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Synthesis and thermal study of SnS nanoflakes

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ABSTRACT

SnS nanoflakes were synthesized by chemical route at a temperature of 80 °C. Stannous chloride and sodium sulphide was used as a source of Sn^{2+} and S^{2-} ions respectively. The elemental stoichiometric analysis of SnS nanoflakes was done by employing energy dispersive analysis of X-rays (EDAX) technique. The structural study of the as-synthesized nanoflakes was studied by X-ray diffraction (XRD). The grain size was determined using X-ray diffraction (XRD) data employing Scherrer's formula and Hall–Williamson plot. The residual strain produced in the synthesized nanoflakes during the synthesis was obtained from Hall–Williamson plot. The transmission electron microscopy (TEM) image showed that the synthesized nanoflakes have average crystallite size of 11 nm. The thermal decomposition of SnS nanoflakes was studied employing thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) techniques. The thermal behaviour of SnS nanoflakes was compared with SnS single crystals. The thermal parameters were evaluated of the SnS nanoflakes using two most common thermal analysis methods; Broido and Coats-Redfern (CR) relations. Thermal activation energy, enthalpy change (ΔH^*), entropy change (ΔS^*) and free energy change (ΔG^*) related to the thermal decomposition process were calculated for the SnS nanoflakes. The obtained results are discussed in details.

1. Introduction

In the past few decades, tin sulfide (SnS) has gained much attention as a possible alternative absorber material for the next generation of solar cells to replace the current best developed technology based on CdTe and $Cu(In,Ga)Se_2$ materials. Reason being it involves toxic cadmium and rare elements gallium, indium and tellurium. Whereas in case of SnS, the constituent elements Sn and S are of low toxicity, low cost and are in natural abundance. Also SnS has high optical absorption ($\alpha > 10^4\ cm^{-1}$) above the direct absorption edge at 1.2–1.5 eV [1,2]. It belongs to IV–VI group compound semiconductor generally showing p-type conduction due to the small enthalpy of formation of tin vacancies, which generate shallow acceptors [3]. SnS is very interesting for the photovoltaic conversion of solar energy into electrical energy, since its band gap is 1.2 eV is comparable to that of silicon. It is seen that SnS in nanoforms especially nanowires, nanorods, etc. have found potential applications in electronic and optoelectronic devices [4,5]. Reason being nanowires of other semiconductors like Si, Ge, GaN and InAs has exhibited high electron mobility in the axial direction due to quasi-ballistic transport of electrons. The field-effect-transistors based on these nanowires showed performance comparable to or even better than the reported for planar devices made from the same materials [6–9]. In same line to nanowires and nanorods, SnS in nanoflakes has found larger interest due to its potential characteristics [10–13]. In this present research paper, the authors report the synthesis of SnS nanoflakes by a simple chemical route method and study their thermal behaviour from ambient temperature to 1223 K.

2. Experimental details

SnS nanoflakes were synthesized by chemical route. The chemicals used for the synthesis of SnS nanoflakes were, stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$; Assay 98%; Alfa Aesar, USA), sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$; Assay 97%; Chiti Chem Corporation, Vadodara, India), oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$; Assay 98%; Chiti Chem Corporation, Vadodara, India) and cetyltrimethyl ammonium bromide (CTAB); ($C_{19}H_{42}BrN$; Assay 98%; Chiti Chem Corporation, Vadodara, India). All the chemicals were of analytical grade and used without any purification.

In the typical SnS nanoflakes synthesis process, firstly 0.02 M $H_2C_2O_4{\cdot}2H_2O$ is added to 350 ml of 4.4 mM CTAB. Then 0.01 mM

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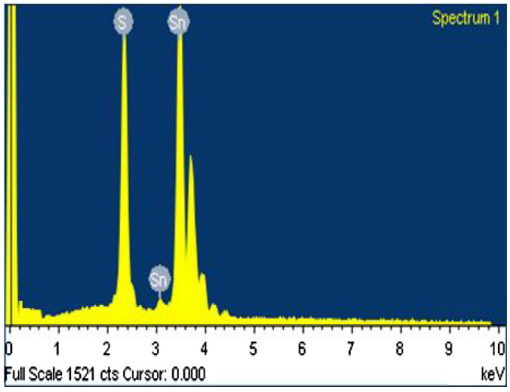

Fig. 1. EDAX spectrum of SnS nanoflakes.

$SnCl_2{\cdot}2H_2O$ is added to the solution. Lastly, 0.01 mM $Na_2S{\cdot}9H_2O$ is added drop by drop into the solution. Here all the solutions were prepared in distilled water and mixing of the respective solutions were done under constant magnetic stirring. The ultimate solution was magnetically stirred for half an hour and the obtained final solution was held at 80 °C for 2 h. At last, the black suspension is filtered and washed several times in distilled water to remove impurities to get resulting nanoflakes yield. After multiple washes, they were dried in oven at 45 °C for 2 h.

In this synthesis mechanism, oxalic acid dihydrate worked as a reducing agent that formed stannous oxalate (SnC_2O_4) after reacting with the stannous chloride. The CTAB acted as a surfactant and Na_2S as a source of S^{2-} ion.

In this paper the thermocurves of as-synthesized SnS nanoflakes were recorded and compared with SnS single crystals thermocurves. The SnS single crystals were taken as-grown. They were grown by direct vapour transport (DVT) technique and comprehensively characterized. The single crystal growth parameters and characterization results are not discussed in this paper and have been reported elsewhere [14].

2.1. Characterization

The EDAX analysis of the as-synthesized SnS nanoflakes were done by energy dispersive analysis of X-rays (EDAX) attached to XL 30 ESEM scanning electron microscope. The X-ray diffraction (XRD) pattern was recorded by a Philips Xpert MPD X-ray diffractometer using graphite monochromatized CuK_α radiation ($\lambda = 1.5405$ Å). The scanning rate of 10° min^{-1} was applied to record the pattern in the 2θ range of 3°–90°. The transmission electron microscopy (TEM) analysis was carried out on Philips, Tecnai 20 microscope by operating at an acceleration voltage of 200 kV. The sample for TEM analysis was prepared by dispersing the nanoflakes in a solvent by sonication and then taking a drop of the solution on carbon coated copper grids. The solvent was allowed to evaporate under ambient condition. The excess solvent was removed by vacuum drying. The curves of thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermogravimetic analysis (DTA) were recorded from ambient temperature to 1223 K at a heating rate of 5 °C/min in inert N_2 atmosphere using Seiko SII-EXSTAR TG/DTA-7200. The same condition and instrument was employed for recording the thermocurves of as-grown SnSe single crystals.

3. Results and discussion

The stoichiometric composition and purity of the synthesized nanoflakes were determined by energy dispersive analysis of X-rays (EDAX) technique. The EDAX spectrum, Fig. 1, shows two elemental peaks of tin (Sn) and sulphur (S). The peaks next to the main Sn peak are also of tin element only, but they are from different energy shell. The obtained weight percentage from EDAX spectrum and the standard weight percentage of tin (Sn) and sulphur (S) elements are tabulated in Table 1 for SnS nanoflakes. The weight percentage data shows that the synthesized SnS nanoflakes are slightly rich in tin content. The EDAX spectrum also showed that the synthesized SnS nanoflakes are free of any other impurities and contaminants. The atomic percentage data of tin and sulphur are tabulated in Table 1.

Table 1
EDAX data of as-synthesized SnS nanoflakes.

	Elements	Standard	EDAX	Resultant compound
Weight (%)	S	21.27	20.80	$Sn_{1.01}$ $S_{0.99}$
	Sn	78.73	79.20	
Atomic (%)	S	50	49.30	
	Sn	50	50.70	

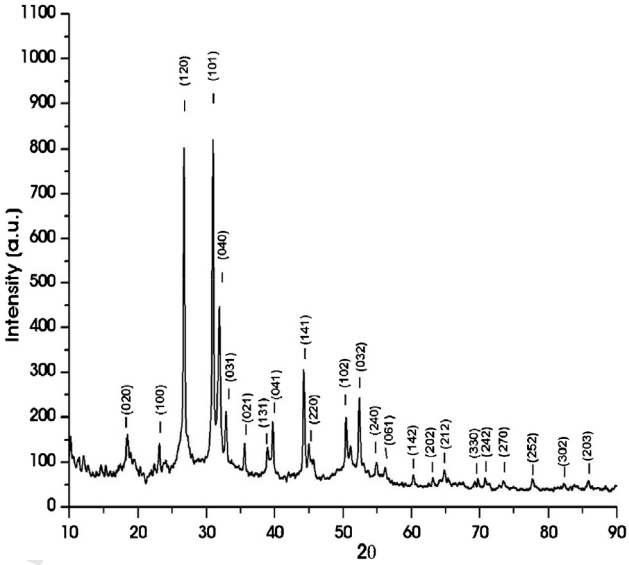

Fig. 2. X-ray diffraction pattern of SnS nanoflakes.

The XRD pattern of the as-synthesized SnS nanoflakes is shown in Fig. 2. All the diffraction peaks can be indexed as those of SnS possessing orthorhombic structure having lattice parameters as; $a = 4.32$ Å, $b = 11.19$ Å and $c = 3.98$ Å in good agreement with the standard data (JCPDS Card No. 39-0354). The XRD did not show any other phases like tin disulphide, tin oxide, etc.

The crystallite size was calculated using below Debye–Scherrer's formula for different X-ray reflections [2];

$$L = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where K is the shape factor taken as 0.9 [15], λ is the wavelength of X-ray (1.5405 Å), β is the angular line width at half maximum intensity and θ is the Bragg angle in degree. The average crystallite size estimated from the XRD analysis using Scherrer's formula came out to be ~13 nm.

The crystallite size and the micro strain in the as-synthesized SnS nanoflakes were estimated by Hall–Williamson relation [2].

$$\frac{\beta \cos\theta}{\lambda} = \frac{K}{L} + \frac{4 \sin\theta}{\lambda} \quad (2)$$

The Hall–Williamson equation incorporates the Scherrer's formula of crystallite size and the micro strain terms. Here β is full width at half maximum (FWHMs) of the diffraction peaks.

The plot of $(\beta \cos\theta)/\lambda$ versus $4(\sin\theta)/\lambda$ for the as-synthesized SnS nanoflakes is shown in Fig. 3. In line to Eq. (2), the plot is a

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