CHAPTER 3

OPTICAL STUDIES ON SnS NANOPARTICLES

3.1 INTRODUCTION

In recent years, considerable interest has been shown on semiconducting nanostructures owing to their enhanced optical and electrical properties, due to the quantum confinement effect. Among the IV-VI group semiconductors, nanostructures of germanium sulfide (GeS), SnS and PbS are important materials. Research on SnS has attracted due to its layer property and less toxic nature compared to other similar materials such as lead and cadmium compounds.

Many researchers have investigated the properties of SnS thin films prepared by various methods such as electrochemical deposition [6], electron beam evaporation [8], chemical deposition [99], thermal evaporation technique [100], plasma-enhanced chemical vapor deposition [101], spray pyrolytic deposition [102] and chemical bath deposition [103]. Tin sulfide nanostructures have been synthesized using solvothermal method [23, 54], aqueous solution route [61] and hydrothermal method [52, 63]. Widely different values of direct and indirect band gap in SnS nanostructures and thin films have been reported [51, 63, 104]. Indirect band gap of 1.1 eV has been reported in SnS quantum dots [51]. Zhao et al. [60], have observed two PL peaks in SnS nanoparticles which are assigned to defect peaks whereas the band gap luminescence from SnS nanoparticles has not been reported so far. Nikolic and Price et al. [105, 106], have reported the Raman spectra of single crystal and thin film of SnS respectively. Liu and Gou et al. [61,107], have reported the Raman spectra of SnS nanoparticles and nanowires respectively wherein only a few Raman modes predicted by group theory have been observed. A
detailed study, comprising of the optical and vibrational properties of SnS nanoparticles, in particular, has not been reported. In the present work, SnS nanoparticles have been synthesized in aqueous medium by wet chemical method and its optical properties are reported.

3.2 SYNTHESIS OF SnS NANOPARTICLES

SnS nanoparticles were synthesized through wet chemical route. All the chemicals used in this work were of analytical grade and were used without further purification. Tin (II) chloride (SnCl₂·2H₂O) and sodium sulfide (Na₂S) were taken as tin and sulfur sources respectively and deionized water was used as solvent. 1.2 g of tin (II) chloride and 1.72 g of sodium sulfide were dissolved in deionized water. Sodium sulfide solution was added drop wise into the solution. The colorless tin (II) chloride solution turns dark brown color with the addition of sodium sulfide solution. This indicates the formation of SnS nanoparticles. This reaction was carried out at room temperature for two hours. The precipitates were centrifuged and washed with deionized water and ethanol for several times and dried at room temperature.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Structural Studies

Figure 3.1 shows the XRD pattern of SnS nanoparticles. All the diffraction peaks are indexed to pure orthorhombic phase of SnS. This is in good agreement with the values of standard card (JCPDS NO 39-0354). The average particle size is calculated using Scherrer’s formula and is approximately equal to 20 nm. This is due to agglomeration of the particles in the powdered sample and hence, XRD was used for phase identification only. Apart from SnS peaks, two
additional peaks were seen in the XRD patterns which are marked as * in XRD and are indexed to the impurity phase of \( \beta \)-Sn (JCPDS NO 04-0673) of very low level.

![XRD pattern of SnS nanoparticles](image)

**Figure 3.1** Powder XRD pattern of SnS nanoparticles and the peaks labeled with * correspond to \( \beta \)-Sn.

For AFM studies, SnS nanoparticles were coated on the silicon substrate using spin coating method. Figure 3.2 (a) shows the AFM image of SnS nanoparticles coated on the silicon substrate.
Figure 3.2 (a) AFM image of SnS nanoparticles, (b) AFM image of SnS single nanoparticles and (c) Line profile of SnS nanoparticle.

AFM image shows uniformly distributed spherical SnS nanoparticles. Size of SnS nanoparticles measured from AFM image is approximately equal to 15 nm.
Figure 3.2 (b) shows the single particle size and Figure 3.2 (c) shows the line profile.

![Figure 3.2](image-url)

Figure 3.3 (a) TEM image of SnS nanoparticles, (b) HRTEM image of SnS nanoparticles and (c) SAED image of SnS nanoparticles.

Figure 3.3 (a) shows the bright field TEM image of SnS nanoparticles. From the TEM image, it is quite evident that the SnS nanoparticles are agglomerated
among themselves due to the high surface energy. The adsorption of polar solvents prevents the further growth of SnS nanoparticles [108]. Size of SnS nanoparticles measured from TEM image is varying from 7 to 15 nm. Figure 3.3 (b) shows the HRTEM from a single SnS nanocrystallites and imaging the 0.324 nm spaced lattice fringes which correspond to (0 2 1) plane of orthorhombic SnS. Figure 3.3 (c) shows the SAED pattern from a region of the SnS nanoparticles. Phase identification was made from scaled SAED images by calculating the lattice spacing and then comparing with standard JCPDS values (39-0354).

### 3.3.2 Optical Studies

Optical absorption measurement was carried out on SnS nanoparticles. For this, the nanoparticles were dispersed in ethanol. Figure 3.4 (a) shows the UV-VIS-NIR absorption spectrum of SnS nanoparticles. For bulk SnS, the direct band gap transition is at 1.3 eV and the indirect transition is at 1.0 eV respectively. The dependence of absorption coefficient ($\alpha$) on the photon energy for semiconductors can be written as

$$ (\alpha h\nu)^n = B(h\nu - E_g) $$

(3.1)

where, $B$ is constant, $n$ is the number that depends on the electronic transitions [63]. The value of $n$ is 2 and 1/2 for direct and indirect transitions respectively. The dependence of $\alpha^2$ on the photon energy ($h\nu$) and ($\alpha$)$^{0.5}$ on the photon energy ($h\nu$) for direct and indirect band gaps are shown in the Figure 3.4 (b) and 3.4 (c) respectively (often referred to as Tauc Plot).
Figure 3.4 (a) Optical absorption spectrum of SnS nanoparticles D: Direct Transition, I : Indirect Transition, (b) plot of $(\alpha h \nu)^2$ versus $h \nu$ showing direct band gap and (c) plot of $(\alpha h \nu)^{1/2}$ versus $h \nu$ showing indirect band gap of SnS nanoparticles.

From the intercepts of plot the direct and indirect band gaps are found to be 1.78 eV and 1.2 eV respectively. Many reports are available with different values of direct and indirect band gap for SnS thin films as well as nanostructures. For example, Zhu et al., have determined both direct and indirect band gaps for SnS nanoflowers
from optical absorption spectrum as 1.53 and 1.43 eV respectively [63]. Using optical absorption spectrum, direct band gap of SnS thin film was reported as 1.92 eV [104] and for SnS quantum dots using N, N-dimethylethanolamine (DMEA) as stabilizing agent, the indirect band gap was reported as 1.1 eV [51]. In semiconductor nanoparticles, the band gap increases as the particle size decreases. This arises due to confinement of carriers [16]. A change in the band gap can also arise due to departure from ideal stoichiometry. The Bohr radius of SnS is 7 nm [65]. The diameter of the SnS nanoparticles is of the order of Bohr radius of SnS and the observed blue shifts of 0.48 and 0.2 eV for direct and indirect transition respectively are attributed to quantum confinement effect.

The room temperature photoluminescence spectrum of as synthesized SnS nanoparticles was recorded using 325 nm He-Cd laser and is presented in Figure 3.5. From the PL spectrum the emission peak is observed at 12680 cm⁻¹ (1.57 eV). As mentioned earlier, bulk SnS has a direct gap of 1.3 eV and indirect gap of 1.0 eV. Hence, the PL emission at 12680 cm⁻¹ can be attributed to the direct band gap transition of SnS nanoparticles. This shows a blue shift of 0.27 eV compared to bulk SnS. This is in good agreement with the optical absorption results.
Figure 3.5 Room temperature photoluminescence spectrum of SnS nanoparticles. The open symbols are experimental data and the solid curve is a Gaussian fit to the data.

Raman scattering measurements were carried out on SnS nanoparticles. Tin sulfide has orthorhombic structure with eight atoms per unit cell. For orthorhombic structure, the 24 vibrational modes are represented by the following irreducible representations at the centre of Brillouin zone as,

$$\Gamma = 4A_g + 2B_{1g} + 4B_{2g} + 2B_{3g} + 2A_u + 4B_{1u} + 2B_{2u} + 4B_{3u}$$ (3.2)
Tin sulfide has 21 optical phonon modes of which 12 are Raman active modes ($4A_g$, $2B_{1g}$, $4B_{2g}$ and $2B_{3g}$), seven are infrared active modes ($3B_{1u}$, $1B_{2u}$ and $3B_{3u}$) and two are inactive ($2A_u$) [105].

Figure 3.6 Room temperature Raman spectrum of SnS nanoparticles. The open symbols are experimental data and the solid curve is a Lorentzian fit to the data. The inset shows the modes in the range from 40 cm$^{-1}$ to 60 cm$^{-1}$.

Figure 3.6 shows the room temperature Raman spectrum of SnS nanoparticles. The Raman modes for SnS nanoparticles are observed at 77 cm$^{-1}$,
109 cm\(^{-1}\), 170 cm\(^{-1}\), 182 cm\(^{-1}\), 229 cm\(^{-1}\) and 260 cm\(^{-1}\) along with some weak intensity modes at 46 cm\(^{-1}\), 52 cm\(^{-1}\), 57 cm\(^{-1}\) and 154 cm\(^{-1}\). Based on the previous report on Raman spectra of SnS single crystal, the observed Raman modes at 109 cm\(^{-1}\) and 260 cm\(^{-1}\) are assigned to A\(_g\) mode and 77 cm\(^{-1}\), 170 cm\(^{-1}\) and 182 cm\(^{-1}\) are assigned to B\(_{2g}\) mode. A mode is observed at 229 cm\(^{-1}\) and this mode is not observed in the Raman spectrum of SnS single crystal [105]. In accordance with Raman spectra of GeS, the Raman mode at 229 cm\(^{-1}\) is assigned to A\(_g\) mode [109]. A prominent B\(_{2g}\) mode is observed at 182 cm\(^{-1}\) for SnS nanoparticles whereas in the case of single crystal spectra, the intensity of B\(_{2g}\) mode at 194 cm\(^{-1}\) is weak. The intensities of various modes of vibration are prominent in the range 40 cm\(^{-1}\) to 60 cm\(^{-1}\) for the single crystal spectrum, [105] whereas in the case of SnS nanoparticles the intensity of these modes is weak. This region of the spectrum is shown as an inset in the Figure 3.6. The mode observed at 52 cm\(^{-1}\) is assigned to A\(_g\) mode and the modes at 57 cm\(^{-1}\) and 154 cm\(^{-1}\) are assigned to B\(_{3g}\) mode. Table 3.1 compares the Raman modes in the present SnS nanoparticles with the single crystal data [105, 109].

**Table: 3.1 Observed Raman modes of SnS nanoparticles**

<table>
<thead>
<tr>
<th>A(_g) modes (cm(^{-1}))</th>
<th>B(_{2g}) modes (cm(^{-1}))</th>
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<tr>
<td>SnS Nanoparticles</td>
<td>SnS Single crystal</td>
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<tr>
<td>-------------------</td>
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<tr>
<td>109</td>
<td>111 [105]</td>
</tr>
<tr>
<td>229</td>
<td>238 [109]</td>
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<td>260</td>
<td>264 [105]</td>
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The Raman modes of SnS nanoparticles show broadening and are shifted towards lower wave number side as compared to Raman modes of SnS single crystal. This is due to phonon confinement effect. Liu et al., [61] have observed $2A_g$ modes at 223 cm$^{-1}$, 273.7 cm$^{-1}$ and one $B_{2g}$ mode at 190.4 cm$^{-1}$ for SnS nanowires. Gou et al. [107], have observed only $2A_g$ modes at 189 cm$^{-1}$ and 220 cm$^{-1}$ for SnS nanoparticles. All the predicted Raman modes observed in Figure 3.6 are related to SnS nanoparticles. A weak peak is observed at 124 cm$^{-1}$ which does not belong to the predicted Raman modes of SnS. Pressure dependent Raman scattering studies on $\beta$-Sn showed longitudinal optical (LO) and transverse optical (TO) modes at 42.4 cm$^{-1}$ and 126.6 cm$^{-1}$ at ambient pressure in which TO mode is prominent [110]. The mode observed at 124 cm$^{-1}$ in the present work can be assigned to TO mode of $\beta$-Sn since stoichiometric variations can lead to the presence of $\beta$-Sn in the system. However, the intensity of this peak is weak, suggesting the presence of small quantity of $\beta$-Sn in the system.

3.4 CONCLUSIONS

SnS nanoparticles were synthesized through wet chemical method. TEM and AFM showed the presence of spherical SnS nanoparticles of size in the range of 7 nm -15 nm. The XRD pattern revealed the orthorhombic structure of SnS nanoparticles. The room temperature PL spectrum showed the band edge emission at 1.57 eV for direct transition. The estimated direct and indirect band gaps from optical absorption spectrum were 1.78 and 1.2 eV respectively. A blue shift of 0.48 eV for direct transition and 0.2 eV for indirect transition were observed compared to that of bulk. This is due to quantum confinement effect. Raman modes of SnS nanoparticles were found to be shifted towards lower wavenumber side due to phonon confinement.