CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF SnS

NANOSHEETS THROUGH SIMPLE CHEMICAL METHOD

4.1 INTRODUCTION

SnS has attracted more attention of many researchers compared to the other IV-VI group narrow band gap semiconductors (PbS, PbTe, SnTe etc.,) because of its constituent elements being abundant in nature and not posing any health and environmental hazards. In the recent years, more effort has been put on the synthesis of nanostructured metal chalcogenide semiconductors by different methods. Most of the properties of nanostructured materials depend on their architectures including geometry, morphology and hierarchical structures [111].

Tin sulfide nanostructures have been synthesized using aqueous solution route [61], microwave - irradiation [53], solvothermal method [23, 57] and hydrothermal method [63]. SnS nanosheets have been synthesized through hydrothermal method in the presence of thioglycolic acid (TGA) and laser ablation method [66, 112, 113]. In the present work, SnS nanosheets were synthesized by simple wet chemical route without surfactants and stabilizing agents and are reported.

4.2 SYNTHESIS OF SnS NANOSHEETS

All the chemicals used were of analytical grade and used as such without further purification. 1.2 g of tin (II) chloride (SnCl₂·2H₂O) and 1.72 g of sodium
sulfide (Na₂S) were taken as tin and sulfur sources respectively and ethylene glycol (EG) was used as solvent. SnCl₂·2H₂O solution was added drop by drop into the Na₂S solution. The solution turns dark brown color with the addition of tin (II) chloride solution. The reaction was carried out at 80 °C. The precipitates were centrifuged and washed with ethanol for several times. The final product was dried at room temperature for further studies.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Structural Studies

![Figure 4.1 Powder XRD pattern of SnS nanosheets.](image)

Figure 4.1 Powder XRD pattern of SnS nanosheets.
Figure 4.1 shows the powder X-ray diffraction pattern of SnS nanosheets. All the diffraction peaks obtained are indexed to pure orthorhombic phase of SnS. This is in good agreement with the values of standard card (JCPDS NO 39-0354). Phase purity is confirmed from powder X-ray diffraction. No other impurity peaks are observed. The broadening of the peaks indicates the nanocrystalline nature of SnS. The particle size is calculated as 12 nm using Scherrer’s formula.

Figure 4.2 (a) shows the bright field image TEM of SnS nanosheets. TEM image shows that the particle size is 13 nm and the SnS nanosheets are formed due to agglomeration of nanoparticles. Figure 4.2 (b) shows the HRTEM micrograph of a single nanosheet. HRTEM micrograph shows that the nanoparticles are overlapped on each other. From the power spectrum [inset in Figure 4.2 (b)], it is observed that the lattice spacing is 0.27 nm which corresponds to plane (1 1 1) and 0.34 nm which corresponds to plane (1 2 0) of orthorhombic SnS. Figure 4.2 (c) shows the SEM image of SnS nanosheet. SEM image also shows agglomeration of SnS nanoparticles resulting in the formation of nanosheets.
Figure 4.2 (a) TEM image of SnS nanosheets, (b) HRTEM image of SnS nanosheets and the inset figure shows the corresponding power spectrum and (c) SEM image of SnS nanosheets.
4.3.2 Optical Studies

For optical absorption measurement, the SnS powder was dispersed in ethanol medium. Figure 4.3 (a) shows the UV-VIS-NIR absorption spectrum of SnS nanosheets. The dependence of \((ahv)^2\) on the photon energy \(hν\) is shown in Figure 4.3 (b). It shows a clear evidence for direct band gap transition in SnS nanosheets. An estimate of direct band gap from the intercept of the plot is 1.88 eV which shows a blue shift of 0.58 eV compared to bulk SnS. Salavati-Niasari et al., have observed large blue shift in the optical absorption spectrum of SnS nanosheets. This is due to quantum confinement of charge carriers in the nanoparticles [64].

![Figure 4.3](image)

*Figure 4.3 (a) Optical absorption spectrum of SnS nanosheets and (b) Plot of \((ahv)^2\) versus \(hν\) showing direct band gap of SnS nanosheets.*
Figure 4.4 Room temperature photoluminescence spectrum of SnS nanosheets. The colored solid curve is a Gaussian fit to the data.

Figure 4.4 shows room temperature PL spectrum of as synthesized SnS nanosheets. The PL spectrum shows two emission peaks at 1.75 eV (705 nm) and 1.57 eV (785 nm). The emission at 1.75 eV can be attributed to the band edge emission of SnS nanosheets. This shows a blue shift of 0.45 eV compared to bulk SnS. The high intensity peak at 1.57 eV can be attributed to defect such as sulfur vacancies. Zhao et al., have observed two strong emission peaks at ~ 480 nm and ~ 415 nm for SnS nanoparticles which are assigned to a high density of sulfur and tin vacancies and various kinds of defects such as interstitials, stacking faults etc.
Ghosh et al., have observed the band gap emission peak and a broad radiative defects peak at ~ 825 and at ~ 710 nm respectively for SnS thin films grown on glass and ITO substrates [114]. Present energies of PL emissions are slightly higher than those reported by Ghosh et al. [114], which may be due to smaller particle size in the present case. Devika et al., have observed band edge emission peak at ~ 720 nm and two different kinds of impurities or crystal defect peaks were observed in the wavelengths between 550 and 530 nm and at 414 nm for SnS thin films grown on amorphous and crystalline lattice matched substrates respectively [104]. Different mechanisms are reported by many researchers to explain their experimental results. But the exact mechanism is still under controversy. In present PL study, the emissions at 1.75 eV and 1.57 eV are explained to arise from band edge and defect like sulfur vacancies respectively.

Initially, SnS nanoparticles are formed by reaction of SnCl$_2$.2H$_2$O and Na$_2$S in EG solution. EG is a polar solvent. Polar solvent EG adsorbs on the surface of SnS nanoparticles due to high surface energy. The adsorption of polar solvents prevents the further growth of SnS nanoparticles. Agglomeration of SnS nanoparticles was found to lead to the formation of nanosheets in order to reduce the high surface energy [108]. For the layered type semiconductor nanocrystals, the two dimensional (2D) nanosheet is the more stable state compared to zero and three dimensional structures [67].

### 4.4 CONCLUSIONS

SnS nanosheets were synthesized through non aqueous route without influence of surfactants and autoclave. XRD and HRTEM studies confirmed that the SnS nanosheets have orthorhombic structure. TEM and SEM studies confirmed the formation of nanosheets. An estimate of direct band gap from optical absorption spectrum was 1.88 eV. Compared to bulk SnS, a blue shift of 0.58 eV observed for
direct transition due to quantum confinement effect. PL spectrum showed band edge emission peak at 1.75 eV and the defect level transition at 1.57 eV arising from sulfur vacancies.