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Synthesis and Characterization of Mn Doped ZnS Nanoparticles by Co-Precipitation Chemical Method

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ABSTRACT

Mn doped ZnS (Zn1-xMnxS) nanoparticles with Mn concentration x = x = 2%, 4%, 6% were synthesized by the chemical co-pricipitation technique. Powder X- ray diffraction (XRD) reveals that Mn incorporates into the ZnS crystal Lattice with a cubic structure. UV–vis measurements show that ZnS nanoparticles prepared from the doping of Mn have more than 70% transmission in the wavelengths above 350 nm and an optical band gap of about 3.76 eV.
Keywords: Mn doped ZnS, concentration, nanoparticles, optical, SEM

I. INTRODUCTION

Research on semiconductor nanoparticles stimulated great interest in recent years because of their unique optical and electrical properties. Among the semiconductor nanoparticles, zinc sulfide as an important II–VI semiconductor has been researched extensively because of its broad spectrum of potential applications such as in catalysts, cathode-ray tubes (CRT), field emission display (FED) phosphors for a long time. It can also be used for electroluminescent devices and photodiodes [1, 2]. In recent years, much effort has been devoted to the research of doped metal chalcogenide nanostructured materials. This kind of nanomaterials exhibits unusual physical and chemical properties in comparison with their bulk materials, such as size-dependent variation of the band gap energy. Furthermore, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities [3]. In particular, when doped with magnetic ions (e.g. Mn^{2+}), these materials can produce unique magnetic and magneto-optical properties and provide unparalleled opportunities for the new field of spintronics [4]. As an important II–VI semiconductor material, ZnS is chemically more stable and technologically better than other chalcogenides (such as ZnSe), so it is considered to be a promising host material. Transitional elements ions (e.g. Mn^{2+}, Ni^{+2} and Cu^{2+} [1, 3-11]) and rare earth ions (e.g. Eu^{2+} [12, 13]) have been incorporated into ZnS nanostructures by thermal evaporation, sol–gel processing, co precipitation, micro emulsion, etc. These doped ZnS semi-conductor materials have a wide range of applications in electro-luminescence devices, phosphors, light emitting displays, and optical sensors.

In this paper we demonstrate successful synthesis of undoped and Mn doped ZnS nanoparticles by simple co-precipitation technique. The morphology and crystallinity of the as prepared particles were carefully investigated by employing various characterization techniques XRD, SEM etc. We discussed the detailed optical properties of both doped and undoped particles based on UV-Vis analysis.

II. METHODS AND MATERIAL

Mn doped Zinc Sulphide ($Zn_{1-x}Mn_xS$, where x = 2%, 4%, 6%) were synthesized by Co-precipitation method. 0.1M Zinc Sulphate, 0.1M Manganese Sulphate and 0.1M Sodium Sulphide were used as reactant materials. Freshly prepared 50 ml of aqueous solution of 0.1M Sodium Sulphide was mixed drop by drop in 50 ml of 0.1M solution of Zinc Sulphate and 50 ml of 0.1M solution of Manganese Sulphate using vigorous stirring and then 0.5 gm of polyethylene glycol added as a capping agent. The precipitate was then separated from the reaction mixture and washed several times with distilled water. The wet precipitate was dried and thoroughly ground and then annealed at 400°C in muffle furnace.

The Co-precipitation samples had taken as three types which contains various ratio of Zns and Mn , these are

i) Sample A - Mn doped ZnS (6% + 94%)
ii) Sample B - Mn doped ZnS (4% + 96%)
iii) Sample C - Mn doped ZnS (2% + 98%)

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis

We have studied the XRD patterns from as synthesized ZnS nanoparticles and heated samples at different doping concentrations (Mn). Source of X-ray was $Cu_{k\alpha}$ with wavelength 1.54 Å. The step of scanning is 0.02° with speed of a step per second. Figure 1, 2 & 3 show the XRD patterns of three samples that the doping concentrations are between 2% to 6% of manganese. From Fig. 1, 2 & 3 the X-ray peaks have been found to correspond to (110), (102), and (201) planes of the pure ZnS cubic phase (JCPDS 05-0566). It is found that widths of peaks are decreasing when amount of Mn concentration increased. This indicates that particle size increasing when doping level is increasing.

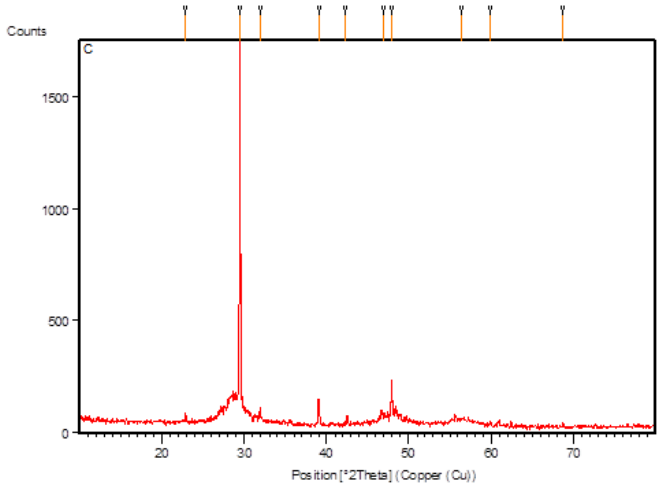

Figure 1: XRD Pattern of Sample A

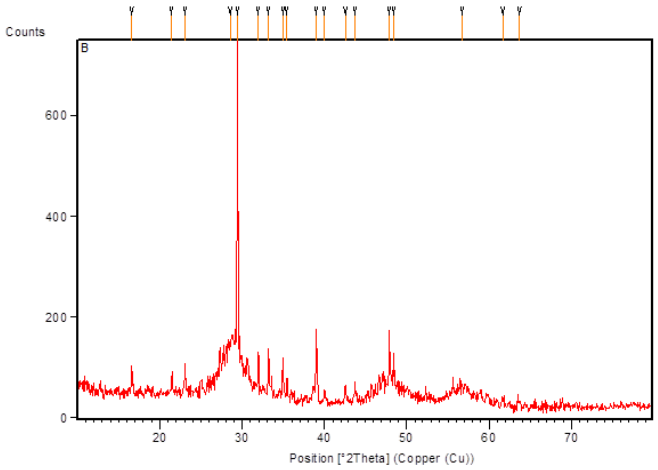

Figure 2: XRD Pattern of Sample B

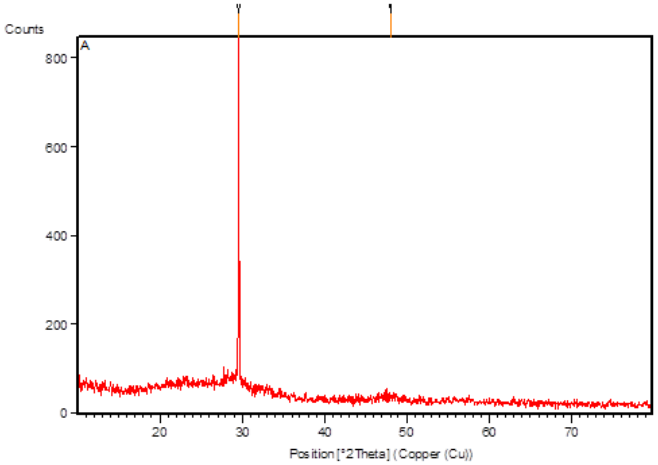

Figure 3: XRD Pattern of Sample C

The grain size of particle for samples that Mn doped at 2% and 6% obtained 0.64 and 2.08 nm by using Sherer's formula, respectively. The mean calculated crystallite size of the Mn doped ZnS nanoparticles show that the synthesized nanoparticles are in the quantum confinement regime as given in table (1). Those results are in agreement with literature [14]. The values of particle size obtained from XRD for different Mn concentrations are listed in Table 1. The lattice parameter (d) of the unit cells is calculated according to the relation [15].

These values are smaller compared to the bulk value of 5.48Å. As already mentioned the XRD peak broadening could also be due to the strain in addition to the crystalline size of the particles. Hence an attempt has been made to estimate the average strain of the ZnS nanoparticles using Stokes-Wilson equation [16]. The Dislocation density (δ) was also calculated from the relation [17]. The average strain and the dislocation densities values are given in Table 1.

Table. 1 XRD patterns in the Zn_{1-x} Mn_x S nanoparticles

S. No	Mn Concentrations (%)	Avg. Lattice Parameter (d) in Å	Av. Strain (ε) in Å	Avg. Dislocation density(δ) x 10^{19}	Avg. Crystallite size (nm)
1	2	1.9370	0.37	2.5529	0.6483
2	4	2.3000	0.42	0.6386	1.3522
3	6	2.9830	0.56	0.2734	2.0837

Optical Analysis

Figs. 4-6 show UV–Vis spectra of the Mn doped ZnS nanoparticles. The UV-Vis absorption spectra Fig 4-6 of the synthesized Mn-doped ZnS nanoparticles have been recorded, to measure their band-gap. The spectra show absorption edge of the nanoparticles in the range 315 to 900nm, showing these nanoparticles being blue-shifted as compared to bulk ZnS for which the peak is at 340 nm. The blue shift in the absorption edge is due to the quantum confinement of the excitons present in the samples, resulting in a more discrete energy spectrum of the individual nanoparticles. The effect of the quantum confinement on impurity depends upon the size of the host crystal. As the size of the host crystal decreases, the degree of confinement and its effect increases [18].

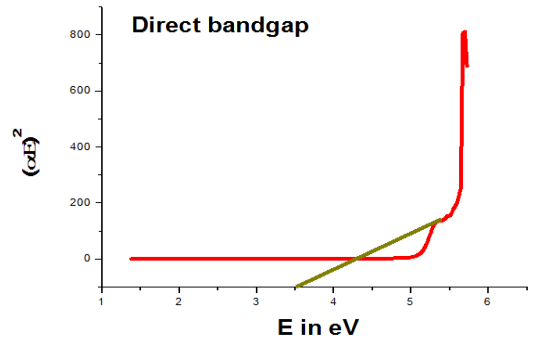

Figure 4: Direct Bandgap for Sample B

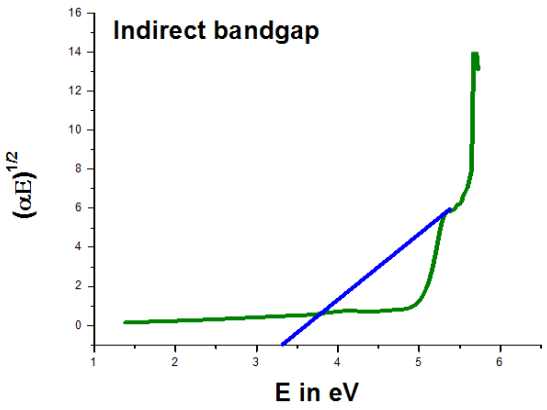

Figure 5: Direct Bandgap for Sample B

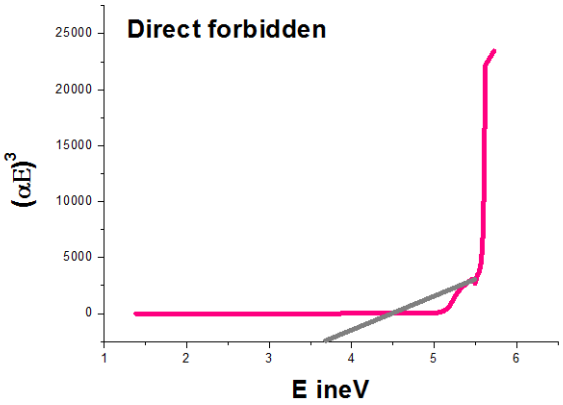

Figure 6: Direct Bandgap for Sample C

On doping Mn in the ZnS nanoparticles, the blue shift further increases, which might be due to the fact Mn forming new energy levels in the ZnS energy band. The obtained band gap and particle size values for different samples are shown in Table 2.

Table 2: Bandgap values in the Zn_{1-x} Mn_x S nanoparticles

S. No	Mn Concentrations (%)	Avg. Crystallite size (nm)	Direct band gap (eV)
1	2	0.6483	3.5513
2	4	1.3522	3.4169
3	6	2.0837	3.2647

From the table, it is clear that the values of optical band gap decreases with the increase in the particle size.

Morphological Studies

In order to study micro-structural surface topography, SEM images have been obtained for Mn- ZnS nanomaterials: Fig. 7 (resp. Fig. 8 & 9) represent micrographs of the surface of the sample prepared from 2% to 6% of Mn dopant. These micrographs reveal that the ZnS thin films grow following the cluster by cluster deposition process. We note the high compactness of these films which are continuous and homogeneous.

Dispersed spherical structures are observed. These nano-sized particles are around 10 nm size in the case of films prepared from 2% of Mn. The surface of films grown with 4 & 6% of Mn displays a smoother and

more homogeneous surface than that prepared from sample A.

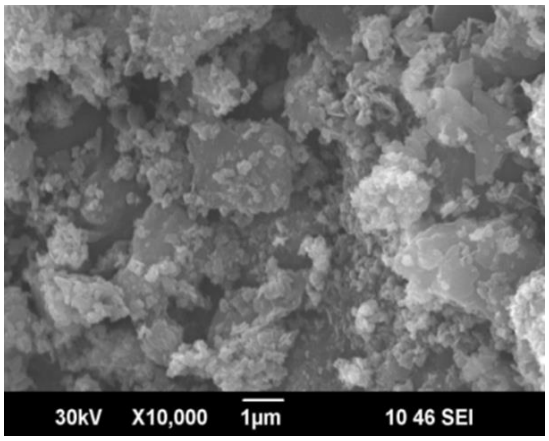

Figure 7: SEM image of Sample A

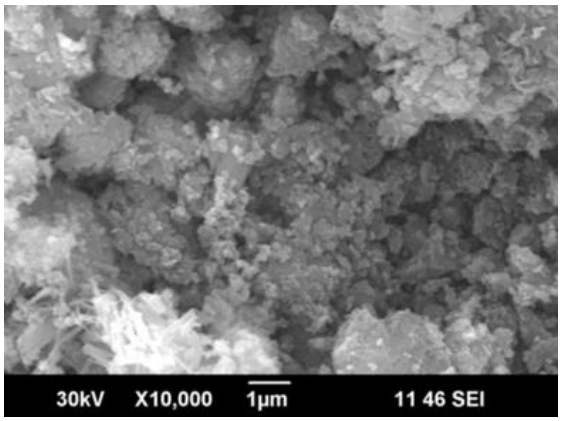

Figure 8: SEM image of Sample B

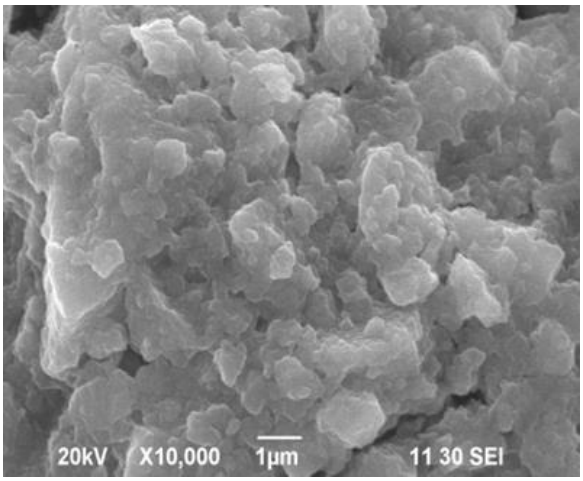

Figure 9: SEM image of Sample C

IV. CONCLUSION

In the present study, Mn doped ZnS ($Zn_{1-x}Mn_xS$) nanoparticles with x= 2%, 4%, 6% have been synthesized successfully through chemical co-pricipitation method. Structural analysis indicates that the Mn doped ZnS nanoparticles crystallize in a cubic structure without forming other secondary phases. The optical studies show the quantum confinement effects in (Zn1-xMnxS) nanoparticles. The present studies demonstrate that very small doping of Ni in ZnS nanoparticles gives rise to room-temperature ferromagnetic ordering which may be useful for spintronic applications.

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