (311) planes of the cubic crystalline ZnS. The crystallite domain size was calculated from the width of the XRD peaks, assuming that they are free from non-uniform strains, using the Scherrer formula.

$$D = 0.94 \lambda / \beta \cos \theta \quad (1)$$

where D is the average crystallite domain size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle. To eliminate additional instrumental broadening, the FWHM was corrected, using the FWHM from a large grained Si sample.

$$\beta_{\text{corrected}} = (\text{FWHM}_{\text{sample}}^2 - \text{FWHM}_{\text{Si}}^2)^{1/2} \quad (2)$$

This modified formula is valid only when the crystallite size is smaller than 100 nm [13]. The average crystallite size of ZnS and ZnS:Mn nanoparticles were found to be 2.8 nm and 3.0 nm, respectively.

3.2 Optical measurements

The absorbance versus wavelength traces for both samples (ZnS and ZnS:Mn) have been recorded in the range 260–1000 nm as shown in Fig. 2.

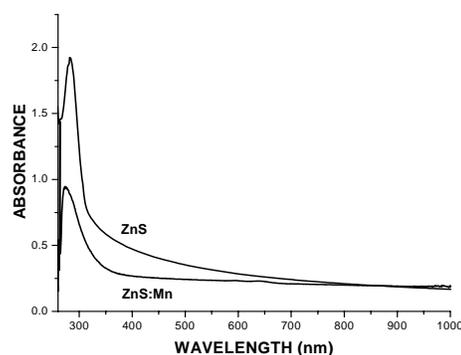


Fig. 2. The absorbance versus wavelength plot for ZnS and ZnS:Mn samples.

The absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficients (α) and the incident photon energy ($h\nu$) can be written as [14]:

$$(\alpha h\nu) = A (h\nu - E_g)^n \quad (3)$$

where A is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. For direct allowed $n = 1/2$, indirect allowed transition, $n = 2$, and for direct forbidden, $n = 3/2$. To measure the energy band gap from the absorption spectra a graph $(\alpha h\nu)^2$ versus $h\nu$ is plotted (Fig. 3). The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap. The direct allowed bandgap values of ZnS and ZnS:Mn have been found to be 4.05 eV and 3.95 eV respectively.

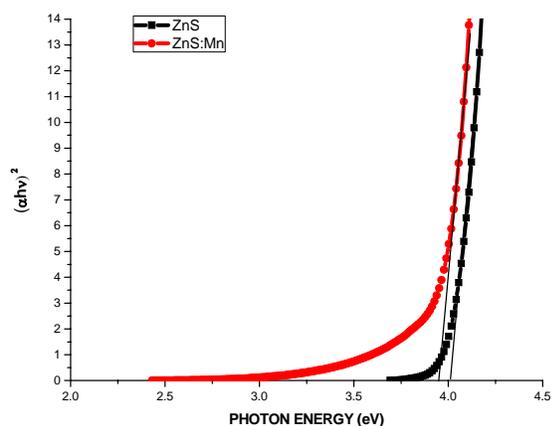


Fig. 3. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnS and ZnS:Mn.

It is clear that band gap decreases on doping with Mn. These can be ascribed to sp-d exchange interaction. The d-orbitals in Mn^{2+} , which are close in energy to Mn^{2+} s-orbitals, are energetically close to the conduction band of the semiconductor (ZnS). This band is primarily composed of metal (Zn) s-orbitals with energy comparable to that of the Mn s-orbitals. For large bandgap like ZnS, the d-orbitals should stay below the conduction band. Now the mixing of d-levels with the conduction band will increase the energy of the host conduction band. Consequently the bandgap will decrease on introduction of Mn in the ZnS matrix [15].

3.3 Photoluminescence studies

The emission spectra of the ZnS and ZnS:Mn nanoparticles recorded at room temperature excited at 308 nm have been shown in Figs. 4 and 5 respectively. Figure 4 shows one peak centered at 425 nm with side band at 464 nm and the tail of the spectrum is extending beyond 600 nm, which is attributed to the presence of sulphur vacancies in the lattice [16]. This emission results from the recombination of photo generated charge carriers in shallow traps [17]. Here, it is seen that when the size of the nanocrystallites decrease, the luminescence is found to be dominated by the band impurities also, surface passivation

by sulphur has resulted in reduced emission intensity of this band indicating involvement of surface traps.

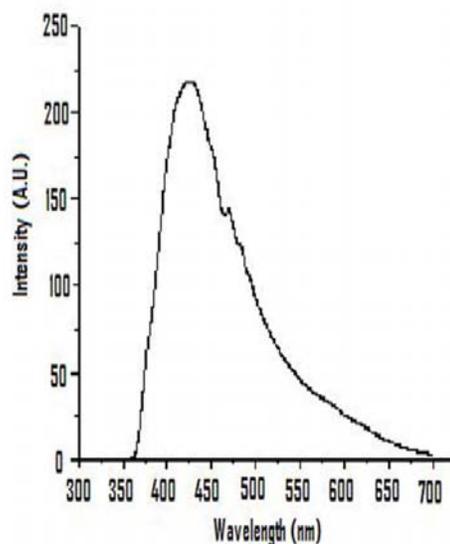


Fig. 4. Emission spectra of the ZnS.

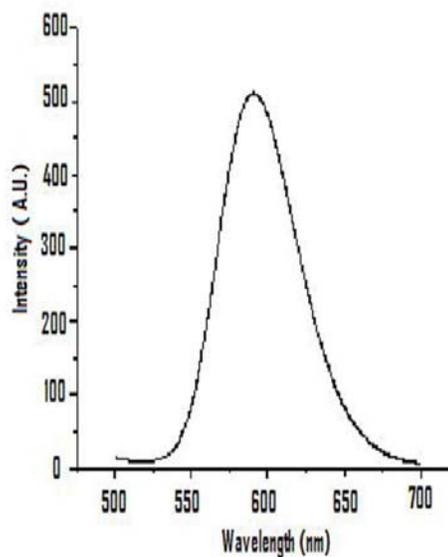


Fig. 5. Emission spectra ZnS:Mn.

For Mn doped ZnS nanocrystallites (Fig.5), the PL peak observed at 590 nm was interpreted as due to an indirect excitation, i.e an excitation into the excited state of the host matrix ZnS, followed by energy transfer from the host to the Mn^{2+} ions and its subsequent de-excitation leading to luminescence [18]. It is associated with ${}^4T_1-{}^6A_1$ transition of Mn^{2+} in ZnS. The characteristics of orange Mn^{2+} emission almost identical to the emission observed for Mn^{2+} in bulk ZnS.

4. Conclusions

From the above studies, it has been established that chemical method for the preparation of efficiently luminescent ZnS nanocrystals doped with significant levels of Mn²⁺ can be realized. The formation of ZnS and ZnS:Mn nanoparticles of ~ 2.8 nm and 3 nm respectively with cubic structure have been obtained by XRD. Emission peak at 425 nm show the presence of blue emission bands in sulphur deficient ZnS, which have been related to the sulphur vacancies V_s . The emission peak at 590 nm for Mn²⁺ incorporation in ZnS matrix, which is associated with ${}^4T_1-{}^6A_1$ transition. With the reduction in particle size the dopant ion dominantly situated near the surface region could be efficiently excited to obtain higher emission intensities in nanophosphors.

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*Corresponding author: kuldeep_ssr@yahoo.com