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Effect of high pressure on chalcogenide glasses*

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Abstract. The effect of high pressures on the various properties of the chalcogenide glasses is reviewed. The properties discussed include the mechanical, electrical, optical and magnetic properties. The phenomena of the crystallization of the chalcogenide glasses under high pressure is also discussed.

Keywords. Glasses; high pressure effects; electrical transport; chalcogenide glasses.

1. Introduction

Chalcogenide glasses have attracted much attention of physicists and chemists after the discovery of the non-destructive fast electrical switching in the multi-component chalcogenide glasses by Ovshinsky (1968). Since then the usage of glassy semiconductors has increased in various fields like photo-voltaic devices, xerography, optical and electrical memory devices etc (Gerluch and Groose 1979; Mott and Davis 1979; Borisova 1981; Hamakawa 1982). However, an understanding of various phenomena like the topology of the glasses, the glass-forming ability, crystallization of glasses, semiconductor-to-metal transitions, photostructural changes, etc is not complete even today (Balian *et al* 1979; Yonezawa 1980; Zallen 1983; Elliott 1984).

In this paper an attempt is made to review the effect of high pressures on the various mechanical, electrical, optical and magnetic properties of the chalcogenide glasses. In the last section the effect of pressure on the crystallization of chalcogenide glasses is also discussed.

Since the general field of high pressure techniques is well reviewed in many places, the topic is not discussed here. In any case the papers describing the high pressure behaviour often discuss the experimental procedures.

2. Mechanical properties

2.1 *Volume compressibility and bulk modulus*

The volume compressibility as well as its pressure and temperature dependence yield direct experimental information on changes in the interatomic forces arising from changes in volume or interatomic spacings. Most of the compressibility data were obtained by measuring the sound velocities of the glasses as a function of pressure and

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* This article is dedicated to the memory of late Dr N S Satya Murthy who had been intimately associated directly and indirectly with the development of condensed matter physics in India.

temperature. The earliest study in this field is done by Bridgman (1925), on the silica rich glasses, where he found that the compressibility increases abnormally with pressure. He suggested that such an anomalous elastic behaviour is associated with the differences in the atomic arrangements between glass and crystal (Bridgman 1925). In the case of chalcogenide glasses, the chalcogen atoms play a crucial role, namely, the bonding forces between the chains and rings of the chalcogen atoms are mostly of the Van der Waals type (Von Hippel 1948; Vedam *et al* 1966). The application of hydrostatic pressure results in a denser packing of the chains. The volume compression being fairly large one must use the methods of finite deformation elasticity to analyse the data. One of the equations widely used is the Murnaghan equation of state

$$V/V_0 = [(K'_T/K_T)P + 1]^{-1/K'_T} \quad , \tag{1}$$

where the bulk modulus K_T is expected to increase linearly (to a first approximation) with pressure and the derivative K'_T is taken at zero pressure. The effect of pressure on the elastic properties of glassy selenium was measured by several authors (Bridgman 1940a, b; Weir 1954; Graham and Chang 1965; Vedam *et al* 1966; Soga *et al* 1973; Singh and Kennedy 1974, 1975; Litov and Anderson 1978). The zero pressure bulk modulus and its pressure derivative for glassy selenium are given in table 1.

In the measurement of compressibility as a function of pressure, two major techniques are used. One is a static method, where the piston displacement versus pressure is recorded. The second technique is the ultrasonic method where the sound velocity is measured accurately as a function of pressure. The variation of bulk modulus and volume compression of amorphous selenium as a function of pressure is shown in figure 1. The pressure dependence of bulk modulus is explained on the basis of the interatomic potentials. In the case of glassy selenium the bonding forces between chains and rings are mostly of the Van der Waals type (Vedam *et al* 1966). It is likely that with

Table 1. High pressure studies on the bulk modulus of amorphous Se

$(K_T)_0$ (GPa)	K'_T	K''_T ((GPa)$^{-1}$)	Pressure range (GPa)	Technique	Reference
9·11	—	—	—	Ultrasonic	Graham and Chang (1965)
9·14	—	—	—	Ultrasonic	Vedam *et al* (1966)
9·16	8·5	—	0–0·5	Ultrasonic	Soga *et al* (1973)
9·29	3·2	—	0–5	Static	Bridgman (1940a)
10·50	3·6	—	0–5	Static	Bridgman (1940b)
6·78	7·4	—	0–1	Static	Weir (1954)
9·02 ± 0·4	6·74 ± 0·7	−1·086 ± 0·7	0–5	Static	Singh and Kennedy (1975)
8·43 ± 0·4	7·40 ± 0·5	−1·214 ± 0·5	0–5	Static	Singh and Kennedy (1975)
8·73	7·07	−1·150	0–5	Static	Singh and Kennedy (1974)
9·10	8·01	—	0–1·6	Ultrasonic	Litov and Anderson (1978)

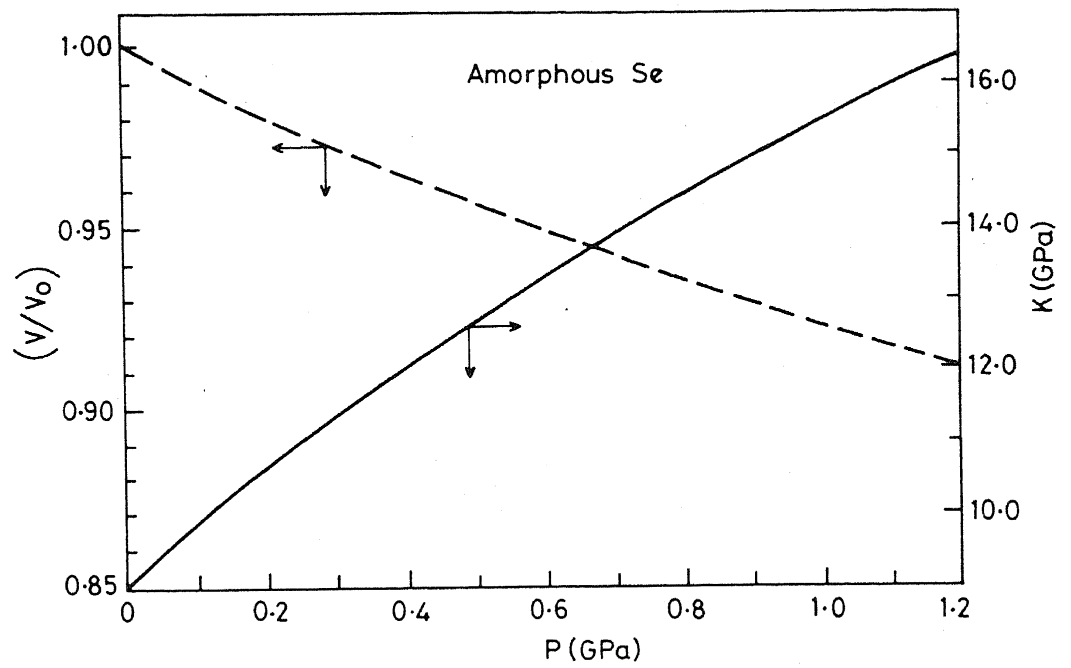

Figure 1. Variation of bulk modulus and volume compression of amorphous selenium as a function of pressure (after Litov and Anderson 1978).

the increase of pressure the promotion of charge from the intra chain orbitals toward inter chain orbitals will increase the attractive interchain forces (Litov and Anderson 1978). So the total energy will be lowered with the increase of pressure, which is responsible for destabilizing the structure, leading to a phase transformation which will be discussed in latter sections. Since the major effect of pressure is to decrease the inter chain distance, Litov and Anderson (1978) assumed that the total potential energy is simply a function of interchain distance rather than intrachain distance. They found that their data are in very good agreement with their theoretical interatomic potential, which consists of a Lennard-Jones term and an attractive term due to intrachain-interchain interaction.

2.1a *Ultrasonic velocity measurements*: The ultrasonic technique is widely used to study the compressibility and its pressure dependence (Soga *et al* 1973; Litov and Anderson 1978). In the three-component glassy $Te_{15}Ge_3As_2$ alloy, the effect of pressure on the ultrasonic velocity and the compressibility has been measured by Bailey and Thompson (1972). They measured the transit time of a short pulse of ultrasonic waves in a cylindrically shaped $Te_{15}Ge_3As_2$ glassy sample and converted the measured transit time to sound speed. Their measurements show that upto 1·0 GPa, the sound velocity increases smoothly with the increase of pressure and the compressibility decreases smoothly with the increase of pressure. The volume change at 1·0 GPa is only 4·6 % in the case of glassy $Te_{15}Ge_3As_2$ alloy (Bailey and Thompson 1972). The value of the isothermal compressibility of $Te_{15}Ge_3As_2$ glass varies from $5{\cdot}66 \times 10^{-12}$ $cm^2/dyne$ at 10^5 Pa of pressure to $3{\cdot}86 \times 10^{-12}$ $cm^2/dyne$ at 1·0 GPa. Similar studies on the pressure dependence of elastic properties of As_2Se_3 glasses have been performed by Soga *et al* (1973) and Ota and Anderson (1977). The value of the isothermal compressibility of As_2Se_3 glass is 14·2 GPa. The magnitude of the pressure coefficient of compression of As_2Se_3 glass reported by Soga *et al* (1973) is less than that of Weir's data (Weir 1965). The pressure and temperature derivatives of bulk modulus at ambient condition for As_2Se_3 glass appear to be normal: i.e., the pressure derivative is positive and the temperature derivative is negative (Soga *et al* 1973; Ota and Anderson 1977).

The next interesting and well-studied sample in the chalcogenide glasses is As_2S_3. The comparison of the similar studies on Se, As_2Se_3 and As_2S_3 glasses will give the information about the effect of dimensionality on the physical properties of the glasses, because Se has a one-dimensional chain-like structure and As_2S_3 and As_2Se_3 possess a highly pronounced layer structure. The effect of pressure on the elastic properties of glassy As_2S_3 alloy has been observed by Gerlich *et al* (1979). They measured the elastic moduli from the velocity and the pressure dependence of longitudinal and shear ultrasonic waves. For the longitudinal waves a pulse-echo method and for the shear waves a superposition technique was used by them. The variation of elastic constants C^l and C^t for glassy As_2S_3 is shown in figure 2. The bulk modulus was calculated from the relation

$$K_T = \frac{1}{1+\alpha\gamma T}\left(C^l - \frac{4}{3}C^t\right), \tag{2}$$

where α = coefficient of expansion, γ = the Gruneisen constant and T = the temperature.

The variation of the bulk modulus of As_2S_3 and As_2Se_3 glasses as a function of pressure is shown in figure 3. Both these two-dimensional chalcogenide glasses have a similar pressure effect. In both cases the chalcogen atom enters into a covalent bonding with a pair of its two nearest neighbours, using two of the six s^2p^4 valence electrons, while the other four form two lone pair orbitals that protrude into the intermolecular regions. With the application of pressure the charge gets promoted from intralayer to the interlayer regions, which is confirmed by the optical studies by Zallen *et al* (1971) under pressure. This will be discussed in a later section. It is observed that two of the intra layer modes decrease with increased pressure, whereas all the interlayer modes increase with pressure. The elastic properties of As_2S_3 and As_2Se_3 glasses under high pressure are explained on the basis of the above microscopic picture (Gerlich *et al* 1979).

The effect of pressure on the elastic properties of germanium based chalcogenide glasses, viz $Ge_x(S, Se)_{1-x}$ has been measured by Ota and Kungi (1977) and Ota *et al*

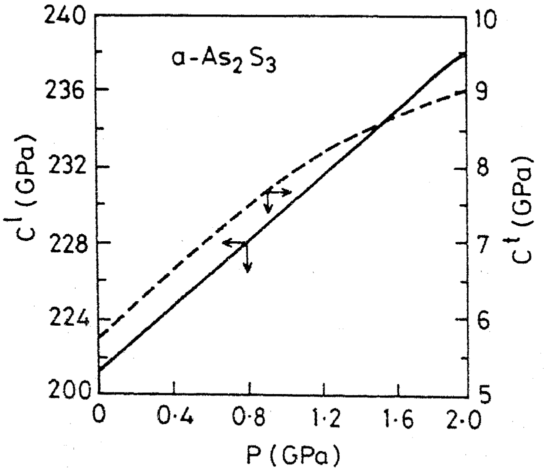

Figure 2. Variation of elastic constants C^l and C^t for As_2S_3 glass as a function of pressure (after Gerlich *et al* 1979).

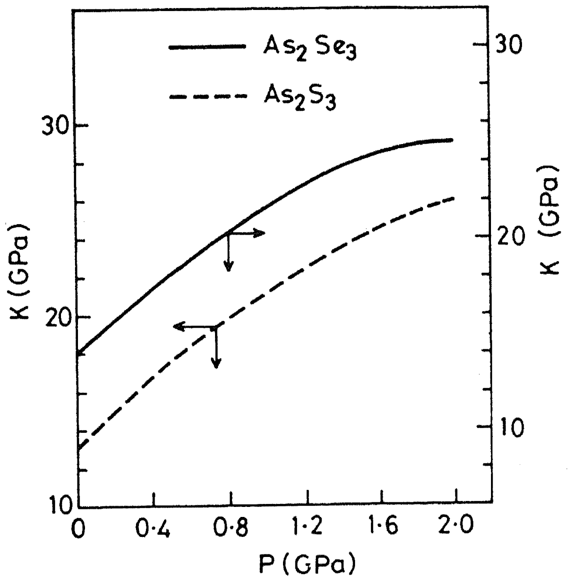

Figure 3. Pressure dependence of the bulk modulus of As_2S_3 and As_2Se_3 glasses.

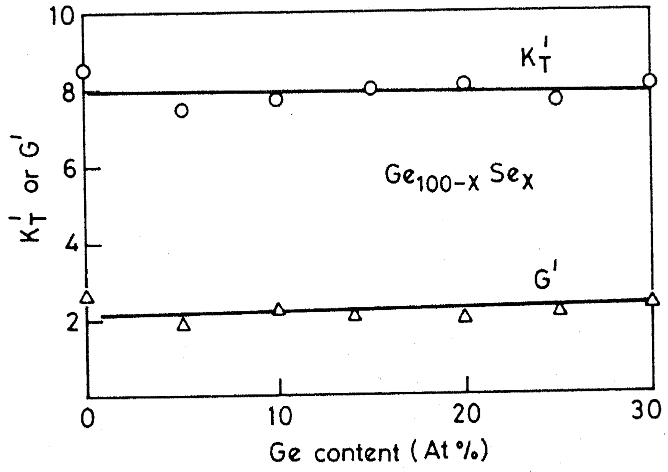

Figure 4. Variation of the pressure derivatives of bulk modulus (K_T') and shear modulus (G_T') as a function of Ge content in Ge_xSe_{1-x} glasses.

(1978), by using ultrasonic interferometry. Figure 4 illustrates the variation of the pressure derivatives of the elastic moduli K_T' and G_T' (bulk modulus K_T and shear modulus G_T). Sound wave velocities (longitudinal wave velocity C_l and transverse wave velocity C_t) and elastic moduli of the Ge_xSe_{1-x} glasses, increased with Ge content and with pressure. The pressure derivatives K_T' and G_T' are in the range $K_T' = 7{\cdot}9 \pm 0{\cdot}3$ and $G_T' = 2{\cdot}2 \pm 0{\cdot}3$, which indicates that Ge_xSe_{1-x} glasses is elastically normal. The temperature dependence of the ultrasonic velocities of the Ge_xSe_{1-x} glasses also confirms the normal elastic behaviour of this system (Kartha *et al* 1981).

Lambson *et al* (1984) have measured the elastic behaviour of TeO_2 glass under uniaxial and hydrostatic pressure. They found that the bulk modulus is consistent with a ring diameter averaging about 8 atoms (Te_4O_4 rings) suggesting that the glass is a disordered version of paratellurite. The pressure derivatives of the second order elastic constants are positive and the third order elastic constants are negative, which is in marked contrast to the anomalous behaviour of silica-based glasses. Lambson *et al* (1984) have also found the long wavelengths acoustic modes stiffen under hydrostatic pressure upto 0·14 GPa.

2.2 *P-V-T relations in glassy selenium*

The pressure-volume-temperature (PVT) properties of amorphous selenium were studied by Berg and Simha (1976) upto 200 MPa pressure in the temperature range 0–70°C. This type of study, earlier common in fluid systems, is not popular in solids. The magnitude of the effort required is not commensurate with the results obtained.

3. Electrical resistivity studies

The primary effect of pressure is to decrease the interatomic distances, which affects the electronic structure. Among the electrical properties, the commonly measured quantity under high pressure is the electrical resistivity. In some cases the effect is pronounced to result in a transition from a semiconductor to a metal in the amorphous semiconductors. The amorphous chalcogenide glasses becomes metallic under high pressure either with a continuous or with a discontinuous decrease in the electrical resistivity and optical gap. The effect of pressure on the optical properties of the chalcogenide glasses will be discussed in the next section.

The explanation for the variation of the electrical resistivity under high pressure is more complex. From the elementary theory one can write

$$\rho = (n\mu e)^{-1}, \tag{3}$$

where ρ is the electrical resistivity, n is the number of carriers, μ is the carrier mobility and e is the charge. In (3) both n and μ depend on pressure and temperature. The number of carriers is determined by the probability of exciting carriers from the Fermi energy to the bottom of the conduction band

$$n \sim \exp\left(-\frac{E_C - E_F}{kT} \right), \tag{4}$$

where k is the Boltzman's constant and T is the temperature. The quantity $E_C - E_F = \Delta E$ in eV is called the activation energy for the electronic conduction. The band picture for the chalcogenide glasses (and the position of the Fermi level) is discussed in detail by Mott and Davis (1979).

3.1 *Elements*

The effect of pressure on the electrical resistivity of glassy selenium has been studied extensively (Bridgman 1952; Balchan and Drickamer 1961; Wittig 1965, 1973; Fuhs *et al* 1973; Moodenbaugh *et al* 1973; Aoki *et al* 1974; Minomura 1978; Gupta and Ruoff 1978; Bundy and Dunn 1979; Parthasarathy *et al* 1984d; Parthasarathy and Gopal 1984a). At room temperature and pressure Se exists in three forms: a chain hexagonal form, a monoclinic form and an amorphous form. Both of the latter are metastable thermodynamically, and transform to the hexagonal form when heated or pressurized.

All the high pressure studies show the following main results:

(i) The electrical resistivity decreases exponentially with the increase of pressure and at 13·0 GPa the resistivity drops by six orders of magnitude and goes to a metallic value.

(ii) Amorphous Se became crystalline under high pressure. The high pressure crystalline phase is yet unsolved and the crystalline phase is retained when the pressure is released to one atmospheric pressure.

(iii) The electronic nature of the (semiconductor-to-metal) transition is found to be reversible in nature.

(iv) The high pressure metallic phase undergoes a superconductivity transition at 7 K (Wittig 1973).

The most controversial thing about the high pressure studies on the glassy selenium is the value of the transition pressure, which varies from 6·0 GPa (McCann and Cartz 1972) to 13·0 GPa (Wittig 1965; Fuhs *et al* 1973; Bundy and Dunn 1979; Parthasarathy *et al* 1984d). The results of the pressure dependence of electrical resistivity of glassy selenium due to various authors are summarized in table 2. The discrepancy arises because of the differences in the method of preparation of the samples.

In the VI group elements, other than selenium no other elements exist in the bulk glassy form. There are a few reports on the existence of amorphous tellurium, which usually crystallizes at 298 K. The other high pressure studies on the bulk glassy elements are on glassy arsenic (Elliott *et al* 1977) and glassy phosphorus (Extance and Elliott 1981), which will be discussed in the last section of this review, where we discuss about the pressure-induced transformation in the chalcogenide glasses.

3.2 *Binary alloys*

The effect of pressure on the electrical resistivity of bulk As-Se glasses has been measured upto 0·2 GPa by Arai *et al* (1973). They found that the conductivity increases with the increase of pressure, which is the characteristic feature of electronically conducting glasses. In amorphous As_2Se_3 both hole transport determined from time-of-flight experiments and dark dc conductivity were measured as a function of pressure by Pfister (1974). He reported that both of them increase with pressure as exp (αp), where $\alpha \simeq 4{\cdot}5\ \mathrm{GPa}^{-1}$. The shape of the current transient and the pressure dependence of the characteristic time strongly support a hopping model of the transport in a-As_2Se_3 (Kolomiets and Raspopova 1970; Ivkin *et al* 1972).

The pressure dependence of the electrical resistivity amorphous thin films As_2S_3 and As_2Se_3 has been measured by Minomura *et al* (1976). The study shows a continuous decrease of resistivity of several orders of magnitude, which lies in 1×10^{-1} and 5×10^{-3} ohm cm for a-As_2S_3 and a-As_2Se_3 films at 25 GPa and these samples remain semiconducting even at 25 GPa pressure. In the case of flash-evaporated amorphous As_2Te_3 films, the resistivity decreases by eight orders of magnitude for 7·0 GPa pressure. The amorphous As_2Te_3 films become metallic near 10 GPa and become superconducting at 4·4 K at 10 GPa pressure (Sakai and Fritzsche 1977).

Figure 5 compares the pressure dependence of the electrical resistivity of amorphous As_2S_3, As_2Se_3 and As_2Te_3 films. The interesting observation in this plot is that with the increase of atomic diameter (from S to Te), the pressure required to transform the semiconducting phase to metallic phase decreases drastically. This indicates that the high pressure studies on the glasses are one of the most useful tools to understand the nature of the bonding in the chalcogenide glasses. Another interesting point

Table 2. High pressure studies of the electrical resistivity of *a*-Se

Author (Ref.)	Sample	Type of study	Transition pressure (GPa)	Results
Balchan and Drickamer (1961)	Bulk	Electrical	11·5–14·0	Transition is sluggish
Wittig (1965)	Bulk	Superconductivity	13·0	$T_c = 7$ K
McCann *et al* (1972)	Bulk	X-ray	6·0–16·5	1) Amorphous Se became crystalline under pressure. 2) The high pressure phase of *a*-Se is the same as high pressure phase of *c*-Se. (unsolved structure). 3) Crystalline state was retained when pressure was released.
Wittig (1973)	Bulk	Superconductivity	13·0	1) Se is not retained in a metallic state. 2) After releasing the pressure to 6 GPa there is no evidence of superconductivity in it down to 1·5 K
Fuhs *et al* (1973)	Thin film	Electrical	13·0	1) Above 11·0 GPa the resistance of film changed irreversibly with pressure. 2) Se crystallizes with hexagonal form above 13·0 GPa.
Moodenbaugh *et al* (1973)	Bulk	Superconductivity	13·0	High pressure phase of *a*-Se is superconducting but hexagonal Se upto 16·0 GPa is not superconducting.
Aoki *et al* (1974)	Thin film	Electrical optical	7·6–14·0	Resistance went upward with time after transformations.
Minomura (1978)	Thin film	Electrical	10·5	Resistance went upward with time after transformations.
Gupta and Ruoff (1978)	Thin film	Electrical optical	9·7	1) Amorphous Se crystallizes at 9·7 GPa at room temperature. 2) At 80°C at $P = 2{\cdot}6$ GPa, amorphous Se becomes metallic. 3) The conducting phase was retained for 18 hours at 2·6 GPa after the temperature was lowered to room temperature.
Bundy and Dunn (1979)	Bulk	Electrical	13·0	1) All the earlier observations were confirmed upto 16·0 GPa. 2) Se undergoes a transition to a stable metallic phase at about 25 GPa. 3) Resistivity of metallic Se is very pressure-sensitive.
Parthasarathy *et al* (1984)	Bulk	Electrical	13·0	Glassy Se undergoes a transition to a stable crystalline phase (unsolved structure)

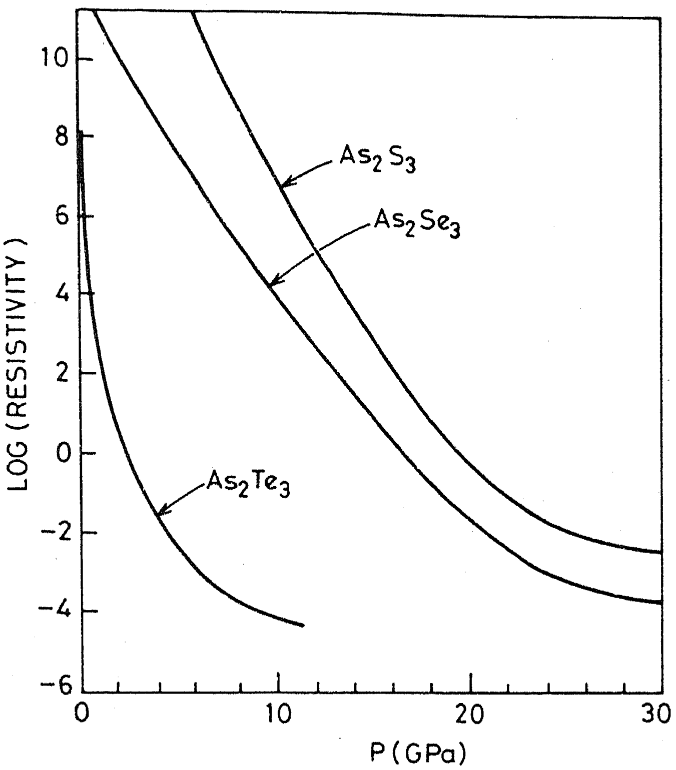

Figure 5. Pressure dependence of electrical resistivity of amorphous As_2S_3, As_2Se_3 and As_2Te_3 films.

reported is that amorphous As_2Te_3 film transforms to crystalline As_2Te_3 under high pressure (10 GPa) with the structure similar to that at room temperature and pressure (Minomura 1982). On the other hand amorphous As_2S_3 and As_2Se_3 films remain amorphous even at 25 GPa pressure. Most of these studies are on the samples in thin film form, but in the case of As_2Te_3 the high pressure results on bulk samples (Ramani *et al* 1979) are in good agreement with those on thin film samples.

The decrease in the electrical resistivity under pressure arises from the gradual decrease of the gap. It is likely that the pressure-induced distortions cause changes in the density of states particularly in the interband gap. This can move the position of the Fermi level and hence decrease the mobility gap; as a consequence the electrons are delocalized. This will result in a pressure-induced semiconductor-to-metal transition, which is observed in glassy chalcogenides.

3.2a *Pressure-induced semiconductor-to-metal transition*: Pressure-induced semiconductor-to-metal transition in amorphous semiconductors is an interesting phenomenon. Amorphous silicon and germanium show the transitions at 10 and 6 GPa respectively (Minomura 1982). In this section let us consider only the binary chalcogenide glasses, which exhibit the transition under pressure. In §3·2 the experimental studies on amorphous As_2Te_3 film under pressure and the pressure-induced semiconductor-to-metal transition in *a*-As_2Te_3 have been discussed. A few other binary chalcogenide glasses like $In_{20}Te_{80}$ (Lakshmikumar *et al* 1981) $Se_{100-x}Te_x$ (Mushiage *et al* 1983; Parthasarathy and Gopal 1984a; Parthasarathy *et al* 1984d), $Ge_{20}Te_{80}$ (Parthasarathy *et al* 1984a, b), $GeSe_2$ (Prasad *et al* 1984), $Al_{23}Te_{77}$

(Parthasarathy *et al* 1985), $Si_{20}Te_{80}$ (Asokan *et al* 1985a), which exhibit the pressure-induced semiconductor-to-metal transition, will now be discussed in detail.

(a) *$In_{20}Te_{80}$ glass*: The sample was prepared in roller quenching technique (Lakshmikumar *et al* 1981). The resistivity drops by 5 to 6 orders of magnitude continuously and becomes independent of pressure beyond 6·0 GPa pressure. The sample recovered from the high pressure cell was identified to have a crystalline structure. The interesting result obtained in $In_{20}Te_{80}$ glass is the time dependent change in the electrical resistivity at each clamped pressure. At higher pressures ($P > 4$ GPa) the time dependence of electrical resistivity is negligible. Lakshmikumar *et al* (1981) explained the observed time dependence on the basis of a slow pressure-induced transformation from the amorphous state to the crystalline state.

(b) *$Se_{100-x}Te_x$ glasses*: The high pressure studies on $Se_{100-x}Te_x$ glasses exhibit two interesting features, namely (i) the pressure-induced glassy semiconductor-to-crystalline metal transition (ii) the composition dependence of the nature of the transition. The second point is extremely interesting, where the discontinuous semiconductor-to-metal transition changes to a continuous one at $6 \leqslant x \leqslant 8$. (Parthasarathy *et al* 1984d). The pressure dependence of the electrical resistivity of glassy $Se_{100-x}Te_x$ alloys with $0 \leqslant x \leqslant 30$ is shown in figures 6 and 7. The glasses, where $0 \leqslant x \leqslant 6$, exhibit a discontinuous drop in resistivity at the transition pressure (figure 6). On the contrary, glasses with $8 \leqslant x \leqslant 30$ show continuous decrease in the electrical resistivity with pressure (figure 7). More extensive studies on the pressure and temperature dependence of the electrical resistivity $Se_{100-x}Te_x$ glasses (Parthasarathy and Gopal 1984a) show that the conductivity is thermally activated in the entire composition range. Glasses with a higher Te content ($x \geqslant 8$) show two activation energies in the conductivity plot, one in the high temperature regime corresponding to the extended state conduction and the other in the low temperature regime corresponding to the localized state conduction through hopping mechanism (Parthasarathy and Gopal 1984a). The variation of the conductivity activation energy as a function pressure for $Se_{100-x}Te_x$ glasses is shown in figures 8 and 9. For $0 \leqslant x \leqslant 6$ the pressure coefficient of electrical resistivity is found to be negative, which is the

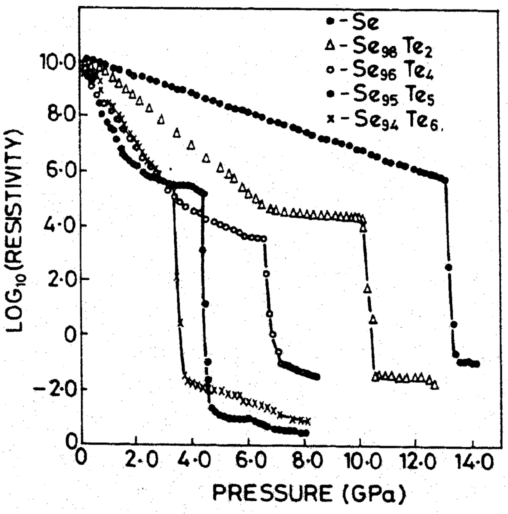

Figure 6. Pressure dependence of electrical resistivity of bulk $Se_{100-x}Te_x$ glasses with $0 \leqslant x \leqslant 6$.

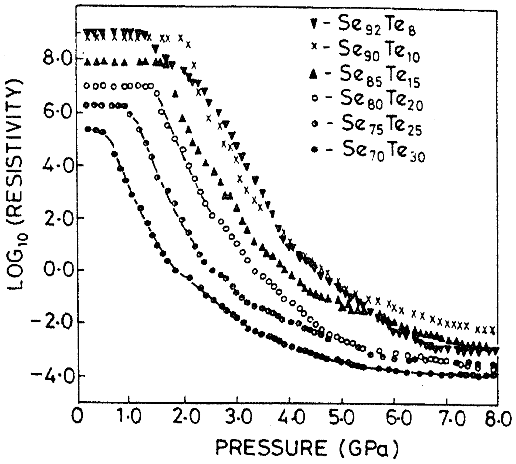

Figure 7. Pressure dependence of electrical resistivity of bulk $Se_{100-x}Te_x$ glasses with $8 \leqslant x \leqslant 30$.

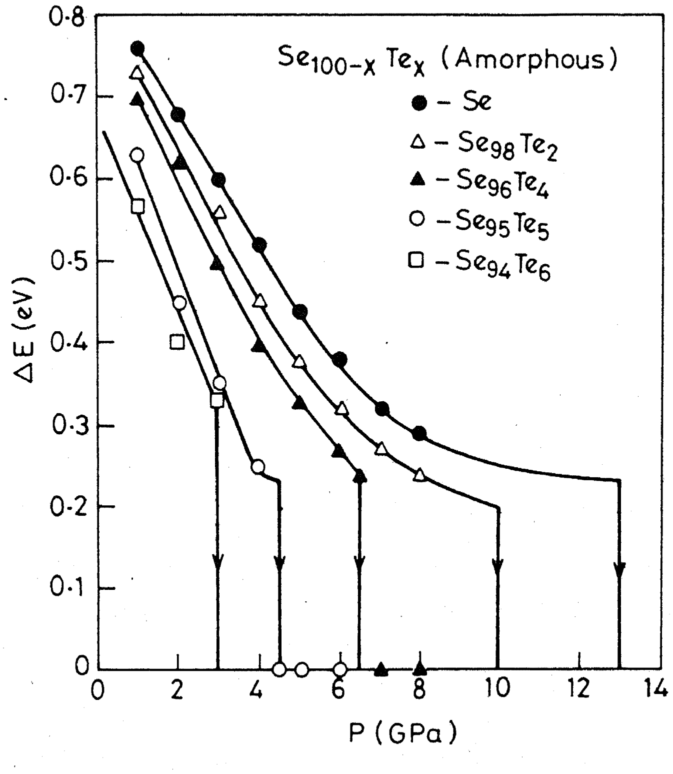

Figure 8. Variation of conductivity activation energy of $Se_{100-x}Te_x$ glasses ($0 \leqslant x \leqslant 6$) as a function of pressure.

characteristic feature of any chalcogenide glasses. For $8 \leqslant x \leqslant 30$, the electrical resistivity shows a rapid and continuous decrease with pressure, above a specific value of P_c (which decreases linearly with the increase of x). The electrical resistivities are almost constant upto P_c, which is interesting (Parthasarathy *et al* 1984d). The most interesting feature of this study is that both the series of these glasses ($0 \leqslant x \leqslant 6$ and $8 \leqslant x \leqslant 30$) become crystalline at high pressure. The crystallization part will be discussed in the last section. The unusual feature in this glassy system is also reflected in our other studies (Parthasarathy and Gopal 1984b; Okuda *et al* 1979). The experimental high pressure studies on amorphous $Se_{80}Te_{20}$ sample by Mushiage *et al* (1983) show not

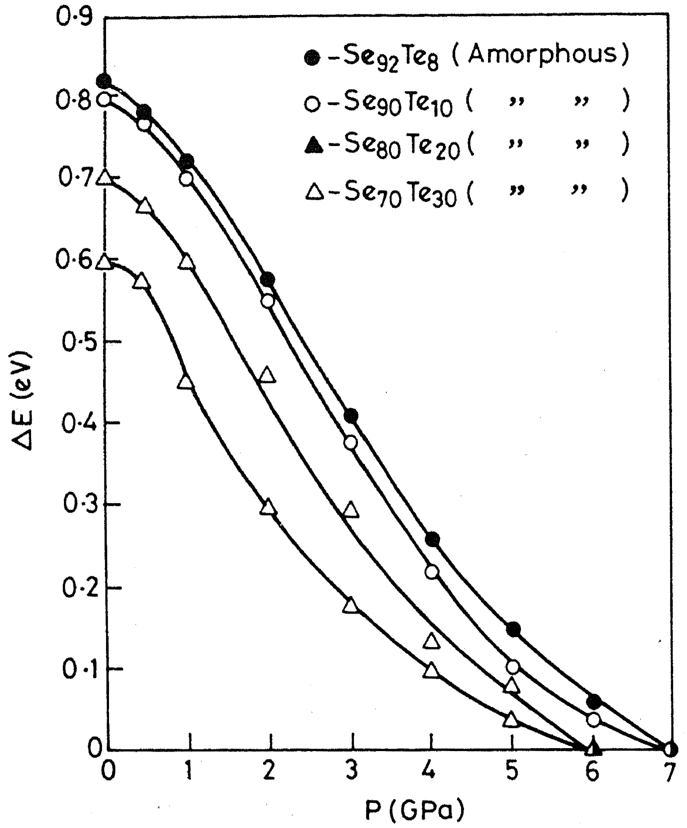

Figure 9. Variation of conductivity activation energy of $Se_{100-x}Te_x$ glasses ($8 \leqslant x \leqslant 30$) as a function of pressure.

only a semiconductor-to-metal transition at 9 GPa pressure, but also a reversible glass-crystal transformation. Until now this latter feature was thought to be thermodynamically improbable. It is very unlikely that the crystalline phase induced by the pressure will transform to the amorphous phase on releasing the pressure, because for a given sample at room temperature the crystalline phase has minimum free energy compared to that of the glassy phase. Moreover it is clear from table 2, that even for amorphous Se, the value of the transition pressure is very much dependent on the method of sample preparation. Mushiage *et al* (1983) have not mentioned about the nature of their sample, whether in the thin film or in the bulk form. The results displayed in figures 6 and 7 are quite reproducible, and it is intuitively obvious that, owing to incorporation of tellurium into selenium, the transport behaviour undergoes a qualitative change above 6% Te. Parthasarathy *et al* (1984d) have explained the observed unusual behaviour on the possibility of a structural change in the Se glass due to the addition of Te beyond 8%. It is very well known that glasses from Se melts contain both rings and chains of Se (Westbury and Cooper 1978). The chain terminations in Se glass are likely to correspond to charged defects. A singly-bonded negative Se_1^- centre is an energetically facile centre to which a tellurium atom can attach itself (Parthasarathy *et al* 1984d).

It is suggested that up to $x = 6$, Te is incorporated at the chain terminations. For $x > 6$, Te atoms are likely to enter the rings rather than the chain, because there is no experimental evidence to suggest further degradation of Se chains with the addition of

Te. The EXAFS study on Se glass (Parthasarathy *et al* 1981) support the above suggestions, by showing the presence of 7 to 8 at.% of Se atoms at the chain terminations. Since upto 6 % Te the substitutions are at the chain end, it does not affect drastically either the structure or the overall cohesion of the alloys, which is possibly the reason for the near-constancy of glass transition temperature and the first-order transition under pressure upto 6 % Te content. Also since the tellurium atoms are larger in size, their presence at the chain ends facilitates pressure-induced crystallization, which manifests itself in lower values of the transition pressure (figure 6). It is also suggested that the three coordinated Te atoms produce localized tail states in the band gap of the *a*-Se. The newly created localized tail states gradually dominate over the defect states. Once the tail state energies cross over the charged defect energies, the band gap begins to decrease. The schematic density of states diagram for $Se_{100-x}Te_x$ glasses is shown in figure 10. The effect of pressure, however, is more influenced at three-coordinated cross linking Te positions, which results in a greater sensitivity of tail states to pressure than the charged defect states. It is assumed by Parthasarathy *et al* (1984d) that the new tail states created by the addition of Te are lower in energy than the top-most negatively-charged defect states. Therefore, at pressures lower than P_c, structural reorganization occurs primarily around Te atoms which are not defect centres, and the gap governed by the defect states is unaffected in the process. This would account for the near-constancy of the electrical resistivities upto P_c. At this stage it is difficult to quantitatively predict the effect of pressure on the band picture or the density of states near the Fermi level or near the mobility edges, and further experiments such as pressure dependence of I-V characteristic, Hall effect, XPS and UPS etc have to be performed.

The unusual behaviour observed in $Se_{100-x}Te_x$ glasses is certainly due to the local atomic arrangements rather than merely the change in conductivity mechanism. This is confirmed by the high pressure study on the crystalline $Se_{100-x}Te_x$ alloys over the entire composition range (Parthasarathy *et al* 1984e). The pressure dependence on the electrical resistivity of the crystalline $Se_{100-x}Te_x$ alloys is shown in figure 11. Here in the entire composition range $0 \leqslant x \leqslant 100$, we observe a discontinuous pressure-

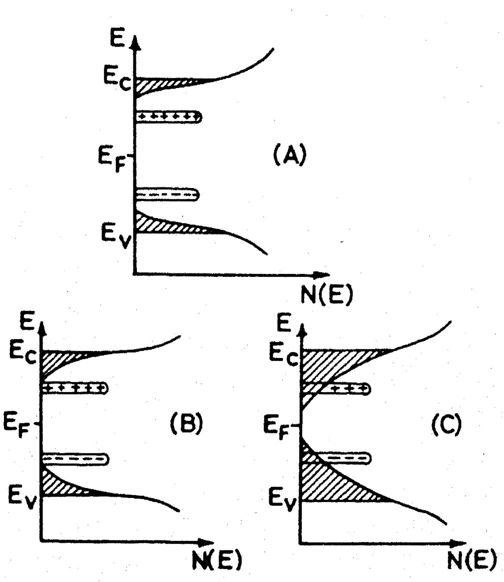

Figure 10. Schematic density of states diagrams for $Se_{100-x}Te_x$ glasses for (**A**) $x \leqslant 6$; (**B**) $x > 6$ and pressures less than the value of the crystallization pressure (**C**) $x > 6$ and pressures greater than the value of crystallization pressure.

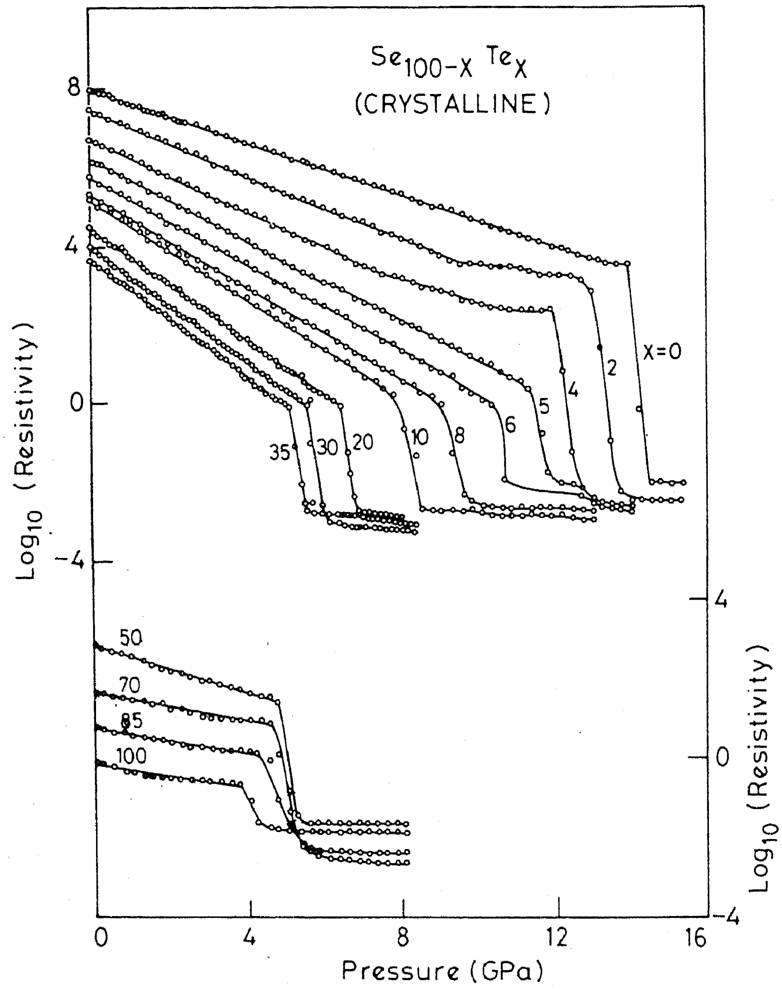

Figure 11. Pressure dependence of electrical resistivity of crystalline $Se_{100-x}Te_x$ alloys.

induced transition. The variation of the electrical resistivity, the activation energy for electronic conduction and the transition pressure as a function of Te concentration exhibit the unusual behaviour at $x = 8$.

These high pressure studies on the glassy and crystalline $Se_{100-x}Te_x$ alloys show that the pressure is a very useful thermodynamic variable to study (qualitatively) the changes in the short range order.

(c) *$Ge_{20}Te_{80}$ glass*: The effect of pressure on the electrical resistivity of Ge-Te glasses (near eutectic composition 83 at.% Te) has been studied by Nakamura *et al* (1975) under hydrostatic pressure environment upto 0·3 GPa. The conductivity of $Ge_{17}Te_{83}$ glass increases by 4 times upto 0·29 GPa. The pressure dependence of electrical resistivity of bulk $Ge_{20}Te_{80}$ glass upto 8 GPa pressure has been reported by Parthasarathy *et al* (1984a, b). The electrical resistivity decreases exponentially with increase of pressure by three orders of magnitude upto 5 GPa, and at 5 GPa, the resistivity drops discontinuously by six orders of magnitude (figure 12). For pressures greater than 5·5 GPa the variation of resistivity with pressure is very small. The pressure-induced transition observed in glassy $Ge_{20}Te_{80}$ sample is

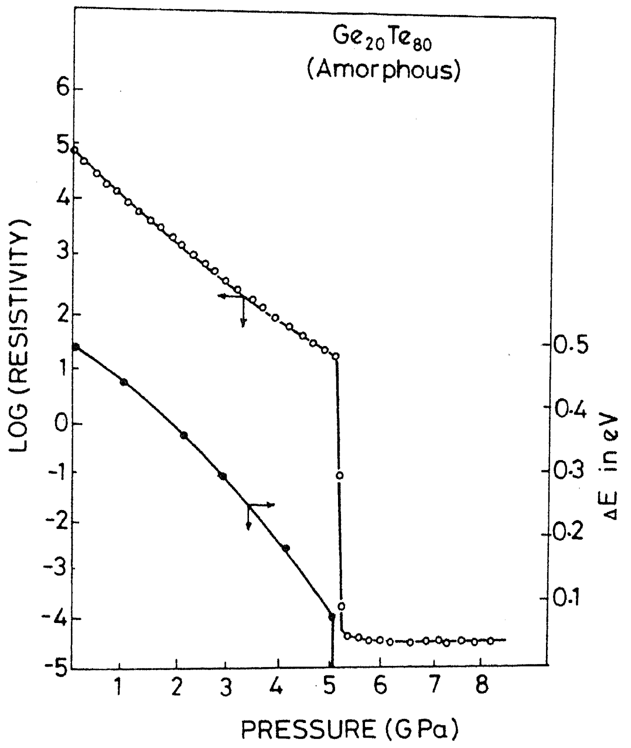

Figure 12. Variation of the electrical resistivity and activation energy for electronic conduction in bulk $Ge_{20}Te_{80}$ glass as a function of pressure.

confirmed to be a semiconductor-to-metal transition by the temperature dependence of electrical resistivity of $Ge_{20}Te_{80}$ glasses at different pressures (Parthasarathy *et al* 1984a). For pressures upto 5 GPa, the variation of resistivity obeys the relation

$$\rho(T) = \rho_0 \exp(\Delta E/kT), \tag{5}$$

where ρ_0 is the pre-exponential factor, ΔE the activation energy for electronic conduction, k the Boltzmann's constant and T the absolute temperature. The variation of the activation energy as a function of pressure is also shown in figure 12. The activation energy decreases to zero at 5 GPa, indicating metallic conduction at high pressures. The pressure coefficient of the activation energy is $-0{\cdot}082$ eV GPa^{-1}. The temperature coefficient of electrical resistivity is positive at 6·0 GPa (Parthasarathy *et al* 1984a). The high pressure metallic phase is found to have a face-centred cubic structure with $a = 6{\cdot}42$ Å.

(d) *$GeSe_2$ glass*: This chalcogenide glass belongs to a special case, where the local bonding is of the tetrahedral type, and is therefore called a tetrahedrally-bonded chalcogenide glass (Zallen 1983). Phillips (1979) described the Ge_xSe_{100-x} glasses by a model of small chemically-ordered clusters embedded in a continuous network. The predominant clusters are $(Se)_n$ chains, $Ge(Se_{1/2})_4$ corner-sharing tetrahedra and $Ge_2(Se_{1/2})_6$ ethane-like structural units, which dominate near $x = 0$, 33 and 40 respectively. The pressure dependence of the electrical resistivity of $GeSe_2$ glass is shown in figure 13. The resistivity increases with pressure upto 2 GPa by two orders of magnitude. Usually the pressure coefficient of electrical resistivity for tetrahedrally-

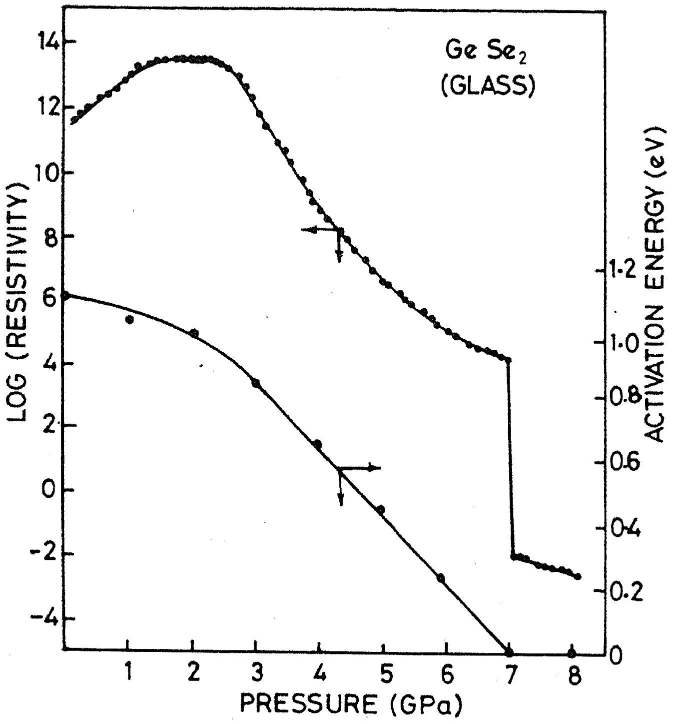

Figure 13. Variation of electrical resistivity and the conductivity activation energy of $GeSe_2$ glass as a function of pressure.

bonded materials like *a*-Si, *a*-Ge, *a*-InSb is positive (Minomura 1982). So the initial increase in resistivity with pressure is certainly due to the local tetrahedrally-bonded $Ge(Se_{1/2})_4$ structures. For pressures above 2·5 GPa, the resistivity decreases exponentially with increase of pressure, which is the behaviour expected for many lone pair semiconductors. At 7 GPa, the resistivity drops by six orders of magnitude and saturates near a value of $3{\cdot}08 \times 10^{-3}$ cm, which is less than the Mott's maximum metallic resistivity value (Mott 1970). The temperature dependence of the electrical resistivity of $GeSe_2$ glass at different pressures obeys the relation (5). The value of the pre-exponential factor in (5) shows that at all pressures upto 5 GPa, the conduction in the sample is due to the excitation of the carriers across the mobility edges (Prasad *et al* 1984).

The temperature coefficient of electrical resistivity of the sample at 7 GPa and 8 GPa is positive and confirms the metallic behaviour of the sample.

(e) *$Al_{23}Te_{77}$ glass*: The chalcogenide $Al_{23}Te_{77}$ glass has very interesting electronic properties like electrical switching (Alegria *et al* 1983). The pressure and temperature dependence of the electrical resistivity of the $Al_{23}Te_{77}$ glass is studied by Parthasarathy *et al* (1985). The variation of electrical resistivity of $Al_{23}Te_{77}$ glass as a function of pressure (at room temperature) is shown in figure 14. The resistivity decreases exponentially with increase of pressure and becomes of the order of 100 $\mu\Omega$cm at 8·0 GPa pressure. The temperature dependence of the electrical resistivity at different pressures obeys the relation (5). At atmospheric pressure there are two activation energies, 0·58 eV for $234\ \mathrm{K} \leqslant T \leqslant 300\ \mathrm{K}$ and 0·30 eV for $185\ \mathrm{K} \leqslant T \leqslant 234\ \mathrm{K}$. Because of high resistance of the sample at low temperature, the temperature range of investigations at low pressures is limited to 185 K. For 1·0 GPa pressure the value of first activation energy decreases to 0·49 eV and the second activation energy increases to 0·41 eV. From the values of the pre-exponential factors it is suggested that the conduction in the lower temperature region is probably through the tail of localized states via thermally activated hopping and at the high temperature region ($T \geqslant 234$ K), conduction occurs through the extended states (Parthasarathy *et al* 1985). The increase in the second activation energy with increase of pressure indicates the increase in width of the localized states near the band tail with the application of pressure.

The variation of the conductivity activation energy as a function of pressure is shown in figure 15. The activation energy also decreases continuously with increase of pressure

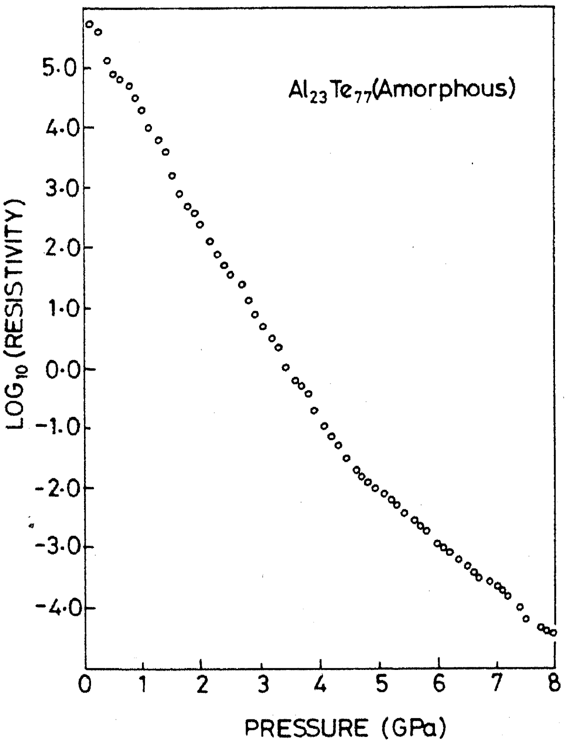

Figure 14. Pressure dependence of electrical resistivity of bulk $Al_{23}Te_{77}$ glass.

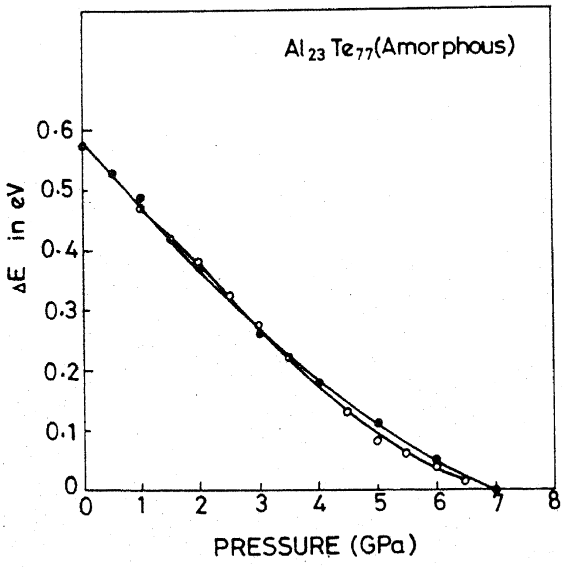

Figure 15. Pressure dependence of conductivity activation energy of bulk $Al_{23}Te_{77}$ glass. The closed circle: Activation energy found from temperature dependence of conductivity. Open circle: Activation energy calculated from the pressure dependence of electrical resistivity which follows

$$(\partial \Delta E/\partial P)_T = kT\frac{\partial \ln \rho}{\partial \ln P}$$

where k is the Boltzmann constant and $T = 300$ K.

and goes to zero at 7·0 GPa pressure. The pressure coefficient of the conductivity activation energy is $-0{\cdot}103\ \mathrm{eV\ GPa^{-1}}$ for $P \leqslant 4$ GPa and $-0{\cdot}06\ \mathrm{eV\ GPa^{-1}}$ for $4\ \mathrm{GPa} \leqslant P \leqslant 7$ GPa respectively. The gradual decrease of activation energy with increase of pressure indicates that the decrease in electrical resistivity under pressure arises from a gradual decrease in the optical band gap.

(f) *$Si_{20}Te_{80}$ glass*: Recent high pressure experiments by Asokan *et al* (1985a) on bulk $Si_{20}Te_{80}$ glass show a pressure-induced glassy semiconductor-to-crystalline metal transition at 7 GPa pressure. The structural transformations will be discussed in the last section. The pressure dependence of electrical resistivity of $Si_{20}Te_{80}$ glass at room temperature is shown in figure 16. In this case also the temperature dependence of the electrical resistivity confirms that the observation transition is the semiconductor-to-metal transition. In all the pressure-induced semiconductor-to-metal transitions, the value of the conductivity in the metallic phase is very near the Mott's minimum metallic conductivity value (Mott 1970).

3.3 *Ternary and multicomponent chalcogenide glasses*

The high pressure studies on the electrical resistivity of $As_{40}Se_{60}Ag_{1{\cdot}0}$ glass (Arai *et al* 1973) $Ge_{16}As_{35}Te_{28}S_{21}$ glass (Minomura *et al* 1976), $As_{40}Se_xTe_{60-x}$ glasses (Ramani *et al* 1979), As-Te-I and As-Te-Ge glasses (Johnson and Quinn 1978a), $Cu_{25}Au_5Te_{70}$

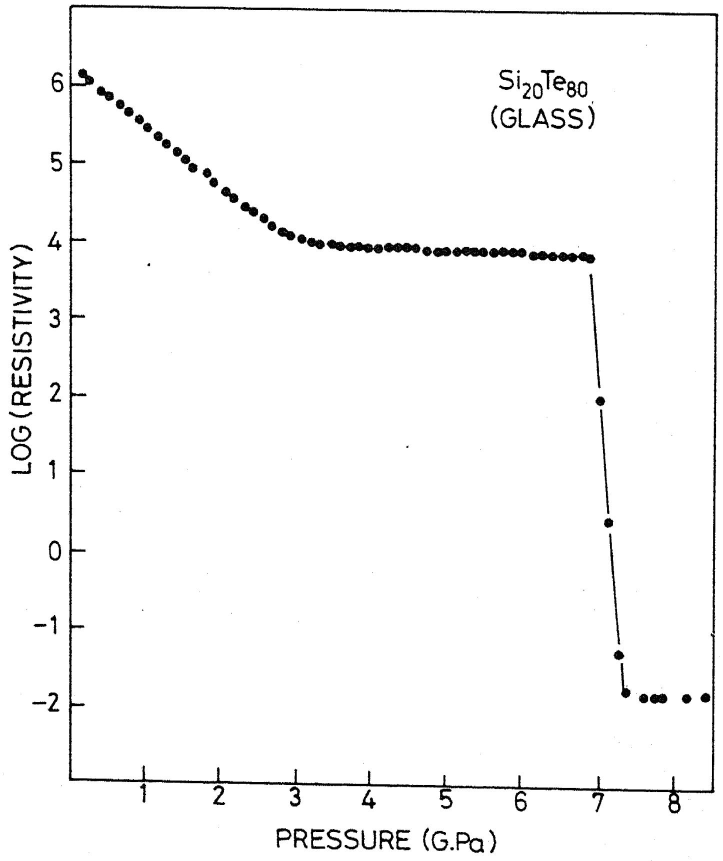

Figure 16. Pressure dependence of electrical resistivity of bulk $Si_{20}Te_{80}$ glass.

glass (Lakshmi Kumar *et al* 1981) Ge-Se-Bi glasses (Bhatia *et al* 1983, 1984, 1985a, b), Ge-Se-Sb glasses (Bhatia *et al* 1984, 1985c), Ge-S-Bi glasses (Gosain *et al* 1985) and Ge-Se-Tl glasses (Naik *et al* 1985) give many interesting results, which will be reviewed in this section.

The conductivity of $As_{40}Se_{60}Ag_x$ glasses increases by 2·5 times for 0·2 GPa pressure. With decrease of silver content the pressure coefficient of conductivity decreases drastically (Arai *et al* 1973). The pressure effects on $As_{40}Se_{60}Ag_x$ glasses suggest that in the electronically conducting glass which contains atleast locally mobile ions such as silver, the conduction process consists of the cooperative processes of electronic and ionic conduction, rather than their simple additive processes.

The multicomponent $Ge_{16}As_{35}Te_{28}S_{21}$ glass becomes metallic under high pressure of 15 GPa with continuous decrease in the activation energy for electronic conduction (Minomura *et al* 1976). On the other hand, the glassy $As_{40}Se_xTe_{60-x}$ alloys remain semiconducting upto 7·0 GPa for $x > 10$ (Ramani *et al* 1979). The magnitude of the pressure coefficient of electrical resistivity and activation energy decreases drastically, with increase of selenium content (Ramani *et al* 1979).

An extensive study of the pressure dependence of electrical conduction on various $As_{50}Te_{50-x}Ge_x$, $As_{50}Te_{50-x}I_x$ and $As_{40}Te_{50}Ge_{10}$ glasses has been made by Johnson and Quinn (1978a). They found that for all the chalcogenide glasses $\Delta \ln\sigma/\Delta P$ varies from about 2 to 8 GPa^{-1} for pressures upto 2·4 GPa. For binary glasses As_2Te_3 and $As_{50}Te_{50}$ the conductivity increases exponentially with pressure with $\Delta \ln\sigma/\Delta P \simeq 4·0\ GPa^{-1}$. The substitution of small concentrations (2 to 5 at. %) of iodine for tellurium in $As_{50}Te_{50}$ reduces $\Delta \ln\sigma/\Delta P$ by about 50 %, whereas the substitution of Ge produces no significant change (Johnson and Quinn 1978a). In the As-Te-I and As-Te-Ge glasses, the conductivity increases more rapidly as a function of time, at high pressure, exhibiting a log t time dependence. The conductivity values increase by a factor of $\simeq 2$ with time at high pressure. They also found the conductivity relaxation phenomena in these glasses after pressure cycling, due to the permanent densification of the glasses at high pressure (Johnson and Quinn 1978a). A similar time dependence on conductivity at high pressure has been observed for $Cu_{25}Au_5Te_{70}$ glass by Lakshmikumar *et al* (1981). They attributed this time dependence of conductivity to the transformation from a glassy state to the crystalline state.

In the past few years bismuth-doped chalcogenide glasses have received much attention because of their capability in transforming from *p*-type to *n*-type semiconductors (Tohge *et al* 1980; Nagels *et al* 1981). Bhatia *et al* (1983, 1984, 1985a, b, c) have investigated the pressure and temperature dependence of the electrical resistivity of bismuth and antimony doped $GeSe_{3.5}$ glasses. For bismuth-doped glasses the variation of electrical resistivity is shown in figure 17. The resistivity of $GeSe_{3.5}$ glass shows a slight increase with pressure upto 1·0 GPa and then saturates, followed by a continuous decrease upto about 7·0 GPa. The addition of Bi dopant significantly alters the picture. For 2 at. % bismuth, the pressure coefficient of electrical resistivity is found to be negative and for higher bismuth content (> 4 at. %) the pressure coefficient of resistivity is positive. The continuous transition in glassy $GeSe_{3.5}$ is drastically influenced by the addition of bismuth (> 4 at. %). The temperature dependence of electrical resistivity at different pressures follows equation (5). The variation of activation energy as a function of pressure for various bismuth concentration is shown in figure 18. Here again the glass with $x = 2$ shows quite a different behaviour as compared to $x = 4$, 10 glasses. Bhatia *et al* (1984, 1985a, b, c) suggested that bismuth,

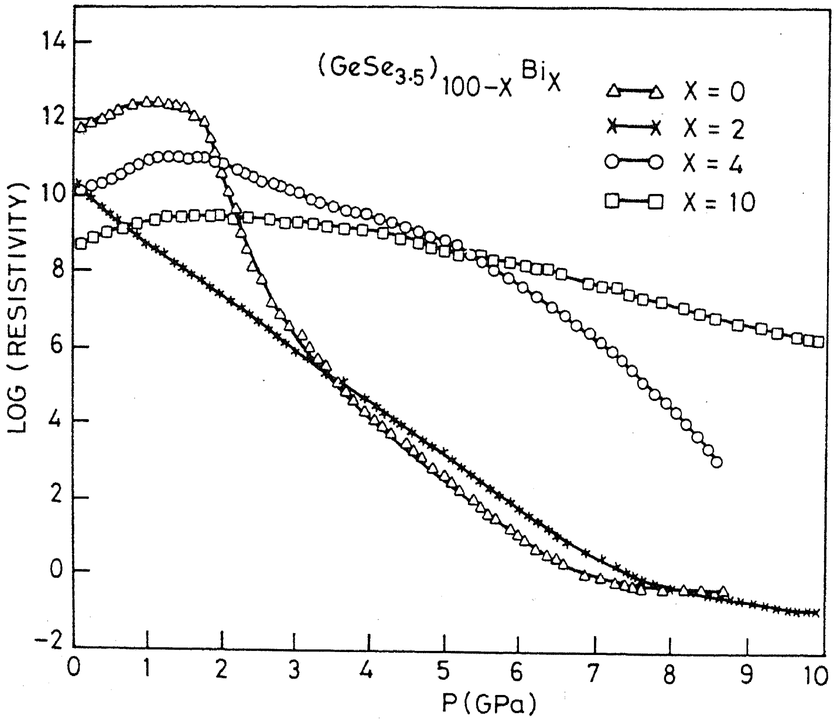

Figure 17. Pressure dependence of electrical resistivity of (GeSe$_{3\cdot5}$)$_{100-x}$Bi$_x$ glasses.

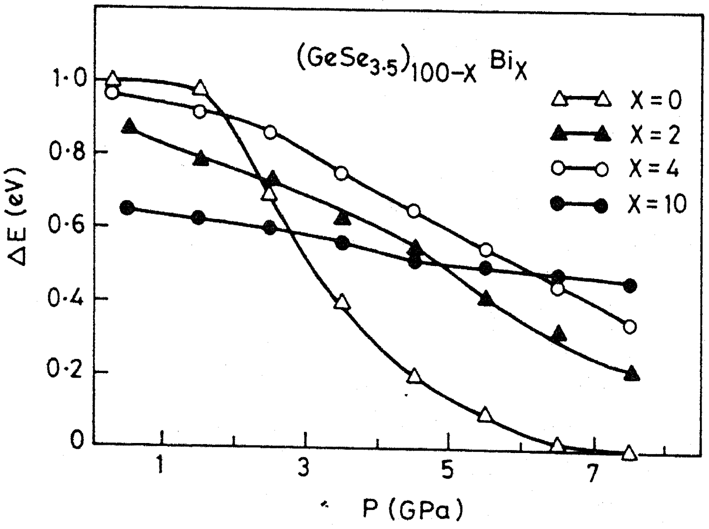

Figure 18. Variation of activation energy as a function of pressure for various (GeSe$_{3\cdot5}$)$_{100-x}$Bi$_x$ glasses.

upto 2 at.%, enters the network of glassy GeSe$_{3.5}$ in such a way that Bi–Se bonds are formed and for higher bismuth content glass, the entry of Bi produces Bi–Ge bonds. These two incorporation behaviours can be understood by considering the Phillips medium range order (Phillips 1981).

The high pressure studies on Ge$_{20}$S$_{80-x}$Bi$_x$ glasses show two pressure-induced discontinuous transitions (Gosain *et al* 1985). The pressure dependence of electrical resistivity of Ge-Se-Tl glasses also exhibits a pressure-induced discontinuous transition

(Naik *et al* 1985). This transition is also attributed to the pressure-induced crystallization phenomena which will be discussed in the last section of this review.

3.4. *Electrical switching*

Among the electrical characteristics of glassy chalcogenide semiconductors, the observation of switching by Ovshinsky (1968) had attracted considerable attention because of their technological applications. Upon the application of a high electric field or current the material switched to a conducting state from an insulating state and this switching on/off could be done many times in a reversible manner. Only a few high pressure investigations on switching behaviour have been performed on $Ge_{15}Te_{81}S_2As_2$ glass (Banik 1973) and $As_{50}Te_{45}I_5$ glass (Johnson and Quinn 1978b). The threshold switching voltage V_t decreases from about 20 V to 3 V at a pressure of 1·6 GPa and the conductivity increases by a factor of about 10. Further the on/off resistance ratio is also adversely affected. At present it is not known whether a better performance is shown by any glass at high pressures.

3.5 *Photoelectric and drift mobility measurements*

The high pressure effects on the electrical conductivity and photoconductivity spectra of amorphous and single crystal samples of As_2Se_3 have been investigated by Kolomiets and Raspopova (1970). They observed that both single crystal and glassy samples exhibit a considerable pressure-induced shift of the photoconductivity spectra. In both cases the spectra shifted toward long wavelengths, which indicates the decrease in band gap with increase of pressure. The value of this co-efficient $dE/dP = -0{\cdot}16\ \mathrm{eV\ GPa^{-1}}$ for glassy sample and $-0{\cdot}17\ \mathrm{eV\ GPa^{-1}}$ for single crystal (Kolomiets and Raspopova 1970).

The pressure dependence of the dark and photocurrent of amorphous selenium has been investigated by Dolezalek and Spear (1970). Both dark current and photocurrent increase with pressure. The pressure coefficient of both photocurrent and dark current is almost equal, which suggests that with the application of pressure the surface conditions gets modified in such a way as to enhance the injecting properties of the contact (Dolezalek and Spear 1970).

The pressure dependence of the drift mobility of electron (μ_e) and hole (μ_h) transport in glassy selenium was measured by Dolezalak and Spear (1970). It is found that both μ_e and μ_h are pressure-independent, which rules out the hopping transport in glassy Se. However they suggested that the presence of a large density of localized states close to the band tails is the main factor which controls the drift mobility.

4. **Optical properties**

In § 3.5 the effect of pressure on photoconductivity has been discussed. Among all the optical properties of glasses, refractive index is one whose pressure dependence has been investigated quite early by Kastner (1972). The pressure dependence on refractive index, optical absorption edge, reflectivity, Raman spectra, photo darkening and photo luminescence spectra of chalcogenide glasses will be discussed in this section. The effect of pressure on the refractive index and the absorption edge of some chalcogenide glasses have been discussed by Lucovsky (1977).

4.1 *Refractive index*

The pressure dependence of the refractive index of semiconducting chalcogenide glasses is related to the pressure-induced shifts of the interband absorption processes. The pressure effect of the refractive index (n) or of the optical path length nl ($l =$ the sample thickness) of glassy As_2S_3, As_2Se_3, $GeSe_2$, GeSeTe and $Ge_{16}As_{35}Te_{28}S_{21}$ alloys has been studied by Kastner (1972) upto 0·2 GPa pressure. It is found that $(1/n)(dn/dp)$ is positive for all the glasses whereas it is negative for the tetrahedral semiconductors. The value of $(1/n)(dn/dp)$ for chalcogenide glasses is an order of magnitude larger than is observed for tetrahedral semiconductors.

The value of dn/dp is positive for all the materials containing group VI elements in two-fold coordination. The local field corrections appear to be the cause of the positive dn/dp. The Lorentz-Lorentz description of the local field predicts dn/dP in agreement with experiment for most of the chalcogenide glasses (Kastner 1972; Zallen *et al* 1981; Weinstein *et al* 1982). In his next paper Kastner (1973) explained the positive pressure coefficient of refractive index for chalcogenide glasses by introducing a new parameter called 'the average bond-free solid angle (BFSA)'. BFSA is the solid angle associated with each atom, which is free of bond charge. When BFSA is large, atoms can move closer together under pressure without compressing bonds. In this case local field corrections cause a positive (dn/dP). The pressure dependence of refractive index of amorphous As_2S_3 has been investigated by Berson *et al* (1981) upto 6·0 GPa pressure. The value of the refractive index of As_2S_3 glass increases from 2·5 (at 10^5 Pa) to 3·25 (at 5·0 GPa), which also agrees with the result of Kastner (1972). According to the Penn dielectric model (Penn 1962) a strong increase in n indicates the decrease in the average bonding-antibonding gap, which will give rise to the negative pressure coefficient of the band gap for chalcogenide glasses.

4.2 *Optical absorption edge*

The optical absorption studies on glassy selenium under pressure have been investigated by Caldwell and Fan (1959), Suchan *et al* (1959), Fuhs *et al* (1973), Kastner (1973), Aoki *et al* (1974) and Lucovsky (1977), which demonstrate the reduction of optical gap to zero at 13·0 GPa pressure. For chalcogenide $Ge_{16}As_{35}Te_{28}S_{21}$, the pressure-induced shift of the energy of the edge is independent of absorption coefficient from 5 to 2×10^3 cm^{-1} (Kastner 1973). The pressure-induced shift is also independent of the temperature in the range $200\,K < T < 350\,K$.

The value of the pressure coefficient of the edge for As_2Se_3 glass is $-0{\cdot}076 \pm 0{\cdot}015$ eV GPa^{-1} (Grant and Yoffe 1970; Kolomiets and Raspopova 1970; Kastner 1973). Kastner's result indicates a lower value for (dE_0/dP) compared to Kolomiets and Raspopova's value and a value higher than that of Grant and Yoffe (1970). Besson *et al* (1981) have investigated the pressure dependence of the absorption edge of crystalline as well as amorphous As_2S_3, which show that for both materials the absorption edge undergoes a rapid red shift of $\simeq$ 1 eV in 10 GPa. The pressure shifts obtained from the initial slopes of the isoabsorption plots ($\alpha = 5 \times 10^3$ cm^{-1}) are $0{\cdot}18 \pm 0{\cdot}02$ eV GPa^{-1} and $0{\cdot}14 \pm 0{\cdot}03$ eV GPa^{-1} for a-As_2S_3 and orpiment respectively. In a later study Weinstein *et al* (1980) found very large effects of pressure on the electronic spectra of As_2S_3 glass. They also found that the main vibrational band is insensitive to pressure. Both these characteristics are explained in terms of the macromolecular character of As_2S_3 (Zallen and Blossey 1976).

The high pressure experiments on the optical properties of a-GeSe$_2$, layer-structure crystalline GeS$_2$ and a quartz-like crystalline form of GeS$_2$ samples were performed by Zallen *et al* (1981) and Weinstein *et al* (1982). They found that pressure causes the absorption edge to red shift and the refractive index to increase, the sensitivity to pressure being largest for glassy GeS$_2$, less for (two-dimensional) layer-structure crystalline GeS$_2$ and the least for the quartz-like crystalline GeS$_2$ sample which is three-dimensional in nature. The pressure coefficient of the band gap of glassy GeS$_2$ sample is $-0{\cdot}23$ eV GPa^{-1}.

The pressure coefficient of the refractive index is also the largest for the glassy GeS$_2$ sample, which suggests that the glassy GeS$_2$ is not a three-dimensional network glass akin to silica but instead has lower network dimensionality (Weinstein *et al* 1982).

4.3 *Reflectivity studies*

The reflectivity studies under high pressure is a very difficult experiment because the refractive indices of the pressure transmitting fluid and the window depend on pressure (Zallen and Paul 1967; Schneider and Vedam 1970; Kastner and Forberg 1976). The pressure dependence of the reflectivity will yield more information about the local field corrections. The reflectivity of glassy selenium was studied under high pressure upto 0·4 GPa, at photon energies between 1 and 4·5 eV. For glassy selenium the pressure coefficient of reflectivity $\Delta R/R\Delta P$ over the entire spectrum is large and positive ($\Delta R/R\Delta P = 0{\cdot}2$ GPa^{-1} at photon energy 1 eV). Kastner and Forberg (1976) have compared their experimental results with the prediction of the Lorentz-Lorentz relation in order to verify the effect of local field corrections on the reflectivity of glassy selenium. The agreement between the Lorentz-Lorentz prediction and experiment suggest that the average value of $\Delta R/R\Delta P$ is the result of local field corrections.

4.4 *Raman spectrum*

The Raman scattering experiment under high pressure has its own difficulty, in the case of the chalcogenide glasses because most of the glasses are opaque to visible light. The Raman scattering experiment should be made in a back-scattering configuration, which usually gives scattered light with very low intensity. For the experimental details the readers can refer the recent review by Jayaraman (1983). Because of the experimental difficulties the Raman scattering studies on chalcogenide glasses under high pressure have been limited to a few systems like glassy As$_2$S$_3$ (Weinstein *et al* 1980; Besson *et al* 1981) and GeS$_2$ alloys (Zallen *et al* 1981). The main Raman band for As$_2$S$_3$ glass is near 350 cm^{-1} corresponding to the As–S covalent bond stretching vibrations. The position of this band is scarcely affected by pressure upto 0·8 GPa. The fractional shift in frequency expressed in units of percent per GPa is $+(1{\cdot}0 \pm 1{\cdot}0)$. The pressure insensitivity of the position of the Raman band in a-As$_2$S$_3$ supports the view that this glass is a molecular solid (Weinstein *et al* 1980).

The influence of pressure on the first-order Raman spectrum of GeS$_2$ glass has been studied by Zallen *et al* (1981). At atmospheric pressure there are five bands at 433, 372, 342, 117 and 20 cm^{-1} for GeS$_2$ glass. The main effect of pressure is to broaden and shift the dominant Ge–S stretching band to a higher frequency. All the other sharp features in the spectrum also broaden with pressure. The observed phonon frequencies increase with increase of pressure.

4.5 *Photodarkening*

Glassy chalcogenide alloys exhibit the phenomenon of photodarkening i.e., a shift of the optical absorption edge to lower energies induced by photons with a greater energy than the band gap (Tanaka 1983). The shift induced by the band-gap illumination can be removed by annealing the glass just below the glass transition temperature. Photodarkening is considered as resulting from distortion of the intermolecular distance between the chalcogen atoms, one of which has been transferred from a stable to a quasistable position by a photon having the band-gap energy. The effect of pressure on these photo-induced changes in chalcogenide glasses has been reported by Kolobov *et al* (1982), Tanaka (1984) and Tsutsu *et al* (1984). High pressure experiments on As_2Se_3 films show that the photodarkening value decreases with increase of pressure. The effect of pressure is very significant, the change in photodarkening value being comparable with the maximum photodarkening value in the absence of pressure (Kolobov *et al* 1982). Photodarkening phenomena in glassy As_2S_3 under high pressure reveal that the pressure derivative of the change of absorption edge $d\Delta E/dP$ is $0{\cdot}12\ \mathrm{eV\ GPa^{-1}}$ (Tanaka 1984; Tsutsu *et al* 1984) which is 30% smaller than that by Weinstein *et al* (1980). When the glassy As_2S_3 sample under high pressure is exposed to light a remarkable shift to lower energy side was observed (Tsutsu *et al* 1984). The values of the shifts are 0·097 eV at 0·1 GPa and 0·121 eV at 0·3 GPa respectively. When the pressure is released, the absorption edge is shifted by the same amount ΔE to higher energy side; however the shift by illumination is quenched even after releasing pressure, which is confirmed by Tanaka (1984). The absorption edge is completely recovered by annealing at 350 K. At atmospheric pressure and at room temperature glassy selenium does not exhibit photodarkening (Tanaka and Odajima 1982). Much effort has been made to search for photodarkening phenomena in amorphous selenium under high pressure. In contrast to As_2S_3, Se glass annealed under pressure exhibits no detectable photodarkening (Tanaka 1984). But in both As_2S_3 and Se glasses, the densification under pressure is induced not only by annealing but also by illumination. The observed differences between As_2S_3 and Se have been explained qualitatively on the basis of the effective coordination number which is the sum of the covalent coordination number and a measure of the strength of the intermolecular bonding proportional to the force constant (Tanaka 1984). The structure of Se is sufficiently flexible that the intermolecular distance may be compressed efficiently by pressure and no space is available for bond twisting. This contributes to the absence of photodarkening in glassy Se under pressure (Tanaka 1983).

4.6 *Photoluminescence studies*

The effect of high pressure on photoluminescence (PL) in crystalline As_2S_3 (upto 11 GPa) and amorphous As_2SeS_2 (upto 17 GPa) has been measured by Weinstein (1984) for the first time. For crystalline As_2S_3 it was conclusively proved that pressure violates the mid-band gap rule. For c-As_2S_3 and PL peak E_{PL} blue-shifts by $+0{\cdot}012\ \mathrm{eV\ GPa^{-1}}$, while the band edge E_g and the PL excitation peak red-shift by $-0{\cdot}14\ \mathrm{eV\ GPa^{-1}}$. The results for As_2SeS_2 glass also indicate a similar pressure dependence. Weinstein (1984) deduced the pressure dependence of the Street-Mott energy level scheme (Street and Mott 1975) from the measurements on c-As_2S_3. He also developed a realistic configuration coordinate model based on layer inter-linking defects (Weinstein 1984).

5. Magnetic properties

High pressure studies on the magnetic properties of glasses mainly discuss the Fe-based metallic glasses (Shirakawa *et al* 1983 and the references therein). Some high pressure investigations on ^{77}Se nuclear magnetic resonance have been made on liquid selenium by Warren Jr and Dupree (1980a, b) in the region from the supercooled liquid (466 K) to the supercritical fluid (1900 K) and at pressures upto 0·08 GPa. Application of pressure at 1800 K induces a rapid delocalization of the paramagnetic centres which coincides with the Mott's minimum metallic conductivity. As far as we are aware no experimental investigations on the pressure dependence of the magnetic properties of bulk chalcogenide glasses have been made. Such a study will be very useful in understanding the phenomena of pressure-induced insulator-to-metal transition in chalcogenide glasses.

6. Crystallization studies

Chalcogenide glasses are considered to be supercooled liquids which are thermodynamically metastable compared to the stable crystalline state. A difference between the free energy of the low pressure glassy phase and that of the high pressure crystalline phase leads to a pressure-induced transition, which can be a sharp discontinuous or a continuous transition. A preliminary review on this aspect and the pressure effects on chalcogenide glasses have been discussed by various scientists (Roy and Cohen 1961; Sakka and Makenzie 1969; Johnson Jr and Quinn 1978a; Gopal 1983a, b, 1985, Parthasarathy and Gopal 1985; Asokan *et al* 1985a). In this section, we will discuss the pressure-induced crystallization in chalcogenide glasses in two parts. The first part deals with materials showing discontinuous transitions and the second part with those showing continuous transitions.

6.1 *Discontinuous transitions to the crystalline state*

In 1972, McCann and Cartz (1972) found that hexagonal and amorphous selenium transform to similar or identical new unsolved structures above about 14 GPa and that the high pressure modification is retained when the pressure is removed. This pressure-induced crystallization of glassy selenium is accompanied with a discontinuous drop in the electrical resistivity by many orders of magnitude at the transition pressure. The high pressure phase is still unsolved though several studies confirm the transition (Balchan and Drickamer 1961; Fuhs *et al* 1973; Aoki *et al* 1974; Minomura 1978; Bundy and Dunn 1979; Parthasarathy *et al* 1984d). Gupta and Ruoff (1978) found that the value of the transition pressure is 9·6 GPa at room temperature, and it is much lower compared to other reported data ($\simeq$ 13·0 GPa). Moreover they found that at 353 K the amorphous selenium crystallizes at 2·6 GPa and goes to a metallic phase (Gupta and Ruoff 1978). The change in the value of the transition pressure might be due to the difference in the nature of the samples like, thickness of the film, evaporation rate, substrate temperature etc.

Other elemental amorphous semiconductors, which exhibit pressure-induced crystallization with discontinuous resistivity drop, are amorphous arsenic (Elliott *et al* 1977) and amorphous red phosphorus (Extance and Elliott 1981). The electrical resistivity of bulk amorphous As decreases continuously by seven orders of magnitude and the sample remains amorphous upto 4·0 GPa pressure. At 4·0 GPa, a discontinuous irreversible transition takes place involving a drop in resistivity by 5 orders of magnitude to a rhombohedral structure. At each clamped pressure the resistance of bulk As is found to change with time. Similar observations have been made for bulk amorphous phosphorus, which has the transition to an orthorhombic structure at 7 GPa pressure. In *a*-P at low pressure ($\simeq 3{\cdot}9$ GPa) the decrease in the resistance values as a function of time is roughly 2 orders of magnitude and at high pressures ($> 4{\cdot}9$ GPa) the time dependence of electrical resistivity is much weaker. This time dependence phenomenon is due to the inhomogeneous nature of the amorphous phosphorous at a microscopic and an atomic level (Extance and Elliott 1981).

Wu and Luo (1975) found the pressure-induced crystallization of amorphous thin film As at 1·8 GPa. The lower value of the transition pressure is certainly due to the nature of the specimen under investigation; for example in the specimens that had been stored for a length of time (of the order of months) crystallization occurs in a much more sluggish manner (Wu and Luo 1975).

Bulk $Se_{100-x}Te_x$ glasses with $(0 < x < 6)$ also exhibit pressure-induced discontinuous crystallization. The high pressure phase is identical to the high pressure phase of amorphous Se (Parthasarathy *et al* 1984d).

The pressure-induced (discontinuous) crystallization in bulk $Ge_{20}Te_{80}$ glass (Parthasarathy *et al* 1984a, b), and $Si_{20}Te_{80}$ glass (Asokan *et al* 1985a) is very interesting. Bulk $Ge_{20}Te_{80}$ glass exhibits a double stage or primary and secondary crystallization under thermal treatment (Parthasarathy *et al* 1984c). On the other hand it undergoes congruent or polymorphous crystallization under high pressure, which can be illustrated by the following reaction.

$$Ge_{20}Te_{80}\text{ (glass)} \xrightarrow{T=492\text{ K}} c\text{-Te} + \text{glass} \xrightarrow{T=555\text{ K}}$$

$$c\text{-Te} + c\text{-GeTe (with distorted NaCl structure with } a = 11{\cdot}02\text{ Å)}$$

$$Ge_{20}Te_{80}\text{ (glass)} \xrightarrow{P=5\text{ GPa}} c\text{-GeTe}_4\text{ (with f.c.c. structure with } a = 6{\cdot}42\text{ Å).}$$

The plausible free energy diagram (schematically) is shown in figure 19 (Gopal and Parthasarathy 1985). The same free energy diagram is also applicable to the bulk $Si_{20}Te_{80}$ glass, where the glass exhibits double stage or primary and secondary crystallization under thermal treatment (Asokan *et al* 1985b), and congruent or polymorphous crystallization under high pressure.

$$\text{i.e. } Si_{20}Te_{80}\text{ (glass)} \xrightarrow{T=494\text{ K}} c\text{-Te} + \text{glass} \xrightarrow{T=575\text{ K}}$$

$$c\text{-Te} + c\text{-SiTe}_2\text{ (with hexagonal structure with}$$

$$c = 6{\cdot}71\text{ Å and } a = 4{\cdot}28\text{ Å)}$$

$$Si_{20}Te_{80}\text{ glass} \xrightarrow{P=7\text{ GPa}} c\text{-SiTe}_4\text{ (Hexagonal crystal with } c = 6{\cdot}0\text{ Å and } a = 4{\cdot}0\text{ Å).}$$

At present it is not clear why pressure and temperature give different types of crystallization for the same glass. Further experiments on this line are in progress.

In a recent work by Gosain *et al* (1985), it is found that the bulk $Ge_{20}S_{80-x}Bi_x$ glasses exhibit discontinuous primary and secondary crystallization under high pressure. The variation of electrical resistivity of bulk $Ge_{20}S_{80-x}$ Bi_x glasses with $x = 0, 4, 11$ and 15 as a function of pressure is shown in figure 20. In the sample with $x = 0$ a slight increase in the electrical resistivity upto 3 GPa, followed by a continuous drop of two orders of

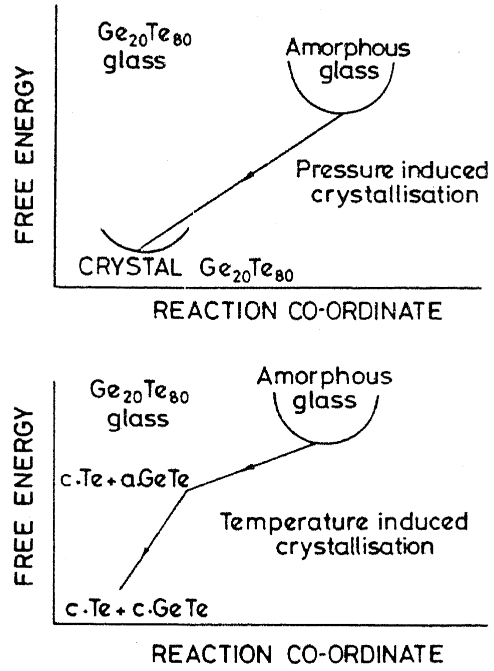

Figure 19. Schematic free energy diagram representing different crystallizations in $Ge_{20}Te_{80}$ glass.

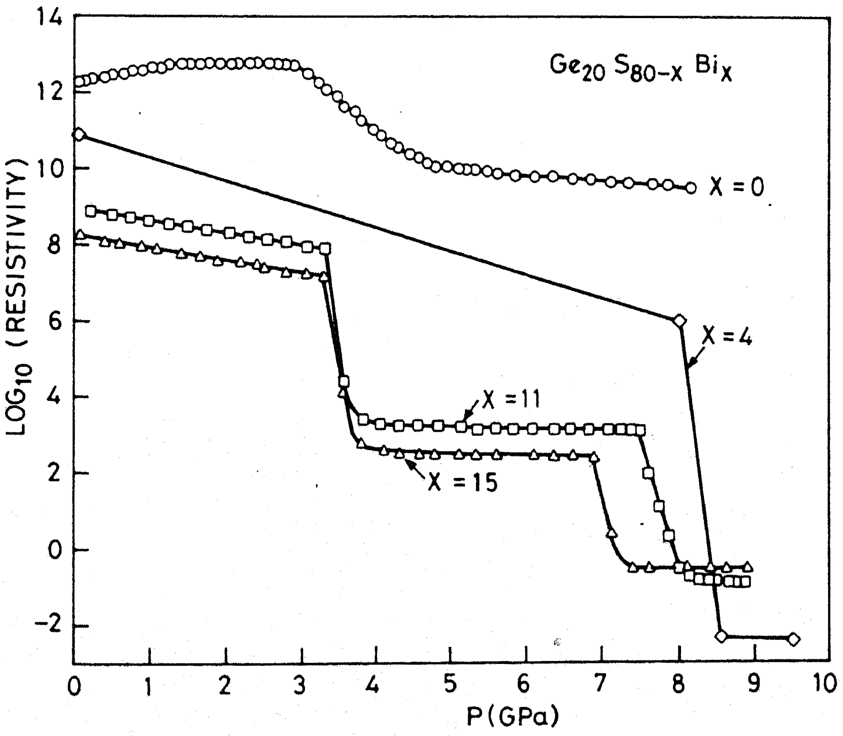

Figure 20. Pressure dependence of electrical resistivity of bulk $Ge_{20}S_{80-x}Bi_x$ glasses.

magnitude of upto about 4·7 GPa is observed. But the glasses with $x = 11$ and 15 exhibit a discontinuous transition at 3·3 GPa and one more transition at 7·0 GPa for $x = 15$ and at 7·5 GPa for $x = 11$ respectively. X-ray studies of the pressure recovered sample show that the first transition is due to the partial crystallization of Bi_2S_3 in $Ge_{20}S_{80-x}Bi_x$ glasses ($x = 11$ and 15) and the second transition is due to the crystallization of the remaining amorphous matrix into GeS_2 crystal (Gosain *et al* 1985). The most interesting result is that the glassy $Ge_{20}S_{76}Bi_4$ alloy exhibit only one pressure-induced transition at 8·0 GPa. The x-ray studies show that the high pressure phase has hexagonal structure with $c = 8·68$ Å and $a = 5·32$ Å. For $x = 11$ and 15 thermal studies also show the primary and secondary crystallization, which confirms the recent percolation model for the bismuth-doped germanium-based chalcogenide glasses (Bhatia *et al* 1985d; Tichy *et al* 1985).

Bulk Ge-Se-Tl glasses also undergo pressure-induced discontinuous transition to crystalline state. The high pressure behaviour of electrical resistivity of Ge-Se-Tl glasses is shown in figure 21. In this glass, the crystallization behaviour is an eutectic crystallization (Naik *et al* 1985).

$Tl_{30}Ge_{20}Se_{50}$ and $Tl_{33}Ge_{23}Se_{44}$ glasses transform to crystalline Tl_2Se with tetragonal structure with $a = 8·54$ Å and $c = 12·71$ Å and crystalline GeSe with orthorhombic structure with $a = 4·40$ Å, $b = 3·82$ Å and $c = 10·80$ Å at the transition pressure. On the other hand $Tl_{15}Ge_{10}Se_{75}$ and $Tl_{20}Ge_{20}Se_{60}$ glasses transform to the crystalline TlSe (with tetragonal structure $a = 8·0$ Å, $c = 7·0$ Å) and crystalline GeSe (orthorhombic structure with $a = 4·40$ Å; $b = 3·82$ Å and $c = 10·80$ Å) at the transition pressure.

Bulk $GeSe_2$ glass undergoes a glass-to-crystal transition at 7·0 GPa where the high pressure phase is found to have f.c.c. structure with $a = 4·06$ Å (Prasad *et al* 1984).

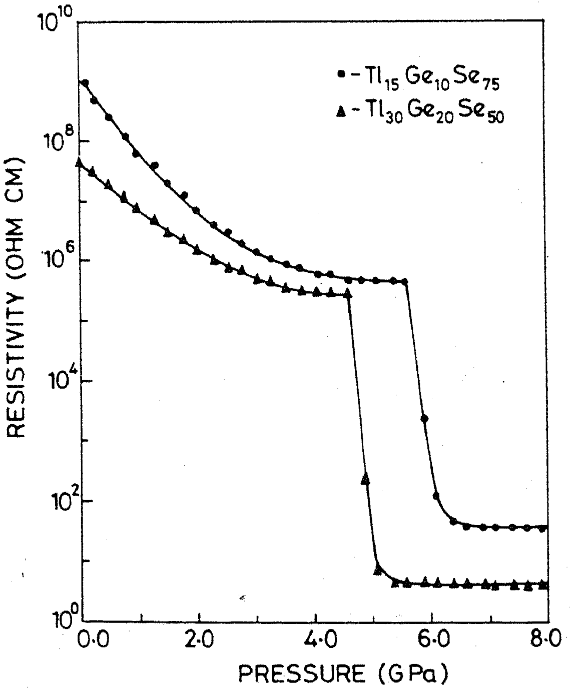

Figure 21. Pressure dependence of electrical resistivity of bulk Ge-Se-Tl glasses.

6.2 *Continuous transition to the crystalline state*

It is well established that the glassy As_2Te_3 alloy (or thin film) undergoes a continuous pressure-induced semi-conductor-to-metal transition (Sakai and Fritzsche 1977). The high pressure phase is found to be crystalline, with the same structure of the crystalline As_2Te_3 alloy (Minomura 1982). It is not clear that this type of crystallization occurs through nucleation and growth. In $Se_{100-x}Te_x$ glasses with $8 \leqslant x \leqslant 30$, the continuous pressure-induced crystallization is explained on the basis of the cluster model (Rao and Rao 1982; Parthasarathy *et al* 1984d). In bulk $In_{20}Te_{80}$ and $Cu_{25}Au_5Te_{70}$ glasses, the pressure-induced crystallization is continuous and also associated with the time dependence on the electrical resistivity. Here the high pressure phase is not identified to have any unique crystal structure (Lakshmikumar *et al* 1981). High pressure studies on $Al_{23}Te_{77}$ glass show that this glass undergoes a polymorphous (or) congruent crystallization under high pressure with a continuous decrease in the electrical resistivity (Parthasarathy *et al* 1985). The high pressure phase has hexagonal structure with $c/a = 1{\cdot}7$. On the other hand under thermal treatment $Al_{23}Te_{77}$ glass exhibits primary and secondary crystallization (Parthasarathy and Gopal 1984c). The $Ga_{20}Te_{80}$ glass behaves in a similar way, as will be reported in due course.

7. Conclusion

In this review an attempt has been made to cover most of the aspects involved in high pressure studies on chalcogenide glasses. Further work has to be done to study the magnetic properties and crystallization phenomena in chalcogenide glasses under high pressure to understand the microscopic picture of the chalcogenide glasses.

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