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Original Research Paper

Study of Optical band gap and microstrain of ZnS nanomaterials prepared by CBD method.

PHYSICS

KEYWORDS: ZnS nanoparticle; X-ray diffraction, Microstrain, Optical bandgap, Doping etc.

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ABSTRACT

We report synthesis and study of optical band gap and microstrain of undoped (ZnS)and doped ZnS nanoparticles prepared by CBD method at 0.0125 M. The prepared nanoparticles are characterised by X-ray diffraction, UV absorption and Transmission Electron Microscopy techniques. The dopant is Fe and doping concentrations are 6 % (ZNS-Fe-6%) and 8 % (ZNS-Fe-8%). The average particle sizes are found to be of the order of 4 nm, 3 nm and 4 nm for ZnS, ZNS-Fe-6% and ZNS-Fe-8%. The microstrains associated with the nanoparticles are found to be 3.13 X 10 -2, 1.5 X 10 -3 and 1.8 X 10 -3 for ZnS, ZNS-Fe-6% and ZNS-Fe-8% doped by Fe. The decreased value of microstrain may be attributed to the decrease in defect density of the nanomaterials after doping. The value of microstrains for ZNS-Fe-6% and ZNS- Fe-8% are almost equal. Which suggests that when doping concentration is increased from 6% to 8%, the structure of ZnS nanoparticles is almost remain same. The values of optical band gap for ZNS-Fe-6% and ZNS-Fe-8% are found to 3.35 eV which also suggests that the structures of both the doped nanoparticles are almost same.

Introduction: Synthesizing nanometer sized semiconductor particles that exhibit size dependent optical and electrical properties which are not shown by their bulk counterparts have attracted much interest from both fundamental and technical researchers. ZnS is prototypical II-IV semiconductor. ZnS exists in two main crystalline form. In each form, the coordination geometry at Zn and S is tetrahedral. The more stable cubic form is known also as zinc blende, or sphalerite.[1-2] The hexagonal form is known as the mineral wurtzite. Both sphalerite and wurtziteare intrinsic, wide bandgap semiconductor. Zinc blende(cubic form) has a band gap of about 3.54 electron volts (eV) at 300 kelvin, but the wurtzite (hexagonal form) has a band gap of about 3.91electronvolts. ZnS is a intrinsic semiconductor and both can be doped as either in n-type or p-type semiconductor [3-4]. ZnS is widely used as a phosphor in optical devices due to its wide band gap of 3.68 eV at room temperature. II-VI groups of semiconductors exhibit interesting size-tunable optical properties due to the strong quantum confinement effect[3, 5-7]. Doped nanometerials are largely studied because their widespread applications in various devices such as solar cells, sensors, optical communication, colour television, light emitting diodes, IR detectors etc [8-9].

This paper reports a simple route for the preparation of undopedZnSand Fe doped nanoparticles by chemical bath deposition method in the presence of polyethylene glycol (PEG) as capping agent [10]. Then the undopedZnS nanoparticles are characterized by the X- ray diffraction.

The mean crystalline size was calculated from the full-width at half maximum (FWHM) of XRD lines by using the Scherrer's equation.

2 Experimental

2.1 CHEMICAL

For the preparation of undopedZnS Fe doped ZnSnanoparticles, the chemical used were polyethylene glycol {M=6000 to 7000 g/mol, $HO(C_2H_4O)_nH$; PEG}, Zinc sulphate { M = 287.54,

$ZnSO_4.7H_2O$}, Sodium sulphide {M=240.18, $Na_2S.9H_2O$}ferrous sulphate { M= 278,

$FeSO_4.7H_2O$}.All chemicals used were from Thermo fisher Scientific India Pvt. Ltd. And used without further purification.

2.2 Synthesis

Nanoparticles of Fe doped ZnS were prepared by chemical bath deposition method.($Zn_{1-X}Fe_xS$)

Freshly prepared aqueous solutions of chemicals were used for the synthesis of nanoparticles.

0.125 M Zinc sulphate,0.125M ferrous sulphate and 0.125 M sodium sulphide were used as reactant materials. Zincsulphate of 0.125 M and ferrous sulphate of 0.125M were mixed with 50mldeionized water using magnetic stirring at about 70 ^{0}C. then 50ml of mixed 0.125M sodium sulphate was mixed drop by drop on it using vigorous stirring at 70^{0}C. Before adding ferrous sulphate to 50ml water we add sulphuric acid .5ml to prevent ferric ion, and then added 05g of polyethylene glycol as capping agent. Before mixing pH ofall the solution are measured by the pH meter. After the completion of reaction , the mixed solution was allowed to settle for sometimes and the supernatant solution was then separated carefully. Then the solution was filtered and washed several times with deionized water. The wet precipitate was dried in oven at 80 ^{0}C.

2.3 Characterization

The X-ray diffraction (XRD) patterns were recorded on a fully automated computerized powder x-ray diffractometer of Model X'Pert Pro, make PANalytical, x-ray tube: Cu.

The diffraction patterrns of undoped (ZnS) and doped ZnS with Fe 6 % (ZnS-Fe-6%) and with 8% (ZnS-Fe-8%) are shown in the Fig. 1. The diffraction patterns of ZnS is matched with the ICDD card No. 80-0020.

The structure of ZnS nanoparticles is cubic in nature. The peaks are obtained at 28.91°,

48.11 $^\circ$, 57.10° ,70.41 $^\circ$, 77.83 $^\circ$ 2ø which are indexed as (*111*), (*220*), (*311*), (*400*), (*331*) respectively.

The peak centre of ZnS-Fe-6% and ZnS-Fe-8% samples which are doped with Fe by 6% and 8% are slightly changed which may be due to the insertion Fe sites. An additional peak is observed around 23° 2ø in these two samples which is the contribution from Fe_2O_3 present in the sample.

The particle sizes are calculated using the Scherrer's equation (Eq. No. 1) [11] which are found to be of the order of 4 nm, 3 nm and 4 nm for ZnS, ZnS-Fe-6% and ZnS-Fe-8% respectively.

$$D = k\ddot{e}/\hat{a}\cos\theta \qquad (1)$$

Where, D is the particle size, k is a constant whose values is 0.89 for spherical shape of particle,

ë is the wavelength and â is the FWHM of the diffraction peak. The Scherrer's equation gives a rough estimate of particle size which mainly calculated from the width (FWHM) of the diffraction peak. The width of the diffraction peak is affected by various effects viz.

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particle size, microstrain etc.

To separate the size effect and strain effect we have used the Williamson-Hall method (W-H) (Eq. 2) [12].âcosθ =4î sinθ + kë/D (2)

Where â is the is the FWHM of the diffraction peak, î is the microstrain associated to the nanomaterials, k is a constant, ë is the wavelength and D is the particle size.

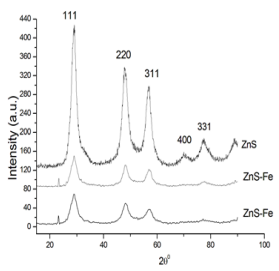

Fig. 1. Diffraction pattern of unoped and doped nanoparticles

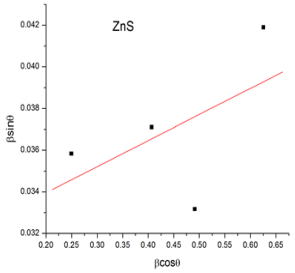

Fig. 2. W-H plot undopedZnS nanoparticles

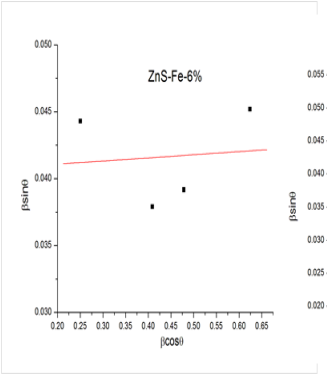

Fig. 3 W-H plot doped ZnS (ZnS-Fe-6%)

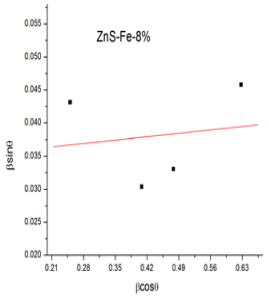

Fig. 4. W-H plot of doped ZnS (ZnS-Fe-8%)

W-H plot of the three samples are shown in Fig.2, Fig.3 and Fig.4. The average particle sizes obtained from W-H plot are found to be of the order of 6 nm, 4 nm and 5 nm for ZnS, ZNS-Fe- 6% and ZNS-Fe-8%.

The average particle sizes obtained by Scherrer's equation for all the samples are greater than that of obtained from W-H Plot. This is due to the fact that broadening of diffraction peaks are affected by size and strain affects. In the Scherrer's method the size and strain affect s are not separated but in the W-H method the size of the particles are measured after separating the stranafftect. The microstrains associated with the nanoparticles are found to be of the order of 3.13 X 10 -2, 1.5 X 10 -3 and 1.8 X 10 -3 for ZnS, ZNS-Fe-6% and ZNS-Fe- 8% respectively.

From the UV-vis-absorption spectrometer the wavelength and absorption are and the wavelength vs. absorbance graph of the ZnS nanoparticles doped with 6% of Fe (ZnS-Fe-6%) is shown in

Fig. 5a. The optical band gap of the ZnS nanoparticles doped with 6% of Fe (ZnS-Fe-6%) is calculated from the optical absorbance spectra by plotting a graph hυ versus (αhυ)2 for direct band gap (Fig. 5b). The optical band gap obtained from the plot of direct band gap is found to be

of the order of 3.35 eV. Similarly the direct band gap of ZnS-Fe-8% is also calculated and found to be of the order of 3.35 eV. The band gap of pureZnS nanoparticles obtained by UV- visabsoption technique is found to be of the order of 3.39 eV. The absorption spectra of pure ZnS nanoparticles are not shown in figure.

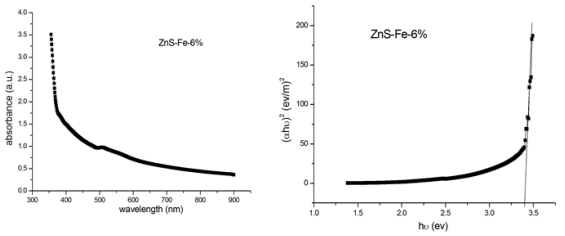

Fig. 5 (a) Absorbancespecra of ZnS –Fe 6% and (b) plot for Optical band Gap

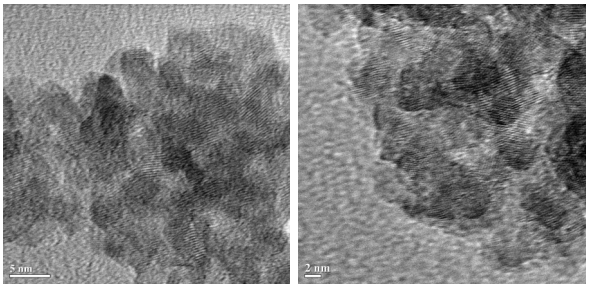

Fig. 6 (a) TEM image of ZnS-Fe-6% **(b)** TEM image of ZnS-Fe-8%

The TEM image of ZnS nanoparticles prepared with 6% Fe (ZnS-fe-6%) and 8% Fe (ZnS-Fe- 8%) are shown in Fig 6. From the TEM study it is found the particles sizes are found to be of the order of 6 nm and 3 nm respectively for the samples ZnS-Fe-6% and ZnS-Fe-8% . The sizes of the particles obtained from XRD and TEM are almost same which confirms that the nanoparticles are successfully prepared.

Conclusions : Fe doped and undopedZnS nanoparticles are successfully prepared. The crystalline nature of the nanoparticles are confirmed by XRD study. The average particle size of the nanoparticles are measured by XRD and TEM studies. The W-H method gives more accurate size of the nanoparticles as the strain associated with the nanoparticles can be separated by this method. The microstarin associated with the pure ZnS nanoparticles is greater than that of Fe doped ZNS nanopartiles.The optical band gap of the nanoparticles is measured with the UV- absorption techniques. The direct band gap of the ZnS-fe-6% and ZnS-fe-8% are found almost equal. This means that impurity level of the Fe dopped semiconductor (Fe-ZnS) is not changed in both 6% and 8% doping with Fe. The band gap of Fe doped ZnS semiconductor is greater than that of pure ZnS semiconductor. Thus the microstarin and band gap of the pure ZnS are decresedand increased respectively when it is doped with Fe.

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