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ELECTRICAL TRANSPORT PROPERTIES OF SnS AND SnSe SINGLE CRYSTALS GROWN BY DIRECT VAPOUR TRANSPORT TECHNIQUE

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Tin monosulphide and Tin monoselenide single crystals have been grown by a direct vapour transport technique. Confirmation of stoichiometric proportion of constituent elements and determination of crystal structure of grown crystals were done by EDAX and powder X-ray diffraction analysis. The resistivity and thermoelectric power measurements were carried out in the temperature range 308 K to 573 K. The Hall coefficient, carrier concentration and Hall mobility were determined from Hall effect measurements at room temperature.

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1. Introduction

Among the IV-VI semiconductor compounds, tin sulphide (SnS), tin selenide (SnSe), germanium sulphide (GeS) and germanium selenide (GeSe) have the layered orthorhombic structure with eight atoms per unit cell forming biplaner layers normal to the largest c axis [1-4]. In unit cell of SnS and SnSe, atoms in a single layer are joined to three nearest neighbors by covalent bonds which forms zigzag chains along the b axis while there is only van der Walls bonding between the layers. This typical crystalline structure results in strong anisotropic optical properties at low energies and more isotropic optical properties at higher energies, which makes them interesting materials intermediate between two dimensional and three-dimensional semiconductors. These compounds have attracted considerable attention because of their important specific properties in the field of optoelectronics [5], holographic recording systems [6-8], electronic switching [9-10] and infrared production and detection [11]. Moreover SnSe is a semiconductor with a band gap of about 1 eV having a potential as an efficient solar cell material [12-13].

2. Experimental procedure

2.1 Crystal growth

For the growth of these crystals highly pure powder of Sn (99.99%), S (99.99%) and Se (99.99%) were taken in a stoichiometric proportion in the ampoule. It was evacuated to a 10^{-5} Torr and then sealed. The sufficient care was taken for vigorous shaking so as to distribute the mixture along the length uniformly. The ampoule was set in a horizontal furnace. Its temperature was slowly raised at the rate of 60 K/hr till it reaches to 1073 K. It was maintained at this temperature for a period of 3 day. The ampoule was then slowly cooled and brought to room temperature. The resulting free flowing shiny homogeneous polycrystalline powder was achieved. This charged ampoule was placed in a dual zone horizontal furnace. For tin monosulphide and tin monoselenide

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the temperatures of hot zone and cold zone of the ampoule were kept as shown in table 1. The temperature was increased at the rate of 30 K/hr, till it attained the required temperature in both the zones. For the growth of SnS, the ampoule was left in the furnace for 3 days after that the temperature was decreased at the rate of 30 K/hr up to the room temperature**.** Then the furnace was switched off and the ampoule was carefully taken out from the furnace. The ampoule was finally broken and resulting crystals were collected.

Table 1 The growth condition of SnS and SnSe single crystals.

Crystal	Temperature distribution		Growth Period (hr)
	Reaction Zone (K)	Growth Zone (K)	
SnS	1073	1023	70
SnSe	1073	1033	48

2.2 Structural characterization

The chemical composition of the grown crystals was studied through Energy Dispersive Analysis of X-rays. The results of EDAX are shown in table 2.

The powder obtained during the growth process for each sample was prepared for the X-ray diffraction study experiment. The X-ray diffraction patterns obtained for SnS and SnSe are shown in Fig. 1 and 2.

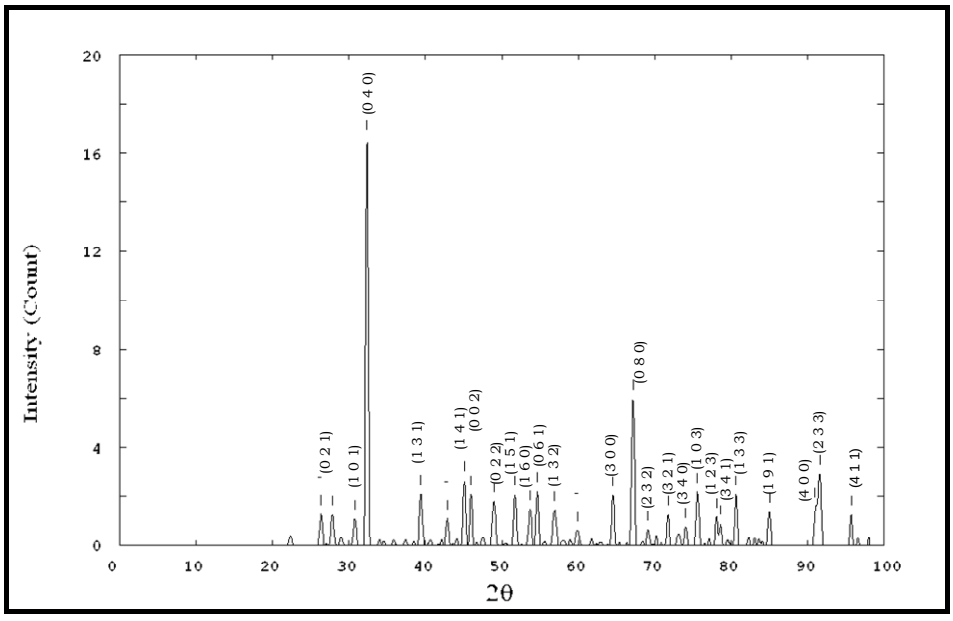

Fig.1. The X-ray diffraction pattern for SnS

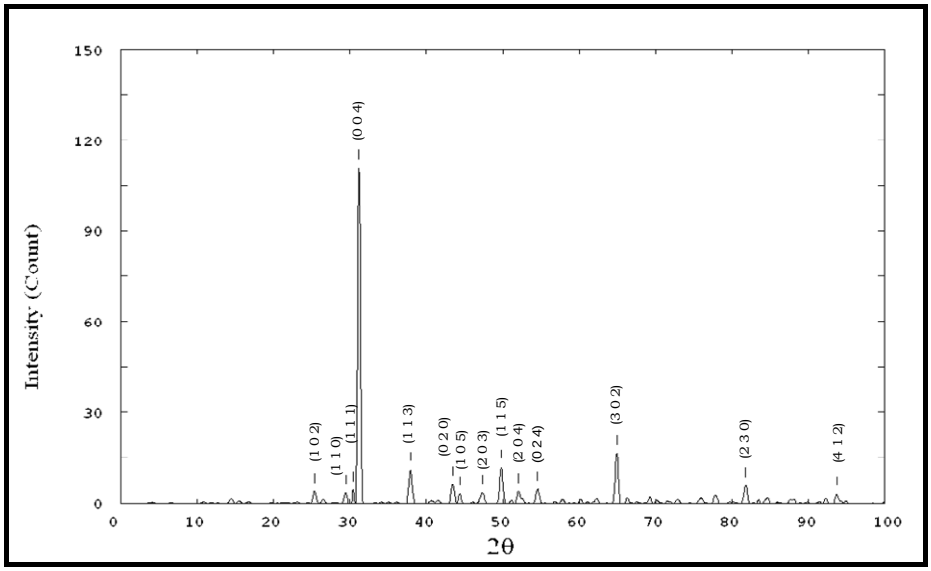

Fig. 2. The X-ray diffraction pattern for SnSe

2.3 Electrical properties measurements

2.3.1 Resistivity measurements

The electrical resistance measurements along the cleavage plane of grown crystals were carried out in the temperature range from 308 K to 573 K at an interval of 5 K. The resistivity of the samples was calculated by using the formula

$$\rho = \frac{RA}{l}$$

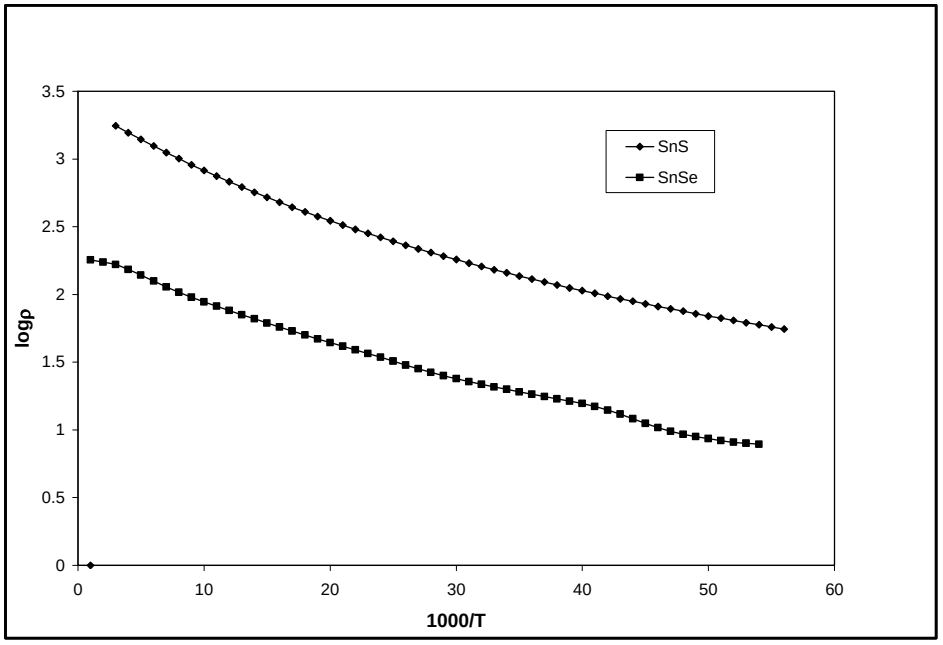

Fig. 3 the plot of logρ versus 1000/T for SnS and SnSe single crystals.

From the slopes of log ρ Vs 1000/T plots the values of activation energies were calculated using the formula,

$$E_a = 2.303 \text{ X } k_B \times 10^3 \text{ X slope (eV)}$$

where $k_B = 8.602 \times 10^{-5}$ eV/K

These values are presented in table 4.

2.3.2 Thermoelectric power measurements

The measurements of the thermoelectric power with temperature were carried out in the temperature range 308 K to 573 K.

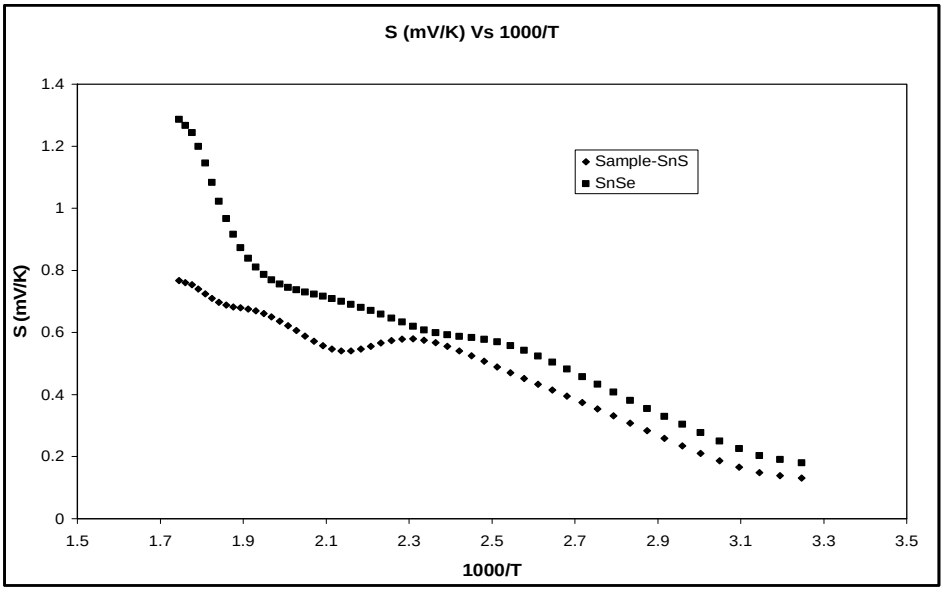

Fig. 4. Variation of TEP with inverse of temperature for SnS and SnSe single crystals

For the study of temperature dependent thermoelectric power S of a p-type semiconductor the expression is given by

$$S = \frac{k}{e}[A + \frac{E_{FV}}{kT}]$$

Where k is Boltzman constant, e is the electronic charge, $E_{FV} = E_F - E_V$ is the separation of the fermi level from the top of the valence band and A is the constant determined by the scattering process and is defined as

$$A = 5/2 - s$$

2.3.3 Measurements of Hall parameters

Hall effect measurements was performed along the cleavage plane of as grown crystals of SnS and SnSe in order to determine the type of the semiconductor, mobility and carrier concentration using the formula

$$\mu_H = \frac{t}{\Delta B} \times \frac{\Delta R}{\rho}, \qquad R_H = \mu_H \times \rho, \qquad \eta = \frac{1}{R_H \cdot e}$$

3. Results and discussion

The single crystals of SnS and SnSe were grown using Direct Vapour Transport (DVT) technique. Single crystal of SnS and SnSe were found to grow in the form of thin shining platelets. Form the results of energy dispersive analysis of X-rays it is confirmed that the chemical compositions of both SnS and SnSe are in good agreement with the calculated data which is shown in table 2. X-ray diffractogram reflect the orthorhombic crystal structure of both SnS and SnSe single crystals. The value of the lattice parameters obtained from the analysis of X-ray diffractogram of both compounds are presented in table 3. The lattice parameters of SnS and SnSe are very well matched with the value obtained by earlier workers [14-30]. The resistivity along the cleavage plane decreases with increase in the temperature which indicates the semiconducting behavior of the as grown crystals. From the high temperature resistivity measurements we get the activation energy of both crystals SnS and SnSe which is presented in table 4 and the value of activation energy indicate that measured resistivity is the results of extrinsic processes in the crystals. From the variation of thermoelectric power with temperature gives the value of scattering parameter and fermi energy are given in table 5. Positive sign of Hall coefficient and seeback coefficient indicate that both crystals SnS and SnSe are p-type in nature and majority in them are holes. All the results obtained from the Hall effect measurements are given in table 6.

Table 2 Results obtained from the EDAX spectra.

Results	**Stoichiometry proportion (Weight %)**			
	SnS		**SnSe**	
	Sn	S	Sn	Se
Calculated	78.73	21.26	60.05	39.94
Experimental	77.98	22.02	59.86	40.14

Table 3 Result obtained from X-ray diffractogram

crystal	**a (Å)**	**b (Å)**	**c (Å)**	**Volume ($Å^3$)**	**X-ray density x 10^3 (kg/m^3)**
SnS	4.327	11.14	3.94	189.91	5.272
SnSe	4.45	4.16	11.45	211.96	6.192

Table 4 Value of activation energies determined by high temperature resistivity measurement for SnS and SnSe single crystals

Crystal	**Activation energy (eV)**
SnS	0.2022
SnSe	0.1856

Table 5 Hall parameters for SnS and SnSe single crystals

Parameter	**SnS**	**SnSe**
Resistivity x 10^{-2} (Ω.m)	893.73	180.65
Hall Coefficient x 10^{-6} (m^3 $coloumb^{-1}$)	10883	15675
Type	p	p
Mobility x 10^{-4} (m^2/V.s)	12.17	86.76
Carrier concentration x 10^6 (m^{-3})	6.78 x 10^{14}	8.53 x 10^{14}

Table 6 Value of parameters A, E_{FV} and s for SnS and SnSe single crystals

Parameter	SnS	SnSe
A	1.458	2.07
E_{FV} (eV)	0.403	0.6034
s	1.042	0.43

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