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Structural,Optical And Magnetic Properties of Dy with Mn Co-Doped Zns Nanoparticles By Using Co-Precipitation Method

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Abstract: *In this present work, Mn, Dy co-doped ZnS nanoparticles were prepared at room temperature using chemical co-precipitation method. The water soluble PVP were used as capping agents for the synthesis of 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 election microscope (SEM), Energy dispersive analysis of X-rays (EDAX), diffuse Reflectance spectroscopy (DRS)and Vibrating Sample Magnetometer (VSM). The size of as prepared Dy, Mn co-doped ZnS nanoparticles is found to be around ~2 nm range. Broadened XRD peaks confirmed the formation of nanoparticles with face centered cubic (FCC) structure. SEM along with EDS gave the size, morphology and compositional analysis of as prepared material. DRS studies show that the effective band gap energy increases with increasing dopent concentration. The M–H loop of Dy, Mn co-doped ZnS Nanoparticleshas been traced using the VSM and magnetic parameters such as saturation magnetization (M_S), coercivity (H_C) and retentivity (M_r) are obtained from VSM data.*
Keywords*: ZnS NPs, Co-Precipitation, XRD, SEM, VSM*

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I. 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. 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- 4]. Transition metal ions play a crucial role to tune optical, electrical and room temperature magnetic properties of the semiconductors[5].

ZnS is chemical stable semiconductor among all II–VI semiconductors as a result of itsdistinctive physical, optical and electrical properties caused by quantum confinement effect, luminescence potency and sensible host for transition metal ion[6].Transition metal doped ZnS DMS is good agent for applications in silicon technology [7]. It is a ferromagnetic nature, sensible conductor of heat, electricity and also its corrosion resistant [8]. Various researchers have been investigating the room temperature ferromagnetic properties of transition metals doped ZnS DMS and perceptive Curie temperature in addition as obstruction temperature higher than room temperature [9]. In this work, we report the structural, room temperature magnetic properties of pure and ZnS: Mn, Dy nanoparticles. Our basic aim is to analyze the magnetic behavior shown by undoped ZnS nanoparticles and enhanced ferromagnetic behavior after doping and co-doping of Dy,Mn ions in ZnS lattice. We examine the influence of surface defects and interaction mechanisms on the structural, magnetic properties of the pure and ZnS: Mn, Dy nanoparticles.

II. EXPERIMENTAL AND CHARACTERIZATION DETAILS

2.1 Experimental details

The ZnS: Dy, Mn nanoparticles were prepared by chemical co-precipitation method. Finally Prepared Dy and Mn co-doped ZnS nanoparticles were subjected to various characterization studies. 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 $Zn(CH_3COO)_2$, Cl_3Dy. $6H_2O$ and $(CH_3COO)_2$ Mn. $4H_2O$ 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, the prepared Mn and Dy co-doped ZnS nanoparticles were subjected to various characterization studies.

2.2 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 (λ=1.5405A°). 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. DRS studies were carried out using Carey-5E UV–VIS–NIR lambda-950 spectrometer.Magnetic properties are recorded by Vibrating Sample Magnetometer (VSM) (Model: 7410 series

III. RESULTS AND DISCUSSION

3.1 Structural Analysis: From the fig.1. 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 and the particle size is ~2 nm. No secondary phase was detected, indicating that Mn and Dy are incorporated into the ZnS host lattice. The average crystalline size of the nanoparticles is estimated using Debye Scherrer formula

$$D = \frac{0.9\lambda}{\beta \text{Cos } \theta}$$

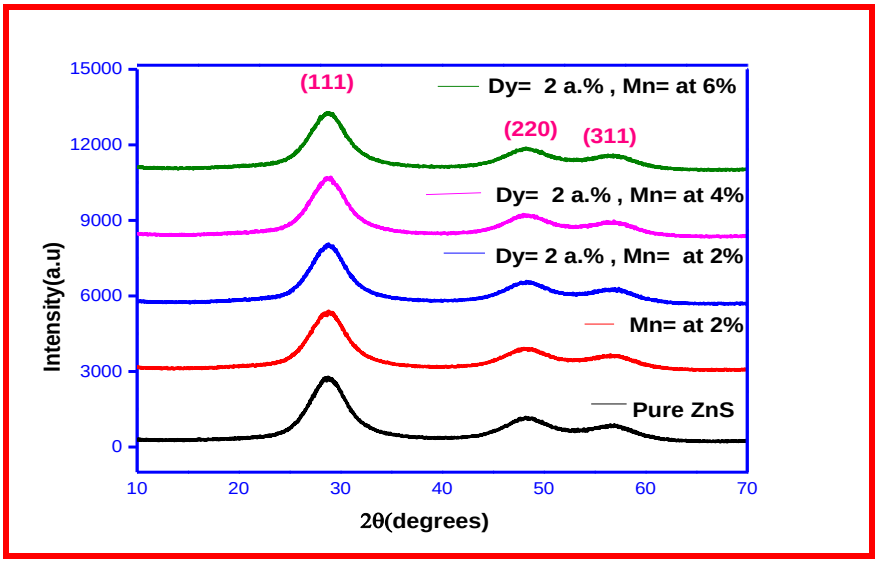


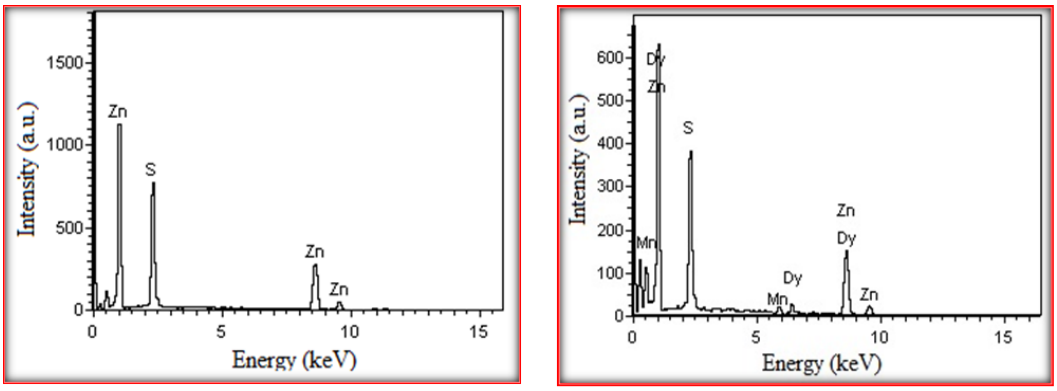
Fig-1: XRD spectra Pure ZnS and Dy with Mn(2 at. %) doped ZnS nanoparticles

given by where, D is the average crystalline size, k is constant (=0.9), βis FWHM and θis the wavelength of X-ray[10].It is also observed that the width of the peaks decreases with increasing Mn concentration, which is an indication of increased crystalline size with increasing Mn concentration. The average crystalline sizes for the pure and ZnS: Mn, Dy nanoparticles are found to be in the range of ~2 nm. The intensity of the XRD peaks is also observed to be decrease with increasing Mn concentration, which is an evidence of reduced crystallinity of the nanoparticles

3.2 Elemental Analysis:

EDS spectra of the samples from (A) confirmed that the amount of Zn, S and from (B) shows that conformed the elements Zn, S, Dy and Mn were close to the nominal (target) values.

The tables 1 & 2 indicates the atomic and weight percentages of pure and Dy(2%) with Mn(2%) co-doped ZnS nanoparticles.



(A) Pure ZnS nanoparticles (B) Dy (2 at.%), Mn (2 at.%) co-doped ZnS NPs

Fig-2:EDS spectra of pure ZnS-PVP, Dy(2%) with Mn(2%) co-doped ZnS nanoparticles

Table:3.2(b) Atomic and weight percentages of pure ZnS nanoparticles

Element	Weight%	Atomic%
S K	28.41	44.73
Zn K	71.59	55.27
Total	100.00	

Table:3.2(a) Atomic and weight percentages of Dy(2%) with Mn(2%) co-doped ZnS nanoparticles

Element	Weight%	Atomic%
S K	28.88	45.29
Mn K	0.38	0.34
Zn K	70.63	54.33
Dy L	0.12	0.04
Total	100.00	

3.3 Morphological Studies

From the Figure-3(A& B) the SEM images is noticed that in the doped samples the agglomerated particles were appear and agglomeration decreased with increasing Mn dopant concentration upto 2 at.%.

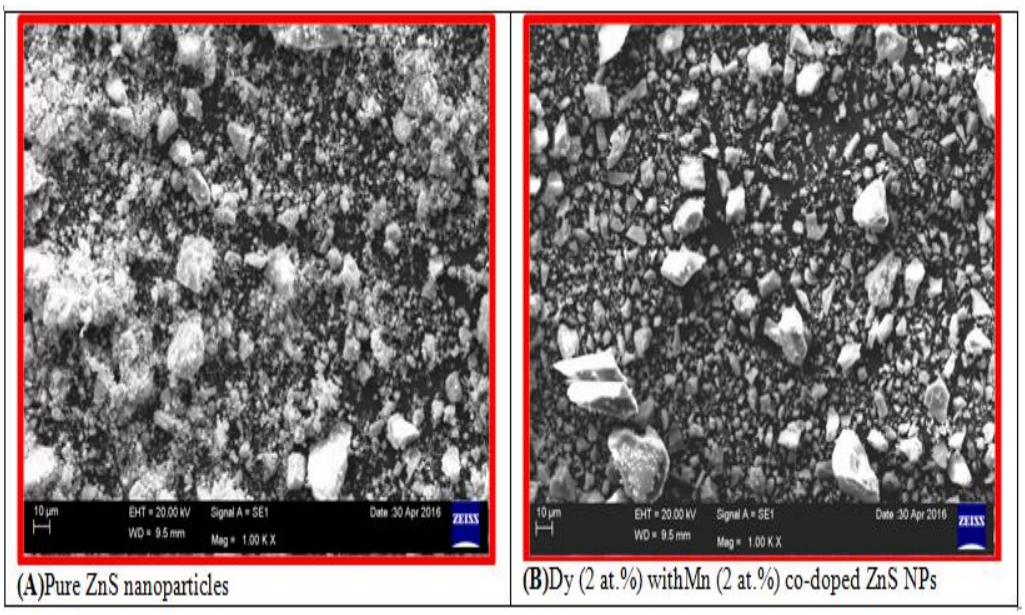


Fig-3:EDS spectra of pure ZnS-PVP, Dy(2%) with Mn(4%) co- doped ZnSnanoparticles

3.4 Diffuse Reflectance Spectroscopy (Drs)

Diffuse Reflectence Spectroscopy was used to study the optical properties of undoped and Dywith Mn (2, 4 and 6 at. %) co-doped ZnS nanoparticles. All spectra were recorded at room temperature in the wavelength

range of 200–800 nm and are shown in Fig.3.4(a). It was observed that the Diffuse Reflectance spectra of the samples shifted towards higher wavelength as the dopant concentration increased.

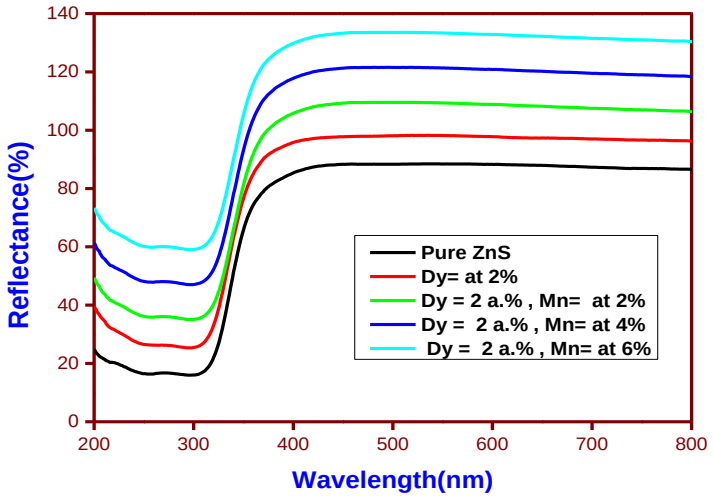


Fig. 3.4.(a) Diffuse reflectance spectra of Pure ZnS and Dy with Mn(2 at. %) doped ZnS nanoparticles

For analysis purposes the diffuse-reflectance (R) of the sample can be related to the Kubelka–Munk function F(R) by the relation $F(R) = (1-R)^2/2R$ [11]. The band gap of the present samples was estimated from the diffuse-reflectance spectra by plotting the square of the Kubelka–Munk function $F(R)^2$versus energy and extrapolating the linear part of the curve to $F(R)^2 = 0$, as shown in Fig..3.4(b).

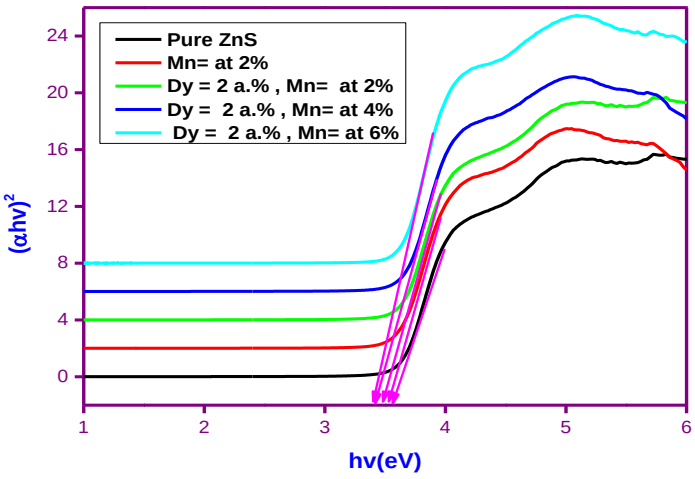


Fig. 3.4.(b) Kubelka–Munk plots and band gap energy estimation for the Pure ZnS and Dy with Mn(2 at. %) doped ZnS nanoparticles

The band gap values estimated from the DRS spectra are given in Table 3.4. As in Fig.3.4(b), the band-gap of the samples increased with an increase in the dopant concentration of Dyand thevariation in band gap may be due to smaller particle size as well as change in dopant concentration.

Table 3.4: Optical band gap values for different concentrations of Pure ZnS and Dy(2 at. %) doped Zn Snanoparticles

S.No	Dopant concentration	Band gap (eV)

	(at.%)	
1	Pure ZnS	3.52
2	Dy(2 at. %)	3.55
3	Dy(2 at. %) Mn(2 at. %)	3.56
4	Dy(2 at. %) Mn (4 at. %)	3.60
5	Dy(2 at. %) Mn (6 at. %)	3.61

3.5 Magnetic Properties (Vsm)

Fig.3.5 illustrates the M-H curves for Dy (2 at.%) and Mn (2,4 and 6 at.%) codoped ZnS nanoparticles at room temperature (300 K) with the magnetic field ranging from -8 to 8 k G. The undoped ZnS nanoparticles showed diamagnetic behavior at room temperature. From the Fig.3.5., it is observed that the sample doped with 2 at.% Dy ($4f^{10}6s^2$) exhibit ferromagnetism and the ferromagnetic behaviour loses with increasing Mn concentration. It may be due to increased dipole-dipole interaction between Mn^{2+}ions and also due to inhomogeneities in the internal field as a result of random distribution of Mn^{2+} ions.

Rare earth atoms have partially filled 4f orbital that carry magnetic moments and may take part in magnetic coupling as in the case of transition metals with partially filled 3d orbital which are delocalized, strongly direct exchange interactions, and have high Curie temperatures, but often the orbital momentum is zero, leading to small total magnetic moment per atom [12, 13]. The 4f electrons are localized, exchange interactions are indirect via 6s conduction electrons, and the high orbitalmomentum leads to high total magnetic moments per atom. Hence, it is expected that the magnetic coupling strength of the f orbital is much weaker than that of the S orbital. Dy ($4f^{10}6s^2$) is an interesting rare earth element that has partially filled 4f orbital, which can take part in a new coupling mechanism proceeding via intra-ion 4f- 6s exchange interaction, followed by inter ion 6s-6s coupling mediated through charge carriers to exhibit the observed ferromagnetism. The Dy doped and Mn Co-doped ZnS nanoparticles showed a weak ferromagnetic response[14]. The magnetic Saturation, coercivityand retentivity values were shown in the Table-3.5. As Mn concentration is increased magnetic Saturation, coercivity and retentivity is decreasing.

Table-3.5: Magnetic parameters of Dy with Mn co-doped ZnS NPs

S.No.	Dy % of concentration	Mn % of concentration	Ms (emu/g)	Hc(G)	Mr(emu/g)	Mr/ Ms	$n_B(\mu_B)$	K(emu/G)
1	2 %	0%	76	75	13	0.171053	1.352384	5816.327
2	2 %	2 %	77.19	53.94	7.12	0.09224	1.370665	4248.601
3	2 %	4 %	74.81	54	6.6	0.088223	1.325604	4122.184
4	2 %	6 %	69	53	6	0.086957	1.220071	3731.633

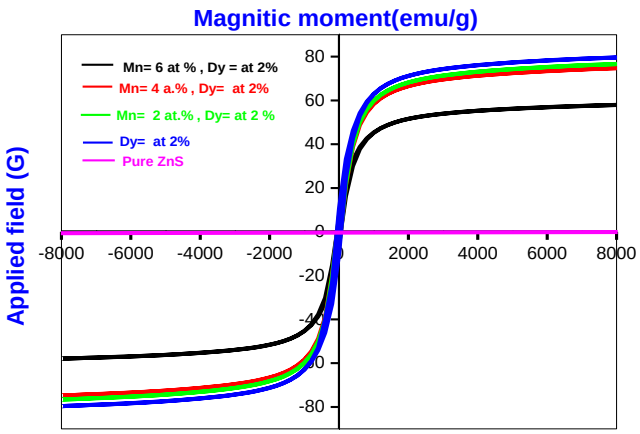


Fig. 3.5(a): The VSM images of pure and Dy(2%) with Mn(2%,4% and 6%) co-doped ZnSnanoparticles.

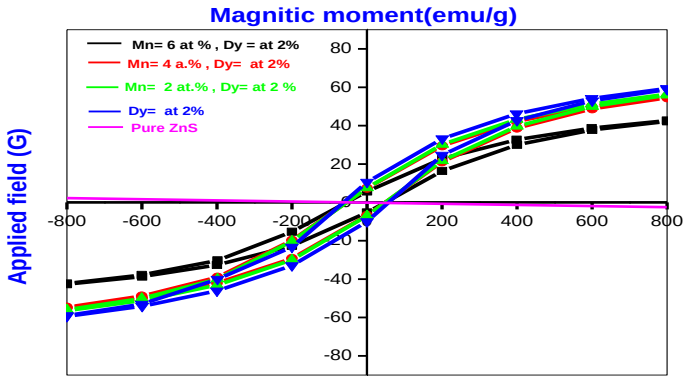


Fig. 3.5(b): The Closed view of hysteresis curves to estimate the Coercity and retentivity values at pure and Dy(2%) with Mn(2%,4% and 6%) co-doped ZnS nanoparticles.

IV. CONCLUSION

Pure Dy (2 at.%), Mn (2, 4 at.%) co-doped ZnS nanoparticles were successfully synthesized by chemical co-precipitation technique at room temperature. X-ray diffraction studies showed the cubic zinc blende structure of the prepared samples. SEM analysis attached with EDAX reveals the surface morphology and effective incorporation of Dy and Mn dopants into ZnS host lattice. SEM images showed slight decrease in agglomeration with increasing Mn concentration. DRS studies showed a decrease in reflectance with increasing Mn concentration. The band gap increased with increase in Mn content.VSM studies revels that Dy doped and Mn Co-doped ZnS nanoparticles showed a weak ferromagnetic nature. With increase in Mnconcentration magnetic saturation, coercivity and retintivity also decreases.

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