Indian Journal of Pure & Applied Physics
Vol. 61, September 2023, pp. 754-758
DOI: 10.56042/ijpap.v61i9.3490

To Study the Impact of Mn Doping on Structural, Morphological and Optical Properties of Zinc Sulfide

Janvi[a], Smriti Sihag[a], Mamta Bulla[a], Rita Dahiya[a], Nitin Bhardwaj[b] & Vinay Kumar[a]*

[a]Department of Physics, COBS&H, CCS Haryana Agricultural University, Hisar, Haryana 125 004, India

[b]Department of Agronomy, COA, CCS Haryana Agricultural University, Hisar, Haryana 125 004, India

Received 9 July 2023; accepted 16 August 2023

By utilising hydrothermal approach undoped and Mn-doped ZnS was synthesized and characterized by using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), Field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR) and UV-Visible spectroscopy. The XRD pattern confirmed the cubic sphalerite crystal structure of prepared nanoparticles. Due to Mn doping, size of crystallite for all the samples was increased. FE-SEM images showed spherical morphology of synthesized samples. The EDX spectrum confirms the presence of Mn in the doped sample. FTIR spectrum showed that doping shifts the position of Zn-S absorption band. A red shift was observed in the absorption maxima and the bandgap was decreased with increasing doping percentage from 0 to 10%.

Keywords: Optical properties; Tuneable band gap; Morphology; Doping; Crystallite size

1 Introduction

Semiconductor materials have been investigated in detail in recent years due to their certain characteristics including an adequate band gap and excellent visible-range absorption[1]. Zinc sulfide (ZnS) is a class II–VI n-type intrinsic semiconductor possessing a wide band gap within the range 3.5 -3.8 eV[2]. Due to its excellent thermal stability and high electronic mobility[3] this material has applications in light emitting diodes, flat panel displays, infrared windows, lasers, optoelectronic devices, as a nano fertilizer and many more. There are two common crystal structures in which ZnS exists: cubic zinc blend and hexagonal wurtzite. ZnS absorbs only high energy UV-radiations as its absorption edge is under 340 nm[4]. By doping with suitable material, the absorption edge of ZnS can be shifted towards longer wavelength. Also, by the addition of dopant to lattice structural, optical and morphological properties of ZnS can be turned[5]. Spin-spin exchange interactions led to the formation of material with more exotic properties when ZnS is doped with transition metals like Ni, Fe, Mn, Co *etc*[6]. Ni-doped ZnS microspheres exhibit better charge storage capacity compared to pristine ZnS[7]. The electrical conductivity of ZnS was modified after doping with Al[8]. Sm-doped ZnS nanoparticles were utilized in optoelectronic devices[9].

In the present study, Mn was selected as doping agent because ofits similar ionic radius as that of ZnS, electrical neutrality of manganese atoms, large exciton binding energy and wide bandgap at room temperature[10]. This study focuses on the impact of Mn doping on the structural, optical and morphological characteristics of ZnS.

2 Materials and Methods

Zinc acetate dihydrate, thiourea and Manganese (II) sulfate monohydrate from Sigma Aldrich were used for the synthesis of zinc sulfide and chemically doped zinc sulphide (AR grade).

For the synthesis of Zinc sulfide and manganese-doped zinc sulphide hydrothermal approach was used[12]. A solution of zinc acetate dihydrate (0.25 M) was chosen as the initial solution and then, a 0.75 M solution of thiourea was gradually added drop by drop into it. The solution was stirred for 30 minutes and then transferred into an autoclave. It was placed in an oven at 200 °C for 24 h, then left to cool naturally to room temperature. Obtained precipitate was washed and dried in an oven at 90 °C for 5 hrs to obtain ZnS powder. The same procedure was adopted for synthesizing 5% and 10% Mn-doped ZnS along with the addition of the appropriate amount of manganese sulfate monohydrate in zinc acetate dihydrate solution.

*Corresponding authors: (E-mail: vinay23@hau.ac.in)

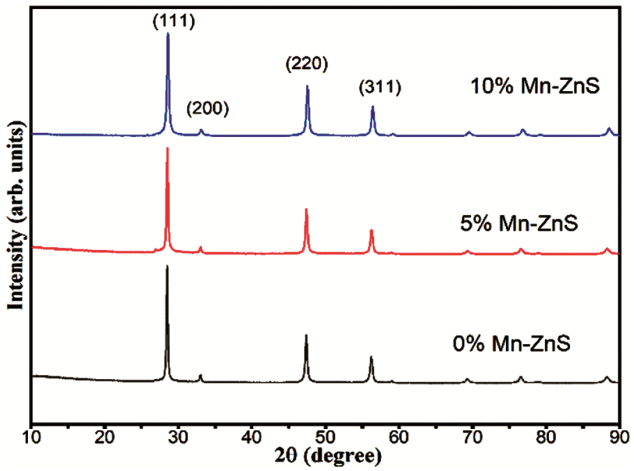

Fig. 1 — XRD patterns of 0 %, 5 % and 10 % Mn-doped ZnS.

3 Results and Discussion

3.1 XRD Analysis

XRD patterns of 0 %, 5 % and 10 % Mn-doped ZnS are shown in Fig. 1. The diffraction peaks at 2θ values of 28.5, 33.1, 47.5 and 56.4 belong to the (111), (200), (220) and (311) planes and represents the cubic sphalerite crystal structure of undoped and Mn doped ZnS. $Zn^{2+}$and Mn^{2+} have nearly similar ionic radii so no significant change was observed in the lattice of ZnS due to doping of Mn. The crystallite size of 0 %, 5 % and 10 % Mn-doped ZnS comes out to be 23.26, 31.52 and 34.52 nm respectively as calculated from the Debye Scherrer formula[11]. As the doping percentage increases from 0 % to 10 %, the size of the crystallites also increases[12].

3.2 FE-SEM and EDX Analysis

Figure 2 displays FE-SEM images of 0 % and 5 % Mn-doped ZnS. Pristine material has spherical morphology (Fig. 2(a)) whereas images of doped ZnS show nearly spherical microspheres. The surface morphology revealed that in case of doped sample particles are agglomerated. In some sites, various sizes of particles are found, so indicating the non-uniform distribution of particle size due to surface tension and interactive forces[13].

The EDX analysis was performed to study the elemental composition of doped sample. The spectrum measurements of 5 % doped ZnS revealed the presence of peaks corresponding to Zn, S and Mn as depicted in Fig. 3. Hence, the EDX spectral measurement confirms that manganese is doped successfully in ZnS.

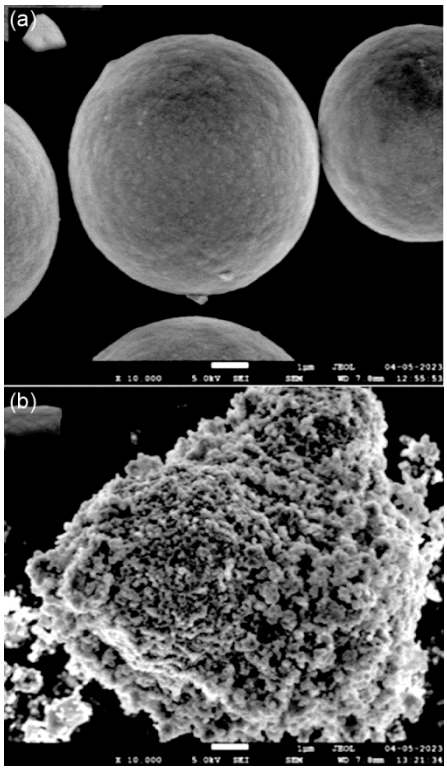

Fig. 2 — FE-SEM image of (a) 0 % Mn-doped ZnS (b) 5 % Mn-doped ZnS.

3.3 FTIR Analysis

The FT-IR spectra of 0 %, 5 % and 10 % Mn-doped ZnS samples are presented in Fig. 4. Due to -OH group stretching a peak around 3400-3500 cm^{-1} appeared[14]. The peak obtained at 636 cm^{-1} for 0 % Mn-doped ZnS corresponds to Zn-S stretching and for the doped sample, peak was shifted little towards the lower wave number. So, doping perturbs the Zn-S-Zn network and changes the peak position of the ZnS absorption band[15]. Peaks were observed at 2424, 2845, 2090 and 1616cm^{-1} due to the formation of microstructures[16]. Weak peaks around 1000 and 800 cm^{-1} were due to the resonance between vibrational modes of sulfide ions[17].

UV-Vis absorption analysis

UV-Vis graphs of 0 %, 5 % and 10 % Mn-doped ZnS are shown in the insets of Fig. 5, 6 & 7 respectively. 0 % Mn-ZnS exhibit the absorption peak at 280 nm, 5 % Mn-ZnS at 300 nm and 10 % Mn-ZnS at 310 nm. For doped samples, absorption maxima were shifted towards longer wavelengths indicating a red shift with increasing concentrations of Mn, and the bandgap of all the samples calculated from Tauc's plot comes out to 3.68 eV for 0 %

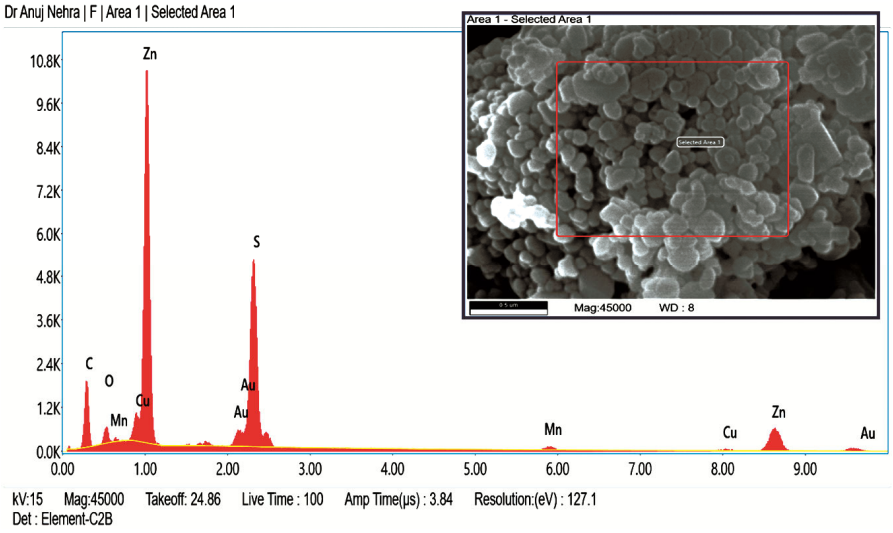

Fig. 3 — The EDX spectrum of 5 % Mn-doped ZnS.

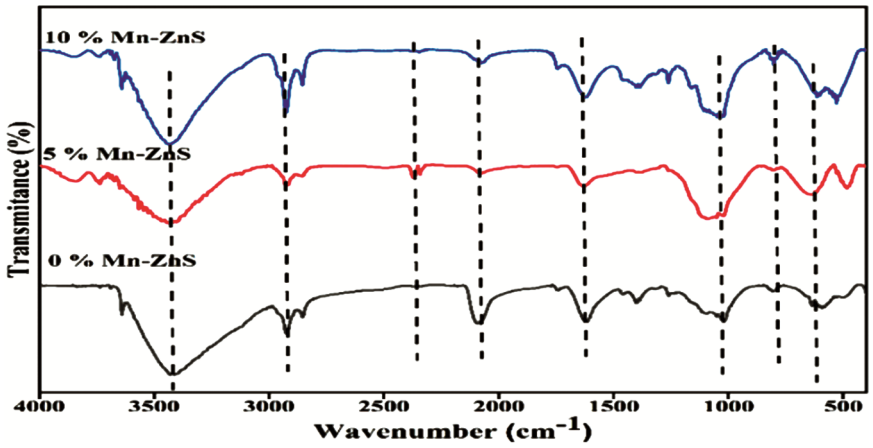

Fig. 4 — FTIR graph of 0 %, 5 % and 10 % Mn-doped ZnS.

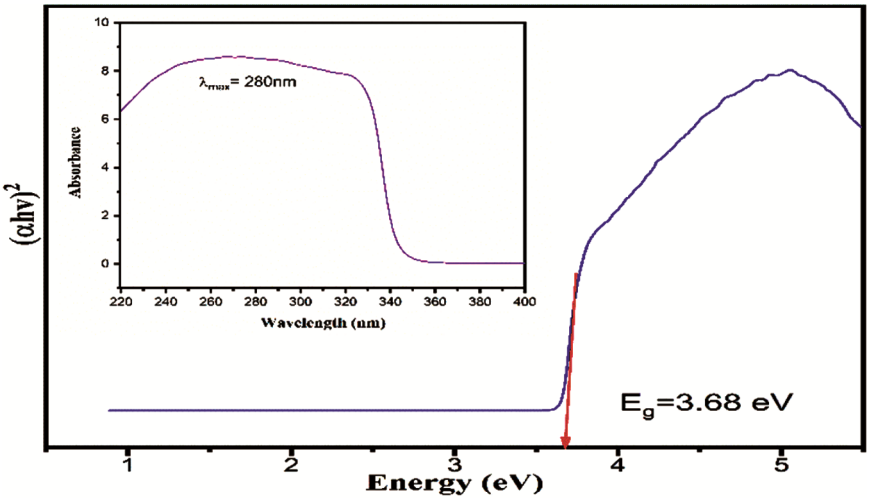

Fig. 5 — Tauc's plot and UV-Vis absorption spectrum of 0 % Mn-doped ZnS.

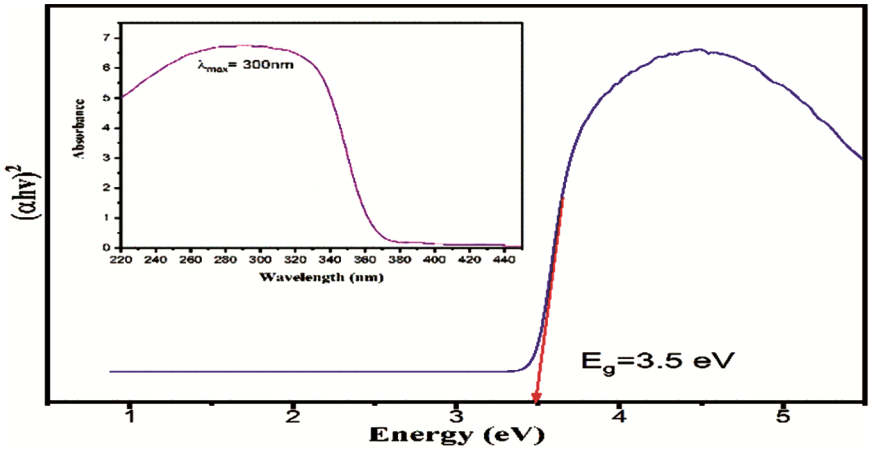

Fig. 6 — Tauc's plot and UV-Vis absorption spectrum of 5 % Mn-doped ZnS.

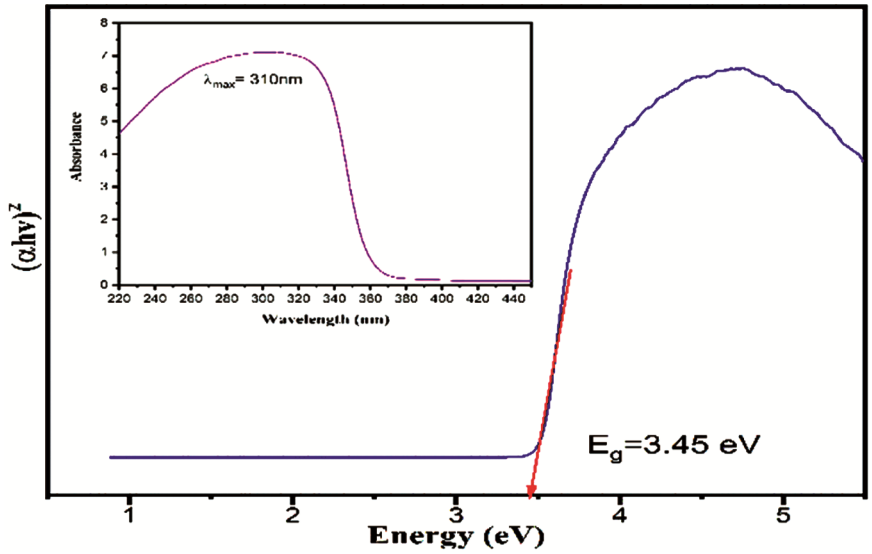

Fig. 7 — Tauc's plot and UV-Vis absorption spectrum of 10 % Mn-doped ZnS.

Mn-ZnS, 3.5 eV for 5 % Mn-ZnS and 3.45 eV for 10 % Mn-ZnS. Therefore, the energy bandgap was decreased with increasing doping percentage because the sample which absorbs UV- light is an aggregate of metal ions spread homogeneously and absorbed peak corresponding to Mn ions, also corroborated with XRD[18]. This minute change suggests that there is direct energy transfer between the semiconductor excited state and the 3d levels of Mn ions[19].

4 Conclusion

The hydrothermal synthesis method was employed to precisely incorporate manganese (Mn) doping into zinc sulfide (ZnS) nanoparticle at three different concentrations, namely 0%, 5%, and 10%.

XRD spectrum shows that ions of Mn get doped in the ZnS without disturbing its crystal structure. The average crystallite size was increased slightly due to Mn- doping. FTIR analysis also confirms the formation of pure and doped ZnS. UV-Visible spectroscopy results show a red shift in the absorption maxima and the band gap value decreased because of doping. So, the optical, structural and morphological characteristics of ZnS can be varied by the doping of manganese in it. The band gap and crystallite size of ZnS can be controlled through doping and the product can find application in the various field.

Acknowledgement

We are grateful to the IIC, IIT, Roorkee, Uttarakhand, for providing necessary ads for characterization tools.

References

1 Zhou H, Qu Y, Zeid T & Duan X *Energy Environ Sci*, 5 (2012) 6732.

2 Baytar O, Sahin O, Kilicvuran H & Horoz S, *J Mater Sci: Mater Electron*, 29 (2018) 4564.
3 Fang X, Zhai T, Gautam U K, Li L, Wu L, Bando Y & Golberg D, *Progress Mater Sci*, 56 (2011) 175.
4 Wang Q, Xu P, Zhang G, Zhang W, Hu L & Wang P, *Phys Chem Chem Phys*, 20 (2018) 18601.
5 Colquitt L, *J Appl Phys*, 36 (1965) 2454.
6 Heiba Z K, Mohamed M B, Ahmed S I & Albassam A, *JMater Sci:Mater Electron*, 31 (2020) 13447.
7 Rose A, Shunmugapriya B, Maiyalagan T & Vijayakumar T, *J Mater Sci:Mater Electron*, 31 (2020) 19204.
8 Sharma S, Singh I, Chitkara N & Kapoor A *Mater Res Exp*, 4 (2017) 075046.
9 Ashwini K, Pandurangappa C, Avinash K, Srinivasanl S & Stefanakos E, *J Lumin*, 221 (2020) 117097.
10 Lu S W, Lee B I, Wang Z L, Tong W, Wagner B K, Park W & Summers C J, *J Lumin*, 92 (2000) 73.
11 Kumar S, Kumar V, Devi R, Sisodia A K, Jatrana A, Singh R B, Dahiya R & Mishra A K, *Adv Mater Sci Eng*, (2022) 1.
12 Hoa, T T Q, The N D, McVitie S, Nam N H, Canh T D, & Long N N, *Opt Mater*, 33 (2011) 308.
13 Kumar V, Bhawna, Yadav S K, Gupta A, Dwivedi B, Kumar, A, Singh P & Deori K, *Chem Select*, 4 (2019) 3722.
14 Sihag S, Dahiya R, Rani S, Kumar A & Kumar V, *Indian J Chem Technol*, 29 (2022) 5.
15 Viswanath R, Naik H S B, Somalanaik Y K G, Neelanjeneallu P K P, Harish K N & Prabhakara M C, *J Nanotechnol*, (2014) 1.
16 Rema D B S, Raveendran R & Vaidyan A V, Parama *J Phys*, 68 (2007) 679.
17 Kurian S K, Sebastian S, Mathew J & George K C, *Indian J Pure Appl Phys*, 42 (2004) 926.
18 Labiadh H, Sellami B, Khazri A,Saidani W & Khemais S, *Opt Mater*, 64 (2017) 79.
19 Kripal R, Gupta A K, Mishra S K, Srivastava R K, Pandey A C & Prakash S G, *Spectrochim Acta Part A: Mol Biomol Spectros*, 76 (2010) 523.