

Effect of pressure on electrical resistance of SnSeRex (x=0.1, 0.2, 0.3, 0.4) (DVT) grown crystals

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Abstract - Rhenium doped Tin monoselenide crystals have been grown by Direct Vapour Transport (DVT) technique using two zone horizontal furnace by trial and error method. The results of electrical resistance measurements under pressure on single crystals of SnSeRex (x = 0.1, 0.2, 0.3, 0.4) (DVT) are reported. Measurements up to 4GPa are carried out using Bridgman anvil set up. There is no clear indication of any phase transition till the highest pressure is reached in these measurements.

Keywords- Crystal growth, Bridgman anvil, high pressure resistance

I. Introduction

The physical properties of layered materials have been a field of intensive study for many years. The binary IV-VI layered semiconducting compounds (SnSe, SnS, GeSe, GeS) generated a great deal of interest during the last two decades due to their interesting electrical and optical properties. Tin selenide has an orthorhombic crystal structure. The lattice parameters a; b and c obtained for SnSe single crystals were compared and found in agreement with those earlier reported by different investigators [1-3]. The single crystals of SnSeRex (x = 0.1, 0.2, 0.3, 0.4) were grown using DVT technique with help of dual zone horizontal furnace. The values of the different lattice parameters of SnSeRex (x = 0.1, 0.2, 0.3, 0.4) have been also reported from the analysis of the X ray diffractogram by author [4]. The SnSe crystal is made up by tightly bound double layers of Sn and Se atoms stacked along the c-axis.

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Each atom has three strongly bonded neighbors within its own layer and three more distant weakly bonded neighbors, one of which lies in an adjacent layer. The bonding between the layers is weak Van der Waals types which permit them to shear easily. At high pressures the fluid lubricants squeeze out from in-contact surfaces, causing high friction and wear. In lamellar solids, shearing takes place more

easily when loads are high. So lamellar solids are well-suited to extreme pressure lubrication. Structural transitions and metallization are of relevance in its application as lubricant. Several studies have been made [5-9] on the physical and transport properties of SnSe. However, there are no reports on the effect of pressure on the electrical resistivity of SnSeRex (x = 0.1, 0.2, 0.3, 0.4) materials. Hence, we have made an attempt to investigate effect of pressure on electrical resistance in SnSeRex (x = 0.1, 0.2, 0.3, 0.4) crystals grown by direct vapor transport technique in view of their growing importance and applications. This paper describes the results obtained.

II. Experimental Technique

Highly pure powder of Sn (99.99%), Se (99.99%) and Re (99.99%) were taken in a stoichiometric proportion in the ampoule for the compound preparation. 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 and maintained at this temperature for a period of 3 days for charge preparation. 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

Growth parameters	SnSeRex (doped by Rhenium)			
	x=0.1	x=0.2	x=0.3	x=0.4
Source zone temp. (°C)	590	580	570	560
Growth zone temp.(°C)	610	600	590	580
Ampoule dimensions (cm × cm)	23 × 2.2			
Vacuum level (torr)	10^{-5}			
Rate of increment of temperature	30 (°C/hour)			
Rate of decrement of temperature	20 (°C/hour)			
Avg. Dimensions (cm × cm)	0.7×0.5	0.9 × 0.5	0.6 ×0.4	0.9×0.5

furnace. The temperatures of source zone and growth zone of the ampoule were kept as shown in Table I.

Table I. Growth conditions of rhenium doped tin selenide single crystals

The ampoule was kept in this temperature gradient of the furnace for 7 days. At the end of this period the furnace was allowed to cool slowly at the rate of 30 °C/h to 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. The appropriate growth conditions for all samples are reported in Table I. These compounds have been characterized by EDAX and XRD analysis [4].

Resistance Measurement Using Bridgman Anvil Cell

The pressure variation of electrical resistance measurements were carried out using Bridgman opposed anvil apparatus [10] up to 4 GPa where we have good control of pressure while increasing or decreasing. A photograph of the high-pressure set-up is shown in Figure 1. The Bridgman anvils consist of a tungsten carbide cylindrical piece, one face of which is ground in a tapered form ending with a flat anvil surface. In a typical anvil, the anvil has a diameter of 100 mm; the WC cylinder is of 25 mm diameter with the flat surface of 10 mm and the taper angle about 10°. The anvil face experiences a high pressure but the material is heavily supported to prevent a failure of the material. Thus the anvil faces can support pressures in excess of 10 GPa. The anvils are pressed against each other four leads electrical resistivity measurements can be done as shown in Figure 2. The sample is enclosed with talc disc and surrounded by pyrophyllite gasket. For the room temperature measurement of resistance as a function of pressure, up to 10 GPa, the sample was set 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 Figure 2.

The sample is contained in a pyrophyllite gasket with talc as pressure transmitting medium [11]. Pressure was calibrated with bismuth transitions at 2.5GPa and 7.65 GPa. The pressure was generated by a hydraulic press on the Bridgman type tungsten carbide opposed anvil apparatus with Bismuth pressure calibration as shown in Figure 2.



Figure .1 The high pressure set-up used for the measurement of resistance using Bridgman opposed anvils up to 10 GPa.

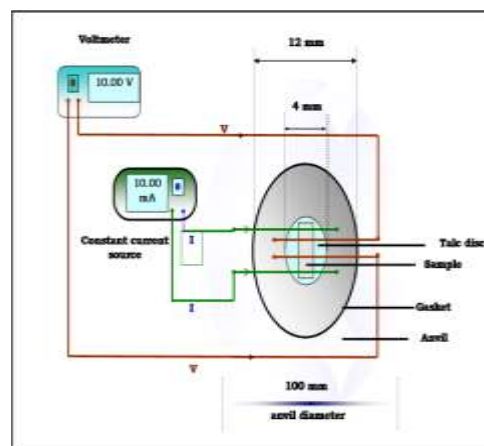


Figure 2. Schematic diagram of the four probe arrangement for measurement of resistance as the function pressure

A four-probe method was used to evaluate the resistance of these samples. Stainless steel wires of 50 μ m thickness were used for this experiment. 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 I-V values of different pressure.

III. Results and Discussions

The variation of electrical resistance with pressure for SnSeRex ($x = 0.1, 0.2, 0.3, 0.4$) crystals are shown in Figure 3. For all the cases, it is clear that the resistance decreases gradually with increase in pressure up to maximum value attained. The results of variation of electrical resistance do not show the presence of any phase transition up to 4GPa. The resistance was measured in several independent runs on these crystals as a function of pressure and found to be reproducible.

In these crystals, the valance band and conduction band are separated by energy band gap. When pressure increases, the separation of bands decreases and charge carriers of rhenium from valance band contribute to the carriers of conduction band and the samples becomes more conducting. This explains the decrease of resistance with increase in pressure. Thus, the decrease in resistance is probably attributed to the charge carriers of valance band contributing to the conduction band carriers. From all the plots we can say that in SnSeRex ($x = 0.1, 0.2, 0.3, 0.4$) crystals the content of rhenium increase the resistance of the crystal increase but in all these crystals the resistance decreases monotonously as the pressure increases.

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.

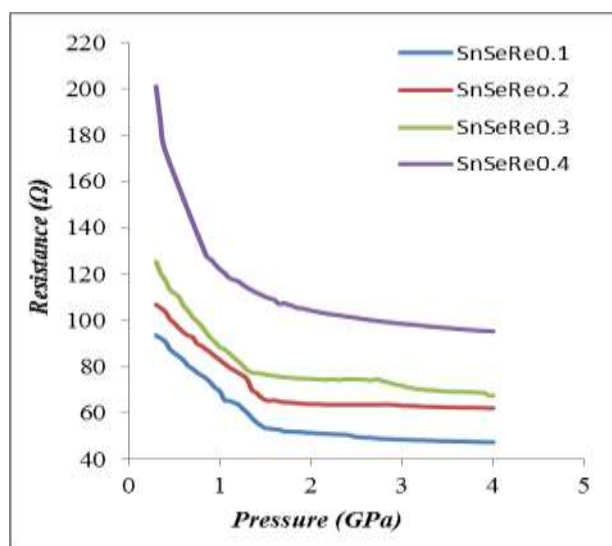


Figure 3. Variation of electrical resistance with pressure for SnSeRe_x($x=0.1, 0.2, 0.3, 0.4$) single crystals using Bridgman anvils

Lattice vibration pressure Raman studies of layer crystals reveals that change in r_0 (the covalent bond length) i.e. (r_0) is one to two orders of magnitude smaller than the change in r_1 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 [15]

The present data on SnSeRe_x ($x = 0.1, 0.2, 0.3, 0.4$) consistent with the above explanation. It will be interesting to carry out Raman and X-ray diffraction measurements under pressure to associate the weak anomaly observed in resistance measurements with any structural transition.

IV. Conclusions

Single crystals of SnSeRe_x ($x = 0.1, 0.2, 0.3, 0.4$) have been grown by direct vapour transport technique. Resistance decreases continuously as pressure increases for all crystals up to 4 GPa using Bridgman Anvil Cell and the crystals become more conducting. Change in conductivity in a semiconductor under pressure mainly arise 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 valance band [16]. No transition is found in further mentioned samples up to 4GPa pressure and the electrical resistance decreases with increase which proves layered structure of the crystals.

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