CHAPTER 5
CONTROLLABLE SYNTHESIS AND CHARACTERIZATION OF
SnS NANOSTRUCTURES

5.1 INTRODUCTION

The versatile bonding nature of tin and sulfur forms many stoichiometric tin sulfide materials like SnS, Sn$_2$S$_3$, Sn$_4$S$_5$ and SnS$_2$ [28]. Among these, SnS has attracted much attention due to its potential applications. Research on the synthesis of semiconductor nanomaterials with specific morphologies has gained attraction due to its optical and electrical properties which depend on both size and shape [115, 116]. SnS nanoparticles with different morphology have been synthesized by various methods such as decomposition of single source precursor [66], simple wet chemical method [117] and hydrothermal method [52]. Among these, solvothermal method is effective method for synthesis since SnS nanoparticles with different morphology and well shaped nanostructures with high crystalline can be possible [54, 118].

In recent years, researchers have been intensely focused on synthesis of SnS nanoparticles with different morphologies. SnS nanowires have been synthesized at room temperature in aqueous solution using cationic surfactant CTAB and with oxalic acid [61]. SnS nanorods have been synthesized by hydrolysis of thiourea under hydrothermal conditions without using any structure directing agent. The reaction temperature and amount of sulfur source can affect the final morphology of SnS nanoparticles [59]. SnS nanostructures such as nanobelts, nanorightangles, nanorods and nanosheets have been synthesized by solvothermal
method. The effect of reaction temperature and sulfur source on the morphologies of SnS nanostructures have been reported [54]. In this chapter, the synthesis of SnS nanostructures via solvothermal method and the influence of reaction time on the morphology of SnS nanostructures are presented.

5.2 SYNTHESIS OF SnS NANOSTRUCTURES

SnS nanostructures were synthesized by solvothermal method at different reaction time and without changes of reaction parameters such as reaction temperature, precursor concentration, etc. In the typical experiment, 0.226 g of SnCl₂. 2H₂O and 0.72 g of Na₂S were dissolved in 30 ml of EG respectively. Na₂S solution was added drop wise into the SnCl₂. 2H₂O solution under magnetic stirring. The colorless solution turned brown on addition of Na₂S solution. After 10 minutes of stirring, the solution was transferred into 100 ml capacity of teflon - lined cylinder. Teflon-lined cylinder was filled with EG upto 80% of its volume and kept inside a furnace at a temperature of 180 °C for the reaction time of 6 hours, 10 hours and 16 hours and then allowed to cool in air to room temperature. The obtained black precipitates were centrifuged and washed several times using water and ethanol. The final products were dried at room temperature for 3 hours.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Structural Studies

Figure 5.1 (a-c) shows the XRD patterns of SnS nanostructures prepared at 180 °C for the reaction time of 6, 10 and 16 hours. The XRD pattern of SnS nanoparticles prepared at 6 h shows a broad peak at 36.2°. This peak corresponds to sodium tin sulfide (Na₄SnS₄, JCPDS NO: 25-0874). This is marked as ↓ in the XRD pattern and shown as inset in Figure 5.1. This is due to the inadequate reaction time for formation single phase SnS nanoparticles. All other diffraction peaks are indexed
to orthorhombic crystal structure of SnS and this is in good agreement with the standard JCPDS card NO 39-0354. For the prolonged reaction time such as 10 hours and 16 hours, only single phase (orthorhombic crystal structure) SnS nanostructures were formed without impurities like sodium tin sulfide, SnS$_2$ and SnO$_2$.

Figure 5.1 XRD patterns of SnS (a) nanoparticles prepared at 180 °C for 6 hours, (b) nanosheets prepared at 180 °C for 10 hours and (c) nanorods prepared at 180 °C for 16 hours and the enlarged portion of Figure 5.1 (a) is shown as inset in Figure 5.1.

Further, it is found that the intensity of the crystalline peaks improved with an increasing in the reaction time. The high intensity plane for the orthorhombic
structure SnS is reported as (1 1 1) plane in the literature (JCPDS NO: 39 - 0354). The intensity of (0 4 0) plane becomes more pronounced compared to that of (1 1 1) plane with increasing reaction time from 6 hours to 16 hours. This indicates the preferential orientated growth of SnS nanoparticles, nanorods and nanosheets.

The influence of reaction time on the morphologies of SnS nanostructures are studied by TEM. Figure 5.2 (a) shows the TEM image of SnS sample prepared at 180 °C for 6 hours. TEM image shows spherical nanoparticles with size less than 10 nm. Figure 5.2 (b) shows the corresponding HRTEM image of SnS nanoparticles. Figure 5.2 (c) shows the TEM image of SnS sample synthesized for the reaction time of 10 hours. TEM image shows sheet like structure. Few nanorods are also formed in addition to nanosheets. The average thickness of the nanosheets is about 200 nm. Figure 5.2 (d) shows the HRTEM image of SnS nanosheets, which represent the single crystalline nature of SnS nanosheet. Figure 5.2 (e) shows the TEM image of SnS sample synthesized for 16 hours. TEM image shows SnS nanorods with average diameter of 150 nm and lengths in the several micrometers. Figure 5.2 (f) shows the enlarged image of Figure 5.2 (e) and this shows that the surface of SnS nanorods is covered by small sized SnS nanoparticles.
Figure 5.2 (a, b) TEM and HRTEM images of SnS nanoparticles prepared at 180 °C for 6 hours, (c, d) TEM and HRTEM of SnS nanosheets prepared at 180 °C for 10 hours, (e) TEM image of SnS nanorods prepared at 180 °C for 16 hours and (f) enlarged image of (e).
5.3.2 Formation Mechanism of SnS Nanostructures

Ethylene glycol is used as solvent in this reaction and also it acts as reducing agent. In order to understand the growth mechanism of the SnS nanoparticles with various dimensions, control experiments were performed by varying the reaction time and keeping the other conditions constant, such as concentration of the Sn, S sources, amount of solvent and temperature. The shape transformation in the nanostructures is mainly derived from the aggregation of small spherical nanoparticles in order to reduce the surface energy. Figure 5.3 shows schematic representation for morphology evolution of SnS nanoparticles. At room temperature, SnS nuclei are formed through the reaction of Na₂S with SnCl₂.2H₂O in EG medium.

Figure 5.3 Schematic representations for the formation of SnS nanostructures.

Under solvothermal conditions, at less reaction time (6 hours) growth of SnS nuclei is fast and leads to the formation of small size SnS nanoparticles along with a few
agglomerated nanoparticles. Increasing the reaction time from 6 to 10 hours, the 2D nanosheets along with a few nanorods were observed (Figure 5.2 c). The formation of SnS nanosheet is due to the adsorption of stabilizing agents (EG) which in turn significantly affects the surface energy of the different facets of growing SnS nanoparticles. Further on increasing the reaction time upto 16 hours, the nanorods were formed due to the high capping ability of EG under prolonged reaction time on low energy crystallography facet of SnS nanosheet, resulting anisotropic growth of nanosheets [23]. The diameter and length of the nanorods were found to increase with increasing reaction time from 10 to 16 hours.

Figure 5.4 (a-c) shows the UV-VIS-NIR optical absorption spectra of SnS nanoparticles, nanosheets and nanorods synthesized at temperature of 180 °C for the reaction time of 6 hours, 10 hours and 16 hours respectively. For bulk SnS, the direct band gap transition is at 980 nm (1.26 eV) and indirect band gap transition is observed at 1100 nm (1.12 eV) [119]. The optical absorption spectra of SnS nanostructures (nanoparticles, nanosheets and nanorods) show the absorption edge at 914 nm (1.35 eV) and 1021 nm (1.21 eV). The transitions observed at 1.35 eV and 1.21 eV are corresponding to the direct and indirect band gap transitions of SnS nanostructures respectively. Only few reports are available for the observation of both direct and indirect band gap transitions in the SnS nanostructures. For SnS nanoflowers [63], direct and indirect band gap transitions were observed at 1.53 eV and 1.43 eV respectively.
Figure 5.4 UV-VIS-NIR absorption spectra of SnS (a) nanoparticles prepared at 180 °C for 6 hours, (b) nanosheets prepared at 180 °C for 10 hours and (c) nanorods prepared at 180 °C for 16 hours.

Sohila et al., have observed direct and indirect transition for SnS nanoparticles at 1.78 and 1.2 eV respectively [120]. Since the diameter and thickness of nanorods and nanosheets is much larger than the exciton Bohr radius of bulk SnS (7 nm) [84]. The quantum confinement effect related shift in the direct and indirect transitions are not observed.
5.5 CONCLUSIONS

SnS nanostructures were synthesized by solvothermal method without using any surfactant. Phase purity of the samples was identified as orthorhombic from the XRD measurements. The influence of reaction time on the morphologies of SnS nanostructures was studied using TEM. The evolution of morphology with respect to reaction was discussed. Direct and indirect band gap transitions were observed at 1.35 eV and 1.21 eV respectively. Quantum confinement effect related blue shift in the optical absorption spectra of SnS nanostructures was not observed.