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CHARACTERIZATION OF CHEMICALLY SYNTHESIZED Mn DOPED ZnS NANOPARTICLES

RUBY CHAUHAN[a,b], ASHAVANI KUMAR[c*], RAM PAL CHAUDHARY[a]
[a]*Department of Chemistry, Sant Longowal Institute of Engg. & Tech. Longowal 148 106 India*
[b]*Technology Education and Research Integrated Institutions, Kurukshetra 136 119 India*
[c]*Department of Physics, National Institute of Technology, Kurukshetra 136 119 India*

Nanoparticles of undoped and manganese doped zinc sulphide ($Zn_{1-x}Mn_xS$, where x = 0.00, 0.03, 0.05 and 0.10) were synthesized by chemical precipitation method. Structural characterization of as synthesized semiconductor nanoparticles were performed by X ray diffraction pattern (XRD) while optical characterization were done by UV-Visible absorption spectroscopy. XRD pattern showed that the synthesized Mn doped ZnS nanoparticles have cubic structure with 3-4 nm average crystallite size. Optical absorption measurements indicated red shift in the absorption band edge upon Mn doping. Direct allowed band gap of undoped and Mn- doped ZnS nanoparticles measured by UV-VIS spectro-photometer were 2.95 to 2.85 eV at 400^oC.

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1. Introduction

Semiconducting nanomaterials have been the key drivers for the growing interest in nano science and technology. Nanoparticles attracted considerable attention in recent years because of their special properties, such as quantum size effects [1−2] and abnormal luminescence phenomenon [3−5]. ZnS is II-VI compound semiconductor with direct and wide band gap of 3.68 eV at room temperature and widely used as a phosphor in optical devices [6-10]. ZnS doped with Mn^{2+} has a potential application in field emission devices (FED) [11]. The band structure of the semiconductor changes with decreasing particle size. ZnS particles have two kinds of structures: zinc blende structure (cubic crystal) and wurtzite structure (hexahedron). ZnS applied in luminescent materials generally has zinc blende structure [12].

There are many methods to prepare ZnS nanoparticles; those can be divided into two categories; physical and chemical methods. The chemical method mainly includes thermal decomposition, micro-emulsion, sol-gel, precipitation and LB techniques. However, these techniques need high reaction temperature, vast use of organic solvents, high cost of equipment operation, and complex process control. In most cases, particles prepared by these methods are of poor uniformity and agglomerate easily [13−14]. Xu et al. [15] succeeded in preparing ZnS nanoparticles by reaction of Zn nanoparticles and Na_2S solution. However, the products are low purity.

In this paper the preparation of Mn doped ZnS nanoparticles were synthesizes by chemical precipitation method using a polyethylene glycol as a capping agent and discussed the structural and optical properties of the prepared nanoparticles.

*Corresponding author: ashavani@yahoo.com

2. Experimental

Chemicals:

For the preparation of undoped and Mn-doped ZnS nanoparticles, the materials used were zinc sulphate [M=288, $ZnSO_4.7H_2O$], manganese sulphate [M=169.6, $MnSO_4.H_2O$], sodium sulphide [M=78, Na_2S] and polyethylene glycol [M=6000, OH $(OCH_2CH_2)_n$ H; PEG]. All chemicals used were AR grade from Sigma Aldrich and used without further purification.

Synthesis:

Mn doped zinc sulphide ($Zn_{1-x}Mn_xS$, where x = 0.00 to 0.10) were synthesized by chemical 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 calcined at 400 ^oC in muffle furnace.

Characterization:

X-ray Diffraction (XRD) patterns were recorded on a Rigaku mini desktop diffractometer using graphite filtered CuK_α radiation (λ = 1.54 Å) at 40 KV and 100 mA with a scanning rate of 3 degree per minute (from $2\theta = 20^o$ to 80^o). Optical absorption spectra were recorded on a Shimadzu double beam double monochromator spectrophotometer (UV-2550), equipped with an integrated sphere assembly ISR-240A in the range of 190 to 900 nm.

3. Results and discussion

X-ray diffraction studies: Fig. 1 shows the XRD diffraction patterns of undoped and Mn doped zinc sulphide ($Zn_{1-x}Mn_xS$, where x = 0.00, 0.03, 0.05 and 0.1) powder samples at 400 ^oC temperature indicating that all the samples were composed of cubic phase. The XRD pattern of annealed samples at 400 ^oC exhibit peaks at (2θ) values of 28.9^o, 48.1^o and 57.1^o which could be indexed to scattering from (111), (220) and (311) planes. The measured d-spacing 3.08, 1.88, and 1.61 Å correspond to the reflection from (111), (220) and (311) crystal planes of the cubic structure.

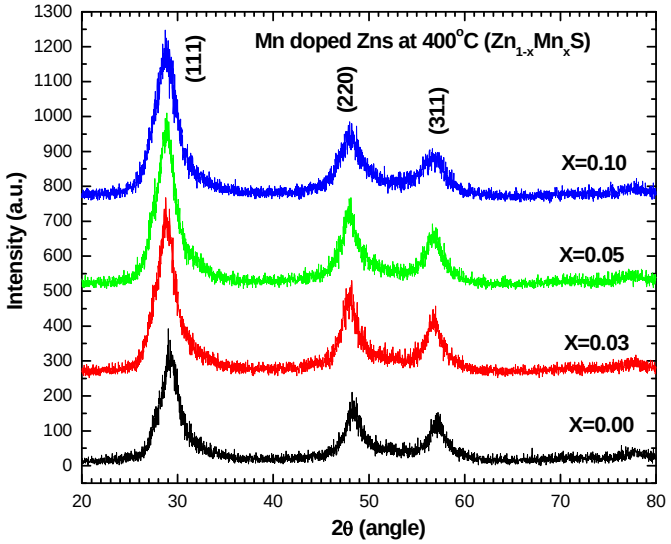

Fig. 1 XRD patterns of Undoped and Mn-doped ZnS nanoparticles calcined at 400 ^oC with PEG.

All the diffraction peaks agreed with the reported JCPDS card no. 80-0020. X-ray diffraction data reveals that the diffraction peak of $Zn_{1-x}Mn_xS$ at (111) plane shifts to lower angle and lattice constant increases with increasing manganese concentration, which is due to the replacement of Mn ions with ionic radii 0.66 Å with smaller ionic radii Zn ions of 0.60 Å in the

host lattice. No additional peaks corresponding to the secondary phases of manganese sulphide were obtained for x = 0.00 to 0.10 at 300 ^{o}C, which indicates that the cubic structure is not disturbed by the Mn addition. Due to size effect, XRD peaks were broadened and their width become larger as the particle becomes smaller. The mean crystalline size was calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherrer formula:

$$D_{h,k,l} = 0.9\lambda / (\beta_{h,k,l}\cos\theta)$$

where D is the average crystalline diameter, λ is the wave-length in angstrom, β is the line width at half–maximum and θ is the Bragg angle. We used the most intense peak (111) in the XRD patterns to calculate the average crystalline size. It can be seen that the average size of nanoparticles decreases as the doping percentage manganese metal is increased. This is due to the change of growth rate between different crystallographic planes. The calculated values of particles size are presented in Table 1 for undoped and Mn doped (3-10%) ZnS at 400 ^{o}C. The particles size are in the range of 3 to 4 nm at 400 ^{o}C corresponding to the $Zn_{1-x}Mn_xS$(x = 0.0 to 0.1) nanoparticles respectively.

Table 1. Size of undoped and Mn doped ZnS nanoparticles with various doping concentration at 400 ^{o}C.

% doping of Mn	Average size of particles for sample annealed at temperature 400 ^{o}C (nm)
0 %	4
3 %	3
5 %	3
10 %	2

Optical studies

The optical absorption spectra of undoped and Mn-doped zinc sulphide ($Zn_{1-x}Mn_xS$ where, x = 0.00, 0.03, 0.05, 0.10) samples at 400^{o}C by a UV-Vis spectrophotometer in the range of 200 to 800 nm are presented in fig. 2. It can be seen that the strongest absorption peak of as prepared sample appears at around 300 nm, which is fairly blue-shifted from the absorption edge of the bulk ZnS (345 nm). ZnS has good absorption for light in the wavelength range of 220-350 nm [16]. The absorption edge shifted towards the longer wavelength side in Mn-doped ZnS nanoparticles.

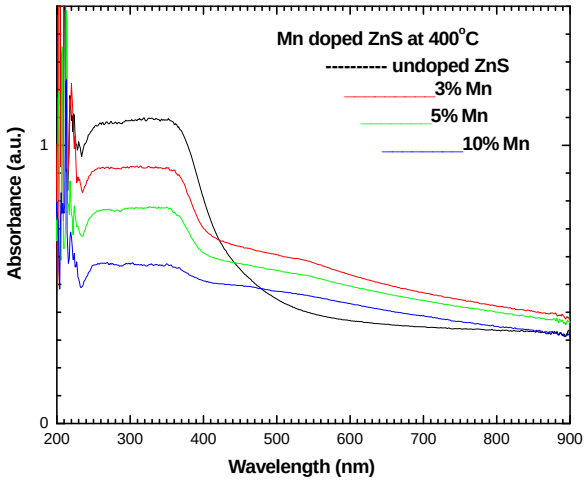

Fig.2 Optical absorption spectra of undoped and 3, 5, 10% Mn-doped ZnS nanoparticles calcined at 400 °C.

A small red shift indicated the decrease of band gap energies for Mn doped ZnS powders. Manifacier model is used to determine the absorption coefficient from the absorbance data [17]. The fundamental absorption which corresponds to the transmission from valance band to conduction band is employed to determine the band gap of the material. The direct band gap energy can be estimated from a plot of $(\alpha h\nu)^2$ versus photon energy (hν). The energy gap was determined by using the relationship:

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

where hν= photon energy, α= absorption coefficient ($\alpha = 4\pi k/\lambda$; k is the absorption index or absorbance, λ is the wavelength in nm), E_g = energy band gap, A=constant, n=1/2 for the allowed direct band gap. The exponent n depends on the type of transition and it may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively [18]. The value of band gap was determined by extrapolating the straight line portion of $(\alpha h\nu)^2 = 0$ axis; as shown in fig. 3 at a temperature of 400 °C. The plots of $(\alpha h\nu)^2$ versus hν are presented in Fig. 3. The intercept of the tangent to the plot will give a good approximation of the direct band gap energies of the samples. The band gap energies of undoped and Mn-doped ZnS powders calcined at 400 °C were depicted in Table 2. The band gap decreases from 2.95 eV to 2.85 eV with manganese (3, 5, 10 %) doping at temperature 400 °C.

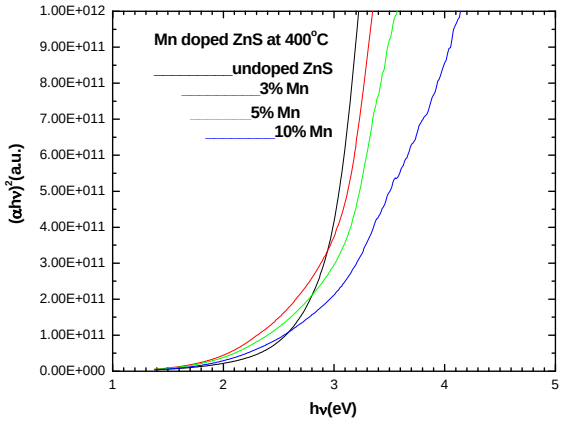

Fig. 3 $(\alpha h\nu)^2$ vs. photon energy (hν) for undoped and 3, 5, 10% Mn-doped ZnS nanoparticles calcined at 400°C.

Table 2. The energy band gap values of undoped and Mn-doped ZnS nanoparticles with various doping concentration at 400 ^{o}C.

% doping of Mn	Band gap for sample annealed at temperature 400 ^{o}C (eV)
0 %	2.95
3 %	2.95
5 %	2.90
10 %	2.85

4. Conclusion

Chemical Precipitation method was successfully used for the preparation of Mn doped ZnS nanoparticles. The XRD pattern of Mn doped ZnS nanoparticles showed that the materials are of the nanometric size regime with a cubic phase and are to be of the order of 3-4 nm. The band gap values of as prepared Mn-doped ZnS samples were found to decrease as compared to undoped ZnS.

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