Yellow light emission from Mn^{2+} doped ZnS nanoparticles

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Zinc sulphide nanoparticle with manganese doped (2-6%), (ZnS: Mn^{2+}) have been investigated. These Mn^{2+} doped ZnS nanoparticles have been synthesized by chemical precipitation method at room temperature. So-prepared Mn^{2+} doped ZnS nanoparticles then characterized by using X-ray diffraction (XRD), Scanning electron microscope (SEM), UV-Vis spectrophotometer, Photoluminescence (PL) using F-2500FL Spectrophotometer. The size of the particle is found to be in 5.24-5.64 nm range. The value of optical band gap has been found to be in range 3.87-4.46 eV. Room temperature photoluminescence (PL) spectrum of the undoped sample exhibit a blue emission peaked at 375 nm under UV excitation. The Mn^{2+} -doped sample exhibits a yellow emission peaked at 577 nm.

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1. Introduction

Luminescent semiconductor nano-crystals, especially II–VI semiconductors, have attracted great deal of attention in the past few decades due to their unique properties and potential applications. The most extensively investigated doped semiconductors are Mn doped ZnS or CdS nano-crystals. 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 [1]. 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 [2]. Bhargava et. al. [3] 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. The Mn^{2+} ion has a $3d^5$ configuration. The Mn^{2+} ion exhibits a broad emission peak. Mn^{2+} d-electron states act as efficient luminescent centers while interacting with s-p state of the ZnS host. The subsequent transfer of electron and hole pairs into the electronic level of the Mn^{2+} ion leads to the yellow emission from the ${}^4T_1$-${}^6A_1$ transition. Some researchers found that the fluorescence intensity of ZnS: Mn nanocrystals showed a maximum at a certain Mn^{2+} concentration and a further increase of Mn^{2+} concentration would lead to the decrease of the luminescence intensity [4, 5]. The effect is called concentration quenching.

The size of the undoped ZnS and ZnS nanoparticles with Mn^{2+} doping (2-6%) is found to be in 5.24-5.64 nm. The PL emission takes place in the yellow region for Mn doped ZnS sample with a peak at 577 nm. Manganese doped ZnS sample has been synthesized using 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 technique is also suitable for industrial large scale production [6].

2. Synthesis of ZnS:Mn^{2+} nanoparticles

The important step in the studies of nanoparticle is their synthesis. There are various methods for synthesis of nanoparticles. We are using here chemical precipitation method 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 are of analytical reagent grade and used without further purification. De-ionized water is used in all synthesis steps. The ZnS nanoparticles doped with different Mn^{2+} concentrations were synthesized in water without using any other agent. We prepare 50 ml solution by mixing 2.195 gm Zn $(CH_3COO)_2.2H_2O$ and 0.049 gm. $Mn(CH_3COO)_2.4H_2O$ with stirring at room temperature for 15 min. Then 50 ml aqueous solution of 2.451 gm $Na_2S.9H_2O$ was added to the solution drop by drop for 25 min with vigorous stirring resulting dull while colloidal solution. Other samples prepared with varying concentration of Mn (4%, 6%). The powder sample was then separated from the solvent and washed with methanol several times to remove the impurity, after wash it is oven dried for 24 hours at 50 ^{o}C. After drying the precipitate is crushed into fine powder with the help of mortar and pestle. The powder obtained is then characterized.

3. Characteristic technique

The size of all the samples are determined by Phillips Expert Pro X-ray diffractometer with Cu Kα radiation (λ=0.154 nm). XRD data are collected over the range 20^0-80^0 at room temperature. The particle size is calculated by using the Debye-Scherrer formula. The morphology of the nanoparticles is determined using scanning electron microscopy (FESEM; QUANTA 3D FEG). Absorption spectra of the samples dispersed in methanol are studied with the help of U-3010 Spectrophotometer. The PL spectrum of the ZnS and ZnS:Mn nanoparticle has been measured at room temperature using Hitachi Hitachi F-2500FL Spectrophotometer.

4. Results and discussion

4.1. X-ray diffraction pattern

The XRD patterns of ZnS and Mn doped ZnS nanoparticle samples are shown in Fig. 1. Three diffraction peaks as shown in Fig. 1 at 2θ values equalto 28.6^0, 47.7^0 and 56.5^0 are appearing 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 [7]. The broadening of the XRD pattern of the prepared ZnS:Mn sample takes place due to the nanocrystalline nature of the sample. The mean crystallite size can be calculated with the help of Scherer's equation as mention below.

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

Where D is the mean grain size, λ is the X-ray wavelength (for Cu Kα radiation, λ = 1.54 nm), θ is the diffraction angle and β is the full width at half maximum of the diffraction peak at 2θ.

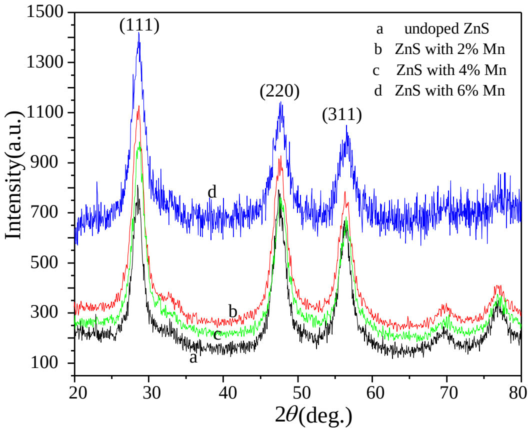
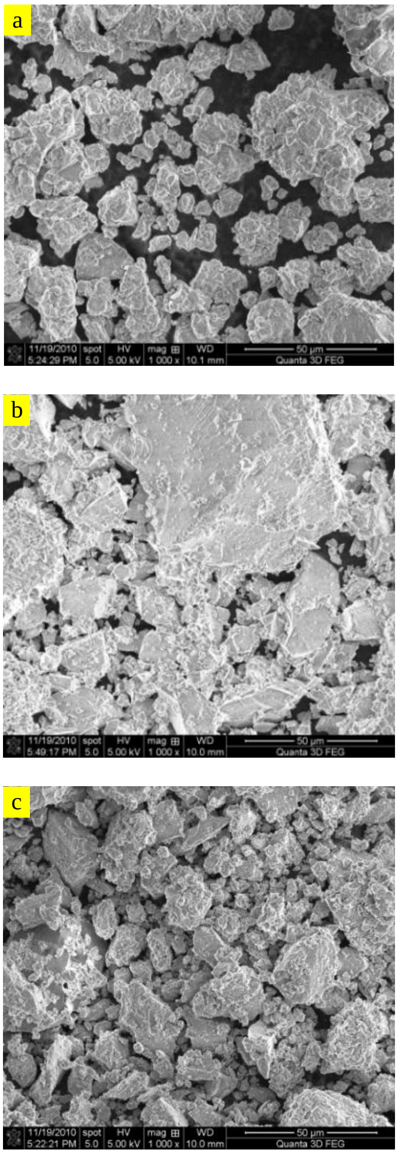


Fig. 1. XRD pattern of ZnS and ZnS:Mn^{2+} nanoparticles.

The grain size of the undoped ZnS and Mn doped ZnS nanoparticle as calculated by using Eq.1. from the most intense peak is 5.64-5.24 nm.

4.2. SEM analyses

Fig. 2 shows the FE-SEM image of undoped ZnS and Mn^{2+} doped ZnS nanoparticles with different Mn (2%, 4%, 6%) concentration. The actual size of the nanoparticle cannot be determined from the FE-SEM images as it is limited by the resolution of the used FE-SEM instrument.



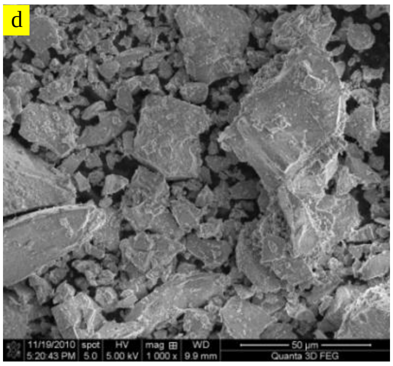


Fig. 2. FE- SEM image of (a) *undoped ZnS,* (b) *2% Mn doped ZnS,* (c) *4% Mn doped ZnS and* (d) *6% Mn doped ZnS.*

4.3. Optical absorption and band gap

The optical absorption spectra have been observed by UV-Visible spectrophotometer (Hitachi U-3010) as shown in Fig. 3. The nanopowders are first dispersed in methanol and taken on a quartz cuvette to study the absorption characteristics of the samples. The characteristic absorption peaks appear in the range 232-350 nm and this peak position reflect the band gap of the synthesized particle. The relation between the incident photon energy (hν) and the absorption coefficient (α) is given by the following relation.

$$(\alpha h\nu)^{\frac{1}{n}} = A\left(h\nu - E_g\right) \qquad (2)$$

Where A is constant and E_g is the band gap of material and the exponent n depends on the type of transition. For direct allowed transition $n = 1/2$, for indirect allowed transition $n = 2$, for direct forbidden $n = 3/2$ and for indirect forbidden $n = 3$. Direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis at $\alpha = 0$.

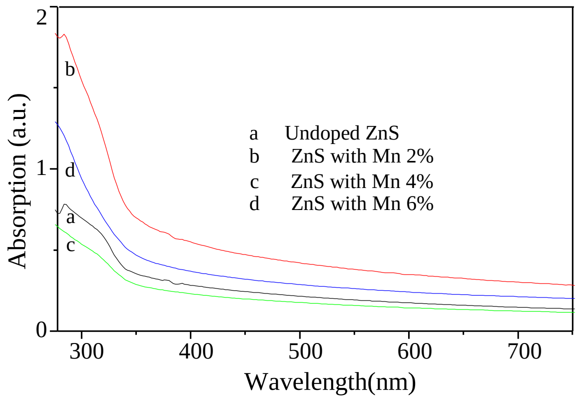


Fig. 3. Absorption spectrum of ZnS and Mn^{2+} doped ZnS nanoparticles.

With the variation of manganese doping, the direct band gap of the samples vary from 4.46 eV to 3.87 eV as shown in Fig. 4. The value of optical band gaps are 4.46 eV, 4.05 eV, 3.99 eV and 3.87 eV respectively, for undoped ZnS, ZnS:Mn (2%), ZnS:Mn (4%) and ZnS:Mn (6%) nanoparticles. The obtained values of the band gap of ZnS and Mn doped ZnS nanoparticles are higher than that of the bulk value of ZnS (3.68 eV). This blue shift of the band gap takes place because of the quantum confinement effect [3].

4.4. Photoluminescence study

Photoluminescence (PL) of ZnS:Mn samples are measured at room temperature using F-2500FL Spectrophotometer. The PL spectrum of Mn^{2+} doped ZnS nanoparticles are shown in Fig. 5, which shows the efficient emission of yellow light with peak at 577 nm. Whereas the undoped ZnS sample shows the blue emission at 375 nm. 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 light from Mn^{2+} doped ZnS nanoparticle. Karar et. al. [1] reported the synthesis of the ZnS:Mn nanoparticle with Mn concentration in the 0-40% range through chemical method using polyvinylpyroledone (PVP) as a capping method. The average size of the nanoparticle was 2 nm. They obtained PL spectra using a Gaussian fit at 460, 600, 640, 680 nm. The PL peak at 460 nm is due to native acceptor level in ZnS. The PL peak at 600nm was attributed to ${}^4T_1$ to ${}^6A_1$ transition of Mn^{2+} doped ZnS. The two other peaks at 640, 680 nm were also attributed to Mn^{2+} Incorporation in to ZnS [1]. Gosh et. al. [8] observed three peaks at 450, 500 and 598 nm with excitation wavelength of 250 nm. The peak at 500 nm is due to the first harmonic of the excitation wavelength. The emission peak at 450 nm is not shifted with variation of Mn concentrations, a peak at 598 nm is due to ${}^4T_1$-${}^6A_1$ transition. ZnS:Mn nanocrystals are found to have increased photoluminescence efficiency with a very short lifetime of the transition associated with the magnetic impurity Mn^{2+} [9]. In the case of ZnS:Mn^{2+} nanoparticles, majority of the Mn^{2+} ions are at the near-surface sites and occupy axial or lower symmetry sites [10]. Tanaka et. al. [11] reported that the energy transfer from the trap state dominates the luminescence from Mn^{2+} under the inter band excitation, the intensity ratio between the trap-related luminescence and the Mn^{2+} luminescence is expected to be almost the same for the inter band excitation and the direct excitation of the trap state.

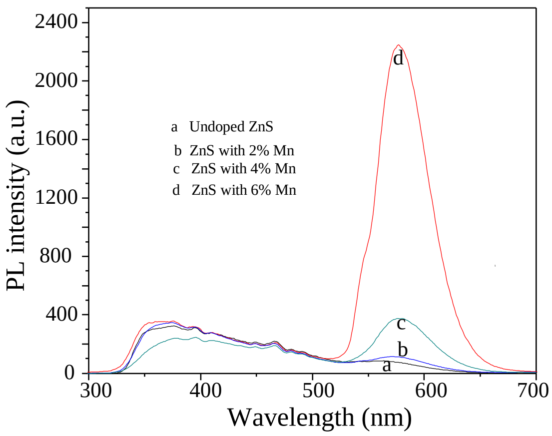


Fig. 5. PL spectrum the ZnS and ZnS:Mn nanoparticles.

PL spectrum of Mn^{2+} doped ZnS nanoparticles in this work are shown in Fig. 5, which shows the efficient emission of yellow light with peak at 577 nm, with excitation wavelength of 270 nm. Whereas the undoped ZnS sample shows the blue emission. With the increase of Mn^{2+} concentration, the intensity of the yellow emission significantly increases while its peak position does not shift. Concentration quenching is not observed in our samples. During the concentration quenching process, the excitation energy is transferred from one Mn^{2+} ion to its nearest Mn^{2+} ion by non radiative transitions and via a number of transfer steps, finally to a quenching site [12]. Khosravi et.al. [4] observed a maximum luminescence at a doping concentration of 0.12%. They found yellow emission peak at 600 nm with excitation wavelength of 312 nm. The emission intensity increases proportionally with the increasing of the doping concentration, the emission intensity of yellow or blue depends upon the transition probabilities and it also depends on the concentrations of Mn^{2+} ions.

5. Conclusion

In this paper we have reported the synthesis of monodispersed undoped and Mn^{2+} doped ZnS nanoparticles using chemical precipitation method. The XRD measurements yielded the particle size in 5.24 nm - 5.64 nm range, the band gap energy of the samples is found in the range 4.46 eV - 3.87 eV. Room temperature photoluminescence (PL) spectrum of the undoped sample exhibit a blue emission peaked at 375 nm under UV excitation, which could be ascribed to a recombination of electrons at the sulfur vacancy donor level with holes trapped at the zinc vacancy acceptor level. The Mn^{2+} -doped sample exhibits a yellow emission peaked at 577nm. 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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