CHAPTER : 10

HIGH PRESSURE STUDIES
OF
GeSe SINGLE CRYSTALS
10.1 INTRODUCTION:

The IV-VI binary compounds of the type AIVBVI are divided into two main groups according to their crystal structure. SnTe, PbS, PbSe and PbTe belong to the \(O_{\text{h}}^1\) (Fm 3m) space group with NaCl type lattice [1]; GeSe, GeS, SnSe and SnS belong to the \(P_{\text{na}}\) \(D_{2h}^{15}\) space group with orthorhombic structure [1]. This orthorhombic subgroup of IV-VI compounds consists of structures intermediate between three- and two dimensional materials, constructed of two dimensional layers weakly bonded to each other to produce a three-dimensional material [2].

Attention has been focussed on single crystals and thin films of lamellar semiconductor GeSe because of the important opportunities they open up particularly in optoelectronics [2]. Thin films and single crystals of GeSe are becoming objects of increasing importance in view of the possibilities for their applications described in detail in Chapter 1.

Anisotropic layered compound GeSe is a well known p-type semiconductor. Its structure, electrical, optical and photoelectrical properties have been investigated quite thoroughly at ambient pressures and described by [2] and references therein. First report on high pressure studies of GeSe are due to Chandrasekhar et al. [3]. They measured the pressure dependence of the Raman active modes in GeSe. The maximum pressure attained in their study was 7 kbar, therefore they could not draw any conclusions regarding the pressure-induced structural transitions in their
samples. They, however showed that pressure coefficients and corresponding Gruneisen parameters of the rigid layer (inter layer) modes were an order of magnitude larger than those of intralayer modes.

Chattopadhyay et al. [4] performed experimental structural studies at high pressure using energy dispersive X-ray diffraction on several members of the IV-VI family. They observed that layered GeSe compounds did not undergo any structural transition up to 340 kbar the maximum pressure up to which these crystals were studied. Bhatia et al. [5] carried out high pressure electrical measurements on single crystal GeSe up to a pressure of 100 kbar. They observed a pressure induced first order phase transition near 6 GPa. The high pressure phase was found to be quenchable and X-ray diffraction study of their quenched material revealed that it had an NaCl – like structure (a=7.37Å). Their transport measurements revealed that the pressure induced metallic character was retained down to ambient pressure. These results are, however, at variance with those of Chattopadhyay et al. [4].

Valiukonis et al. [5] showed a decrease in $E_g$ with pressure for single crystals of GeSe type having a layered structure. Belenkii et al. [6] carried out experimental investigations of the influence of hydrostatic pressure on the energy band structures of layered crystals. In most of the cases they observed that hydrostatic pressure reduced the band gap of the layered crystals.
Ignatchenko et al. [8] studied the changes in the electronic properties of GeSe at pressures in the range 20-50 GPa. Upon increasing the pressure at room temperature from 20 to 50 GPa they noticed a monotonic fall in resistance by more than two orders of magnitude. They suggested a semiconductor I – semimetal – semiconductor II transition in their samples at pressures in excess of 40 GPa. Their results pointed out a possibility of a phase transition in GeSe at an applied pressure of 8-10 GPa. Rabinal et al. [9] have studied the effect of high pressure on the electrical conductivity of Tl In X₂ layered semiconductor. They observed that similar to GeSe these materials also showed continuous metallisation under pressure. They attributed this metallisation to the narrowing of band gap under pressure.

Recently Hsueh et al. [10] carried out studies on theoretical as well as experimental dependence of the unit cell parameters a, b, and c in GeSe on hydrostatic pressure up to 135 kbar. Their calculated results were in good agreement with the experiment. They found no evidence in their experiments to support the claim that GeSe undergoes a pressure induced first order structural phase transition to a metallic modification at approximately 60 kbar, as was reported by Bhatia et al. on single crystal GeSe.

The diffraction of their GeSe samples at 130 kbar was found to be almost identical to that obtained from the starting material at ambient pressure. They found no experimental evidence in their studies to support
the claim made by Bhatia et al. that a NaCl like structure is formed upon decompression.

Thus, it appears from the literature that there are conflicting accounts of pressure effect in GeSe and there is no report on the ac conductivity measurements at different pressures in GeSe. Hence, in view of the importance of understanding pressure-induced electronic effects in materials, author has undertaken simultaneous measurements of ac conductivity and thermoelectric power at different pressures on single crystals of GeSe grown by different techniques.

10.2 EXPERIMENTAL PROCEDURE:

Sample Preparation:

Single crystals of germanium monoselenide (GeSe) were grown by PVT (Physical Vapour Transport) and by a CVT (Chemical Vapour Transport) technique using different transporting agents. Complete details of the growth procedure by both the methods are described in detail in Chapter 5.

High Pressure Measurements:

For the room temperature measurements of electrical resistivity as a function of pressure up to 10 GPa, pressure was generated with a Bridgman type tungsten carbide opposed anvil apparatus with in situ Bi
pressure calibration (Chapter 9). Similarly the simultaneous measurement of room temperature ac resistivity and thermoelectric power of these GeSe single crystals as a function of pressure was taken up to 8 GPa. As already described in Chapter 9, the measurements were made in a Bridgman anvil apparatus and as before here also Bismuth I-II and Bismuth III-IV transitions at 25.5 and 76.7 kbar were used for the pressure calibration.

10.3 EXPERIMENTAL RESULTS:

10.3.1 VARIATION OF RESISTANCE WITH PRESSURE:

The results on pressure dependence of resistance for GeSe crystals grown using different transporting agents are shown in Figs. 10.1 (a) and 10.1(b). The results on GeSe (NH₄Cl) were similar to that obtained for GeSe (I₂), therefore they have not been included here. In the case of GeSe (I₂) [Fig. 10.1(a)], there is a symmetric peak in resistance at about 0.76 GPa pressure at 30 Hz. The peak refers to a small maximum in the resistance which is followed by a large drop from about 0.96 to 2.2 GPa.

We clearly observe an increase in ac conductivity with increasing frequency and a shift in resistance maximum to higher pressures. Fig. 10.1(a) [GeSe (I₂)] shows a splitting of the resistance maximum at 28.6 kHz and 66.6 kHz. At 28.6 KHz one peak lies at 0.96 GPa and the second peak lies at 1.84 GPa. At 66.6 kHz there is a shift in the two peaks and as a result one peak lies at 1.28 GPa and the other one lies at 2.2 GPa.
Fig. 10.1 (a) Variation of resistance $R_n$ with pressure at different frequencies for GeSe crystals grown by CVT technique using $I_2$ as the transporting agent.
Fig. 10.1 (b) Variation of resistance $R_m$ with pressure at different frequencies for GeSe crystals grown by PVT (no transporting agent) technique.
In GeSe (PVT) [Fig. 10.1 (b)] resistivity is independent of frequency. This material shows a monotonous decrease in R up to 7 GPa.

10.3.2 VARIATION OF TEP WITH PRESSURE:

The pressure dependence of TEP as obtained for various samples of GeSe (l2), and GeSe (PVT) is shown in Figs. 10.2 (a) and 10.2 (b) respectively. A careful study of these figures reveals the following:

1. The TEP of GeSe (l2) [Fig. 10.2 (a)] samples increases from a value of 200 μVK'1 at 0.5 GPa reaching a maximum of 2900 μVK'1 at 1.8 GPa and decreases thereafter with further increase in pressure.
2. The TEP of GeSe (PVT) [Fig. 10.2 (b)] samples decreases monotonically with increase in pressure.
3. The sign of TEP for all the samples is positive indicating that all of them are p-type and remain p-type even with an increase in pressure.
4. The values of TEP at all pressures are very high for GeSe (l2) and go on decreasing substantially as we go from GeSe (l2) to GeSe (PVT).

10.4 DISCUSSION:

Similar to GeS (Chapter 9), here also there are two possibilities which can explain the conduction mechanism in GeSe (l2). Either there is thermally activated hopping near the band edges or there is trap limited
Fig. 10.2 (a) Variation of thermoelectric power ($S$) with pressure for GeSe crystals grown by CVT technique using $I_2$ as the transporting agent.
Fig. 10.2 (b) Variation of thermoelectric power ($S$) with pressure for GeSe crystals grown by PVT (no transporting agent) technique.
conduction. Both the models can explain the increase in the resistivity with pressure. In the first mechanism of conduction it is possible that the charge carriers are excited across a large band gap preceded and followed by the hopping mechanism among the localized states near the band edges i.e. far away from the Fermi level [Mott 11]. The localized states in GeSe (I2) can arise from the presence of defects and impurities. The fact that these crystals do contain a large concentration of defects is evidenced from the observations on Hall effect measurements described in Chapter 5.

On the other hand, the trap limited mechanism can explain the saturation of electrical resistance of the samples at high pressures as traps are limited in number and excess electrons then contribute to conduction. The presence of sharp maxima in resistance at different pressures rules out this possibility.

Further, the decrease in the resistivity in the high pressure range can be attributed to the averaging over the specific directions due to increased dimensionality of electronic transport at high pressures.

The symmetric peaks at different frequencies can be associated with acoustic or optical phonons. This can be done by fitting the data with the relation [12,13]

\[ R = A + B P^{*1/2} (1-P^*)^{1/2} \]

For acoustic phonons
or

$$R = A + B P^2 (1-P^*)^2$$

For optical phonons

In these relations $P^* = \frac{P - a}{b}$ where $a$ is the starting pressure of the peak and $b$ is the base width of the peak. By plotting the graphs of $R - A \over P^*^2$ versus $(1-P^*)^2$ for the different peaks observed at frequencies 30 Hz, 1 kHz, 28.6 kHz and 66.6 kHz [Figs. 10.3 (a), (b), (c), (d)] respectively, it can be clearly seen that the peaks nearly fit with the relation for optical phonons. The presence of such optical phonons in GeSe has been shown in Chapter [7] on the optical properties of GeSe. These optical phonons couple the delocalised electrons related with ionic part of the bonding between Ge and S. The observation of two peaks at 28.6 kHz and 66.6 kHz correspond to two phonons suggesting thereby a multiphonon process induced by frequency. The shift in peaks at higher frequencies of 66.6 kHz can be associated with the momentum imparted to the lattice by the increased applied frequency. The applied frequency changes the wave-vector and so the phonon frequency proportional peak value of pressure changes due a dispersion relation of the optical phonon.

Frequency independent $R_m$ in GeSe (PVT) crystals can be due to the low concentration of defects in these crystals. The presence of low density of defects in these crystals can be clearly judged from the Hall effect data and study of microstructures presented in Chapter 5.
Fig. 10.3 (a) Verification of beta density, i.e. $R = A + B P^2 (1-P^*)^2$ for GeSe crystals grown by CVT technique using $I_2$ as the transporting agent.
Fig. 10.3 (b) Verification of beta density, i.e. $R = A + B P^* (1-P^*)^2$ for GeSe crystals grown by CVT technique using $I_2$ as the transporting agent.
Fig 10.3 (c) Verification of beta density, i.e. $R = A + B P^{1-P}$ for GeSe crystals grown by CVT technique using $I_2$ as the transporting agent.
Fig. 10.3 (d) Verification of beta density, i.e. $R = A + B P^2 (1-P^2)^2$ for GeSe crystals grown by CVT technique using $l_2$ as the transporting agent.
The difference in the values of thermoelectric power for different samples of GeSe (I₂) and GeSe (PVT) can be attributed to the difference in their defect concentrations.

The anomalies in R and TEP (S) occurring at different pressures are not attributed to a phase transition. In all the different samples, the monotonous decrease in resistance with increase in pressure to very low values is similar to that observed by other research workers in GeSe, and clearly shows a tendency of the materials towards metallisation at higher pressures. The decrease in S at higher pressures in all the samples [GeSe (I₂) and GeSe (PVT)] is similar to decrease in R and also suggests the setting up of metallisation [14,15] in GeSe with increasing pressure. This occurrence of metallisation has also been observed in the case of other semiconductors having a layered structures [9, and references there in]. Recently, Hsueh et al. [10] observed a pressure induced closure of the indirect band gap in their valence band structure calculations performed at different values of pressures. Such a band gap closure can be responsible for the occurrence of metallisation in our samples of GeSe.

10.5 CONCLUSIONS:

It is generally known that the crystals grown by the vapour transport method under similar but not identical conditions, have different residual resistance and resistance anisotropy, which is often taken as an index of crystal perfection. We have observed in this chapter that GeSe
crystals, grown by vapour transport method using different transporting agent or no transporting agents show significant differences in the ac resistivity and its dependence on frequency. Author suggests that these properties can be taken as an index of crystal perfection. The type of carrier used in the CVT crystal growth also influences these properties. The results presented here clearly confirm that crystals of GeSe grown using the PVT technique are more perfect as compared to those grown by CVT technique using iodine as the transporting agent. That this is indeed true can be verified from the EDAX results for GeSe (PVT) and GeSe (I$_2$) described in Chapter 5.
REFERENCES:


