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Structural Properties of Ce Doped Zns

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Abstract

Ce^{+3} doped ZnS (Ce_x:$Zn_{1-x}S$ where x=0.1,0.5 and 1.0 mol%) and undoped ZnS nano powder were prepared by wet chemical technique sintered at 120^oC for 4 hrs. Optical properties were analyzed by Fourier infrared spectroscopy (FTIR) and UV absorption .Structural properties were studied by using XRD data. FTIR peak at 610 cm^{-1} confirmed the formation of ZnS. In UV absorption study blue shift was observed w.r.t. increase in Ce doping concentration in ZnS. From XRD data , dislocation per cm^2 were calculated which showed that Ce doped ZnS has improved crystal lattice structure as compared to the pure Zinc sulphide.

Key words: Ce, ZnS, XRD and lattice

1. Introduction

Semiconductor compounds of II-VI groups show massive significance in different area of science. Material belong to this category have comparatively large excitonic energy, easily synthesized and band gap tunability. ZnO, CdS, ZnS, ZnSe and ZnTe, so forth are significant individuals from II-VI compound[1-5]. An important effect called Quantum confinement effect which attracts the attention of the researcher is observed in semiconductor material belongs to this category. In this effect, the particle size is so small that it can be compared with the bohr's radius (2.34nm) .Due to quantum size of the particle it become heavy and its band gap increases significantly[6-10]. Quantum confinement effect changes the optical properties of the material. Semiconductor material showing quantum confinement effect is very useful in solar cell fabrication, light emitting diode, laser system[6-9] etc.

ZnS is one of the individual from wide band gap semiconductor has band gap of about 3.6 eV emits UV light[11,12]. The reducing the particle size to nano improves the chemical reactivity of a material because of increment in number of particles on the surface. ZnS has two types of structure: Zinc blende and hexagonal wurtizite structure belong to A_2B_6 group[13-16].Quantum

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size material optical properties, concentration of defects, size modification can be achieved by substituting the impurity atom[10].

Rare earth due to their 4f 4f transition can be used as substitution atom which has the ability to alter the structural and optical properties of the host. Cerium (Ce^{3+}) is the one of the rare earth which emits yellow light.

In this paper, Ce was doped in the ZnS. Pure ZnS and doped ZnS structural and optical properties were analyzed.

2. Experimental and characterization Detail

In the present work , Ce doping effect on the structural parameter of ZnS were studied. Ce doped ZnS ($Ce_x:Zn_{1-x}S$ where x=0.1,0.5 and 1.0 mol%) and pure ZnS were synthesized by wet chemical technique [10]. The chemical used to synthesize Zinc sulphide and Cerium doped Zinc sulphide were Zinc acetate, Oxalic acid and Cerium nitrate. Structural morphology of the material was studied by XRD. Optical parameters were evaluated from UV absorption data.

3. Results and Discussions

3.1 Room temperature FT-IR study

In the spectra for Ce doped Zinc Sulphide , the peak at 610 cm^{-1} is due to the Zinc sulphide band for all samples and result well resembled with the literature .The peaks at 900 cm^{-1} to 1400 cm^{-1} are because of oxygen bending and stretching frequency. Broad peak from 3000 to 3400 cm^{-1} are due to moisture present in the sample.

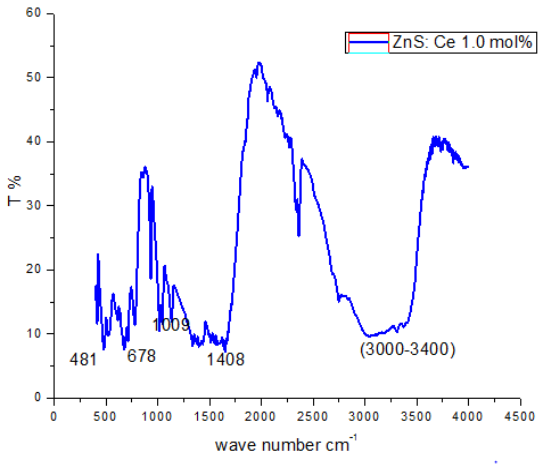

Fig.1: Fourier Infra red spectroscopy for Ce 1.0 mol% doped ZnS

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3.2 UV-Vis absorption spectroscopy

Zinc sulphide and Ce doped zinc sulphide, spectrum were scanned from 200- 800 nm as shown in the figure 2. Strong absorption peak for pure zinc sulphide is at 235 nm and peak width increases from 200 nm to 294 nm on doping.

Blue shift was observed on comparing the zinc Sulfide with doping absorption spectra. Optical band gap was increased on Ce doping in zinc Sulfide. The particle size (S=2r, r is radius) was calculated from the effective mass model mentioned in table1. [14]. UV studied clear show the Quantum confinement effect in the prepared samples.

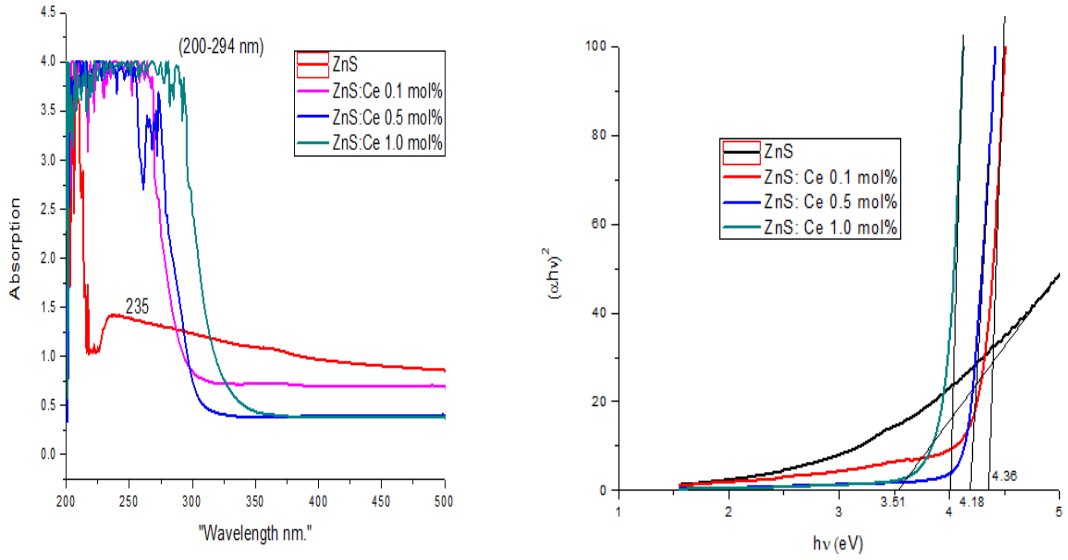

Fig.2: (a) UV plot of Zinc sulphide and Cerium doped Zinc sulphide and (b) plot between $(\alpha h\nu)^2$ Vs $h\nu$ where ν is the frequesny and α is absorption.

Table 1 : Energy band gap, Particle size (S) and surface area(A) to volume(V) ratio of pure Zinc suphide and Cerium doped Zinc Sulphide.

S.No.	Samples	E_g (eV)	S (nm)	A $(nm)^2$	V $(nm)^3$	A/V (nm^{-1})
1.	Pure ZnS	3.52	18.03	1016	3053	0.32
2.	ZnS: Ce 0.1 mol%	4.36	5.55	97	269	0.36

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3.	ZnS: Ce 0.5 mol%	4.18	6.14	118	121	0.97
4.	ZnS: Ce 1.0 mol%	4.00	7.00	154	180	0.86

3.3 Structural properties (XRD)

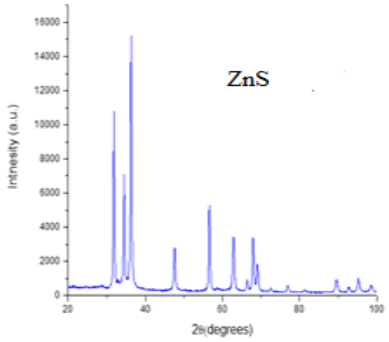
The crystallite size 'S' is calculated from the Scherrer formula given below in the relation (1).

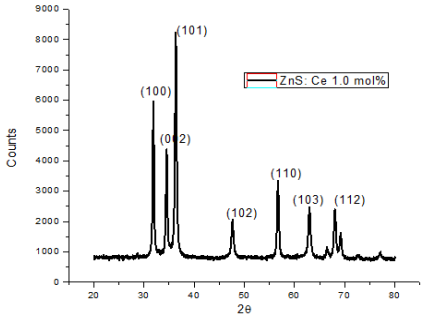
$$S=k\,\lambda / B\cos\theta \qquad \text{----------(1)}$$

' λ' is wavelength of X beam incident on the sample placed at an edge 2 θ . B is the peak width where k =0.94 telling crystallite shape. B is measured in 2θ is in radians.

Figure 3(a, b) are the X ray diffraction of Zinc Sulphide and Cerium 1.0 mol% doped Zinc sulphide. The wurtzite structure has been observed indexed by using JCPDS record No. 36-1451. No change had been observed in the XRD pattern on Ce doping in Zinc Sulphide. Nano crystal size was determined utilizing by using equation (1). Zinc sulphide nano crystal size was 31 nm (approx.) which is 13 nm (approx.) more contrasted with that of Zinc sulphide doped Ce with 1.0 mol% which is 18 nm. This lessening in the Zinc sulphide nano crystal size is because of the increase in the width of the XRD peak .This is due to ionic size of Ce (~1.01A) is more when compared with the ionic range of Zn(~0.7A)) which initiated strain in Zinc Sulphide particle due to doping of Ce.

The lattice parameters (a and c) , bond length (L) and c/a ratio had been determined for Zinc Sulphide and Ce doped Zinc sulphide and is recorded in the table 1.2.





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(a) (b)

Fig.3: XRD pattern of (a) Zinc Sulphide & (b) Ce 1.0 mol% doped Zinc Sulphide

Lattice Parameters had been increased with increment of cerium doping. This fact concluded that change in the lattice constants is an effect of a hydro static strain in the Zinc sulphide because of the Cerium substitution. Cerium ionic size is bigger than that of Zn therefore it is expected that strain will developed in Zinc sulphide.

Sample	**2 θ (Deg)**	**(hkl)**	**S (nm)**	**a (Å)**	**c(Å)**	**c/a**	**L (Å)**
ZnS	32	(100)	38	3.233	5.202	1.61	1.880
	34	(002)	26				
	36	(101)	31				
ZnS:(1.0 mol%) Ce	32	(100)	21	3.239	5.207	1.61	1.973
	34	(002)	15				
	36	(101)	22				

Table 2: Crystallite size (S), Lattice Parameters (a,c and c/a) and bond length (L) from XRD data of Zinc sulphide and Cerium doped Zinc sulphide.

The widening of X-beam diffraction is because of the both molecule size and inward strain. In this manner utilizing the Williamson and Hall (W-H) technique (Nelson and Riley, 1945) for Cauchy nature of expanded profile, we have the relation

$$B = \frac{1}{S\cos\theta} + 4\varepsilon \tan\theta \qquad \text{----------(2)}$$

$$\frac{B\cos\theta}{\lambda} = \frac{1}{S} + \frac{4\varepsilon \sin\theta}{\lambda} \qquad \text{----------(3)}$$

In equation (2) and (3) , ε is the normal interior strain. For a plot between B cosθ /λ versus 2 sinθ / λ gave a straight line. Intercept of the plot gave the nano crystal size (S) and the slope represents the strain in the lattice.

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Table 3: Dislocation density of ZnS and Cerium doped Zinc sulphide.

S.No.	Sample	S (nm)	$\Delta(10^{15})$ line $/m^2$
1.	ZnS	12	83
2.	ZnS:Ce 1.0 mol%	19	53

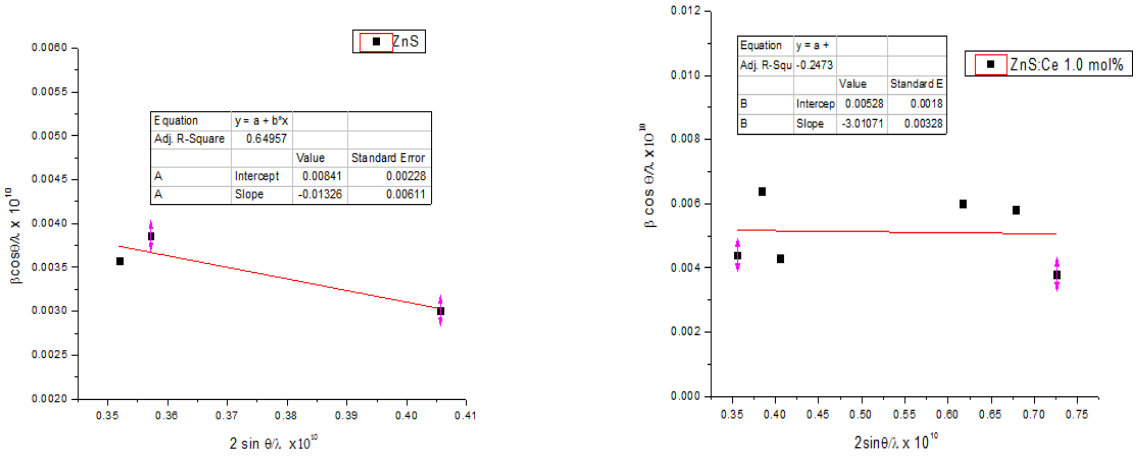

Fig. : 4 Williamson and Hall plot for (a) Zinc sulphide (b) Ce doped Zinc sulphide.

Dislocation density Δ is defined as the length of dislocation lines per unit volume of the material. Δ was calculated from the Williamson and Small man's formula [9].

$$\Delta = n/S^2$$

Dislocation density by taking n=1 for both doped and pure Zinc suphide nano powder has been tabulated in Table 3. Density(Δ) is seen to be decrease in case of Zinc sulphide doped Cerium. This might be because of the large crystal size.

3.4 Summary

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Surface to volume ratio was calculated for all the samples from UV absorption which increase with the increase of doping concentration of Ce in ZnS i.e. blue shift is observed in energy band gap. This showed the Quantum confinement effect. Dislocation density was calculated which conclude that Cerium doped Zinc sulphide has improved crystal structure as compared to the pure Zinc sulphide .

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