Growth, microtopography and effect of pressure on electrical resistance of DVT grown SnS and SnSe single crystals

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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 respectively. The surface microtopographic study of as grown crystals showed that they are grown by lateral layer mechanism. Pressure dependent electrical resistance was studied using Bridgeman opposed anvils experimental system up to 6 GPa for SnS and SnSe single crystals.

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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]. These compounds have at low temperature the orthorhombic structure but at high temperature a more symmetric structure with space group, Cmcm. In unit cell of SnS and SnSe, atoms in a single layer are joined to three nearest neighbors by covalent bond which forms zigzag chains along the b axis while there is only Van der Waals bonding between the layers. These layered semiconductors have been attracting the attention of scientist because of their potential application in optoelectronic device [5-8]. They are also used in holographic recording systems [4]. The electronic and optical properties of SnS and isostrucutral IV-VI semiconductors have been extensively studied by electron-energy-loss spectroscopy, photo emission spectroscopy and ellipsometry [9-11]. Experimental studies showed that SnS is narrow gap semiconductor with an indirect gap of 1.07ev and direct gap is located at energy of 1.3 eV. But theoretical calculation gave the value of 1.19-1.6 eV for the indirect gap and 1.8eV for the direct gap [12]. The influence of high pressure and temperature on the band gap in SnS was studied by Parenteau and Carlone (1990) [4] using optical absorption spectroscopy. They have observed that under pressure there is a reduction of direct and indirect band gaps. The motivation for the present work emerged from the above mentioned experimental work.

2. Experimental

2.1 Crystal growth and surface microtopography

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 quartz ampoule. It was evacuated to a 10^{-4} 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 days. The ampoule was then slowly cooled at the rate of 60 K/hr 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 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 60 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 60 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 which are shown in Fig. 1.

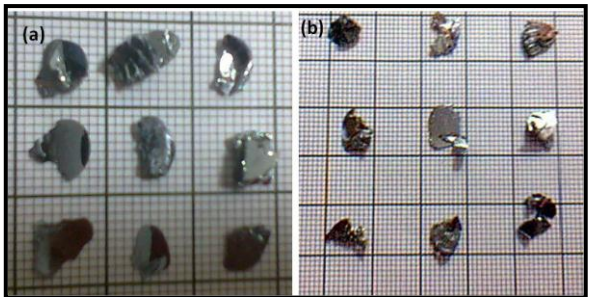

Fig. 1. Photographs of (a) SnS single crystal (b) SnSe single crystal.

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

Crystal	Temperature distribution		Growth Period (hr)	Remark
	Reaction Zone (K)	Growth Zone (K)		
SnS	750	700	60	Crystals not found
	900	850	74	Crystals not found
	1073	1023	70	Crystals found shown in Fig. 1
SnSe	810	760	78	Crystals not found
	890	840	85	Crystals not found
	950	900	60	Crystals not found
	1073	1033	48	Crystals found shown in Fig. 1

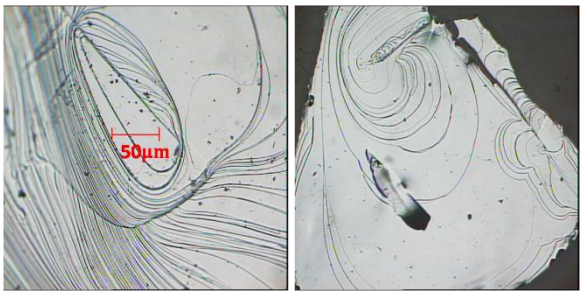

Fig. 2. Micro-topography of SnS single crystals.

In the present work observation of microstructure on crystal surfaces was accomplished with the help of metallurgical microscope designed by 'Carl Zeiss' for rapid examination of grind, polished and as grown surfaces of objects. Figs. 2 and 3 shows the microtopography of their surface growth structures.

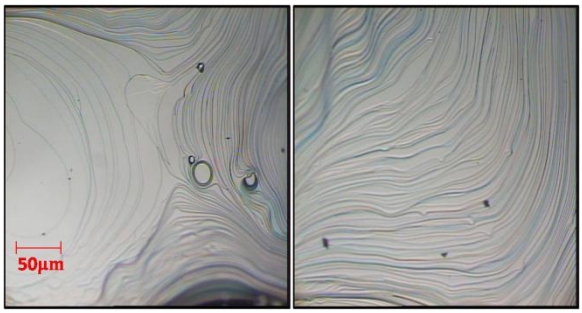

Fig. 3. Micro-topography of SnSe single crystals.

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. 4 and 5.

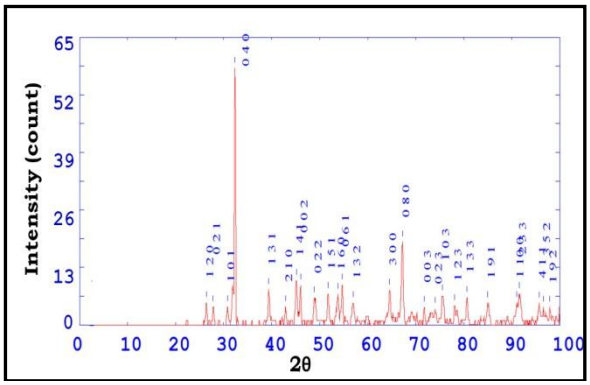

Fig. 4. The X-ray diffraction pattern for SnS.

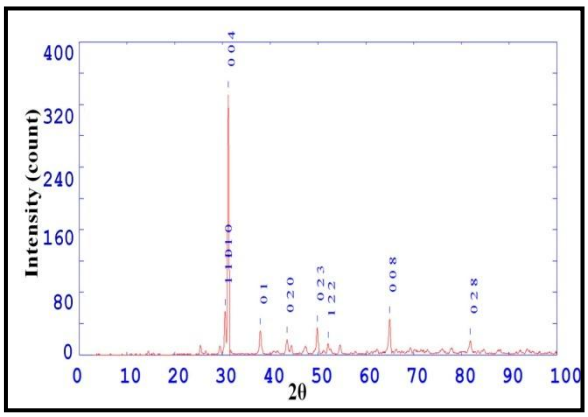

Fig. 5. The X-ray diffraction patterns for SnSe.

2.3 Pressure dependent electrical resistance

For the room temperature measurement of resistance as a function of pressure up to 6 GPa, the sample was kept at the centre of the talc disc on the lower anvil. The schematic diagram of the experimental arrangement for the resistance measurement with pressure is shown in Fig. 6. The pressure was generated by a hydraulic press on the Bridgman type tungsten carbide opposed anvils which is shown in Fig. 7. The sample was contained in a pyrophyllite gasket with talc as pressure transmitting medium. A four-probe method was employed in order to measure the resistance of this sample. Stainless steel wires of thickness 50 μm were used. For the measurements of resistance, suitable current (~1-10 mA range) was passed through outer leads and the voltage drop across the inner leads was measured. Resistance has been calculated out using the I-V values for different pressure.

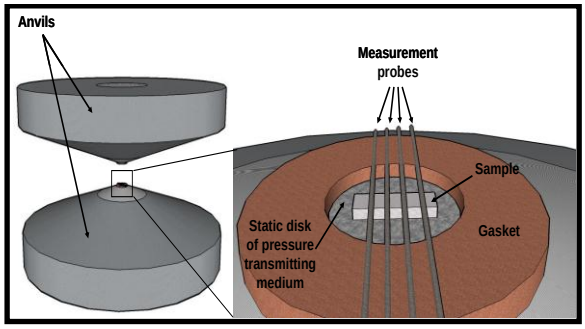

Fig. 6. Arrangement of sample and probes in the pressure dependent electrical resistivity measurement system.

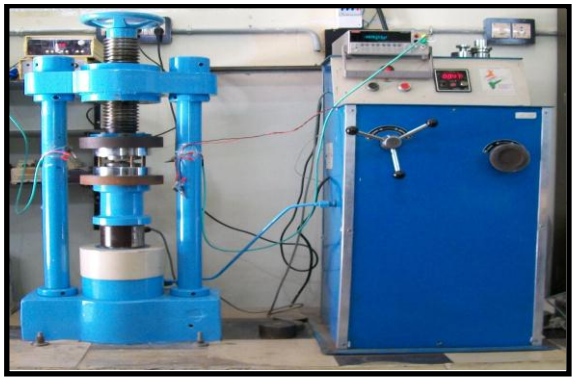

Fig. 7. Hydraulic press used to generate high pressure.

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. From 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 [13-29].

Table 2. Results obtained from the EDAX spectra.

Results	**Stoichiometric 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. Parameters 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

Since the as grown faces of SnS and SnSe crystals did not show any growth spiral patterns, one can deduce that growth was not promoted by screw dislocation mechanism. The irregular shape of the growth layers indicates that the growth is rapid. Fig. 2 shows that impurities on the surface serve as the starting point for the growth layers.

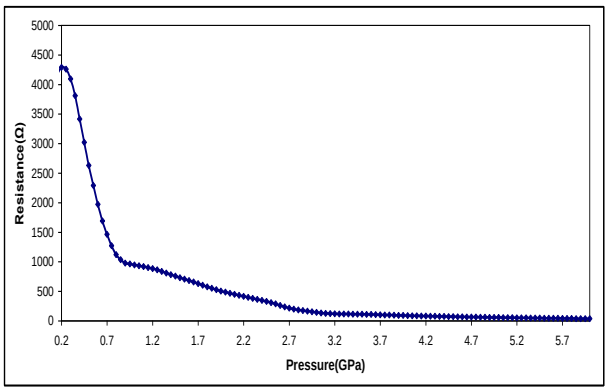

Fig. 8. Variation of electrical resistance with pressure for SnS single crystal using Bridgman anvils.

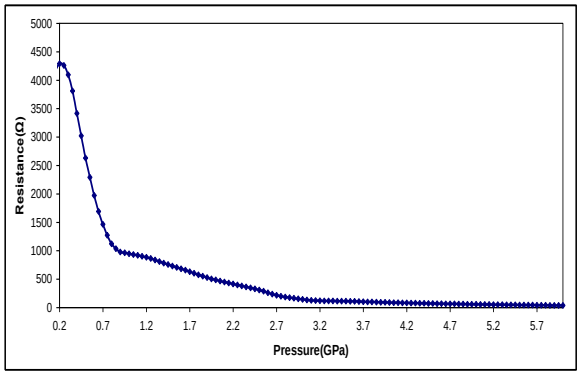

Fig. 9. Variation of electrical resistance with pressure for SnSe single crystal using Bridgman anvils.

The variation of the resistance with pressure for SnS and SnSe single crystals grown by direct vapour transport technique are shown in Figs. 8 and 9. For SnS and SnSe, it is seen that the resistance decreases exponentially with increases in pressure up to maximum pressure attained and result of variation of electrical resistance do not show any transition up to 6 GPa. The resistance was measured in several independents runs on these crystals as a function of pressure and was found to be reproducible.

When the layered material is subjected to pressure the interlayer spacing will change more rapidly than the intralayer spacing since the interlayer bonds are much weaker than the intralayer bonds. For such materials compression therefore forces the layers closer together without affecting the nearest neighbor distances. Lattice vibration pressure Raman studies of layer crystals reveals that change in r_0 (the covalent bond length) i.e. $\Delta(r_0)$ is one to two orders of magnitude smaller than the change in r_1 (the intralayer spacing) i.e. $\Delta(r_1)$. Accordingly, pressure induced modifications in the electron energy levels of the layered semiconductors like WS_2, WSe_2 and WTe_2 should show a decrease in the resistance with increasing pressure [30]. The present data on SnS and SnSe upto 6 GPa are consistent with the above explanation.

4. Conclusions

1. Single crystals of SnS and SnSe have been grown by direct vapour transport method. Single crystal of SnS and SnSe were found to grow in the form of thin shiny platelet. Optimum growth conditions for the growth of large sized SnS and SnSe single crystals have been determine by trial and error method.
2. EDAX results confirm fairly good stoichiometric proportion of constituent elements in both SnS and SnSe.
3. X-ray diffraction analysis of these crystals has shown that these crystals possess orthorhombic structure. The lattice parameters are very well matched with the value obtained by earlier workers.
4. The surface microtopographic studies of the as grown single crystals showed no spiral traces, confirming that the growth is not driven by screw dislocation mechanism. The irregular nature of the growth layers seen at the edges of the smooth flat faces, substantiated the rapid growth by lateral spreading of layers.
5. Using Bridgman anvils author achieved pressure maximum up to ~6 GPa. As shown in Fig. 8 and 9, resistance decreases continuously as pressure increases. With increase in pressure samples become more conducting. Change in conductivity in a semiconductor under pressure mainly arises from the change in the energy band gap and therefore the applied pressure influences the number of electrons in the conduction band and holes in the otherwise filled valence band [31]. No transition is found in SnS and SnSe up to 6 GPa pressure and the electrical resistance decreases with increase in pressure which shows layered structure of the single crystals.

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