

Luminescent Behaviour of Divalent Impurity Doped ZnS Nanophosphors**D.P.Bisen¹ and Ravi Sharma²**

¹School of studies in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur (C.G.) 492010, India

²Department of Physics, Arts & Commerce Girls College, Devendra Nagar, Raipur (C.G.) 492001, India

E-mail: dpbisen@rediffmail.com

Abstract

Divalent impurity (Mn) doped ZnS nanoparticles, having average diameter 3–5 nm, have been synthesized using chemical precipitation technique using mercaptoethanol as external capping agent. Zinc blende crystal structure has been confirmed by the X-ray diffraction studies. The effect of Mn doping on the photoluminescent properties of ZnS nanophosphor has been studied. PL spectra show two peaks, first at 425nm and second at 583nm. The UV–Visible absorption spectra show blue shift as compared to the bulk ZnS. The FTIR spectra show incorporation of Mn in the ZnS matrix.

Introduction

Luminescence is defined as the phenomenon in which the electronic state of a substance is excited by some kind of external energy and the excitation energy is given off in the form of light. At certain frequencies, this radiation is significantly in excess of the thermal radiation, which is emitted by a substance at that particular temperature. The so-produced electromagnetic radiation, generally in the visible region, is characteristic of the particular luminescent material under examination, termed as phosphor. The word phosphor means “light bearer” in Greek, it can be defined as any material that will emit light when an external excitation source is applied. This source can include photons, electrons, heat etc. These phosphors may either be in the powder or thin film form. The phosphor materials are doped intentionally with certain impurities to get the desired wavelength. These phosphor powders and thin films are critical in the development and also in the improvement of display technologies. Smaller size phosphor particles are needed for high-resolution images.

In recent years, research involving Mn-doped nanocrystalline ZnS (ZnS:Mn) has grown extensively, mainly due to the high quantum luminescence efficiencies that have been reported [1, 2]. ZnS is an important and one among the oldest member of the family of wide-gap (3.66 eV, at room temperature) semiconductors and probably the most important material used as phosphor host [3]. Due to unique optical properties and potential applications, doped semiconductor nanocrystals have attracted extensive research interests [4]. These II–VI compound semiconductors have been studied for a variety of applications such as optical coatings, photoconductors, optic modulators, electro-optic modulators, flat panel displays, electroluminescent devices, sensors etc. [5, 6]. Numerous researchers have investigated the structural and luminescent properties of doped nanophosphors, especially Mn²⁺ doped ZnS nanocrystals, as ZnS can be doped with Mn very easily [7]. These nanomaterials behave differently from bulk semiconductors as they are influenced by various surface states arising due to quantum confinement effect and large surface-to-volume ratio. ZnS nanoparticles have been mostly

synthesized with methods like inverse micelle [9], zeolite [10], or vapor-phase condensation method [11]. Chemical precipitation method is better than other techniques for producing efficiently luminescent nanophosphors in terms of process simplicity, effectiveness of doping, higher yield and has a very simple procedure with low-cost apparatus [12].

Experimental

The powder of ZnS nanoparticles were prepared by using chemical precipitation technique described by Khosravi [13]. For synthesis, the 1M aqueous solution of $ZnCl_2$ and 1M aqueous solution of Na_2S were mixed in the presence of various concentration of mercaptoethanol solution. $MnCl_2$ was also mixed in the solution in various ratio, while stirring the solution continuously. The obtained precipitate was washed thoroughly three to four times with double distilled water and then separated by centrifuge at 3500 rpm, and finally air-dried.

The crystal structure were determined by XRD technique with $Cu K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and the particle size was calculated by Debye-Scherrer formula.

X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer. The Perkin Elmer, USA Lambda 950 model UV-VIS spectrometer is used to obtain the optical absorption spectra of ZnS:Mn nanoparticle. The PL measurement was performed by Shimadzu Spectrofluorophotometer RF 5301PC. The FTIR measurement was performed by using a Shimadzu IR affinity 1 Spectrophotometer.

Results and Discussion

The XRD patterns for the samples are shown in Fig. 1. Three different peaks are obtained at 2θ values of 29.50° , 48.80° and

57.80° . This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes, respectively [14]. The lattice parameter has been computed as 5.31 \AA , which is very 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 not only in the first peak, but also in the second as well as third peak for different samples. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [15].

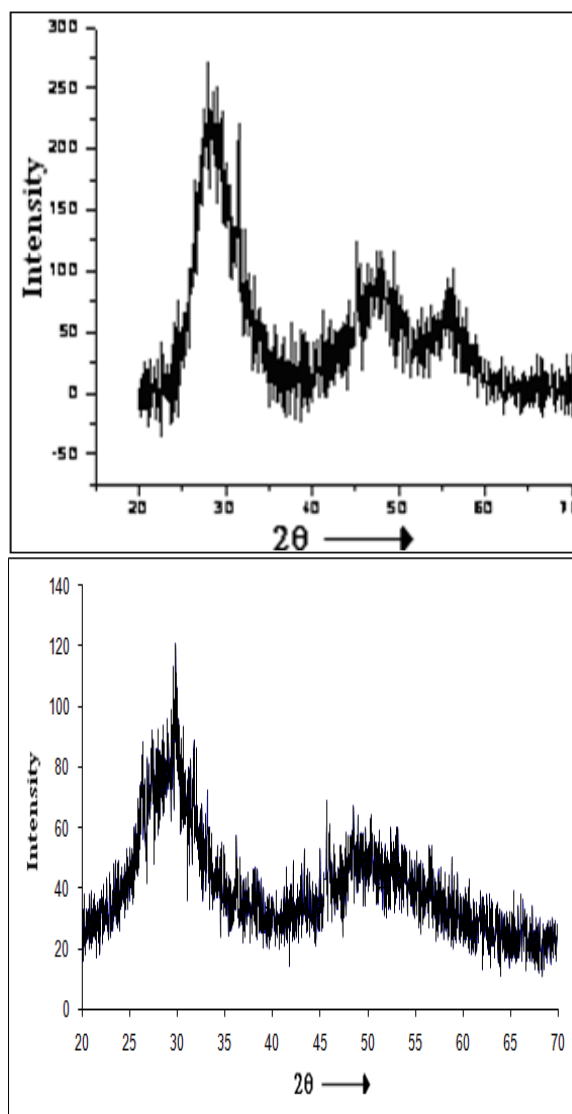


Fig.1 XRD pattern of ZnS and ZnS:Mn nanophosphor

Figure 2 shows the absorption spectra of the bulk ZnS:Mn and ZnS:Mn nanoparticle. The optical absorption spectra of the samples are in the range of 400 nm-200 nm. Absorption edge was obtained at shorter wavelength. The characteristic absorption peak due to ZnS nanoparticles appears in the wavelength range 250-340 nm and this peak position reflects the band gap of the material. For the ZnS:Mn nanoparticle an absorption peak appears at around 300 nm. This peak is blue-shifted from the absorption peak of bulk ZnS:Mn at 345nm.

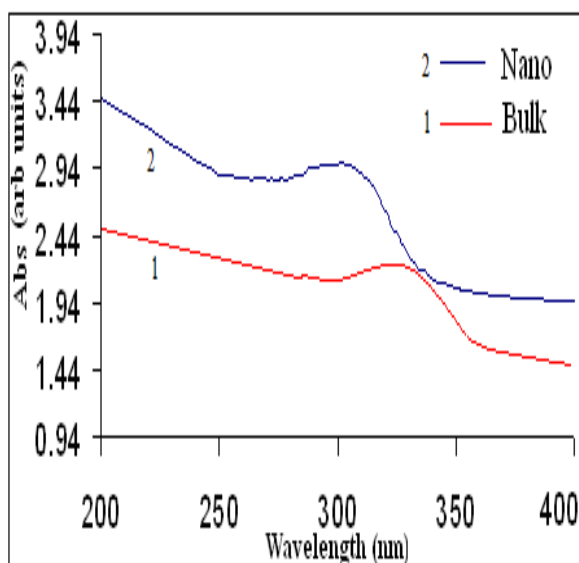


Fig.2 Absorption spectra of the bulk and ZnS:Mn nanophosphor

Figure 3 shows the PL spectrum of ZnS nanoparticles doped with Mn. The first peak around 293 nm is the excitation peak. It was found that only one peak at 425 nm was found for the undoped ZnS nanoparticles, whereas two peaks were found for ZnS:Mn nanoparticles. The first peak was at 425 nm and the second peak was at 583 nm. This confirms the incorporation of Mn in the ZnS matrix. The emission at around 425 nm is typical luminescence of undoped ZnS resulting from the transition of electrons from shallow traps near the conduction band to sulfur vacancies present near the valence band. The PL band at 583 nm is

a characteristic emission of Mn^{2+} ion, which can be attributed to a ${}^4T_1 - {}^6A_1$ transition.

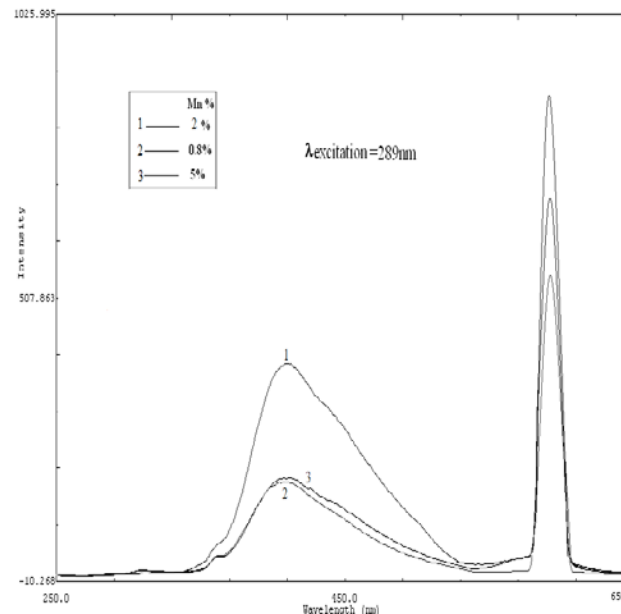


Fig. 3 PL spectrum of ZnS:Mn nanophosphor

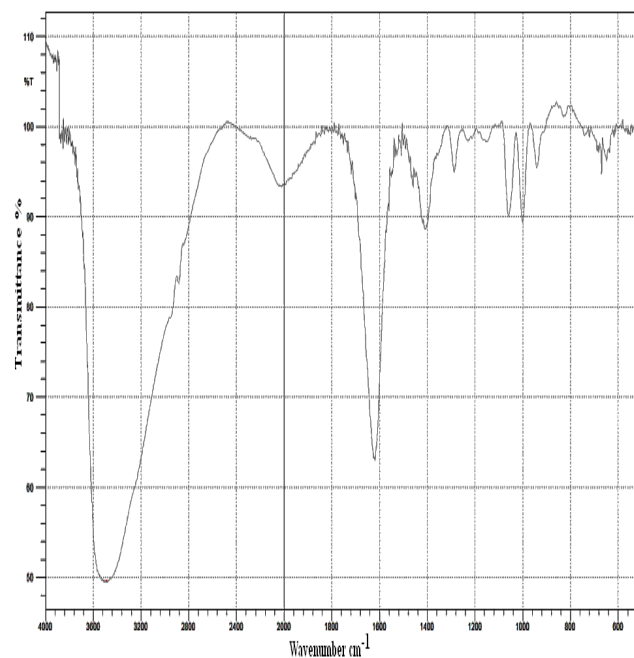


Fig. 4 FTIR spectra of ZnS:Mn nanophosphor

Figure 4 shows the typical FTIR spectra of synthesized ZnS : Mn nanoparticles. The organic composition of the samples and the presence of various bonds have been studied. The spectra show characteristic peaks at 501, 651, 673, 742,

941, 1,001, 1,058, 1,286, 1,406, 1,460, 1,618, 2,011, 2,848, 2,951, 3,450 cm^{-1} and some other associated peaks. The bands around 501 and 640 cm^{-1} are assigned to the Mn-O band. A strong intensity band at 1,019 cm^{-1} may be due to S-O-C stretching. The peaks at 651 cm^{-1} is assigned to the ZnS band (i.e., corresponding to sulphides). Bands around 900- 1,500 cm^{-1} are due to the oxygen stretching and bending frequency. The peaks at 2,951, 2,848 and 1,406–1,460 cm^{-1} are assigned to the characteristic vibrations of the methylene groups in ME. The stretching vibration bands of the C-O groups on ME located at 1000–1300 cm^{-1} are due to the characteristic frequency of inorganic ions. These modes indicate the presence of resonance interaction between vibrational modes of sulphide ions in the crystal [16]. Band around 3,000–3,600 cm^{-1} are due to the hydrogen stretching frequency (OH stretching). The band at 3,450 cm^{-1} corresponds to characteristic vibration band of hydroxyl groups of ME molecules. Our measurement of the spectrum of powdered sample yields the bands, which are in good agreement with the reported values [17,18].

Conclusions

In summary, we have synthesized ZnS nanophosphors (~3 nm) doped with Mn using mercaptoethanol as the external capping agent. The cubic (zinc blende) structure of the synthesized nanophosphors has been observed using XRD studies. UV–visible absorption spectra have been studied and the band gap of synthesized ZnS:Mn nanophosphor was calculated (~4.6 eV). Quantum confinement effect was observed, as a blue shift has been observed in the optical absorption spectra. The maximum PL intensity occurred at 2 mol% of Mn and then the PL intensity decreases, which is due to the concentration quenching effect in the ZnS host. The FTIR spectra show incorporation of Mn in the ZnS matrix.

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