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Optical Properties of Mn^{2+} Doped ZnS Nanoparticles

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Mn^{2+} doped ZnS nanoparticles have been synthesized by chemical precipitation method at room temperature. During synthesis process a stabilizing agent EDTA has been used to study its effect on the particle size of the synthesized material. The morphology of the prepared Mn^{2+} doped ZnS nanoparticles have been characterized by using X-ray diffraction and scanning electron microscope. The optical properties of the synthesized Mn^{2+} doped ZnS nanoparticles have been done using UV-VIS spectrophotometer and photoluminescence using F-2500 FL spectrophotometer. The size of the particle when EDTA is not used as a stabilizer is found to be 5.52 nm and when EDTA used as a stabilizer the particle size is reduced to 4.77 nm. The value of the band gap energy estimated from spectrophotometer data has been found to be in range of 3.85- 4.36 eV. Room temperature photoluminescence spectrum shows that the Mn^{2+} doped sample exhibits a yellow emission peak at 575 nm.

Key Words: ZnS, Nanoparticle, XRD, UV-VIS, Optical absorption, Band gap energy.

INTRODUCTION

Doped semiconductors have been studied extensively in the past few decades; especially II-VI semiconductors have attracted great deal of attention due to their unique properties and potential applications. However, certain properties pertaining to ZnS are unique and advantageous compared to ZnO. To name a few, ZnS has a larger band gap of 3.72 eV (for cubic zinc blende (ZB)) and 3.77 eV (for hexagonal wurtzite (WZ)) respectively than ZnO (3.4 eV) and thus it is more suitable for visible-blind ultraviolet (UV) light based devices such as sensors/photo detectors. On the other hand, ZnS is traditionally the most suitable candidate for electroluminescence devices. However, the nanostructures of ZnS have not been investigated in much detail relative to ZnO nanostructures[1]. The doping ions act as recombination centers for the excited electron-hole pairs and result in strong and characteristic luminescence. This II-VI compound semiconductor material has been studied for a variety of applications, such as optical coating, electro-optic modulator, photoconductors, field effect transistors, optical sensors, phosphors and other light emitting materials. Zinc sulphide doped with transition metal ion is known to have efficient light emitting properties[2]. In doped compound semiconductors, in contrast to the undoped semiconductors, the impurity states can play a special role in affecting the electronic energy structures and transition probabilities[3]. Bhargava *et al.*[4] reported that Mn doped nanocrystalline semiconductors yield both high luminescent efficiencies and life time shortening. It was shown that ZnS:Mn nanocrystal exhibit an orange luminescence with high quantum efficiency of approximately 18 % at room temperature. The quantum efficiency increases with decreasing particle size[4].

The objective of this work is to study the effect of EDTA on the size of Mn^{2+} doped ZnS nanoparticles. The role of EDTA is to stabilize the particle against aggregation, which may lead to decrease the nanoparticle size. The size of the particle when EDTA is not used as a stabilizer is found to be 5.52 nm and when EDTA used as a stabilizer the particle size is reduced to 4.77 nm. The photoluminescence emission takes place in the yellow region for Mn doped ZnS sample with a peak at 575 nm. The material synthesis technique used here is chemical precipitation method, which is the most popular technique because of its several advantages like easy handeling, simpler and with low-cost chemical compounds. This synthesis method is suitable for industrial large scale production[5].

EXPERIMENTAL

Preparation of the ZnS: Mn nanoparticles: The important step in the studies of nanoparticle is their synthesis. The chemical precipitation method is performed at room temperature using $Zn(CH_3COO)_2.2H_2O$, $Mn(CH_3COO)_2.4H_2O$ and $Na_2S.9H_2O$ as source materials. All chemicals used are of AR grade. A 50 mL solution was prepared by mixing 2.195 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.049 g of $Mn(CH_3COO)_2{\cdot}4H_2O$ with

stirring at room temperature for 15 min. Then 50 mL aqueous solution of 2.451gm $Na_2S.9H_2O$ was added to the solution drop by drop for 25 min with vigorous stirring resulting dull white colloidal solution. After that 50 mL solution of 1.861 g EDTA was added drop by drop and mixed for 20 min. The powder sample was then separated from the solvent and washed with methanol several times to remove the impurity and traces of EDTA, after wash it was oven dried for 24 h at 50 ºC. After drying the precipitate is crushed in to fine powder with the help of mortar and pestle. The powder obtained is then characterized.

Sample characterization: The size of all the samples are determined by phillips expert pro X-ray diffractometer with CuK_α radiation (λ = 0.15406 nm). XRD data are collected over the range 20º-80º at room temperature. The particle size is calculated by using the debye-scherrer formula. Absorption spectra of the samples dispersed in methanol are studied with the help of U-3010 spectrophotometer. The photoluminescence spectrum of the ZnS: Mn nanoparticles have been measured at room temperature using Hitachi F-2500FL spectrophotometer. The morphology of the nanoparticles is determined using scanning electron microscopy (FESEM; QUANTA 3D FEG).

RESULTS AND DISCUSSION

The XRD pattern of the Mn^{2+} doped ZnS nanoparticles with and without EDTA are shown in Fig. 1. Three diffraction peaks at the value of 2θ equal to 28.7º, 47.6º and 56.5º are present in Fig. 1. appears due to reflection from the 111, 220 and 311 of the cubic phase of the ZnS. The XRD pattern of the nanocrystal is well matched with the standard cubic ZnS[6].The broadening of the XRD pattern of the prepared ZnS:Mn sample takes place due to the nanocrystalline nature of the sample. The crystalline size can be calculated with the help of Scherrer's equation.

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

where D is the mean grain size, l is the X-ray wavelength (for CuK_α radiation, λ = 1.5406 Å), θ is the diffraction angle and β is the half-width of the diffraction peak at 2θ. The average grain size of the ZnS:Mn doped nanoparticle calculated using above equation (**1**) is 5.52 nm without EDTA and with EDTA it is 4.77 nm. The role of EDTA is to stabilize the particle against aggregation, which may lead to decrease the nanoparticle size. The strain of ZnS:Mn nanoparticles are also calculated by using the stokes-wilson equation as mention below.

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (2)$$

The latice strain for ZnS without EDTA is 2.3×10^{-2} and for ZnS with EDTA it is found to be 1.5×10^{-2}.

Fig. 2. shows the FESEM image of the Mn^{2+} doped ZnS nanoparticles. The actual size of the nanoparticle cannot be determined from the FESEM images as it is limited by the resolution of the used FESEM instrument.

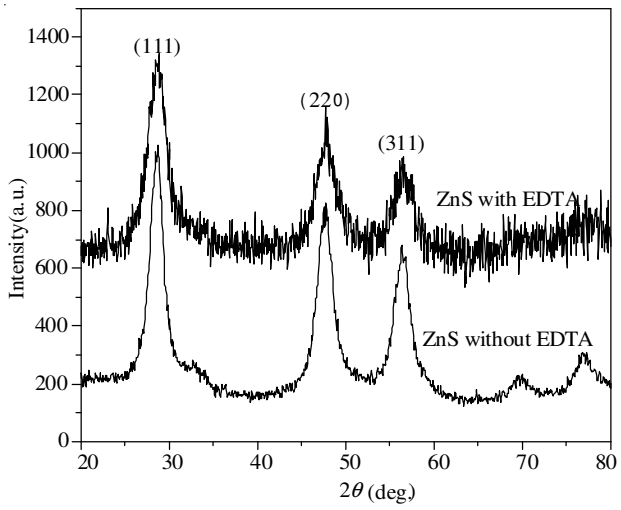

Fig. 1. XRD pattern of ZnS:Mn nanoparticle

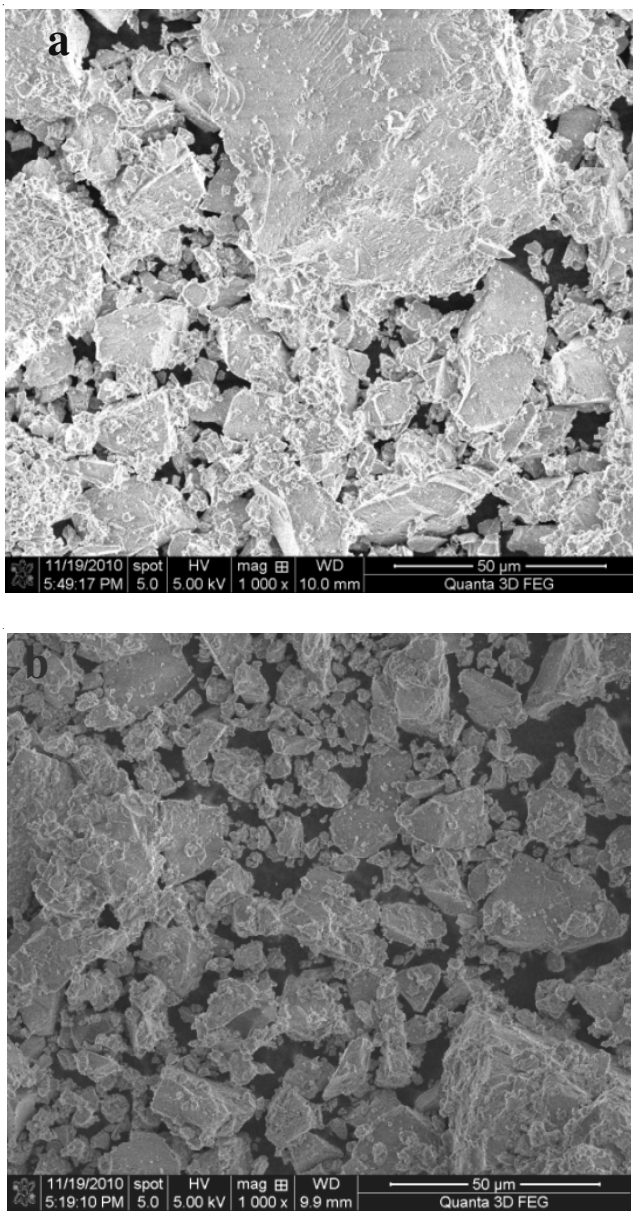

Fig. 2. FESEM image of (a) ZnS:Mn without EDTA (b) ZnS:Mn with EDTA

The optical absorption spectra have been observed by UV-visible spectrophotometer (Hitachi U-3010) as shown in

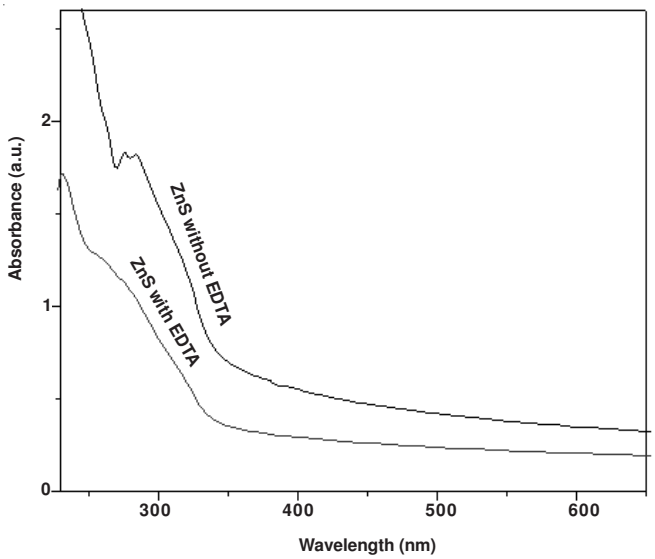

Fig. 3. Absorption spectrum of Mn^{2+} doped ZnS nanoparticles

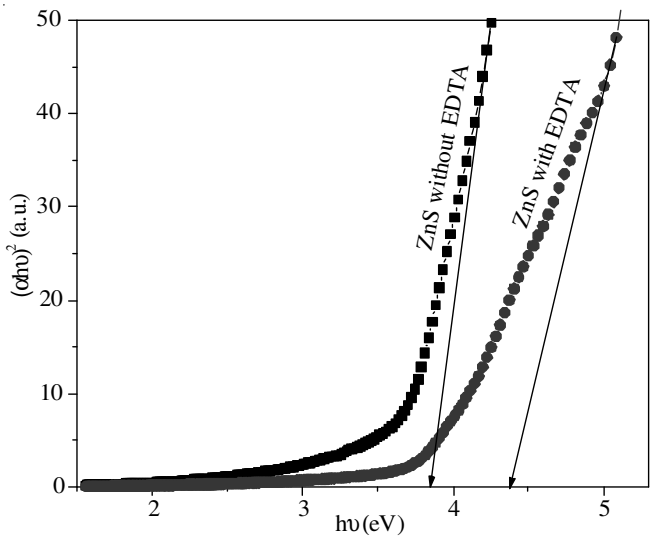

Fig. 4. Calculation of the band gap energy from the UV-VIS absorption spectra

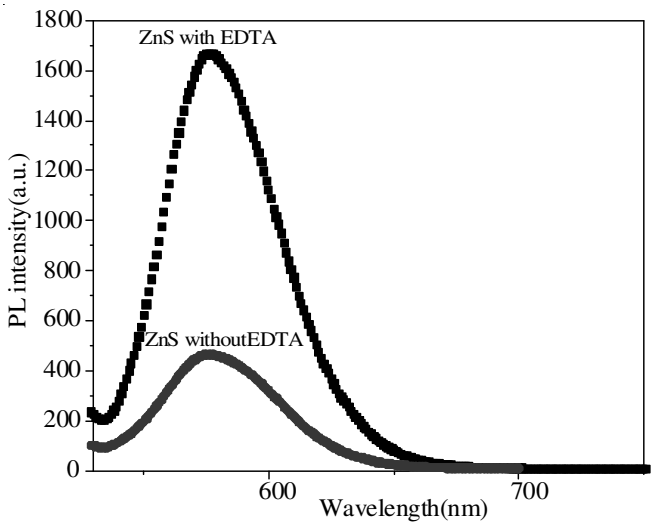

Fig. 5. Show the PL emission from the ZnS:Mn nanoparticle

Fig. 3. For measuring the absorption characteristics, the nanopowders are first dispersed in methanol and taken on a quartz cuvette. The characteristic absorption peaks appear in the range 232-340 nm and this peak position reflect the band gap of particle. The relation between the incident photon energy (hν) and the absorption coefficient (α) is given by the following relation.

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g) \quad (3)$$

where A is constant and E_g is the band gap energy of the material and the exponent *n* depends on the type of transition. For direct allowed transition $n = \frac{1}{2}$, for indirect allowed transition n = 2, for direct forbidden $n = \frac{3}{2}$ and for indirect forbidden n = 3. Direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ *vs.* hν and then extrapolating the straight portion of the curve on hν axis at $\alpha = 0$ as shown in Fig. 4. The band gap energy of the samples is found in the range of 3.85 - 4.36 eV. The obtained values of the band gap energy of ZnS:Mn nanoparticles are higher than that of the bulk value of ZnS (3.72 eV). This blue shift of the band gap takes place because of the quantum confinement effect[4]. The particle size calculated from XRD pattern, optical band gap and strain are summarized in Table-1.

TABLE-1
PARTICLE SIZE ENERGY BAND GAP AND STRAIN ANALYSES

Sample	Band gap energy (E_g)	Particle size	Lattice Strain
ZnS:Mn without EDTA	3.85 eV	5.52 nm	2.3×10^{-2}
ZnS:Mn with EDTA	4.36 eV	4.77 nm	1.5×10^{-2}

The photoluminescence of ZnS:Mn samples are measured at room temperature using F-2500 FL spectrophotometer. The doping of Mn^{2+} in host ZnS produce energy levels between the conduction band and valence band of the ZnS, leads to the emission of yellow colour light from Mn^{2+} doped ZnS nanoparticle[2]. ZnS:Mn nanocrystals are found to have increased photoluminescence efficiency with a very short life-time of the transition associated[7] with the magnetic impurity Mn^{2+}. The Mn^{2+} ions, as a dopant in the ZnS:Mn^{2+} nanoparticles may exist either inside the ZnS or attaching to the outside. Different types of Mn^{2+} centers presented in the ZnS:Mn^{2+} nanoparticles result in different luminescence properties[8]. The PL spectrum of Mn^{2+} doped ZnS nanoparticles are shown in Fig. 5. This shows the efficient emission of yellow colour light with peak at 575 nm, due to the excitation wavelength of 260 nm. The yellow emission originates from a transition between the $^4T_1$ excited state and $^6A_1$ ground state of Mn^{2+} ion. The emission takes place *via* energy transfer from the excited state of the ZnS host lattice to the d electrons of Mn^{2+}.

Conclusion

Manganese doped zinc sulphide (ZnS:Mn^{2+}) nanoparticles are prepared using EDTA as a stabilizer by chemical method at room temperature. The XRD measurements yielded the particle size in 5.52-4.77 nm range. Particle size of the synthesized ZnS:Mn^{2+} nanoparticles are controlled by EDTA. The band gap energy of the samples is found in the range 3.85-4.36 eV. Room temperature photoluminescence (PL) spectrum

of the Mn^{2+} doped sample exhibits a yellow emission peaked at 575 nm. The yellow emission originates from a transition between the $^4T_1$ excited state and $^6A_1$ ground state of Mn^{2+} ion.

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