Investigation Of La Doped Zns For Visible Emission

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Abstract : La doped ZnS nanopowder was synthesized by co precipitation method. In FTIR spectra, the major peak at 676 cm^{-1} and 661 cm^{-1} was due to Zn-S stretching bond. Crystallite size was calculated by effective mass model from UV absorption data, Scherer formula and W-H plot and found to be almost same. The crystallite size lies between 1 to 5 nm indicating quantum confinements. Dislocation density was observed to be decreased in case of ZnS: La0.5 mol%. This might be due to the higher growth in crystallite size. Board emission peak was observed at 489nm which conclude the utilization of nanophosphor for display devices
Key words: ZnS, La, quantum confinements, Dislocation density , emission.

1.   Introduction

Semiconductor belongs to group of II-VI attract the attention of scientists due to their broad area of application in optoelectronics devices like solar cell, Lithium-ion batteries, chemical sensor, optoelectronic detectors etc. ZnS, ZnO, CdS and ZnSe etc. are the examples of some of the semiconductor compound belong to the category. ZnS based material has wide variety of applications [1-6] .During the synthesis of ZnS, surface and interfacial defects are formed which is responsible for blue, green and orange emission. Cations , anions and antisite defects introduces deep defect levels in the band gap and can be act as donors and acceptors depending upon the position of Fermi level. Movement of electron from sulfur vacancy to interstitial site is responsible for green emission[7-8]. . Controlling defects formation makes ZnS a capability material for optical devices. Rare-earth element is mostly used as dopants due to 4f-4f intra shell transition known for visible light emission.

2. Experimental Details

In the present work , La doping effect on the structural and optical properties of ZnS were studied. La doped ZnS ($La_x:Zn_{1-x}S$ where x=0.1,0.5 and 1.0 mol%) and pure ZnS were synthesized by wet chemical technique [4,9,10]. The chemical used to synthesize Zinc sulphide and La doped Zinc sulphide were Zinc acetate, thiourea and Lanthanum nitrate.

3.   Result detail

3.1 Fourier-transform infrared spectroscopy

FTIR spectra of undoped ZnS and La: ZnS is shown in figure1.Absorption peak at 661 cm^{-1} is due to Zn-S stretching bond . FTIR spectra for ZnS and La:ZnS are same and no additional peak was found on doping .Peak at 3343 cm^{-1} is due to moisture present in the sample.
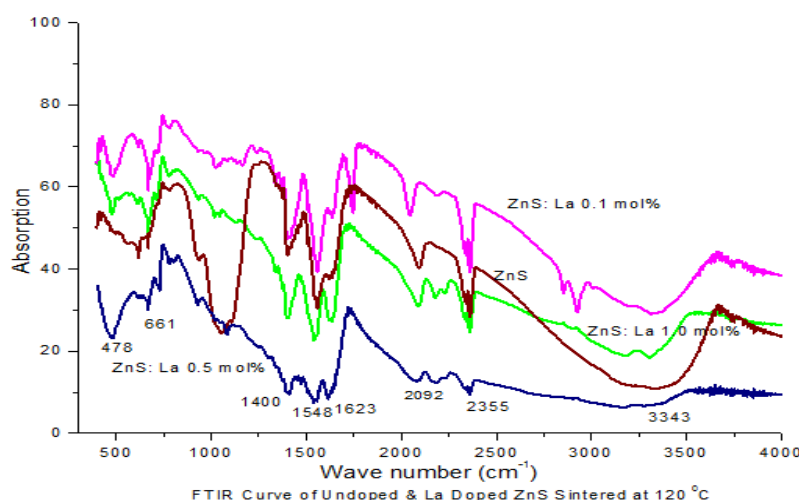
Fig. 1: Shows the Fourier-transform infrared spectroscopy spectra La doped and undoped ZnS variation

3 .2 UV -Vis Absorption

UV absorption spectra were recorded from 200 to 800 nm^{-1} range are shown in figure 2.Absorption peak was at 235 nm for undoped ZnS and got broaden on doping which may be due to the increase of defect center. Red shift was observed in absorption edge on doping. The particle size was calculated by using the effective mass model [4,11-12] and is tabulated in table 2.
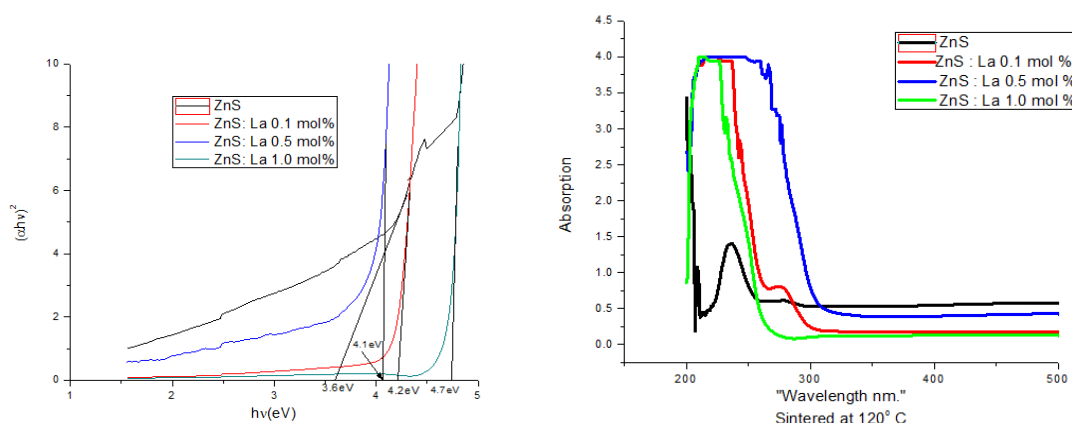
**Fig. 2: (a) UV absorption spectra of undoped and La doped ZnS at different doping concentration.**

Table 1: Particle size(D) , Optical band gap(E_g) ,and surface(S) to volume(V) ratio of particle of ZnS and La doped ZnS

S.No.	Nano phosphor	E_g(eV)	D (nm)	S $(nm)^2$	V $(nm)^3$	S/V (nm^{-1})
1.	ZnS	3.70	10.10	319.69	537.60	0.61
2.	0.1 La: ZnS	4.10	6.50	131.86	142.43	0.94
3.	0.5 La : ZnS	4.20	4.45	61.89	45.84	1.37
4.	1.0 La: ZnS	4.70	4.07	51.77	35.04	1.48

From table 1 ,it clearly visible that optical band gap increases which lead to decrease in particle size and hence surface to volume ratio increase which attributes to the Quantum confinement effect.

3.3 X ray Diffraction(XRD)

XRD spectra of La doped ZnS has been shown in the figure 3 and calculated value of crystallite size resemble with the literature and summarized in table2. Nano phosphor has cubic structure confirmed by JCPDS card 00-027-1402.
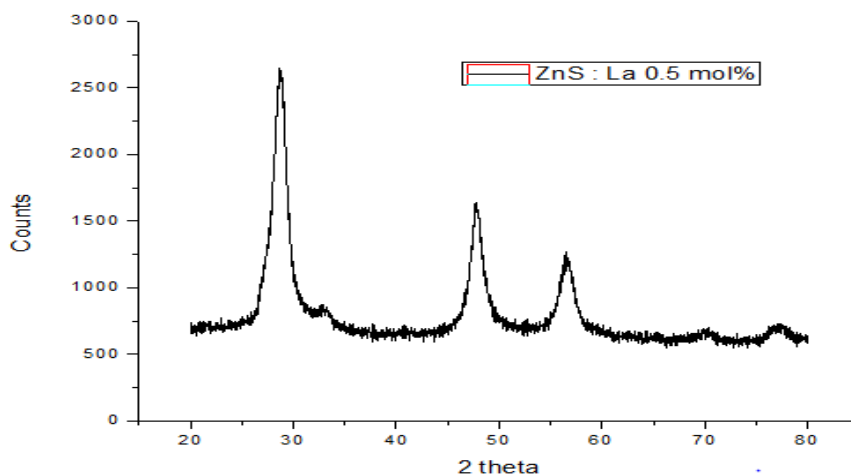

Fig. 3:   XRD pattern of ZnS doped La with 0.5 mol% each.

The calculated crystallite size(nm) were tabulated in table 2.From the table it was observed that crystallite size were increased on doping .This may be due to the large ionic radius of La^{3+}(103pm) as compared to Zn (74 pm). Increase in crystallite size indicates that the La entered at lattice or at some interstitial site.

Table 2 : Crystallite size(D), d-spacing and lattice constant(a) of undoped ZnS and La doped ZnS

S.No.	Sample	2θ (deg.)	(hkl)	FWHM Degrees	D(nm)	d-spacing (Å)	a (Å)	Lattice strain
1	ZnS	28.59	(111)	3.56	2.42	3.12042	5.4118	0.0600
2		47.71	(220)	4.00	2.33	1.90471	5.3609	0.0395
3		56.56	(311)	3.89	2.43	1.62577	5.4054	0.0315
4.	ZnS: La	28.95	(111)	2.06	4.16	3.08141	5.3372	0.0348
6.		47.68	(220)	3.36	2.70	1.89345	5.3555	0.0332
7.		56.54	(311)	5.22	1.81	1.62580	5.3913	0.0424
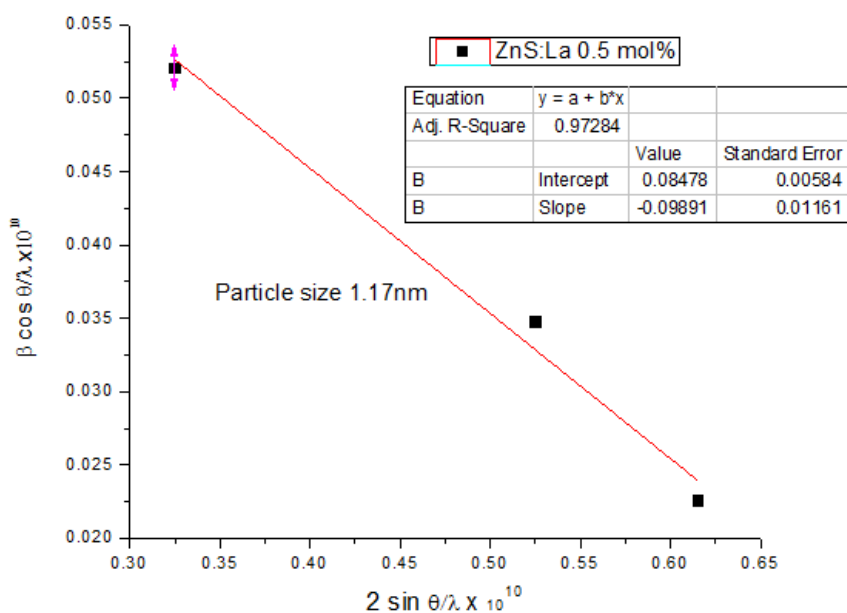
Fig. 4 : W-H plot for ZnS:La 0.5 mol%

Average crystallite size from W-H plot is 1.17 nm less than that calculated by using Scherrer's equation[13-17].

Table 4: Particle Size, strain and dislocation density (δ)of undoped ZnS and La doped ZnS.

| S.No.	Sample	Particle size(nm)	Strain	Dislocation density (10^{16})line /m^2 ($\delta = n/D^2$)
1.	Undoped ZnS	2.26	0.013	44.
2.	ZnS: La 0.5 mol%	1.16	0.050	29

Dislocation density for both the doped and undoped films has been given in Table 3. Decrease in dislocation density with larger crystallite size, ZnS: La 0.5 mol% represents better lattice quality than the undoped ZnS film[18, 19]. Crystallite size was calculated by effective mass model(EMM) from UV absorption data, Scherer formula(SF) and W-H plot and found to be almost same.

Table 5: Comparison of Particle size calculated from UV absorption data, XRD data.

Samples	Particle Size (nm)		
	EMM	SF	W-H plot
Undoped ZnS	10.10	2.40	2.26
ZnS: La 0.5 mol%	4.45	2.90	1.16

3.4   Fluorescence spectra of ZnS and La doped ZnS

ZnS and La doped ZnS emission spectra was obtained by excited the powder with 235 nm wavelength. A broad emission spectra peak at 483nm has been obtained as shown in figure 5. Intensity and full width half maximum (FWHM) is maximum for ZnS as compared to La doped ZnS. Intensity and FWHM deceases on La doping. The broad emission peak at 483nm (475-490)nm is due to the singly ionized Zn and S vacancies[7] .i.e. This green emission is due to the electron transfer from sulfur vacancies to interstitial sulfur vacancies[8] . The decrease in intensity may be due decrease in dislocation density on doping as shown in table2 .Mainly the emission is obtained from the defects which decreases with doping hence decrease in intensity and FWHM.
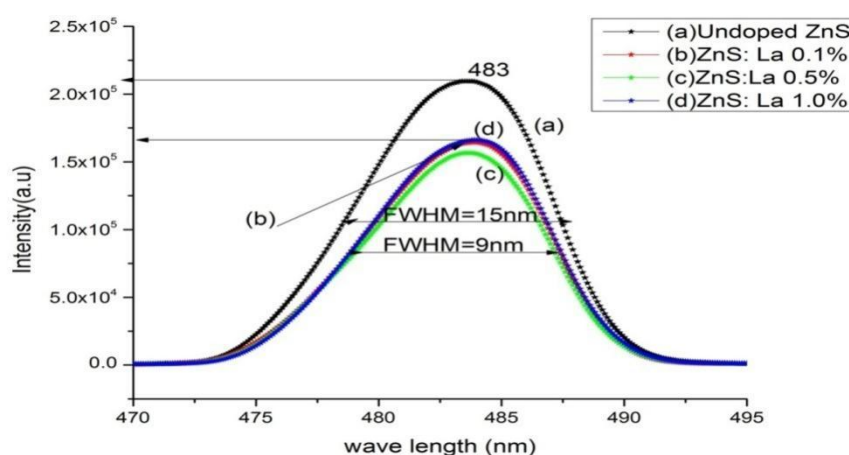
Fig.5: Emission spectra of ZnS and La doped ZnS excited by 235nm

4.   Conclusion

ZnS and La doped ZnS were prepared by co precipitation method. In FTIR analysis the major peak at 661 cm^{-1} is attributed to Zn-S stretching bond. From the XRD analysis of La doped ZnS, it was concluded that crystal structure of ZnS remain same on doping and has Zinc blende structure. Decrease in dislocation density with larger crystallite size, ZnS: La 0.5 mol% represents better lattice quality than the undoped ZnS film. Bluish green light was observed in the emission spectra of ZnS and La doped ZnS concluded that prepared material can be explore for the optoelectronic devices specially display devices.

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