IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

Impact Of Mn Doping On The Structural And Optical Features Of Zns Nanoparticles

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Abstract: In this study, we describe the synthesis and characterization of ZnS and manganese-doped ZnS nanoparticles using a simple and cost-effective chemical method with a polyvinyl alcohol (PVA) matrix. This approach is particularly well-suited for the industrial-scale production of nanoparticles. The synthesized materials were characterized through various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible absorption spectroscopy, and photoluminescence (PL) analysis. Notably, the PL spectrum of the ZnS:Mn nanoparticles revealed a peak at 603 nm, which is attributed to the $^4T_1$-$^6A_1$ transition of the manganese dopant.

***Index Terms* - Nanoparticles, photoluminescence analysis, X-ray diffraction, ZnS**

I. INTRODUCTION

Nanostructured materials are intriguing for both scientific exploration and practical uses. Zinc Sulfide (ZnS) is an II-VI semiconductor characterized by a direct band gap of 3.68 eV at room temperature [1-4]. It holds significant potential in diverse applications, including phosphors, solar cells, and infrared (IR) windows [5-7]. Over the last twenty years, there has been considerable focus on semiconductor nanoparticles doped with transition metals, primarily due to their distinctive luminescent properties caused by quantum confinement effects. Bhargava et al. [8] were the pioneers in reporting the luminescence characteristics of Mn-doped ZnS:Mn nanocrystals synthesized through a chemical method at room temperature. The photoluminescence (PL) and electroluminescence (EL) properties are significantly influenced by manganese doping [9]. Doped semiconductors demonstrate unique optical characteristics, making them suitable for a range of optical applications. Consequently, semiconductor nanocrystals with doping have garnered considerable research attention [10]. Nanocrystalline chalcogenides illustrate fascinating electronic behaviors and transition probabilities, finding relevance in spintronics [11]. These II-VI compound semiconductors have been examined for numerous applications, including optical coatings, photoconductors, and optical as well as electro-optical modulators. ZnS nanoparticles doped with manganese are particularly appealing due to their elevated fluorescence quantum efficiencies [12].

II. RESEARCH METHODOLOGY

Manganese-doped ZnS nanoparticles were produced through a chemical method utilizing polyvinyl alcohol (PVA) as a capping agent. A homogeneous solution was prepared containing 0.1 M zinc acetate, 0.1 M sodium sulfide, and 0.1 M manganese acetate to synthesize both ZnS and ZnS:Mn nanoparticles. A solution of zinc acetate and manganese acetate was added dropwise to a vigorously stirred solution of sodium sulfide. The mixture was then stirred for an additional four hours at room temperature with a magnetic stirrer. To eliminate any impurities from the sample, the nanoparticles were washed multiple times with deionized water. The resultant products were subsequently characterized.

III. RESULTS AND DISCUSSION

The surface morphology of the synthesized ZnS and ZnS:Mn nanoparticles was examined using scanning electron microscopy (SEM). The SEM picture ZnS:Mn nanoparticles was shown in fig.1.

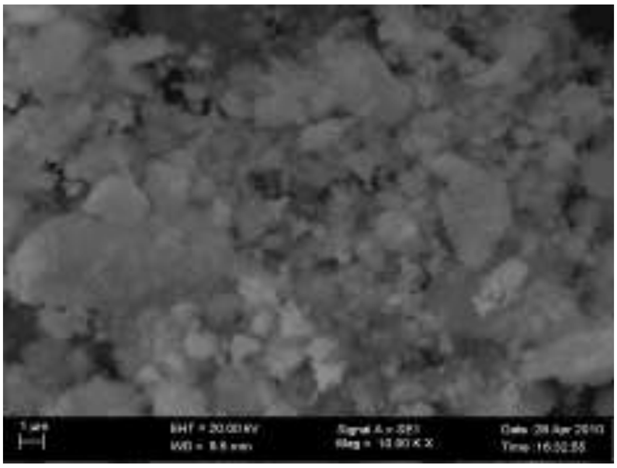

Fig 1. SEM image of Zn 0.95 Mn 0.05S nanoparticles

The chemical compositions of the synthesized nanoparticles were analyzed using Energy Dispersive X-ray Spectroscopy (EDAX), which confirmed that the actual compositions matched the intended target compositions. This analysis provides insights into the elemental makeup of the nanoparticles, ensuring the successful incorporation of manganese into the ZnS structure. Additionally, X-ray diffraction (XRD) patterns were collected over a 2θ range of 20° to 70° at room temperature using a Seifert 3003 TT XRD instrument. This technique was employed to determine the crystalline phases of the materials and to assess the crystallinity and structural properties of both ZnS and ZnS:Mn nanoparticles.

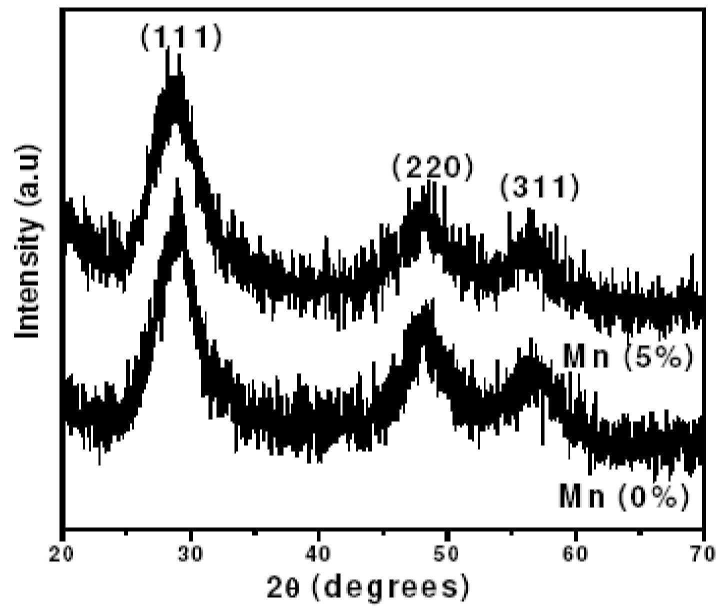

Fig 2. XRD pattern of the undoped and Mn doped ZnS nanoparticles

The X-ray diffraction (XRD) patterns for both ZnS and ZnS:Mn nanoparticles are depicted in Fig 2, revealing that all analysed samples exhibit a cubic zinc blende structure. This observation is supported by the presence of strong and broad diffraction peaks corresponding to the (111), (220), and (311) planes, which align well with the Joint Committee on Powder Diffraction Standards (JCPDS) data, confirming the crystallinity of the samples. To estimate the average size of the nanoparticles, we utilized the line broadening of the XRD peaks in conjunction with Scherrer's formula, which is represented as:

$$D = \frac{0.9\lambda}{\beta_{2\theta} \, Cos\,\theta} \qquad (1)$$

Here, D represents the particle size, λ is the wavelength of the X-ray used, and $\beta_{2\theta}$ is the full width at half maximum (FWHM) of the diffraction peak. The calculated average size of the ZnS and ZnS:Mn nanoparticles is approximately 3 nm, indicating that the synthesis method produces very fine particles, essential for various applications. Lattice parameters were derived from the XRD data, and the values obtained were 5.325 Å for pure ZnS and 5.324 Å for the ZnS:Mn nanoparticles [13]. Notably, the doping of manganese at a concentration of 5% did not alter the crystalline phase of the nanoparticles, suggesting successful incorporation of Mn without changing the fundamental structure of ZnS [14].

In addition, the optical properties were analyzed using UV-Vis absorption spectroscopy to determine the band gap values of the synthesized materials. The calculated band gaps were found to be slightly higher for pure ZnS at 4.137 eV compared to the Mn-doped Zn 0.95 Mn 0.05S nanoparticles, which exhibited a band gap of 4.112 eV [15]. This slight reduction in band gap upon doping indicates a potential redshift, suggesting that the presence of manganese influences the electronic structure of the host ZnS lattice [16].

Room temperature Photoluminescence (PL) spectra for both ZnS and ZnS:Mn nanoparticles were recorded, using an excitation wavelength of 335 nm, and are presented in Fig 3. The PL spectrum of pure ZnS nanoparticles reveals an emission peak at 460 nm, which is attributed to defect-related emissions, characteristic of ZnS materials. Additionally, an orange emission peak at 595 nm is observed, linked to the luminescent properties of the ZnS material. For the ZnS:Mn nanoparticles, a prominent broad emission peak is noted around 603 nm [17]. This orange emission is directly related to the incorporation of manganese into the ZnS lattice, and it can be attributed to the $^4T_1$ to $^6A_1$ transition of the Mn impurity [18]. The observed photoluminescence characteristics further reinforce the successful doping of Mn and highlight the material's potential for various optoelectronic applications.

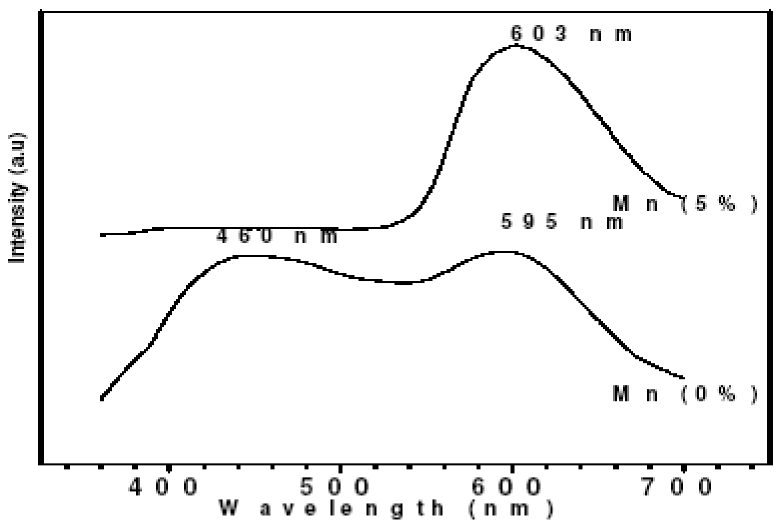

Fig 3. PL spectra of the undoped and Mn doped ZnS nanoparticles.

IV. CONCLUSIONS

The synthesized ZnS nanoparticles were characterized using X-ray Diffraction (XRD), revealing a single-phase cubic zinc blende structure, which indicates that the material is pure and retains its crystalline form despite the incorporation of 5% manganese (Mn) as a dopant. The average particle size was approximately 3 nm, suggesting they are in the nanoscale range, which often enhances certain physical properties due to quantum effects. Optical analysis showed an orange emission peak at around 603 nm, attributed to the Mn doping within the ZnS host material. This emission is linked to electronic transitions occurring in the manganese ions; specifically, it corresponds to the transition from the excited state $^4T_1$ to the ground state $^6A_1$ of Mn ions. This photoluminescent property is significant for applications in optoelectronics, as it indicates the ability of the doped nanoparticles to emit light effectively.

V. ACKNOWLEDGMENTS

The Authors thank the University Grants Commission, NERO, Guwahati, India for the financial assistance through Minor Research Project

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