
EFFECT OF PVP DYSPROSIUM DOPED AND MANGANESE CO- DOPING ON STRUCTURAL, MORPHOLOGICAL PROPERTIES OF ZNS NANOPARTICLES BY CHEMICAL CO-PRECIPIATION METHOD

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Abstract: Dysprosium doped and Manganese co- Doping ZnS nanoparticles were synthesized at room temperature through a soft chemical route, by chemical co-precipitation method at open atmosphere. The water soluble PVP were used as capping agents of synthesis Dy, Mn co-doped ZnS nanoparticles. The nanostructure of the synthesized Dy, Mn co-doped ZnS nanoparticles were characterized by powder X-ray diffraction (XRD), Scanning electron microscope (SEM), Energy dispersive analysis of X-rays (EDAX) and High Resolution Raman spectroscopic techniques. The size of as prepared Dy, Mn co-doped ZnS nanoparticles is found to be around 6-12 nm range. SEM attached with EDS gave the size, morphology and compositional analysis of as prepared material. The Raman spectra of unimplanted and Mn, Dy ions implanted samples of nanostructured ZnS showed LO mode and TO mode. Compared with the Raman modes (276 and 351 cm^{-1}) of undoped ZnS nanoparticles, the Raman modes of Mn, Dy co- doped ZnS nanoparticles are slightly shifted towards lower frequency side.

Keywords: ZnS, Nanoparticles, co-precipitation, PVP, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Raman spectra..

Introduction: Nanoparticles have been very much attracted the researchers in the field as the transition from micro particles to nanoparticles was seen to lead to huge changes in the physical and chemical properties of a material. Nano-sized materials with uniform morphology have received great interest due to their importance in basic scientific research and potential knowledge applications. Due to their small size, nanoparticles exhibit novel material properties that are significantly different from those of their bulk counterparts. Because of these physical properties they find many potential applications in areas such as nonlinear optics, photoluminescence, electronics, catalysis, solar cells and optoelectronics [1- 6].

Semiconductor nanoparticles are themselves highly unstable, and in the absence of capping agent, they agglomerate very rapidly. For this reason bonding of capping agents to nanoparticles is necessary to provide chemical passivation and also to improve the surface state which has substantial influence on the optical and electronic properties of nanoparticles. Luminescence properties of ZnS can be controlled using various dopants such as Ni, Fe, Mn, Cu etc. Various transition metal ions and rare-earth ions as impurities doped in nanocrystalline ZnS host, such as Cu^{2+} , Mn^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Eu^{3+} , Sm^{3+} , Tb^{3+} , Er^{3+} etc not only give luminescence in various regions but also can add to the excellent properties of ZnS. In this paper, Mn and Dy are co-doped into ZnS host lattice by using simple and cost-effective chemical co-precipitation method and the effect of dopant concentration on various properties of ZnS were studied.

Experimental and Characterization details

Experimental details: All the chemicals were of analytical reagent grade and were used without any further purification. The ZnS: Mn, Dy nanoparticles were prepared by chemical reduction method. The samples were prepared by chemical co-precipitation method using pure zinc acetate, Dysprosium (III) chloride hexahydrate, Manganese (II) acetate (Tetra hydrate) and Sodium sulfide. Appropriate amounts of $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Cl}_3\text{Dy} \cdot 6\text{H}_2\text{O}$ and $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ were dissolved in 50 ml distilled water. To this solution, 50 ml of Sodium sulfide solution is added drop wise under constant stirring until to get fine precipitate of Mn and Dy co-doped ZnS nanoparticles. After the completion of the reaction, products were collected and thoroughly washed for several times with distilled water and ethanol, Mn and Dy co-doped ZnS nanoparticles were subjected to various characterization studies.

Characterization details: The X-ray diffraction patterns of the samples were collected on a Seifert 3003 TT X- Ray Diffractometer with the Cu K_α radiation ($\lambda=1.5405\text{ \AA}$). Elemental composition for the prepared samples were analyzed through EDAX using Oxford Inca Penta FeTX3 EDS instrument attached to Carl Zeiss EVO MA 15 Scanning Electron Microscope. Photoluminescence spectra of the present nanopowders have been recorded using a Horiba-Fluorolog-3 (Model FL3-22) spectrofluorometer at room temperature (300 K).

Results and discussion:

Structural Analysis: The XRD patterns of the doped and undoped nanoparticles show a single-phase with cubic zinc blende structure with three diffraction peaks corresponding to (111), (220) and (311)

diffraction planes of cubic zinc blende structure as per the standard card (JCPDS No. 80-0020). No secondary phase was detected indicating that Dy and Mn are incorporated into the ZnS host lattice. The broadened XRD peaks indicate that the nanocrystalline nature of the prepared samples. The average crystallite size was obtained from the most prominent XRD peak, (111) using Debye-Scherrer's formula [7] $D = 0.9 \lambda / \beta \cos \theta$, where D is the average particle size, λ is wavelength of Cu-K α irradiation, β is the full width at half maximum intensity of the diffraction peak and θ is the diffraction angle. The particle size of the prepared samples lies in the range of 6- 12 nm. The XRD spectra of Mn and Dy co-doped ZnS nanoparticles are shown in fig.1.

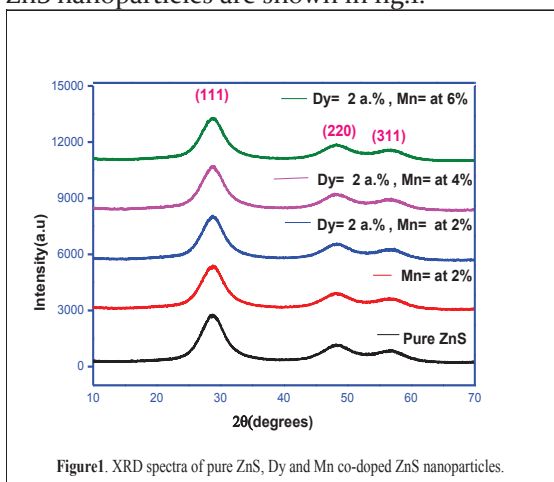


Figure1. XRD spectra of pure ZnS, Dy and Mn co-doped ZnS nanoparticles.

Elemental Analysis: Chemical composition analysis of all the prepared nano samples was done by EDAX technique. In order to analyze the amount of Mn and Dy content and distribution in doped ZnS this technique is much useful. Figure 2 (a), (b), (c), (d) and (e) shows EDAX spectra of Pure ZnS, Dy (2 at.%) doped ZnS and Dy (2 at.%) & Mn (2, 4 and 6 at.%) co-doped ZnS nanoparticles respectively. EDS spectra of the samples confirmed that the amount of Zn, S, Dy and Mn were close to the nominal (target) values. This confirms the effective doping of Dy and Mn into ZnS host lattice matrix.

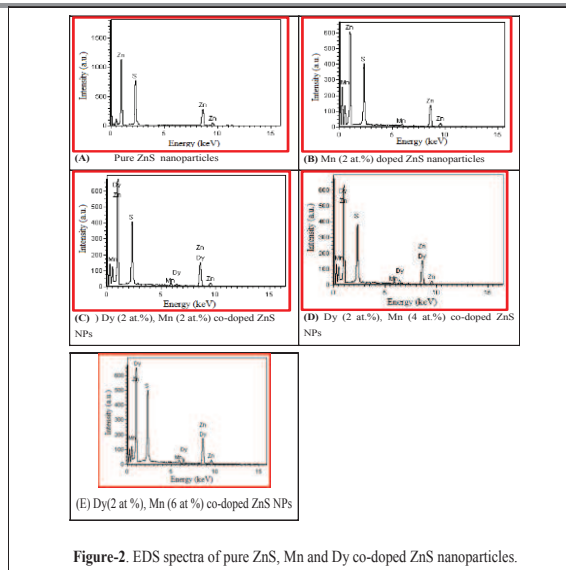


Figure-2. EDS spectra of pure ZnS, Mn and Dy co-doped ZnS nanoparticles.

Morphological Studies: The surface morphology is studied by a powerful tool called Scanning Electron Microscope, especially by observing the top and cross-sectional views of the sample. The surface morphologies of the Pure ZnS, Mn (2 at.%) doped ZnS and Dy (2 at.%) & Mn (2, 4 and 6 at.%) co-doped ZnS nanoparticles were shown in figure 3 (a), (b), (c), (d) and (e) respectively. It is noticed that in the doped samples the agglomerated particles were appear and agglomeration decreased with increasing Mn dopant concentration upto 4 at.%.

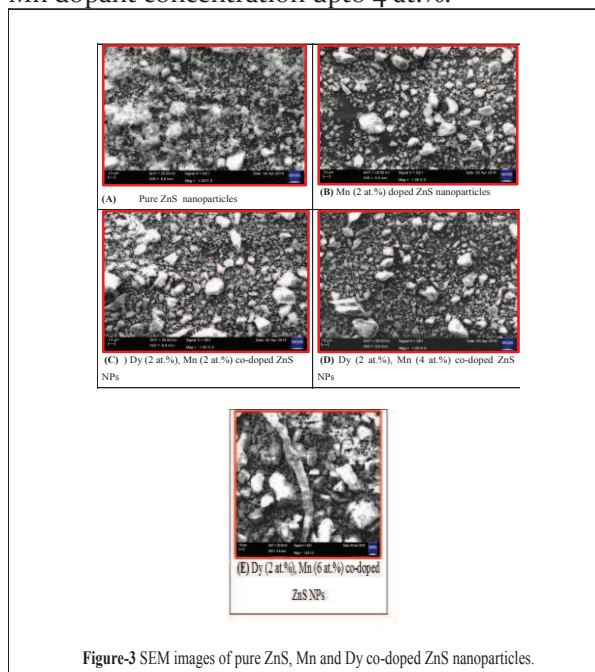


Figure-3 SEM images of pure ZnS, Mn and Dy co-doped ZnS nanoparticles.

FTIR spectroscopy: FTIR spectroscopy was carried out to understand the formation of ZnS-PVP nanoparticles. FTIR spectrum for PVP, PVP-ZnS and PVP-ZnS/Dy, Mn (4%) nanoparticles were recorded on a Shimadzu (model: IR Prestige 21, with ZnSe ATR crystals) spectrometer and are shown in Figs. 4 and 5. In pure PVP, the COO- stretch band is observed at

1658 cm^{-1} and it is red shifted to 1642 cm^{-1} in ZnS-PVP nanocomposites, indicating a strong interaction between ZnS nanoparticles and COO- of PVP [8,9]. The other bands observed in the FTIR spectrum are

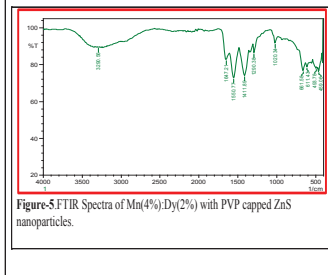
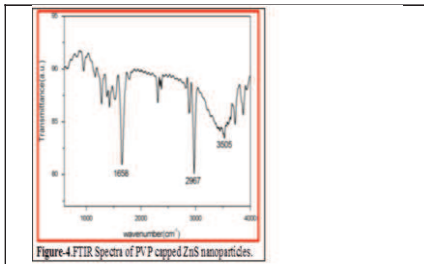


Table-1

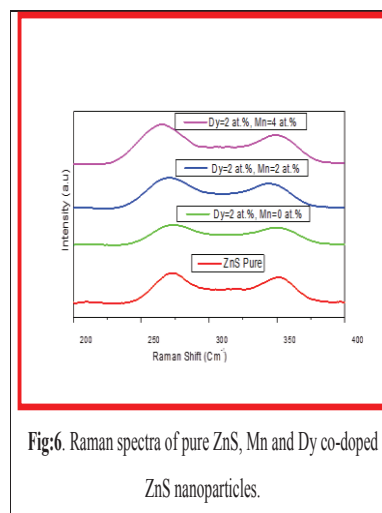
Vibrational assignments of Mn(4%):Dy(2%) with PVP capped ZnS nanoparticles.

Wavenumber (cm ⁻¹)	Vibrational assignment
3290.56	O-H stretching
1647.21	O-H bending
1550.77	COO---
1411.89	C-H stretching
1290.38	C-N stretching
1020.34	S-O stretching
661.58	Mn-S vibration
611.43	Zn-S stretching
493.78	Dy-S vibration
459.06	Dy-O stretching

Raman Spectroscopy: Raman spectra of uncapped and PVP capped ZnS: Mn, Dy nanoparticles recorded in the frequency range 200 - 400 cm^{-1} are shown in Figure 4. The Raman spectrum of undoped ZnS nanoparticles exhibits strong but broad peak at 276 and weak broad peak at 351 cm^{-1} . Asymmetric broadening in the Raman bands of Dy³⁺ and Mn²⁺ ions co-doped ZnS nanoparticles and PVP capped ZnS: Mn, Dy nanoparticles is due to phonon confinement effect and the possible reason for the Raman shift is the ionic radius of Dy³⁺ is higher than that of Zn²⁺, lattice defects get introduced or intrinsic host lattice defects are activated when Dy³⁺ ions are incorporated. The Dy³⁺ ions and Mn²⁺ ions tend to occupy the substitutional cationic sites resulting in host lattice defects. Further, no additional Raman modes due to Mn, Dy impurities are observed in co-doped ZnS: Mn, Dy nanoparticles.

listed in Table -1. It is inferred from Fig. 5 that by the addition of dopants the bands are shifted to lower wavelength side this indicating the presence of dopants (Dy, Mn) in the host matrix.

Also, no additional peaks were observed due to the presence of capping agent which reveals the absence of impurity phases. In the case of large surface-to-volume ratio, surface scattering contributes more to the Raman signal than the volume scattering. The frequency shift of the Raman bands towards lower frequency side could be due to large surface to volume ratio. Therefore, the frequency shifts of the TO and LO modes observed in the present samples may be attributed to the smaller size and larger surface-to-volume ratio compared with that of the undoped ZnS. They represent Transverse Optical (TO) and Longitudinal Optical (LO) zone center phonons of cubic ZnS crystals respectively and these are similar to Brafman and Mitra [10] reports.



Conclusion: Pure, Dy (2 at.%), Mn (2, 4 & 6 at.%) co-doped ZnS nanoparticles were successfully synthesized by facile chemical co-precipitation technique at room temperature. X-ray diffraction studies showed the cubic zinc blende structure of the prepared samples and the broadened peaks in the X-ray diffractograms indicates the nanocrystalline nature of the prepared samples. SEM analysis attached with EDAX reveals the surface morphology and effective incorporation of Mn and Dy dopants into ZnS host lattice. SEM images showed slight decrease in agglomeration with increasing Dy concentration. The Raman spectra of unplanted and Mn, Dy ions implanted samples of nanostructured ZnS showed LO mode and TO mode. Compared with the Raman modes (276 and 351 cm^{-1}) of undoped ZnS nanoparticles, the Raman modes of Dy, Mn co-doped ZnS nanoparticles are slightly shifted towards lower frequency side.

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