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INVESTIGATION OF MORPHOLOGICAL AND OPTICAL PROPERTIES OF MN DOPED ZNS.

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Abstract: The Mn doped ZnS nanoparticles were prepared by co- precipitation method at room temperature. The structural (morphological) and optical properties the resultant ZnS:Mn^{2+} nanoparticles were studied by different characterization techniques likely X-ray diffraction (XRD), UV-vis spectroscopy, Photoluminescence (PL) and FTIR . UV-vis spectra analysis accurately predicted the band gap and Urbach energy. The prepared ZnS:Mn^{2+} nanoparticles have zinc blend structure with their crystalline size of nearly 2.65nm which were confirmed by XRD. The presence of various functional groups was designated by FTIR. PL analysis was carried out which shows emission at 594nm monitored at 341nm excitation. Thus, Mn doped ZnS nanoparticles causes the changing its morphology structural optical and Photoluminescence properties.

Key words: Urbach energy, Tauc's plot, Nanoparticles.

INTRODUCTION

Various researcher has been attracted in the filled of nanoscience and nanotechnology owing to their large number of applications regarding its size and photoluminescence properties [1]. ZnS nanoparticles have large number of applications in the filled of semiconductor material as Optoelectronics devices, Solar cell, fluorescence microscopy, Photodetector [2,3,4]. various transition metal has been doped in ZnS but doping of Mn^{2+} and Cu^{2+} is an important aspect in different nanostructure [5]. ZnS compound have direct and wide band gap of 3.6ev. These properties employed in Optical sensor and electroluminescence devices LED [7,8]. A large number of methods has used to prepare Mn doped ZnS nanoparticles including Sputtering ultrasound radiation, Co evaporation, Sol gel, Solid state reaction, Liquid phase, Chemical precipitation, Gas phase condensation, Microwave radiation and biological synthesis [11,12,13,14]. In this research paper, we present a comprehensive characterization of Mn-doped ZnS nanoparticles utilizing a combination of advanced spectroscopic techniques. X-ray diffraction (XRD), UV-visible spectroscopy (UV-Vis), Photoluminescence spectroscopy (PL), and Fourier-transform infrared spectroscopy (FTIR). XRD analysis provides invaluable insights into the crystalline structure, phase purity, and lattice parameters of Mn-doped ZnS nanoparticles [6,9]. By analyzing the diffraction patterns, the crystallographic phases and crystallite size distribution of the nanoparticles can be determined, offering fundamental information about their structural properties. UV-vis spectroscopy is employed to investigate the optical properties of Mn-doped ZnS nanoparticles, including their absorption and transmission spectra. This technique enablesthe determination of the band gap energy, optical band-edge transitions, and electronic structure of the nanoparticles, crucial for understanding their optical behavior and potential applications in photonic devices [15,16]. Photoluminescence spectroscopy offers a deeper understanding of the luminescent properties of Mn-doped ZnS nanoparticles [10]. By analyzing the emitted light spectra upon excitation, valuable information regarding the energy levels, defect states, and emission mechanisms can be elucidated, facilitating the optimization of the luminescent performance for applications such as light-emitting diodes (LED's) and biomedical imaging probes. FTIR spectroscopy is employed to probe the chemical composition, surface functionalization, and bonding configurations of Mn-doped ZnS nanoparticles. This technique provides insights into the vibrational modes of functional groups and surface ligands, enabling a comprehensive analysis of the chemical structure and surface properties of the nanoparticles [17].

By integrating these advanced spectroscopic techniques, this research aims to provide a thorough understanding of the structural,optical, luminescent, and chemical properties of Mn-doped ZnS nanoparticles, thereby contributing to the advancement of their synthesis, characterization, and application in various technological fields.

MATERIAL AND SYNTHESIS METHOD

ZnS: Mn nanomaterials were prepared by Co-precipitation method:
Zinc Acetate [$Zn(CH_3COO)_2.H_2O$], Manganese Acetate [$Mn(CH_3COO)_2.4H_2O$], Sodium Sulphide [Na_2S], Distilled Water.
75ml of double distilled water were used to dilute 10ml of 1.0M zinc acetate and 5ml of 0.1M manganese acetate solution for 5% Mn^{2+} doping. After that, 10ml of 1M Na_2S was added drop wise while being vigorously stirred for 1hr. After centrifugation white

precipitated was produced, which was then repeatedly clean with ethanol and double distilled water. The precipitated was dried

for 6-7 hr. at 200^0 C to get powder sample. The samples were investigated using FTIR, PL, UV- Vis and XRD. Each and every observation made at room temperature. More than 99% of chemical are pure. All laboratory glass beaker objects used in this practical action is acid clean. As shown in fig. (1)

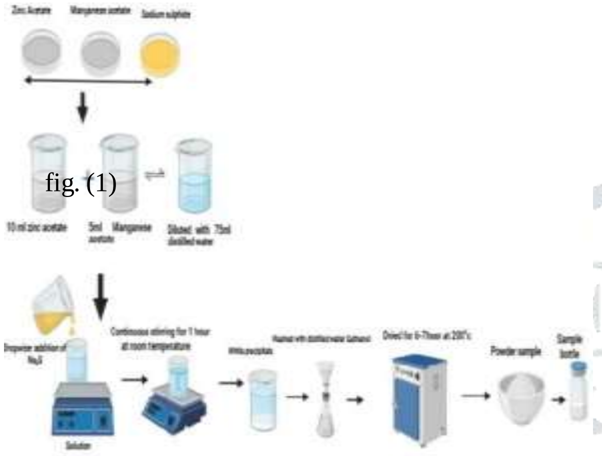


fig. (1)

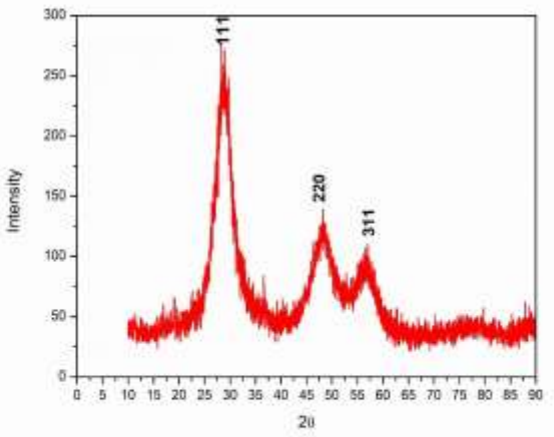


fig. (2)

CHARACTERIZATION TECHNIQUES

(A) **X-ray Diffraction:** Fig. (2) shows the XRD patterns of ZnS:Mn^{2+} nanoparticles with 5% concentration of Mn^{2+} at room temperature. The XRD patterns of the prepared Mn^{2+} doped ZnS samples were show various diffraction peaks for 2ϴ values of 28.91^0, 48.11^0, and 57.11^0 corresponding to the planes (1 1 1), (2 2 0) and (3 1 1) respectively of cubic zinc blend structure. They are well match with the standard JCPDS card (JCPDS no. 80-0020). Table (1).

h, k, l) values	θ (Degree) Standard	θ (Degree) Observed
1,1,1)	8.6	8.91
2,2,0)	7.7	8.11
3,1,1)	6.3	7.11

There were no significant changes due to substitution of Mn^{2+} ions in ZnS lattice because Zn^{2+} ($0.74A^0$) and Mn^{2+} ($0.67A^0$) have approximately similar ionic radii. The grain size was estimated by using the Debye–Scherrer formula.

$$D = \frac{0.89\lambda}{\beta cos\theta}$$

Vhere, 0.89 - Scherrer constant. λ - Wavelength (1.54 A^0)

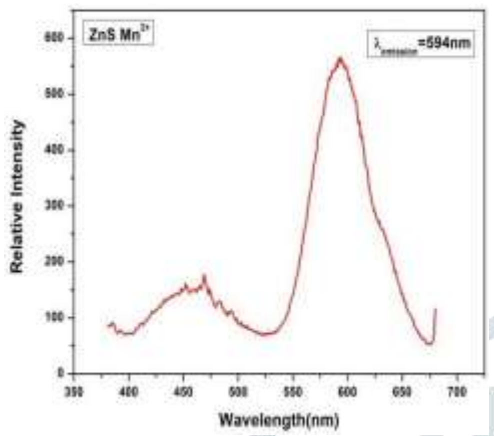
θ - Bragg's angle

β - Full width at maximum height (FWHM)

The calculated grain size was 2.68nm corresponding to (111) plane. Crystalline size indicates that the doping concentration doesnot affect the particle size. The broadening of the XRD peaks indicates the nanocrystalline nature of the samples. In addition, no diffraction peaks from manganese impurities were detected.

(B) **Photoluminescence (PL):** Fig. (3,4) Shows PL spectra of Mn^{2+} doped ZnS nanoparticles at room temperature. It shows the excitation (λ_{ex} = 341nm) and emission (λ_{em} = 594nm) spectrum of ZnS:Mn^{2+}. It can clearly see that the excitation wavelength at 341nm. For the sample, the blue green emissions centered at 450nm and 460nm arise due to interstitial sulfur vacancies (V_s) and zinc vacancies (V_{zn}) respectively. Since sulfur ion have larger ionic radius (1.7 Å) than that of zinc ion (0.74 Å). The graph shows narrow size distribution of nanoparticles. Interstitial sulfur produces more strain in the ZnS lattice and thus the electron levels due to this site will have smaller binding energy. The wavelength 450nm and 460nm assigned to sulfur vacancies and zinc

vacancies respectively in the defect states. For the ZnS nanoparticles doped with Mn2+, an orange peak centered at 594nm isobserved in addition to blue green emissions, which arises due to $^4T1–^6A1$ transition within the 3d shell of Mn^{2+}.



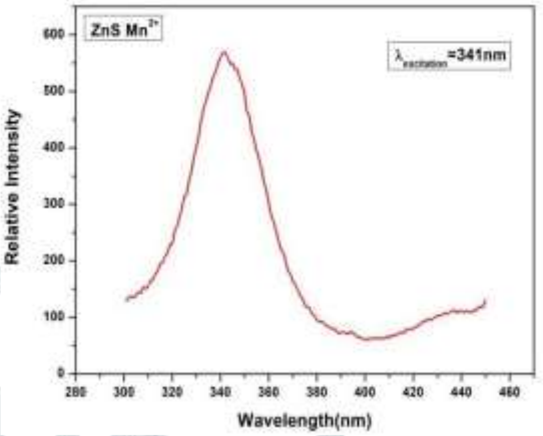


fig. (3)

fig. (4)

(C) **Fourier Transform Infrared Radiation:** FTIR spectra of synthesized ZnS:Mn^{2+} nanoparticles were used to identify the functional group in the prepared ZnS:Mn^{2+}. It also analyzed equality and compositions of compound. The FTIR spectra as shown in fig. (5) along with different peak corresponding to different wavenumber. FTIR graph show's several absorption bands immersed between the wavenumber range 5000cm^{-1} to 400cm^{-1}. The peak at 3427 cm^{-1} corresponds to O-H group stretching andvibration. The peak at 1587.48cm^{-1}, 1425.46cm^{-1}, 1026.17cm^{-1} and 666.43cm^{-1} corresponds to S-O, C-O, C-C and Zn-S (stretching) respectively.

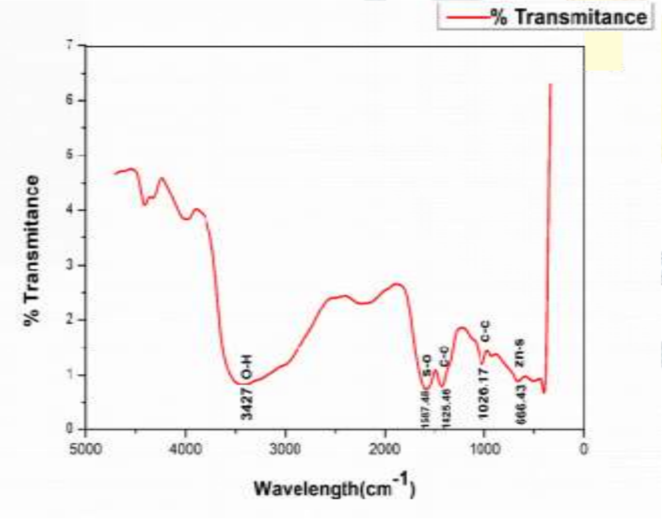


fig. (5)

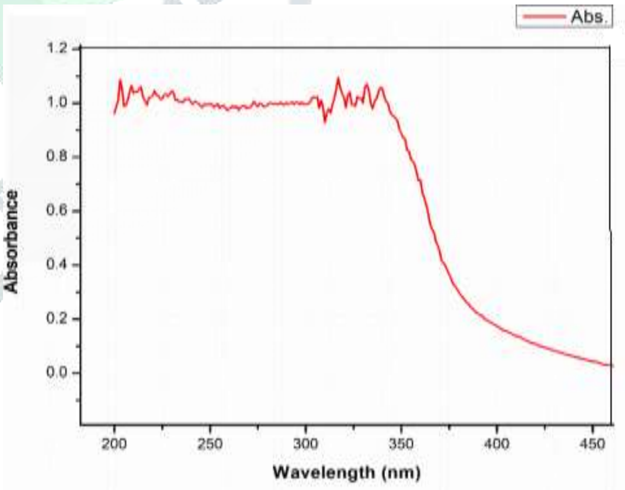


fig. (6)

(D) **UV- Vis Spectroscopy:** The UV-Vis absorption spectrum of Mn-doped ZnS nanoparticles exhibited a broad absorption band in the UV region. The UV spectrum was found in 200nm to 460nm range (in fig.(6)) and centered around 300-350 nm. This absorption peak corresponds to the band gap energy (E_g =3.22ev) of the nanoparticles as shown in fig. (8) and Urbach energy (E_u =0.1029ev) as shown in fig. (7) indicating the transition of electrons from the valence band to the conduction band. Additionally, doping Mn into the ZnS lattice resulted in a red shift of the absorption peak compared to undoped ZnS nanoparticles. This shift can be attributed to the incorporation of Mn ions into the ZnS crystal structure, leading to changes in theelectronic band structure and optical properties. The observed blue shift in the absorption edge is reflection of the
band gap is 3.22ev.

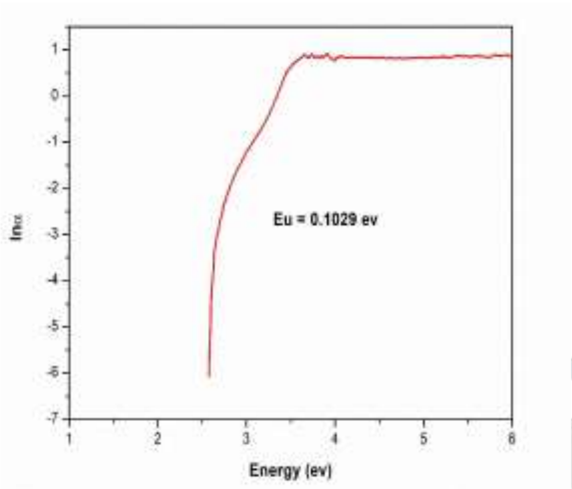


fig. (7)

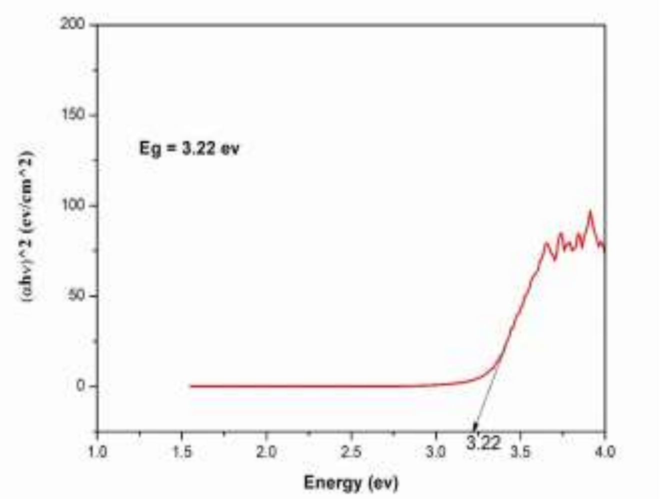


fig. (8)

CONCLUSION

In the present work, the Mn doped ZnS were synthesized by using Co-precipitation method. The morphology and optical propertywere studied by using XRD, FTIR, UV and PL. The grain size 2.68nm and energy band gap E_g =3.22ev confirmed accurately andprecision of prepared $ZnS:Mn^{2+}$.

The FTIR spectra provided additional confirmation of the functional group and their different effects of nanoparticles and confirmation of ZnO Nanoparticles. PL show wavelength range for the Sulphur and zinc vacancies in interstitial defect site anddoped Mn orange peak centered at 594nm showing the transition with in 3d shell.

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