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Microstructure and Optical Properties of Undoped and Ni-Doped ZnS Nanocrystalllites

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ABSTRACT

Wet Chemical Synthesis method was used to synthesis undoped and Ni doped ZnS. The as-prepared products were characterized using XRD, FE-SEM, UV-VIS and PL analysis. The crystal structures, morphologies and optical properties of as-prepared samples along with the particle size, micro strain and dislocation density have been investigated**.** The results exhibit a crystalline hexagonal structure in particles, rod shape size about 2nm and optical bandgap of 5.56 ev.

Introduction

In recent years, considerable efforts have been devoted to design and control fabrication of nanostructures materials with functional properties. Much attention has been devoted to synthesis of group Transition metal(TM) and rare earth (RE) doped II – VI semiconductor materials due to their excellent values in catalysis, optical devices, magnetic fields and spintronic devices.[1,2]. The electronic properties of nanosized ZnS are also strongly influenced by doping of transition and rare earth metals [3, 4].

Zinc sulphide (ZnS), a wide band gap II–VI compound semiconductor is very much promising material for its wide applications in electroluminescence and optoelectronic devices. Various chemical and physical techniques are employed to investigate the optical properties of nanocrystalline ZnS [5– 8]. The emission efficiency and thermal stability increased upon reduction of ZnS particle size [9–11]. The confinement of electrons within nano dimension leads to unusual behavior. The introduction of surface states with miniaturization of sample size also affects the electronic energy states of wide band gap semiconductor. In fact, by doping ZnS with different metal ions, novel characteristics, such as stable and tunable optical properties could be obtained [12-14]**.**

Various deposition techniques such as Hydrothermal method [15], solvothermal synthesis [16], Chemical bath deposition [17], successive ionic layer adsorption and reaction (SILAR) [18], molecular beam epitaxy (MBE) [19] and radio-frequency sputtering [20, 21] have been adopted for the fabrication of ZnS. The wet chemical synthesis (WCS) route is simple, low cost method and has a large scale production potential [22]. WCS can be successfully used to obtain uniform ZnS nanocrystalline powders at low temperature.

In this article undoped and Ni – doped ZnS nanocrystalline powders have been synthesized by WCS.

The average particle size, morphology, optical band gap and emission spectrum of the products have been examined using X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), UV–Visible absorption and photoluminescence (PL) studies, respectively.

Experimental

Materials

For the preparation of Undoped and Ni doped ZnS nanocrystalline powder the materials used are Analytical reagent grade chemicals: zinc acetate ($C_4H_6O_4Zn{\cdot}2H_2O$), nickel acetate ($Ni(CH_3CO_2)_2{\cdot}2H_2O$), sodium sulphide ($Na_2S.H_2O$), and polyvinyl pyrrolidone (PVP) [$(C_6H_9NO)n$] were used without further purification. Deionized water is used for all the preparation process.

Synthesis

ZnMnS nanocrystals have been synthesized using wet chemical co-precipitation method [23] for the synthesis of Eu3+ doped Cd1-**x**Zn**x**S quantum dots. All synthesis was carried out at room temperature in aqueous media for its inherent advantages of being simple and environmental friendly. Solutions of 0.3 M zinc acetate, 0.6 M sodium sulphide, and 0.001 M nickel acetate were prepared in separate beakers. Then zinc and nickel precursor solutions were mixed in the stoichiometric proportion under vigorous stirring, 4 ml of 2% PVP solution was added to total 50 ml volume, before drop wise addition of sulfur precursor. PVP will act as the capping agent to avoid the agglomeration of nanocrystals. The resulting precipitates were centrifuged and dried in oven for 4 to 6 h continuously.

Characterization

The crystal structure of the obtained undoped and Ni – doped ZnS nanocrystalline powders is examined by XRD

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using a XPERT PRO diffractometer. The morphology of the samples is observed by FE-SEM which is performed on a ZESIS.

Optical Absorption spectra of as-prepared samples are recorded with an UV scanning spectrophotometer (JASCO V-570) in the range 200–800 nm. The PL measurements have been carried out using a HORIBA JOBIN–YVON has been carried out using a HORIBA JOBIN–YVON Fluorolog at the excitation wavelength of 350 nm.

Result and Discussion

XRD Analysis

The crystalline phase and orientation of undoped and Ni – doped ZnS nanocrystalline powders have been studied by XRD pattern using the X-ray diffractometer which is shown in Fig. 1. The sharp and high intensity diffraction peaks imply good crystallinity of the samples. Figure 1a represents the XRD pattern for the sample (1:2 molar ratio of Zn and sulfur source). The diffraction peaks can be indexed to hexagonal structured with lattice constants a = b = 3.823 c= 68.728 which is in good agreement with the standard data from JCPDS Card 89 – 2144. Figure 1b represents the XRD pattern for the sample (1:2 molar ratio of Zn and sulfur source along with Nickel doped). The diffraction can be indexed to hexagonal structured with lattice constants a = b = 3.823 c = 62.480 which is in good agreement with standard data from JCPDS Card 89-2165.

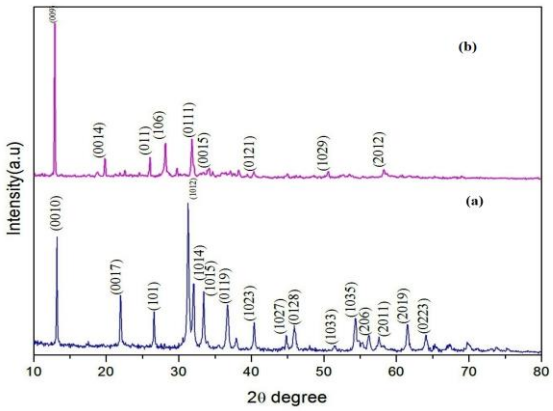

Figure 1. XRD Patterns of (a) Undoped ZnS, (b) Ni – doped ZnS.

The average crystallite size (D) from the XRD ray line broadening has been estimated using Scherrer equation [24]:

$$D = C\lambda / \beta_r \cos\theta$$

here, C is a constant whose value is typically between 0.89 and 0.90 of rod crystals; k is wavelength of incident X-ray beam (1.5406 A˚); β is the full width half maximum (FWHM) of the peak after correcting the peak broadening of the selected XRD reflection peak in radians and h is diffraction angle or Bragg's angle. Thus, the corrected peak broadening (β_r) may be represented as

$$\beta_r^2 = \beta_0^2 - \beta_i^2$$

where, β_0 is the observed peak broadening in radians; β_i is the broadening due to instrumental factors. The above conventional Scherrer method uses any one of the diffraction peak to calculate the crystallite size which gave considerably larger errors. In order to decrease the errors, we must use modified Scherrer formula that use all the diffraction peaks or any number of selected peaks to obtain the average crystallite size by using least squares method. To estimate more accurate crystallite size from XRD data by modified Scherrer equation [25] as follows

Taking logarithm on both sides of basic Scherrer formula:

$$\text{In}\ \beta_r = \text{In}(c\lambda / D.\cos\theta) = \text{In}(c\lambda / D.) + \text{In}(1+\text{In}\cos\theta)$$

The linear regression plot is obta*ined* from the results of In (β_r) against In (1/cosθ), then the single straight line through the points to give an intercept In(cλ/ D.)

The linear equation for Undoped ZnS is shown on the chart (Fig 2.a) is Y = 4.3528x-2.5719

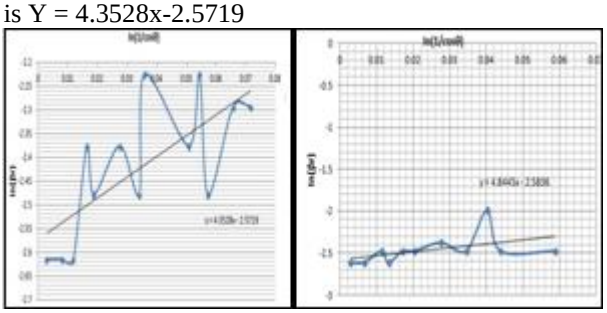

Figure 2. Linear plots of modified equation of (a) undoped ZnS & (b) Ni – doped ZnS

Finally the average nanocrystalline size of Undoped ZnS was calculated 1.8 nm and for Ni doped ZnS was about 1.7 nm were calculated which is shown in Table 1.

Table 1. XRD Analysis for Crystal size, Micro strain and dislocation density.

Samples	β_0= FWHM	Crystal sizes (nm)	Micro Strain	Dis location
Undoped ZnS	0.0025748	1.815	0.0602	0.30353
	0.0025748		0.0594	
	0.0025748		0.0589	
	0.0042913		0.0012	
	0.0034330		0.0795	
Ni –doped Zns	0.0025748	1.756	0.0006	0.32441
	0.0025748		0.0006	
	0.0034330		0.0008	
	0.0025748		0.0006	
	0.0034330		0.0008	

The micro strain (€) and dislocation density (δ) have been calculated by using the following relations [26]:

$$€ = (¼)\ \beta\cos\theta$$

$$\delta = 1/D^2$$

The micro strain and dislocation density of as – prepared samples have listed in Table 1.

FE-SEM Analysis

The surface morphology of synthesized nanoparticles has been studied by using FE-SEM. Figure 3 shows the FESEM images of undoped ZnS and Ni doped ZnS. The accelerating voltage, magnification, spot size and instrumental parameters indicated on FE – SEM image. The surface morphology can be found from the analysis of the obtained FE – SEM images at different magnification. The FE-SEM indicates that the appearance of as undoped Zns and Ni doped ZnS nanocrystalline powders are in rod shaped arranged in regularly pattern.

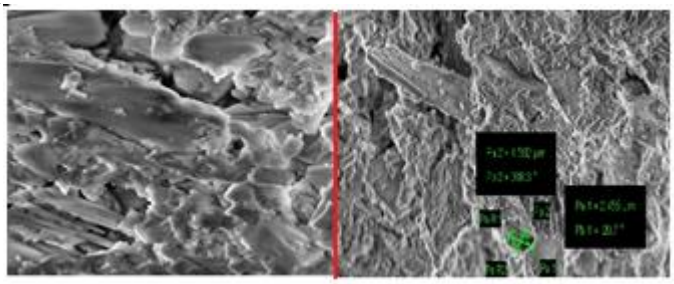

Figure 3. FE – SEM images of of (a) Undoped ZnS, (b) Ni – doped ZnS.

The average diameter of Ni – doped ZnS is in rod shape and its diameter is about 2.45 µm.

UV–Visible optical absorbance and band gap

The UV–Visible optical absorption spectrum of the samples recorded in room temperature is shown in Figure. 4. UV–Visible absorbance spectrum indicates that undoped ZnS having absorption peak at 208 nm while Ni doped ZnS is having an absorption peak at 228 nm. Undoped and Ni – doped ZnS have very good absorption extended up to 800 nm. The as prepared samples show a wide range of absorption from UV to NIR which indicates that the prepared material is good for sun light absorption. The optical band gap of undoped Zns is 3.6 eV and for Ni – doped ZnS is 5.6 eV , from its evident that doping of Transition Metal increase the optical band gap.

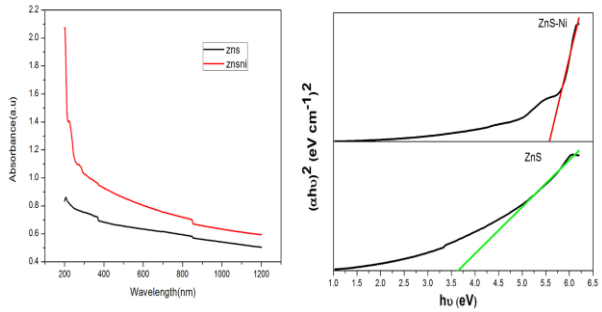

Figure 4. UV – Visible Spectrum and optical bandgap of Undoped and Ni – doped ZnS

Photoluminescence studies

Figure 5 shows the PL spectrum measured at room temperature of synthesized Undoped and Ni – doped ZnS nanocrystalline powder. The excitation wavelength is set to as 350 nm. The PL spectrum contains two emission peaks centered at 380 nm and 540 nm for undoped ZnS and 411 nm and 480 nm for Ni – doped ZnS. The undoped ZnS exhibit a strong UV blue emission and UV green emission. The Ni – doped ZnS exhibit a strong UV Violet emission and UV blue emission. This kind of emission peaks may be attributes to sulfur vacancy with holes at the valance band[29].

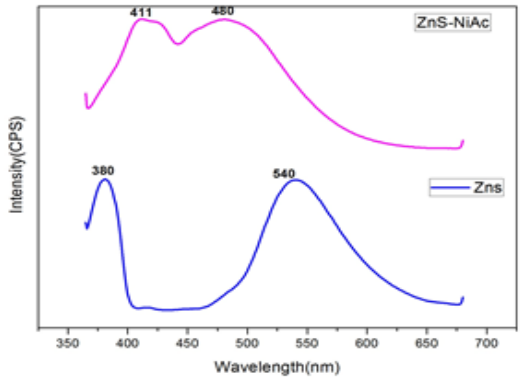

Figure 5. PL Spectrum of Undoped and Ni – doped ZnS.

Conclusion

The Undoped and Ni – doped ZnS nanocrystalline powder have been successfully synthesized by using WCS method. The average crystallite size using modified Scherrer equation, micro strain and dislocation density have been calculated from the XRD data. The average crystallite size was estimated as 1.815 nm and 1.765 nm FE - SEM images indicates that as – synthesized Undoped and Ni – doped ZnS nanocrystalline powder are rod in shape.

UV–Visible absorbance spectrum indicates the large blue shift with the optical band gap of 3.6eV and 5.6 eV. The PL spectrum reveals the two emission peaks around 380 nm and 540 nm and for Ni doped ZnS its about 411nm and 480nm which is strong in UV violet and blue emission.

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