

Electronic conduction in bulk $\text{Se}_{1-x}\text{Te}_x$ glasses at high pressures and at low temperatures

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Abstract. The electrical resistivity of bulk $\text{Se}_{1-x}\text{Te}_x$ glasses is reported as a function of pressure (up to 8 GPa) and temperature (down to 77 K). The activation energy for electronic conduction has been calculated at different pressures. The samples with $0 \leq x \leq 0.06$ show a single activation energy throughout the temperature range of investigations. On the other hand samples with $0.08 \leq x \leq 0.3$ show two activation energies in the different regions of temperature. The observed behaviour has been explained on the basis of band picture of amorphous semiconductors.

Keywords. Chalcogenide glasses; pressure-induced semiconductor-to-metal transitions; amorphous semiconductors.

1. Introduction

In amorphous semiconductors pressure-induced effects, phase transitions and semiconductor-to-metal transitions are the most interesting phenomena (Minomura 1982). Many amorphous chalcogenides become metallic under pressure with a continuous decrease in band gap and resistivity even as they retain their molecular structure (Sakai and Fritzsche 1977; Minomura 1982; Parthasarathy *et al* 1984a). On the other hand tetrahedrally-bonded glasses undergo discontinuous transition with changes in structure to high coordination (Shimomura *et al* 1974). In amorphous selenium the resistivity decreases continuously with pressure by many orders of magnitude and goes to a metallic state with a discontinuous change in the electrical resistivity at high pressures. The value of the transition pressure is about 100–130 kb, which varies from work to work (Witting 1973; Fuhs *et al* 1973; Minomura 1978; Gupta and Ruoff 1978; Bundy and Dunn 1979). The most accepted value of transition pressure is about 13 GPa (= 130 kb).

In our study we find that the nature of the pressure-induced semiconductor-to-metal transition in $\text{Se}_{1-x}\text{Te}_x$ glasses, changes as a function of tellurium composition (Parthasarathy *et al* 1984 a,b). In this paper we report a systematic study on the pressure and temperature dependence on the electrical resistivity of $\text{Se}_{1-x}\text{Te}_x$ glasses for $0 \leq x \leq 0.3$.

2. Experimental details

2.1 High pressure cell assembly

The high pressure apparatus to measure the electrical resistance of $\text{Se}_{1-x}\text{Te}_x$ glasses as a function of pressure and temperature consists of a hydraulic press and a high pressure

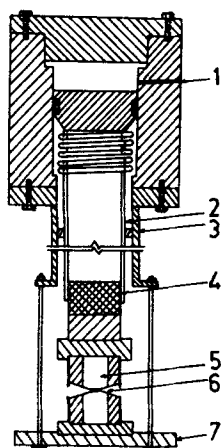


Figure 1. Schematic diagram of the high pressure cell assembly. 1. Oil inlet 2. Compression member 3. Tension member 4. High pressure plug 5. Tungsten carbide anvil 6. Sample 7. Bottom flange.

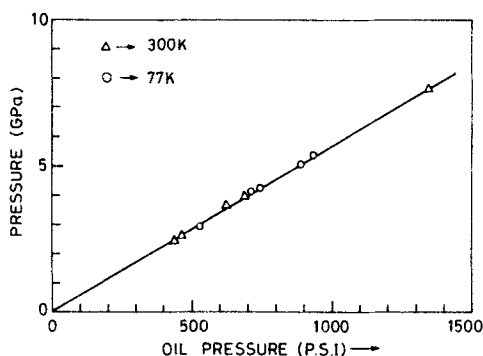


Figure 2. Plot of actual pressure vs oil pressure. Triangle for calibration at room temperature and circle for calibration points at liquid nitrogen temperature.

cell for low temperatures. The hydraulic press for low temperatures is similar to that which was discussed by Fujii and Nagano (1971). The compression member and the tension member are made of stainless steel 304 type. The high pressure cell is constructed with opposed tungsten carbide anvils with 6% cobalt binder, with heat treated EN-24 steel binding rings. The schematic diagram of the apparatus is shown in figure 1.

2.2 Pressure calibration

The pressures were calibrated at 300 K using as fixed points the Bi transitions at 2.54, 2.7 and 7.7 GPa, Yb transition at 4 GPa and Tl transition at 3.75 GPa. The pressure-induced transitions in Bi, Yb and Tl at 77 K have been studied. The calibration at low temperature shows that in this system the pressures at low temperatures were the same as those calibrated at room temperature.

The fixed points are plotted as a function of oil pressure in figure 2. The detailed analysis of the low temperature calibration will be discussed elsewhere (Parthasarathy *et al* 1984c).

2.3 Sample preparations and characterization

Bulk $\text{Se}_{1-x}\text{Te}_x$ glasses, with $x = 0, 0.02, 0.04, 0.05, 0.06, 0.08, 0.1, 0.2, 0.3$, were prepared by melting together appropriate amounts of the elements (5N purity), in sealed, evacuated quartz tubes (10^{-6} torr). The tubes were kept in a rotary furnace for 30 hr at a temperature of 1200 K, and subsequently quenched in an ice water mixture. These samples were confirmed to be amorphous by x-ray diffractometry differential scanning calorimetry and electron microscopic technique.

The room temperature and atmospheric pressure resistivity values are measured by the Van der Pauw (1958) technique. For high pressure and low temperature resistivity values, the change in the dimensions of the samples under pressure is not taken into account; the effect of this on the resistivity is comparatively small compared with the total change in the resistivity. A two-probe method (in sandwich geometry) is used to measure resistance, where the value of the resistance is more than 500 ohms. For measuring the resistances below 500 ohms a conventional four-probe method is employed. An electrometer (Keithley 616), a constant current source (Keithley 225) and a digital multimeter (Keithley 177) were used as measuring units. A copper-constantan thermocouple was used to measure the temperature. Because of the heavy thermal mass of the system, the temperature is controlled within ± 1 K. The error involved in the measurement of temperature is within ± 0.3 K.

3. Results

The variation of dc conductivity with temperature for $\text{Se}_{1-x}\text{Te}_x$ glasses at different pressures is shown in figures 3 to 11. For all the samples dc conductivity follows the Arrhenius relation

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (1)$$

where σ_0 ($\Omega^{-1}\text{cm}^{-1}$) is the pre-exponential factor, ΔE (eV) the activation energy, T (K) the temperature, and k the Boltzmann constant. For $\text{Se}_{1-x}\text{Te}_x$ glasses with $0 \leq x \leq 0.06$ we realise that the electronic conduction process is thermally activated with a single activation energy for all the pressures, in the temperature range of investigations (figures 3 to 7). On the other hand the glasses with $0.08 \leq x \leq 0.30$ show double activation energies in the same temperature range. The conductivity activation energy (ΔE) has been estimated by fitting the conductivity data in (1). The variation of the activation energy (ΔE) as a function of pressure for $\text{Se}_{1-x}\text{Te}_x$ glasses is shown in figures 12 and 13. The values of the activation energy and the pre-exponential factor σ_0 have been summarised in tables 1 and 2.

4. Discussion

In figure 3 we see that the room temperature and atmospheric pressure resistivity of pure selenium is of the order of 10^{10} ohm cm. Most of the experimental data on pure selenium show that the resistivity is of the order of 10^{10} to 10^{12} ohm cm at normal condition. It has been reported that the room temperature resistivity of pure deoxygenated selenium is of the order of 10^{17} ohm cm, and it drops by seven orders of magnitude through the addition of 20 ppm of oxygen added as SeO_2 to the melt

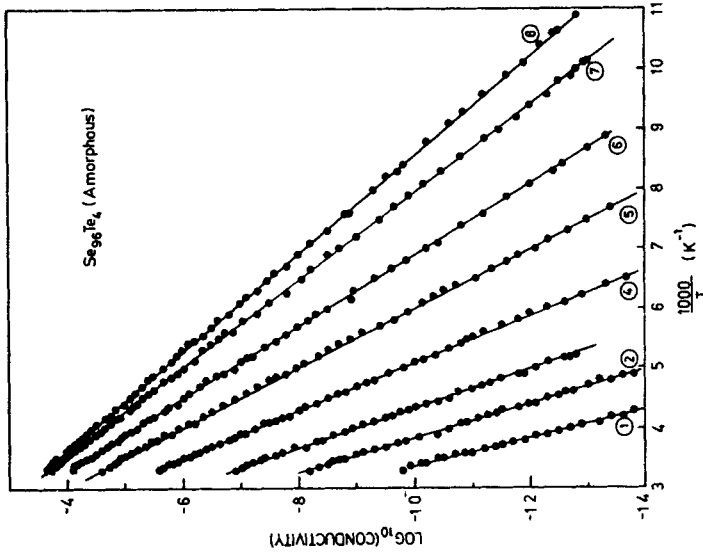


Figure 5. Semilog plot of dc conductivity vs $(1000/T)$ for $Se_{0.6}Te_4$ glass at different pressures: Curves (1) 10^2 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa (7) 6 GPa (8) 6.5 GPa.

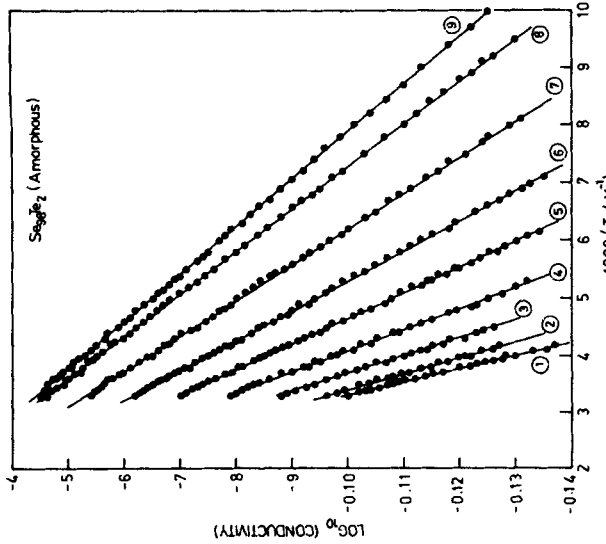


Figure 4. Semilog plot of dc conductivity vs $(1000/T)$ for $Se_{0.8}Te_2$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa (7) 6 GPa (8) 7 GPa (9) 8 GPa.

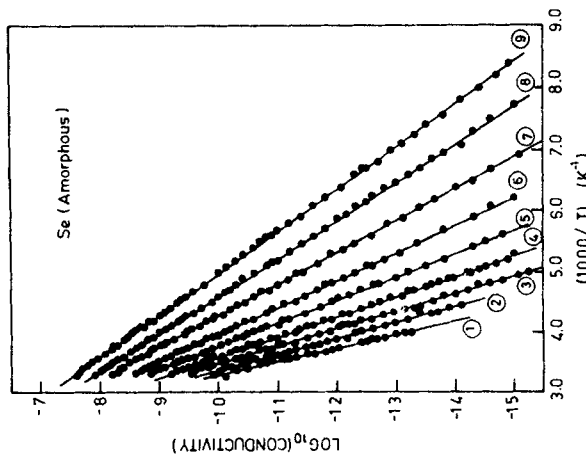


Figure 3. Semilog plot of dc conductivity vs $(1000/T)$ for selenium glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa (7) 6 GPa (8) 7 GPa (9) 8 GPa.

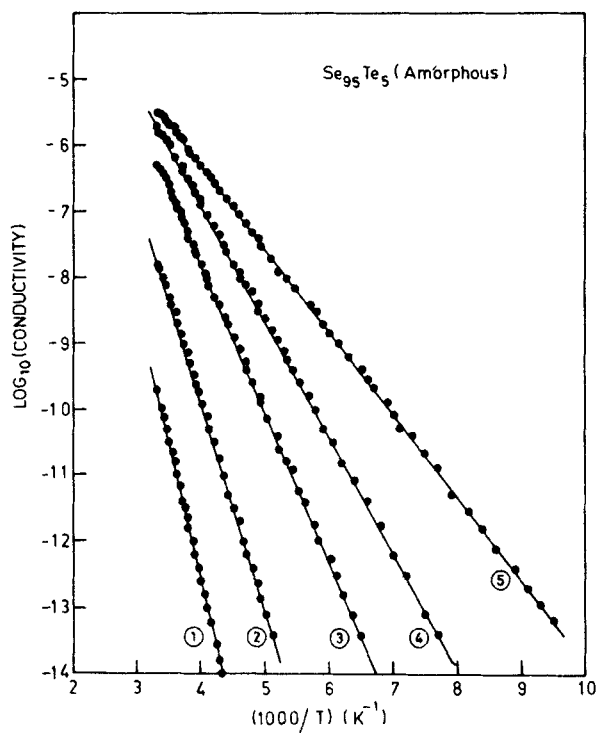


Figure 6. Semilog plot of dc conductivity vs $(1000/T)$ for $\text{Se}_{95}\text{Te}_5$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa.

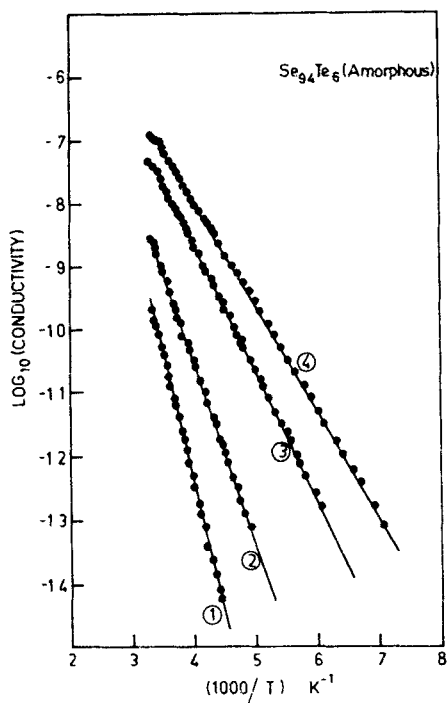


Figure 7. Semilog plot of dc conductivity vs $(1000/T)$ for $\text{Se}_{94}\text{Te}_6$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa.

(Lacourse *et al* 1970). Mott (1976) has explained this phenomena in terms of the charged dangling bonds (Street and Mott 1975). The conductivity activation energy for pure selenium is given by (Mott 1976)

$$\Delta E = \frac{1}{2} B - \varepsilon \quad (2)$$

and for oxygenated selenium it is

$$(\Delta E)_{\text{ox}} = \frac{2}{3} (\frac{1}{2} B - \varepsilon), \quad (3)$$

where ΔE and $(\Delta E)_{\text{ox}}$ are the activation energies for pure selenium and oxygenated selenium respectively. B is the band gap and ε is the difference in energy between the middle of the band gap and the Fermi level *i.e.* Fermi level is pinned in pure selenium by D^+ and D^- defects at an energy below midgap by an amount ε . The ε value is estimated to be roughly 0.13 eV (Mott 1976). The value of the optical band gap B of pure amorphous selenium is equal to 2.05 eV (Davis 1970) which is roughly the same value obtained by other workers (Lanyon 1964; Dawar *et al* 1981; Bhatnagar and Subramanyam 1983). If we substitute the B value in (2) and (3), we get $\Delta E = 0.895$ eV and $(\Delta E)_{\text{ox}} = 0.60$ eV. Our experimental data on selenium give the value of activation energy (at 10^5 Pa pressure) = 0.896 eV. Recent conductivity experiments by Kotkata *et al* (1982) on amorphous and liquid selenium show that the activation energy is equal to 0.525 eV for the glassy state and 0.6 eV in the liquid state. Moreover their resistivity value is of the order of $10^8 \Omega \text{cm}$. These results are in good agreement with the value of the oxygenated selenium, which is estimated from (3). These effects of the oxygen doping in amorphous selenium require more systematic experiments on transport properties.

Figure 12 shows that the activation energy of electronic conduction for all the samples decreases with the increase of pressure. For pure selenium the pressure coefficient of activation energy is found to be -0.08 eV/GPa, which is in excellent agreement with the data reported by Fuhs *et al* (1973).

The variation of d.c. conductivity of $\text{Se}_{1-x}\text{Te}_x$ glasses for $0 \leq x \leq 0.06$ shows that in all the samples at all the pressures the conduction is thermally activated with a single activation energy. If we fit the conductivity data to equation (1), we get the numerical value of activation energy and the pre-exponential factor. These factors are presented in table 1. Our experimental value of σ_0 for Se is in good agreement with the value reported by Davis and Mott (1970). In most of the cases the pre-exponential factor σ_0 is of the order of $10^4 \Omega^{-1} \text{cm}^{-1}$, which indicates that at atmospheric pressure the conduction in all the samples ($0 \leq x \leq 0.06$) is through extended states in the temperature range of investigations. With the increase of pressure the σ_0 value decreases continuously by seven orders of magnitude (in the case of selenium, table 1), which indicates that the process of electronic conduction changes from the extended states conduction to the localized state conduction. The decrease of activation energy ΔE with the increase of pressure shows the movement of the Fermi level towards the conduction band edge, by the application of the pressure. The variation of ΔE and σ_0 with pressure for other samples also ($0 \leq x \leq 0.06$) can be explained in the same way.

The variation of conductivity with temperature for $\text{Se}_{1-x}\text{Te}_x$ glasses with $0.08 \leq x \leq 0.3$ show a somewhat different behaviour from that for $0 \leq x \leq 0.06$ (figures 8–11). For $0.08 \leq x \leq 0.3$ the conduction at high temperature region is across mobility edges and at low temperature region, the conduction process is in the localized states near the Fermi level by thermally-activated hopping. The first activation energy

Table 1. Constants related to dc conductivities at different pressures; σ_0 (in $\Omega^{-1} \text{cm}^{-1}$) and ΔE (in eV) are the least-square-fit values of the pre-exponential factor and the activation energy of the Arrhenius formula

Pressure	Se		$\text{Se}_{98}\text{Te}_2$		$\text{Se}_{96}\text{Te}_4$		$\text{Se}_{95}\text{Te}_5$		$\text{Se}_{96}\text{Te}_4$	
	ΔE	σ_0	ΔE	σ_0	ΔE	σ_0	ΔE	σ_0	ΔE	σ_0
10^5 Pa	0.896	8.74×10^4	0.874	4.90×10^4	0.85	3.37×10^4	0.84	2.44×10^4	0.83	2.06×10^4
1 GPa	0.76	3.39×10^3	0.73	3.96×10^2	0.70	3.61×10^3	0.63	607.2	0.57	8.32
2 GPa	0.68	74.57	0.62	40.63	0.62	3.55×10^3	0.45	19.01	0.40	0.269
3 GPa	0.60	7.49	0.56	34.67	0.50	623.7	0.35	1.53	0.33	4.47×10^{-2}
4 GPa	0.52	0.75	0.45	3.64	0.40	130.8	0.25	18.6	—	—
5 GPa	0.44	5.92×10^{-2}	0.38	1.50	0.33	30.2	—	—	—	—
6 GPa	0.38	3.95×10^{-2}	0.32	1.04	0.27	6.44	—	—	—	—
7 GPa	0.32	2.84×10^{-3}	0.27	0.83	—	—	—	—	—	—
8 GPa	0.29	1.92×10^{-3}	0.24	0.35	—	—	—	—	—	—

Table 2. Values of the activation energies and the pre-exponential factors at different pressures for $\text{Se}_{1-x}\text{Te}_x$ glasses ($0.08 \leq x \leq 0.30$) (ΔE is in eV and σ_0 is in $\Omega^{-1} \text{cm}^{-1}$)

Pressure	$\text{Se}_{92}\text{Te}_8$		$\text{Se}_{90}\text{Te}_{10}$		$\text{Se}_{80}\text{Te}_{20}$		$\text{Se}_{70}\text{Te}_{30}$	
	ΔE	σ_0	ΔE	σ_0	ΔE	σ_0	ΔE	σ_0
10^5 Pa	0.82	4.81×10^4	0.797	4.145×10^4	0.70	5.66×10^4	0.60	6.02×10^4
1 GPa	0.72	1.04×10^4	0.70	9.99×10^2	0.60	1.39×10^3	0.45	5.16×10^4
2 GPa	0.19	2.44×10^{-8}	0.19	1.00×10^{-8}	0.14	6.64×10^{-8}	0.10	5.00×10^{-6}
3 GPa	0.575	105.6	0.55	3.07	0.46	5.17×10^3	0.30	1.65×10^5
4 GPa	0.100	1.00×10^{-8}	0.12	1.46×10^{-10}	0.10	2.0×10^{-4}	0.09	3.607
5 GPa	0.41	112.4	0.38	1.53×10^{-2}	0.30	1.15×10^4	0.18	7.19×10^4
6 GPa	0.05	3.34×10^{-8}	0.06	5.07×10^{-8}	0.05	6.64×10^{-2}	0.04	30
7 GPa	0.26	2.09×10^3	0.22	382	0.14	3.51×10^3	0.10	3.90×10^4
8 GPa	0.03	1.00×10^{-5}	0.03	1.0×10^{-4}	0.03	16.67	—	—
9 GPa	0.15	1.36×10^5	0.10	365	0.08	1.11×10^4	0.04	1.10×10^4
10 GPa	0.014	1.25×10^{-2}	0.018	0.278	0.014	2.86×10^2	—	—
11 GPa	0.06	1.48×10^3	0.04	1.926×10^3	—	—	—	—

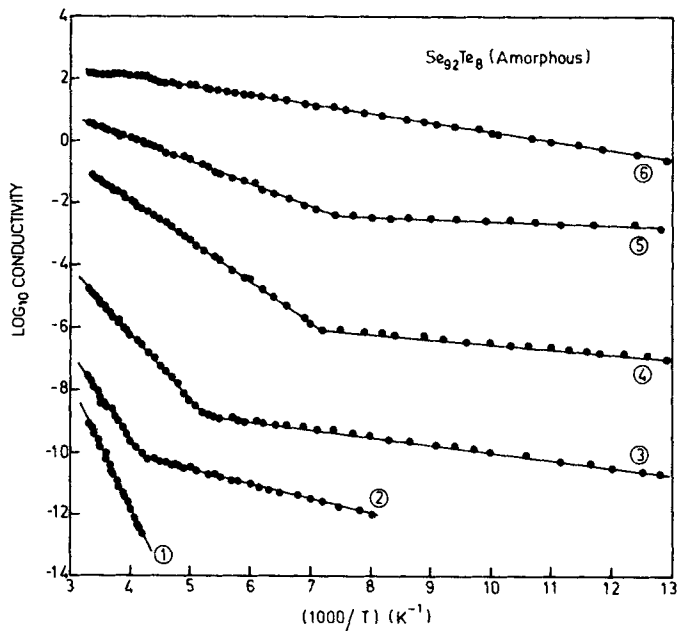


Figure 8. Semilog plot of dc conductivity vs $(1000/T)$ for $\text{Se}_{92}\text{Te}_8$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa (7) 6 GPa.

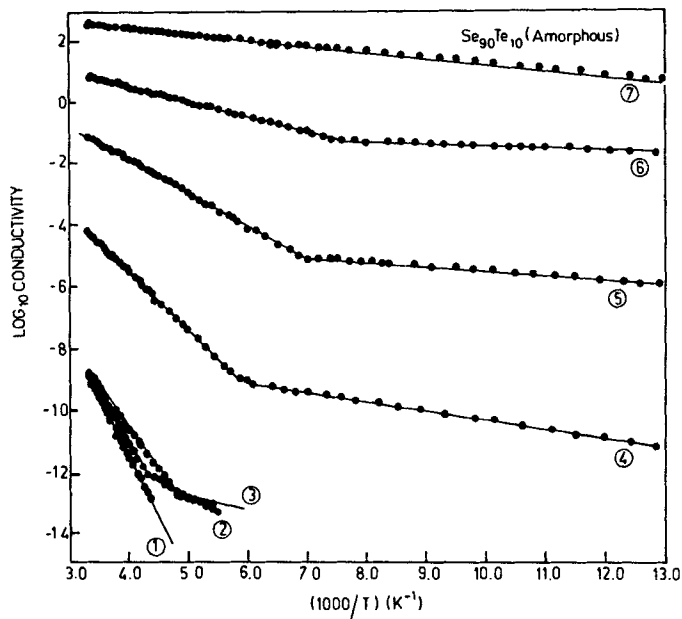


Figure 9. Semilog plot of dc conductivity vs $(1000/T)$ for $\text{Se}_{90}\text{Te}_{10}$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa (7) 6 GPa.

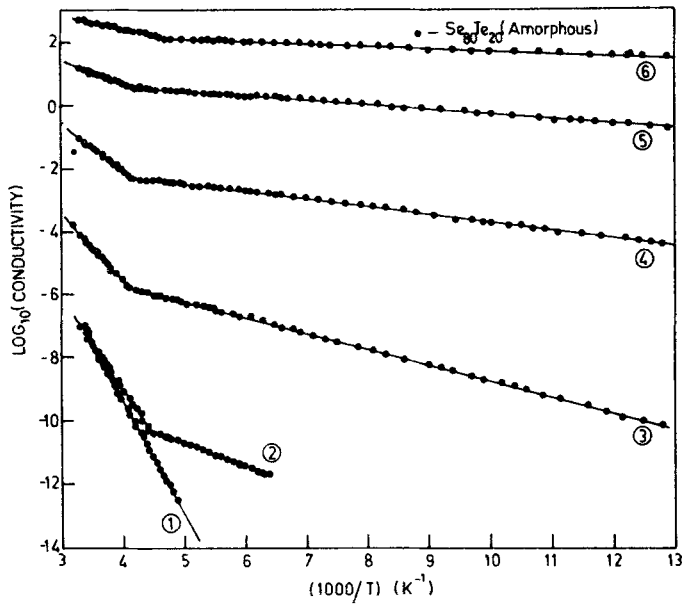


Figure 10. Semilog plot of dc conductivity vs $(1000/T)$ for $\text{Se}_{80}\text{Te}_{20}$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa.

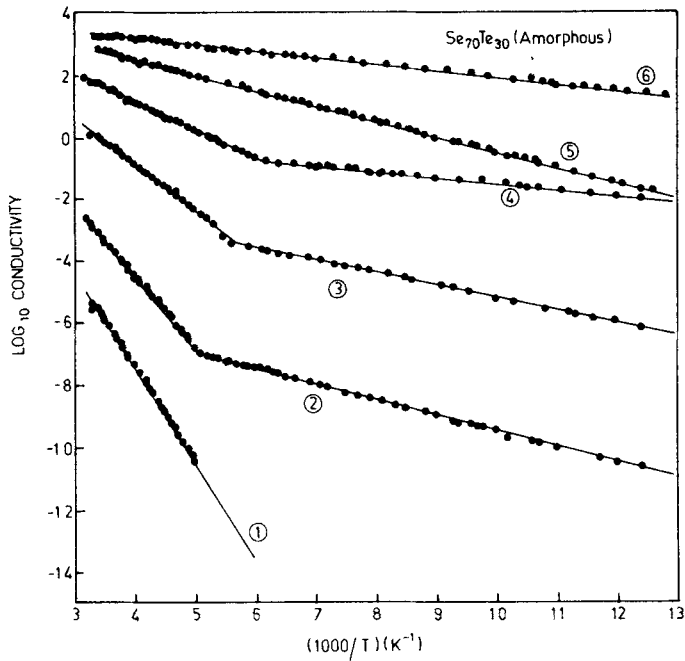


Figure 11. Semilog plot of dc conductivity vs $(1000/T)$ for $\text{Se}_{70}\text{Te}_{30}$ glass at different pressures: Curves (1) 10^5 Pa (2) 1 GPa (3) 2 GPa (4) 3 GPa (5) 4 GPa (6) 5 GPa.

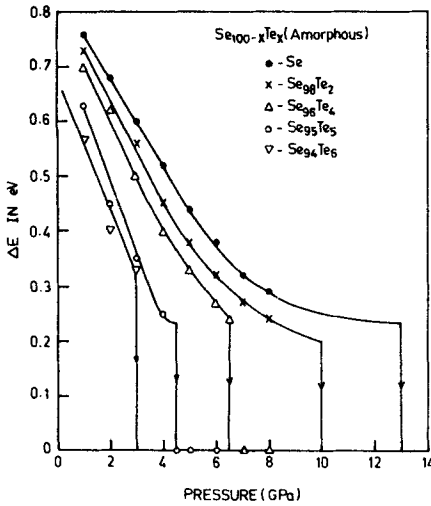


Figure 12. Variation of conductivity activation energy as a function of pressure for $\text{Se}_{1-x}\text{Te}_x$ glasses ($0 \leq x \leq 0.06$).

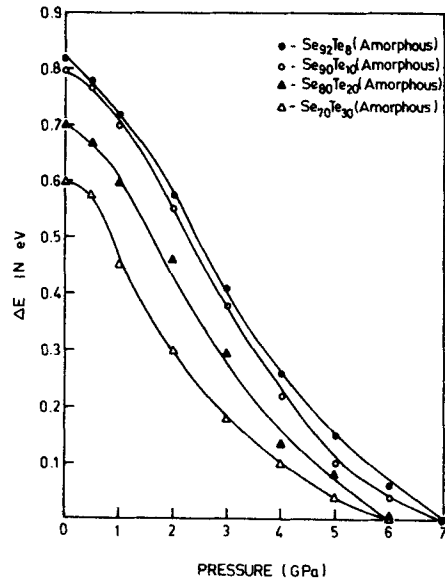


Figure 13. Variation of conductivity activation energy as a function of pressure for $\text{Se}_{1-x}\text{Te}_x$ glasses ($0.08 \leq x \leq 0.30$).

(in high temperature region) represents the value of $E_c - E_f$ and the second activation energy gives the value of half the width of the localized states near the Fermi level. We find (table 2) that both the activation energies decrease with increase of pressure, which implies that the fundamental energy gap or in other words the mobility gap decreases with increase of pressure. The decrease in the second activation energy indicates a decrease in the localization of the gap states. The decrease in both activation energies leads to a metallic phase beyond 7 GPa pressure.

For calling the high pressure phase as metallic we follow the operational definition of metallic conduction put forward by Sakai and Fritzsche (1977) and Mott (1970), which says that the conductivity is metallic if its temperature coefficient is zero or negative and if its value is equal or larger than Mott's minimum metallic conductivity. The interpretation of the pressure dependence on electrical resistivity is more complicated because, the behaviour is determined by the gap, the mobility and also the position of the Fermi level.

From figures 12 and 13 we notice the differences in the variation of the activation energy with pressure. For $0 \leq x \leq 0.06$ the activation energy decreases continuously with the increase of pressure and drops to zero at a certain pressure. On the other hand for $0.08 \leq x \leq 0.3$, the activation energy decreases continuously to a zero value. Moreover for $0 \leq x \leq 0.06$, the conductivity activation energy is found to be single over the temperature range of our experiments at all the pressures. On the other hand for $0.08 \leq x \leq 0.3$ we find two activation energies in different temperature ranges. These observations indicate that there should be some change in the band structure of $\text{Se}_{1-x}\text{Te}_x$ glasses at the value of x between $x = 0.06$ and $x = 0.08$ (Parthasarathy *et al* 1984b).

In the defect model (Mott *et al* 1975; Kastner *et al* 1976; Kastner and Fritzsche 1978)

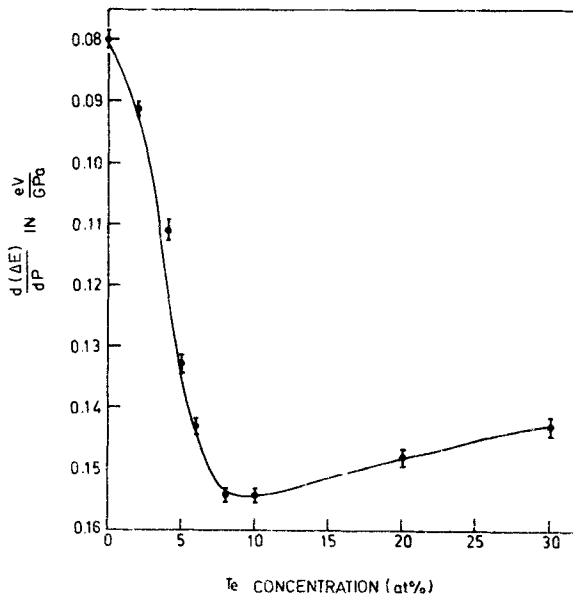


Figure 14. Variation of the pressure coefficient of activation energy as a function of tellurium concentration.

selenium glass is considered to a continuous random network consisting of chains (and few rings) of atoms with two-fold coordination. The defects in glassy selenium may consist of dangling chain ends, which are called as charged dangling bonds denoted by C_3^+ , C_1^0 and C_1^- depending on whether 0, 1 or 2 electrons occupy the gap state. We expect that the addition of tellurium (figure 14) in glassy selenium up to 6 atomic percentage does not affect the structure of Se and hence the band picture. But beyond 6 atomic percentage the tellurium atoms create new defect states inside the mid gap which may be over-coordinated (C_3^+) type or under-coordinated (C_1^-) type or both. Hence we observe the single activation energy for $0 \leq x \leq 0.06$ and double activation energies for $0.08 \leq x \leq 0.3$ in the same range of temperature. A more detailed discussion on this change in the electronic transport behaviour as a function of tellurium composition will be published elsewhere (Parthasarathy *et al* 1984a).

In conclusion, a systematic study of the electrical conductivity of $Se_{1-x}Te_x$ glasses as a function pressure and temperature is reported. There appears to be some drastic change in the electronic behaviour of these glasses at $x = 0.06$ to 0.08 . This has to be related to the details of the models for these glasses.

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