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Investigation of Structural and Spectroscopic Behaviour of Fe^{2+} Substituted ZnS Nanostructures

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Abstract: *Pure ZnS and Fe^{2+} based ZnS semiconducting nanostructures have been produced by a simple chemical precipitation process using their acetate salts and sodium sulphide in the presence of N-N dimethyl Formamide as the reaction catalyst. The structure and optical behaviour of synthesized nanostructures have been investigated by means of XRD and diffused reflectance spectra. X-ray diffraction analysis confirms cubic zinc blend phase with no any secondary phase for pure and Fe^{2+} incorporated ZnS nanocrystals. The average crystallite size as computed to be around 3.8-4.7 nm range. The crystallite size shows decrement due to the substitution of Fe^{2+} impurity ions. Diffused reflectance spectra show increment in the optical band gap from 3.83- 4.0 eV as the doping concentration of Fe^{2+} increase*

Keywords: ZnS:Fe, chemical precipitation, XRD, DRS, Optical band gap, refractive index

I. INTRODUCTION

Zinc sulphide is a large band gap, 3.7-3.9 eV range II-VI semiconductor, extensively studied due to its elementary physical properties, versatility, non-toxicity, chemical stability and huge potential for variety of scientific use. ZnS is frequently applied in various optical devices such as UV LEDs, flat panel display, optical sensors, lasers, photodectors, solar cells, photovoltaic devices, optical fibres, electroluminescence devices and field emission [1]. Band gap is one of the major and key features of the semiconductor material which play an elemental job in electrical and optical features of semiconductor material [2]. Doped semiconductors have been comprehensively investigated during recent decades. The optical behaviour can be tuned as a result of quantum confinement effect, which efficiently escort to a size dependent discrepancy of band gap energy [3]. ZnS has been doped with different metals, transition metals, rare earth metals to manage its electrical, optical and magnetic behaviour. ZnS incorporated with Fe^{2+} provides excellent optical and magnetic features [4]. The refractive index is one of the key aspects of a material as it is directly related to the electronic polarizability of ions and the local field inside the material. The estimation of refractive indices of semiconductors is of significant value for use in integrated optic devices, where refractive index of the material is the key factor for device design. The refractive index and the energy gap of semiconductors signify two basic physical features that describe their optical and electronic behaviour [5-6].

In view of the above discussion, we report the synthesis, structural and optical behaviour of Fe^{2+} included ZnS nanoparticles in this paper by altering impurity content. Our main purpose is to investigate the influence of Fe^{2+} incorporation on the structural and optical behaviour of ZnS nanocrystals produced by a simple and low cost chemical precipitation route. The synthesized samples have been characterized by XRD, and UV-Visible DRS Spectrometer.

II. MATERIALS AND METHODS

Experimental:

Pure and Fe^{2+} incorporated ZnS nanocrystals have been produced by a chemical precipitation process, using zinc acetate [$(CH_3COO)_2$ Zn, $2H_2O$] (extra pure Merck) as the zinc source, Ferrous sulphate [$FeSO_4$, $7H_2O$] (Merck) as the impurity material and sodium sulphide [Na_2S, H_2O] (extra pure Loba Chemie) used as the sulphur source in this reaction. DMF, $(CH_3)_2NC(O)H$ (Merck) has been used as a stabilizer and also the reaction catalyst. All the chemicals

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used in this reaction were of analytical reagent (AR) grade obtained commercially and used as obtained with no additional decontamination. The double distilled water was used for solution preparation in this reaction throughout the experiment.

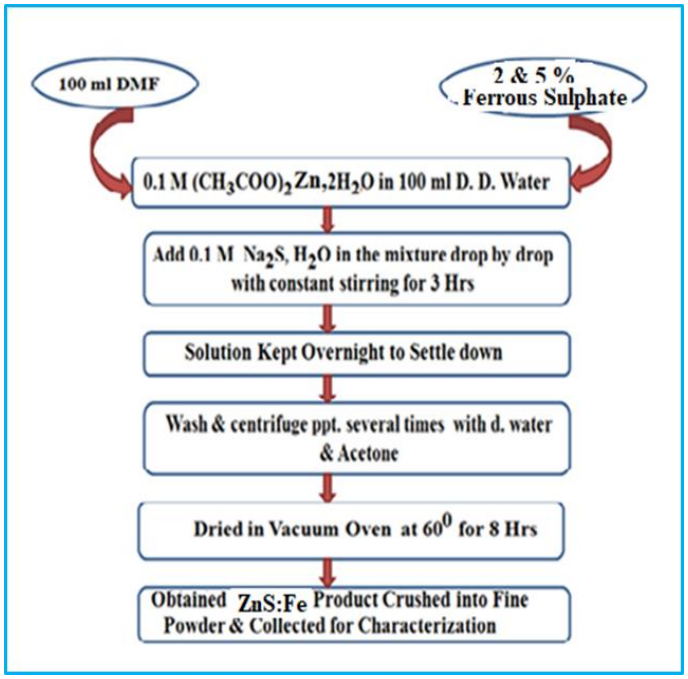

Figure 1: Flowchart of the synthesis of ZnS:Fe Nanoparticles

ZnS:Fe powder samples were obtained by the chemical route using their acetate salts. The process involved is as follows. First, 0.1 M zinc acetate [Zn^{2+}] solution was made by dissolving zinc acetate in 100 ml double distilled water and 0.1 M sodium sulphide [S^{2-}] was also made in 100 ml double distilled water separately. Then 2 and 5 at % ferrous sulphate [$FeSO_4$, $7H_2O$] was simply added to zinc acetate solution with continuous stirring by magnetic stirrer to mix the solution. Then appropriate amount of DMF is added in the mixture and stir for 20 minutes. Afterwards, 100 ml sodium sulphide solution was inserted in the mixture drop wise with continuous stirring for 4 Hours. The resulting solution was kept for settled down to form the precipitate overnight. The precipitate so formed was isolated by centrifugation, washed several times with double distilled water and finally with acetone to remove any impurities and dried in vacuum oven at 60 ^{0}C for 8 H. The samples then crushed into a fine powder and then collected in a sample bottle for the characterizations. Pure ZnS sample also have been produced by the same procedure without impurity material.

Characterization of ZnS:Fe nanoparticles

The structural investigation of ZnS and ZnS:Fe nanocrystals were carried out using X-ray powder diffractometer (Model: D-8 Advance) with CuKα radiation (λ = 0.15406 nm) scanning 2θ in the range 10^0- 80^0. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.1541 nm. The X-rays were identified using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). UV-Vis diffused reflectance spectra were recorded using double beam UV-Vis-NIR spectrometer, Make: Perkin Elmer, USA; Model: Lambda 950.

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III. RESULTS AND DISCUSSION

X-ray diffraction:

XRD is a non-destructive method exploited to characterize the phase and structure of the nanoparticles. The X-ray diffraction pattern for pure and Fe^{2+} included ZnS nanocrystals with varying Fe^{2+} (2 & 5 %) content at room temperature are presented in Figure 2.

The outcome of Fe^{2+} ions in ZnS crystal structure can be analyzed by studying the result of XRD pattern for pure ZnS and incorporated with Fe^{2+} ions. Figure-2 shows XRD pattern of pure and Fe^{2+} substituted ZnS, shows three key diffraction peaks at 2θ values around 2θ = 28.87°, 48.03°, & 56.81°, which corresponds to the reflections from (111), (220) and (311) crystal planes reveals the products so produced exhibited cubic (zinc blend) lattice structure for the prepared samples which matches very well with the standard **JCPDS** database **(80-0020)**, confirms the purity of the ZnS sample The highest intense peak of the synthesized products at 2θ = 28.87° is the characteristics of cubic (111) plane [7].

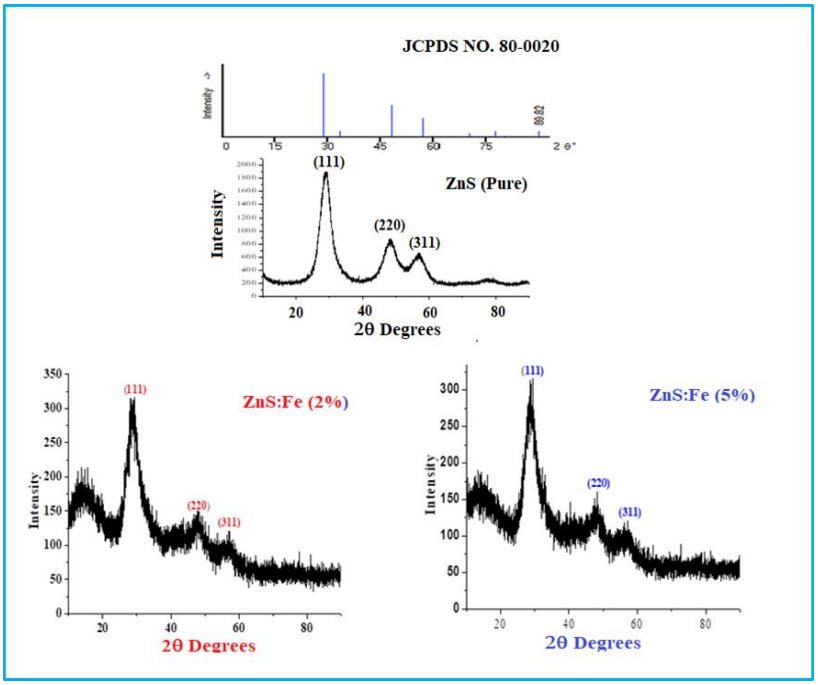

Figure 2: XRD pattern of ZnS and ZnS:Fe nanoparticles

Fe^{2+} impurity did not contribute any other diffraction peaks due to substitution of Fe^{2+} impurity to ZnS host, which confirms the highest purity of synthesized samples. Moreover, the cubic phase of ZnS host remains unaltered due to Fe^{2+} inclusion. The broadening of XRD peaks indicates the nanodimensional development of the particles. The mean crystallite size for the products has been evaluated applying Debye-Scherer formula [8-9] for (111) reflection in the X-ray diffraction pattern based on Full Width at Half Maximum (FWHM).

$$D = \frac{0.9\,\lambda}{\beta\,cos\theta} \qquad (1)$$

Where λ = 0.1541 nm is the wavelength of X-ray diffraction, β is the FWHM in radian of the highest intensity peaks and θ is the Bragg's angle.

The average crystallite size of the as-prepared samples estimated using Debye-Scherer formula decreases with the addition of Fe impurity and found to be lying in the range of 3 - 5 nm

The lattice parameter **'a'** for ZnS and ZnS: Fe nanoparticles has been computed using [10] equation 2

$$a = \frac{\lambda}{2sin\theta} \times \sqrt{h^2 + k^2 + l^2}\ \text{Å} \qquad (2)$$

The d-spacing for cubic system for $2\theta_{(111)}$ has been computed by using [11] equation 3

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$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \text{ Å} \quad (3)$$

The microstrain determined using [12] equation 4

$$\varepsilon = \frac{\beta cos\theta}{4} \quad 4)$$

The dislocation density (δ), defined as the length of dislocaton lines per unit volume has been estimated using [12] equation 5

$$\delta = \frac{1}{D^2} \quad (5)$$

The calculated structural parameters of the prepared products are tabulated in Table 1

Samples	Peak position $2\theta_{(111)}$ (degree)	FWHM β (degree)	Particle Size D (nm)	Lattice parameter (a) Å	Unit Cell Volume a^3	Micro strain (ε)	Dislocation Density (δ) (10^{-14} lines/cm^2)	d spacing A^0 for $2\theta_{(111)}$
ZnS (Pure)	28.80	1.7570	4.7	5.3659	154.5	0.4255	0.0453	3.0981
ZnS:Fe (2%)	28.49	2.1525	3.8	5.4072	158.1	0.5215	0.0688	3.1217
ZnS:Fe (5%)	28. 77	1.9724	4.16	5.3723	155.1	0.4776	0.0577	3.1016

Table 1: Structural parameters of ZnS and ZnS:Fe nanoparticles

Optical analysis of ZnS and ZnS:Fe nanoparticles

To inspect the optical performance of the semiconducting nanomaterials, a versatile technique diffused reflectance spectroscopy have been employed. The most spectacular characteristic of semiconductor nanocrystals that can potentially be estimated from the diffused reflectance is the optical band gap energy.

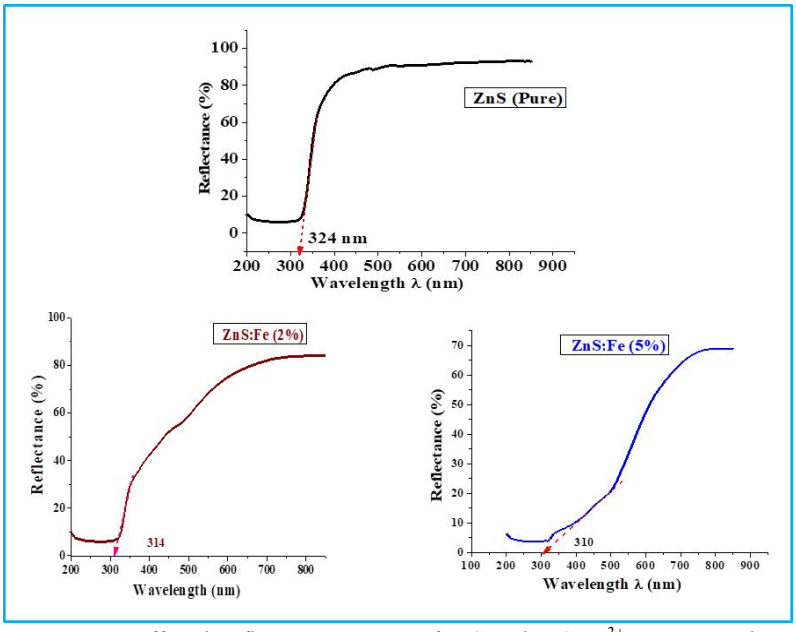

Figure 4: Diffused Reflectance spectra of ZnS and ZnS:Fe^{2+} Nanoparticles

According to quantum confinement theory, electrons in the conduction band and the holes in the valence band are spatially confined by the potential barrier up to the surface which effectively increases the energy separation between

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the valence and the conduction band increasing the energy value of optical transition [13]. The DRS spectra of pure and Fe^{2+} included ZnS samples measured over the spectral region 200-850 nm with respect to $BaSO_4$ as the reference sample is presented in Figure 3. From the DRS spectra, the reflectance has been seen to be reduces slightly in comparison with the pure sample with the enhancement of doping quantity.

The DRS spectra are slightly shifted to the inferior wavelength section. Pure ZnS shows band edge absorption at 324 nm. Due to the inclusion of Fe^{2+} impurity content (2 & 5%) undoubtedly. the band edge absorption swing to inferior wavelength section with respect to pure ZnS sample from 324 nm to 314 nm. The absorption edge of the material shows blue shift with respect bulk ZnS (334 nm) [13] due to quantum confinement impact. Furthermore, quantum confinement effect takes place owing to the reduction in particle size with respect to the bulk materials which modify the band gap values.

Values of the optical band gap for the products have been estimated with the help of diffused reflectance spectra (DRS) employing the Einstein's well known energy wavelength equation [14-15]

$$Eg = \frac{hc}{\lambda} \text{ eV} \qquad (6)$$

The values of optical band gap for pure and Fe^{2+} included ZnS has been estimated to be 3.83 eV and 3.89 eV respectively. The estimated values of the optical band gap show increment in its values due to the inclusion of Fe^{2+} quantity. The optical band gap value enhances due to the substitution of Fe^{2+} impurity ions, resulting in to the reduction in particle size as a result of the quantum confinement cause.

The particle radius of the samples is determined using the mathematical model of effective mass approximation [16] according equation 7.

$$r(E) = \frac{0.3\ 2\text{-}2.9\sqrt{E-3.49}}{2(3.5\ 0\text{-}E)} \text{ nm} \qquad (7)$$

Where, r is the particle radius (2r is the diameter and hence the particle size) and E is the optical band gap energy. The optical band gap and the average particle size of pure and Fe^{2+} inserted ZnS nanostructures have been estimated using equation (6) and (7) and are summarized in Table 2.

Refractive Index (n):

Refractive index is one of the fundamental and key physical parameters to study II-VI and III-V sets of semiconductors. The evaluation of refractive indices of semiconductors is of giant significance for prospective relevance in integrated optical devices for instance switches, filters and modulators, while refractive index of materials is the crucial parameter to design a range of devices. Energy band gap may be the largely imperative one among the variety of factors controlling the refractive index, accordingly, to enlarge a correspondence between refractive index and the energy gap in solid materials is of enormous importance. These materials, predominantly semiconductors, have potential applications in the field of light emitting diodes (LEDs), photo-detectors (PDs), laser diodes (LDs) optoelectronic devices and integrated circuits and currently in nanotechnology and biotechnology [17-18]. The refractive indexes of the synthesized products are estimated according to Herve and Vandamme [19] relation and are summarized in table 2.

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \qquad (8)$$

Where A = 13.6 eV and B = 3.4 eV, n = refractive index and E_g = band gap energy

Table 2: Optical parameters of ZnS and ZnS: Fe^{2+} samples.

Samples	Absorption edge λ (nm)	Band gap Eg (eV)	Particle size (nm)	Refractive Index (n)
ZnS	324	3.83	4.12	2.1301
ZnS:Fe(2%)	314	3.95	3.66	2.1032
ZnS:Fe(5%)	310	4.0	3.50	2.0922

The band gap values summarized in the above Table 2 are greater than the bulk band gap of ZnS (3.7 eV) on account of quantum confinement impact. Refractive index decreases due to insertion of impurity content.

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IV. CONCLUSION

ZnS and ZnS:Fe nanoparticles were synthesized fruitfully by a very simple and efficient chemical precipitation process. The structural study done through XRD exhibits cubic phase crystal structure for the synthesized materials and no any additional peaks of Fe^{2+} impurity were contributed. The crystallite sizes of the prepared material estimated reveals decreasing trend with the inclusion of Fe^{2+} impurity ions. The UV-Visible DRS spectrum reveals enhancement in the optical band gap of the prepared samples with Fe^{2+} impurity concentration due to quantum confinement effect. The refractive index exhibits slight decrease in its value as the concentration of Fe^{2+} enhances. Thus the prepared material has a good potential to be used in solar cells and optoelectronic devices applications.

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