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Synthesis and Study of Optical Molecular Spectroscopic Characteristics of ZnS and ZnS-ZnO nanocomposites

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Abstract:

Here the research work is synthesis of ZnS and ZnS-ZnO nanocomposites by solvothermal synthesis method. For investigating the crystalline materials X-ray diffraction was carried out and from Fourier Transform Infrared Spectroscopy (FTIR) we can get the information about the presence of symmetric stretching vibration, weak vibration and symmetric stretching vibration of molecular bond. The UV-Visible spectroscopy indicates blue shift of ZnS-ZnO in UV region as compared to ZnS and Photoluminescence (PL) spectra informs that emission at red shift.

Keywords: Nano composite, XRD, UV-Vis, FTIR, Photoluminescence (PL).

1. **Introduction:** Nano scale semiconductors have been achieving more concentration sine last decades due to their extended physical and optical properties which are not same as their bulk materials. Now in present time these are being extensively used in different field of optoelectro device [1], nano laser [2], solar cell [3], sensor and biomedical imaging [4], ZnS & ZnO are the such ionic semiconductors that having wide band gap values of 3.7 and 3.3 eV respectively make them attractive to researchers. There several methods have been noticed in lots open literatures, here author used the solvothernal method [5-7]. The purpose of our present work is to study the characteristics of structural analysis, optical properties and molecular study of ZnS and ZnS-ZnO.

2. **Materials & Methods:** Here two samples were synthesized one is pure zinc sulphide (ZnS) and other is zinc sulphide-zinc oxide (ZnS-ZnO) nano composite with the help of sovothermal synthesis method by using zinc acetate [$Zn(CH_3COO)_2$], thiorea [$Sc(NH_2)_2$] and sodium sulphide as precursor [8].

2.1 Synthesis of ZnS nanoparticles: For synthesis of pure ZnS nano particles initially we added 2.45 gm zinc acetate in 45 ml distilled water and stir it by magnetic stirrer for 1 hour to prepare 45 ml 0.5 M solution of zinc acetate, similar method was followed to prepare 0.5 M Na_2S solution. Then Na_2S solution was mixed with the previous solution by burette keeping normal stirring for 1 hour and put it 100 ml Teflon line stainless steel autoclave which was enliven into furnace for 12 hours at 180^0 C and let it be cooled until become at room temperature. In next step it was washed several times with distilled and water and ethanol consecutively to washed out the contaminating elements and dried it for 24 hours at 100^0 C.

2.2 Synthesis of ZnS-ZnO nanocomposites: For preparing the ZnS-ZnO nano composites we used 2.45 gm zinc acetate in 27 ml distilled water to obtain 0.5 M solution, stirring by magnetic stirrer for 1 hour. Similar method was followed to prepare 0.5 m theoria and 0.5 M NaOH by adding separately 27 ml distilled water with 1.027 gm theoria and 0.27 gm NaOH respectively. After that thioria solution was mixed with zinc acetate solution drop wise on normal stirring then it was mixed with the NaOH solution on stirring well for 1 hour. In the next step final solution was put into Teflon lined stainless steel autoclave which kept at furnace for 12 hours keeping temperature at 180^0 C and cooled it to room temperature. The final stage is to wash several times with distilled water and ethanol consecutively and dried at 100^0 C for 24 hours.

3. Results and Discussion:

3.1 Crystalline Structure: In fig. 1 here it is XRD pattern from where it is explained the crystalline structure of pure ZnS and ZnS-ZnO nanocomposites. We got the nano particles in powder forms and grain size was measured by Scherar formula, as follows [9]

$$D = \frac{k\lambda}{ß\cos\theta} \quad \textbf{(1)}$$

where, D = mean diameter of grain, size factor k = 0.9, ß = full width half maximum (in radians) and wave length λ= 1.54 Å. Here the size measured of nano crystal is very small (<10 nm). The XRD of pure ZnS nano particles matched with JCPDS card number (039-1363) where three broad peaks are noticed at 2θ values (28.58^0), (47.75^0) and (56.55^0) which correspond to crystal plane (008), (110) and (118) respectively. Similarly for ZnO matched with the JCPDS card number (036-1451) having broad peaks at (31.77^0), (34.42^0), (36.25^0) and (62.83^0) corresponding to (110), (002), (101) and (103) respectively.

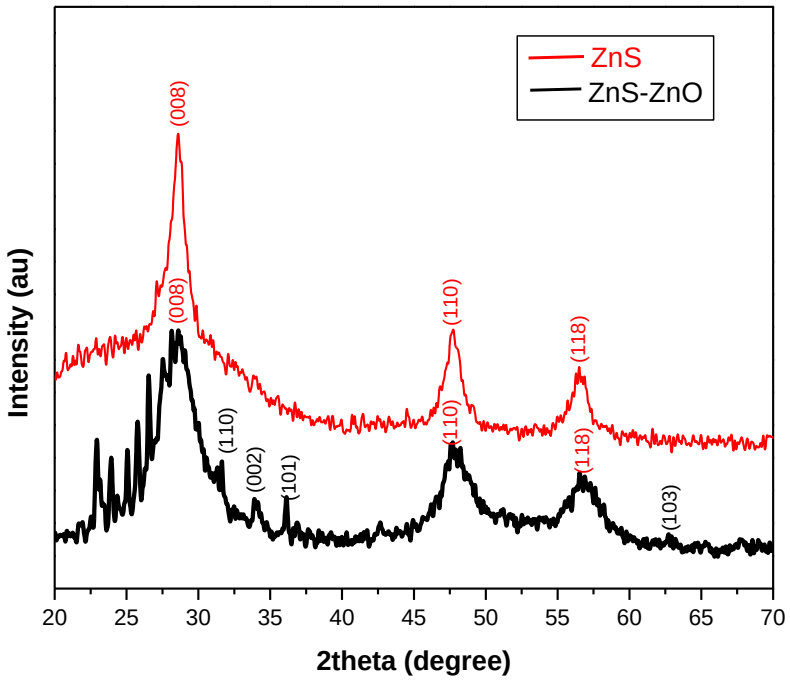

Fig.1: XRD pattern of ZnS and ZnS-ZnO

3.2 Ultraviolet-visible (UV–vis) spectroscopy: In fig.2 shows UV-visible absorption spectra of pure ZnS and ZnS-ZnO nanocomposites where we find peaks aried for pure ZnS at 238 nm and for ZnS-ZnO at 230 nm. The blue shift in the absorption for ZnS-ZnO because of more vicinity of optical component of ZnS-ZnO as compared to pure ZnS [10].

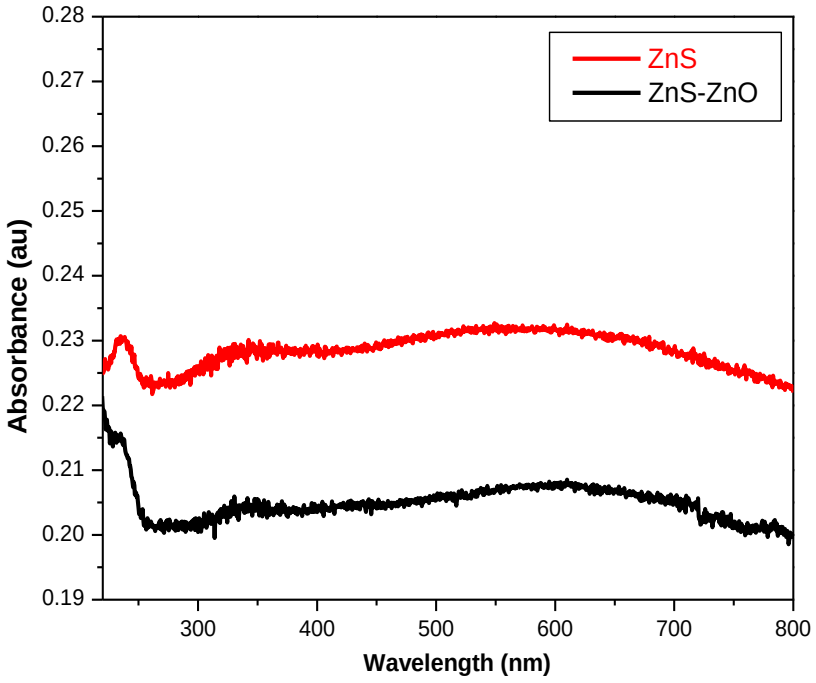

Fig. 2: UV visible spectra of ZnS and ZnS-ZnO

3.3 Band Gap Study: The optical band gap of ZnS and ZnS-ZnO were measured from Tauc formula from absorption spectrum, as follows [11].

$$\alpha h\nu = c(h\nu - E_g)^n \qquad (2)$$

where α = molar excitation coefficient hν = incident photon energy, c= constant, E_g = band gap energy and n decides type of transition i.e. having value ½ gives direct allowed band gap.The curve drawn in between hν and with best linear fitting $(\alpha h\nu)^2$ is shown in fig 3**.** The estimated E_g from the intercept gives the value for pure ZnS and ZnS-ZnO composite are 3.23 eV and 3.51 eV respectively which are very close to expected value as reported by many researcher [12-15]**,** shown in fig.3. The tunability of band gap makes suitable for optoelectronic application. The alternation of band gap may be due to many complicated parameters, these are crystalline and particle average size, phase concentration, morphology and so on [16].

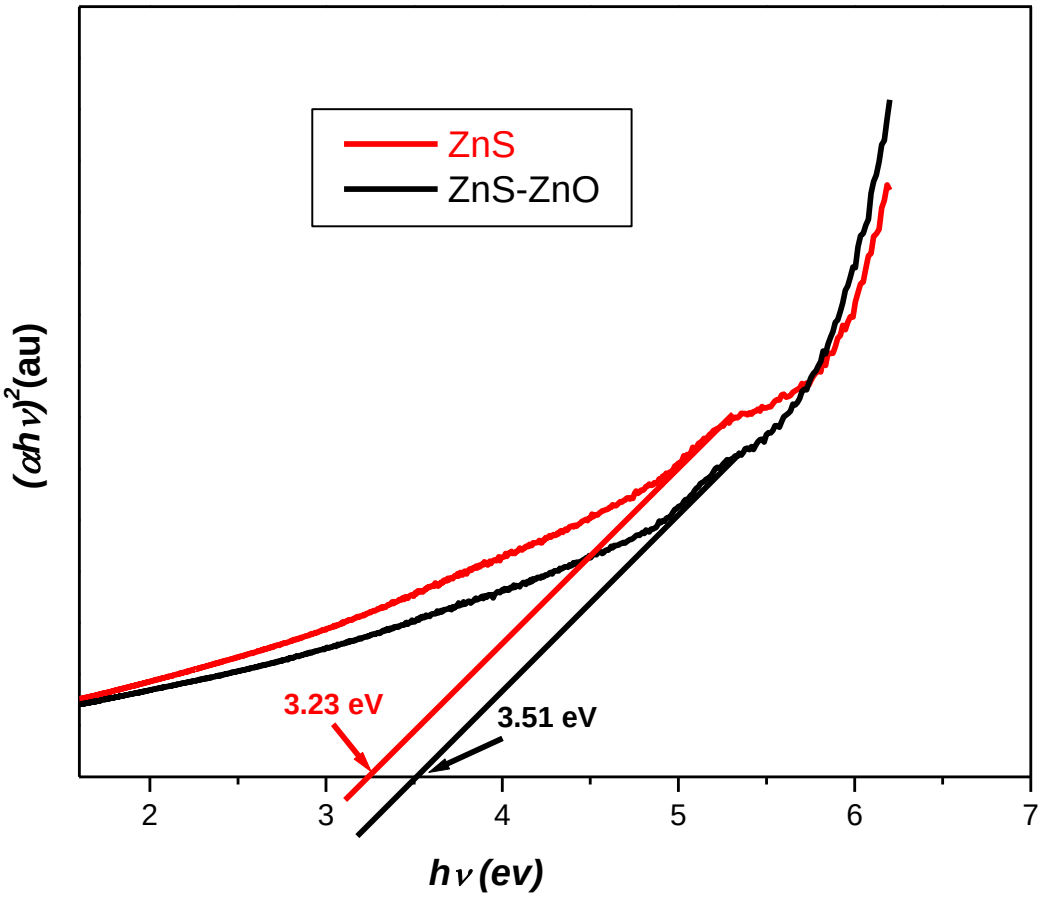

Fig. 3: Tauc plot of ZnS and ZnS-ZnO to estimate the bang gap.

3.4 Photoluminescence (PL) spectra Study: PL spectra is very powerful tool to investigate the optical property and to get information about the crystal defects. In fig.4 here is shown PL spectra for pure ZnS and ZnS-ZnO nanocomposites with excitation wave length is 325 nm, strong peaks are distinguished at 438.15 nm and 463.84 nm respectively. The wavelength's peak at red shift might be due to particle or cause of phase change [17].

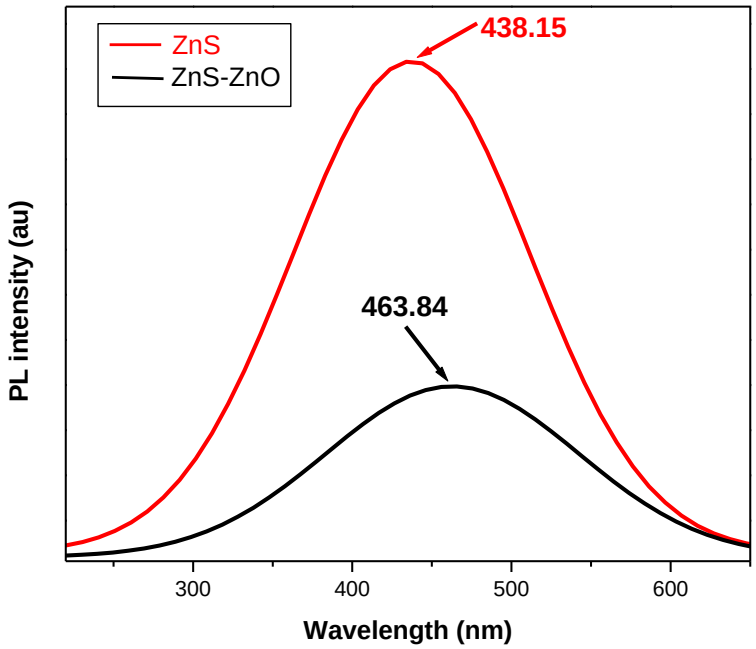

Fig. 4: PL spectra of ZnS and ZnS-ZnO

3.5 Molecular Study: In molecular study through Fourier Transform Infrared (FTIR) spectra we will search the identification of Zn-S and Zn-O bond. In fig.5 at ZnS curve some band observed at 626 cm^{-1} , 773 cm^{-1}, 1123 cm^{-1} are the characteristic of ZnS peak [18]. Band at 1123 cm^{-1} and 2370 cm^{-1} are due to surface absorbs water molecules and air molecule [19] respectively. The others at 2925 cm^{-1} is related to CH_2, CH_3 asymetry stretching [20] band at 3411 cm^{-1} is due tob water evaporation [21-22].

In fig 5 at ZnS-ZnO curve we will identify the capping of ZnS Nps with ZnO. The observed peak at 507 cm^{-1} is due to Zn-O. It can be seen the bands in the range of (500 cm^{-1} to 900 cm^{-1}) are attributed to Zn-O and Zn-S bond while 959 cm^{-1} , 1020 cm^{-1} and 1123 cm^{-1} are related to Zn-S bond [18]. The band noticed at 1177 cm^{-1} is for C-N or C-N stretching which is due to calcinations [23] and at 1424 cm^{-1} due to N-O bonds from residual nitrate source. Again peaks at 1624 cm^{-1} and 2062 cm^{-1} belong to H-O-H bond and

air molecules respectively [19]. Lastly the bands at 3300 cm^{-1} is related to O-H bonds of water evaporation [21-22].

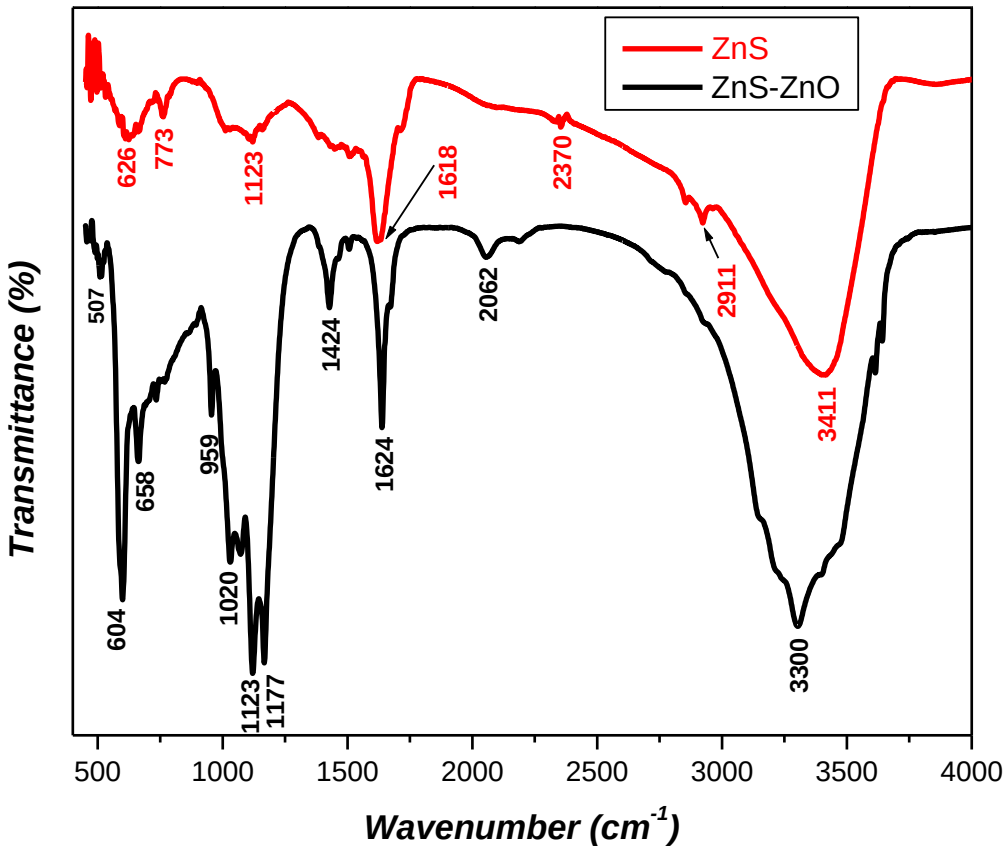

Fig. 5: FTIR spectra of ZnS and ZnS-ZnO

4. **Conclusion:** In this research work pure ZnS and ZnS-ZnO nanocomposites have been synthesizes successfully using simple solvothermal method. We studied structural, optical and molecular properties which confirmed that ZnS and ZnS-ZnO nanocomposite had been formed properly. XRD studies says us ZnS is cubic and ZnO is wurtizes in core shell nanocomposites, UV visible

spectra confirmed that the band gap can be tuned and PL studies showed the emission wave length towards the blue region and also bond formation of ZnS and ZnS-ZnO nanocomposites was identified by molecular study (FTIR).

5. **Conflicts of Interest:** No conflicts of interest is declared by the authors.

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