

## Thermal diffusion near glass transition in Ge–Se glasses measured by photoacoustics

K N MADHUSOODANAN and JACOB PHILIP

Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India

MS received 29 September 1988; revised 30 January 1989

**Abstract.** The glass transition in  $\text{Ge}_x\text{Se}_{1-x}$  ( $0.1 \leq x \leq 0.25$ ) glasses has been investigated using the photoacoustic (PA) technique. It is found that the PA amplitude and phase undergo anomalous changes at the glass transition temperature  $T_g$ . The amplitude has critical minimum and phase has maximum values at  $T_g$ . The variation of the thermal diffusivity, determined by measuring the frequency dependence of the PA amplitude and phase, with temperature shows sharp decrease near the glass transition temperature. The temperature dependence of the optical energy gap also has been measured and it shows a decrease with temperature for all compositions, the rate of decrease being higher for temperatures greater than  $T_g$ .

**Keywords.** Thermal diffusivity; glass transition; photoacoustic technique.

PACS Nos 61-40; 63-50; 66-70

### 1. Introduction

Recent developments in the microscopic and topological description of glass-formation in covalent semiconducting glasses have contributed remarkably to our understanding of the glass forming tendency in these materials (Phillips 1979, 1980, 1981; Thorpe 1983). According to Phillips (1979), the glass forming tendency of a solid is optimized mechanically by equating the number of valence force field constraints which are intact at the glass transition temperature with the number of atomic degrees of freedom. He explained the existence of deep minimum occurring in the glass transition width in the specific heat curves of  $\text{As}_x\text{Se}_{1-x}$  glasses at  $x = 0.4$  using a molecular model for cluster formation based on a topological approach using constraints theory (Phillips 1982). Later Thorpe (1983) pointed out that in the range of glass forming composition, a system contains both overconstrained (rigid) and underconstrained (floppy) regions. As the mean coordination  $\langle m \rangle$  increases the rigid regions increase in volume until at  $\langle m \rangle = m_p$ , where  $m_p$  is a critical average coordination, a percolation transition takes place from a polymeric glassy state to a rigid network. It is the threshold percolation of rigidity that drives this transition and the most stable glass is formed for  $\langle m \rangle = m_p$ . Arguments based on mean field theory leads to the result that in covalent glasses such as chalcogenides, percolation transition takes place at  $m_p = 2.4$  for a three-dimensional network if the bond-bending and rotationally invariant bond-stretching constraints are taken into account (Phillips and Thorpe 1985). Evidences for the existence of such a critical composition in chalcogenide glasses such as  $\text{As}_x\text{Se}_{1-x}$  and  $\text{Ge}_x\text{Se}_{1-x}$  have been provided by several

experimental results (Phillips 1985; Brasser *et al* 1986; Philip and Madhusoodanan 1988; Gilroy and Phillips 1983; Murase *et al* 1983). For As-Se type glasses both the mechanical and chemical critical points coincide at  $x = 0.4$  ( $\langle m \rangle = 2.4$ ) composition whereas Ge-Se type glasses show a mechanical threshold at  $x = 0.2$  and chemical threshold at  $x = 0.33$ .

Recently photoacoustic (PA) technique (Rosencwaig 1980) has successfully been applied to the determination of the optical and thermal parameters such as optical energy gap and thermal diffusivity of solids. The use of the PA effect for studying first- and second-order phase transitions has been demonstrated by several authors (Bechthold *et al* 1980; Etxebarria *et al* 1984; Korpiun and Tilgner 1980; Somasundaram *et al* 1986). This has become possible because the PA signal depends largely on the thermal properties such as specific heat, thermal expansion and thermal conductivity of the sample. Due to this dependence, on going through a phase transition, the PA response reflects the thermodynamic changes that are taking place in the sample. However, not much work on probing the features of glass transitions using this technique has been reported in literature. Such studies will give information about the changes in the thermal properties of samples at the glass transition temperature, which in turn can provide valuable information about the mechanism of glass transition (Büchner and Korpiun 1987).

We have used the PA technique to locate the glass transition temperature  $T_g$  in Ge-Se glasses and determined the temperature dependence of thermal diffusivity and optical absorption in them up to temperatures larger than  $T_g$ . The experimental method used, the results obtained and a discussion based on them are given in the following sections.

## 2. Experimental method

In the present investigations we have fabricated a high temperature Helmholtz resonator type PA cell with which measurements can be made up to a temperature of  $\approx 500$  K. Essentially the microphone compartment is isolated from the sample compartment to avoid direct heating of the sensitive electret microphone which detects the PA signal. These two compartments are connected by a thin walled stainless steel tube. The other parts of the PA spectrometer are the same as that described in a previous paper (Madhusoodanan *et al* 1988). The cell has been initially calibrated with a standard carbon black sample. The  $\text{Ge}_x\text{Se}_{1-x}$  samples with  $0.1 \leq x \leq 0.25$  used for these measurements have been prepared by the usual melt-quenching technique. For this appropriate amounts of 5N purity constituent elements are taken in an evacuated quartz ampoule. The ampoule is then kept in a furnace at  $900^\circ\text{C}$  for 24 h with periodic rotation of the ampoule for homogeneous mixing. Finally the ampoule is quenched in ice water. The amorphous nature of the samples are checked by X-ray diffractometry. For thermal diffusivity measurements, bulk samples have been thinned down to a thickness of  $\approx 0.1$  mm by hand lapping and polishing.

First of all the variation of the PA amplitude and phase has been measured as a function of temperature with white light from a Xe lamp chopped at a frequency of 22 Hz with the intention of studying their variations near the glass transition temperature. These measurements have been repeated for two other chopping frequencies viz. 180 Hz and 330 Hz. The samples are thermally thick at these chopping

frequencies so that the thermal properties of the backing medium do not affect the PA signal. The thermal diffusivity  $\alpha$  is determined by measuring the variation of the PA signal amplitude and phase as a function of the chopping frequency. From this variation, the characteristic chopping frequency  $f_c$ , above which the sample is thermally thick, is determined. The sample is fixed on a brass disc which acts as a thermally thick backing medium during measurements. For determining  $f_c$  the PA phase of a thermally thick reference sample (thickness = 1 mm) and that of the experimental sample are measured as a function of the chopping frequency. The thickness of the experimental sample is 0.1 mm for all compositions and the error in its determination is within  $\pm 3\%$ . Then  $f_c$ , above which the PA signal is independent of the effect of backing material, is obtained as the frequency at which the difference between these two phases tends to zero. Once  $f_c$  is determined the thermal diffusivity  $\alpha$  is calculated using the formula  $f_c l^2 = \alpha$  where  $l$  is the sample thickness (Charpentier *et al* 1982; Lachain and Poulet 1984). In this way  $\alpha$  has been determined at various fixed temperatures up to  $T > T_g$ . The total error in the measurement of  $\alpha$  is within  $\pm 5\%$ . We have also recorded the PA spectra of the samples at various temperatures by plotting the normalized PA signal amplitude as a function of the incident wavelength. The normalization is done with the power spectrum of the light source obtained using carbon black as the sample. From this data optical energy gap at various temperatures have been evaluated.

### 3. Results and discussion

From the results obtained on the variation of the PA signal with temperature it is observed that the PA signal amplitude decreases as we approach the glass transition temperature  $T_g$  from below and it shows a minimum value at  $T_g$  as shown in figure 1. The corresponding PA phase plotted in figure 2 shows a critical maximum again at  $T_g$ . The values of  $T_g$  of  $\text{Ge}_x\text{Se}_{1-x}$  glasses with  $0.1 \leq x \leq 0.25$  thus determined is plotted against the composition parameter  $x$  and is shown in figure 3. This does not show any anomalous change at  $x = 0.2$  which is the mechanical threshold, where  $m_p = 2.4$  for this system. The  $T_g$  values determined by the present technique agrees well with the reported data from calorimetric measurements which also does not exhibit any anomaly at  $x = 0.2$  (Feltz *et al* 1983). The temperature-amplitude plots taken at three different chopping frequencies are shown in figure 4 for  $\text{Ge}_{0.15}\text{Se}_{0.85}$  sample. The corresponding phase plots are given in figure 5. Even though these measurements have been carried out on other samples as well, all the curves are not shown here as the nature of all of them is same. From these measurements it is found that  $T_g$  shifts slightly to higher temperatures as the chopping frequency is increased. The slight chopping frequency dependence of  $T_g$  indicates that the opto-thermal-acoustic conversion mechanism in PA effect is directly related to the relaxation occurring near  $T_g$ .

Figure 6 gives the variation of the thermal diffusivity as a function of temperature for compositions with  $x = 0.1, 0.15, 0.2$  and  $0.25$ . Thermal diffusivity decreases with increase in temperature and it shows a sharp decrease at the glass transition temperature in all samples. The Rosencwaig–Gersho (RG) theory (Rosencwaig and Gersho 1976) predicts that the PA signal for optically opaque ( $l_p \ll l$ ) and thermally thick ( $\mu < l; \mu > l_p$ ) samples, where  $l$  is the thickness and  $l_p$  is the optical absorption

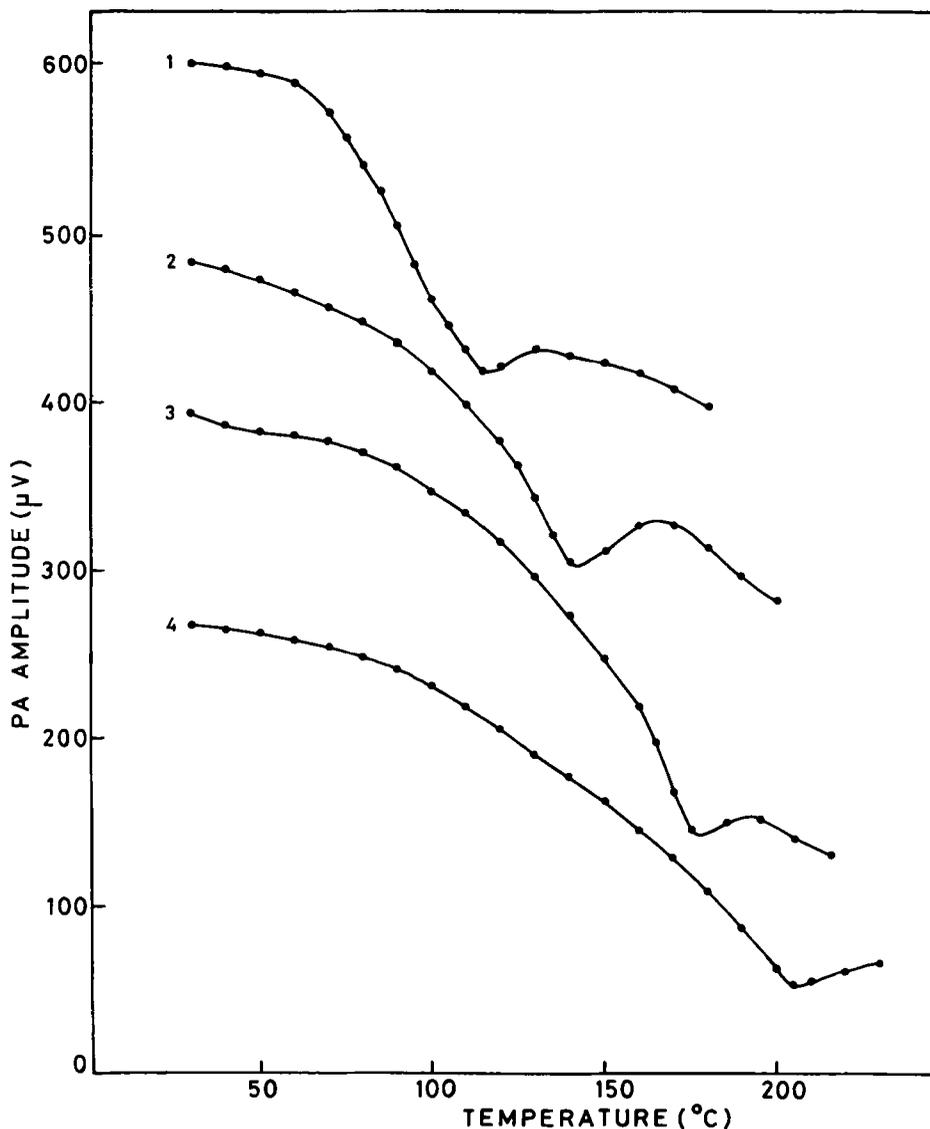


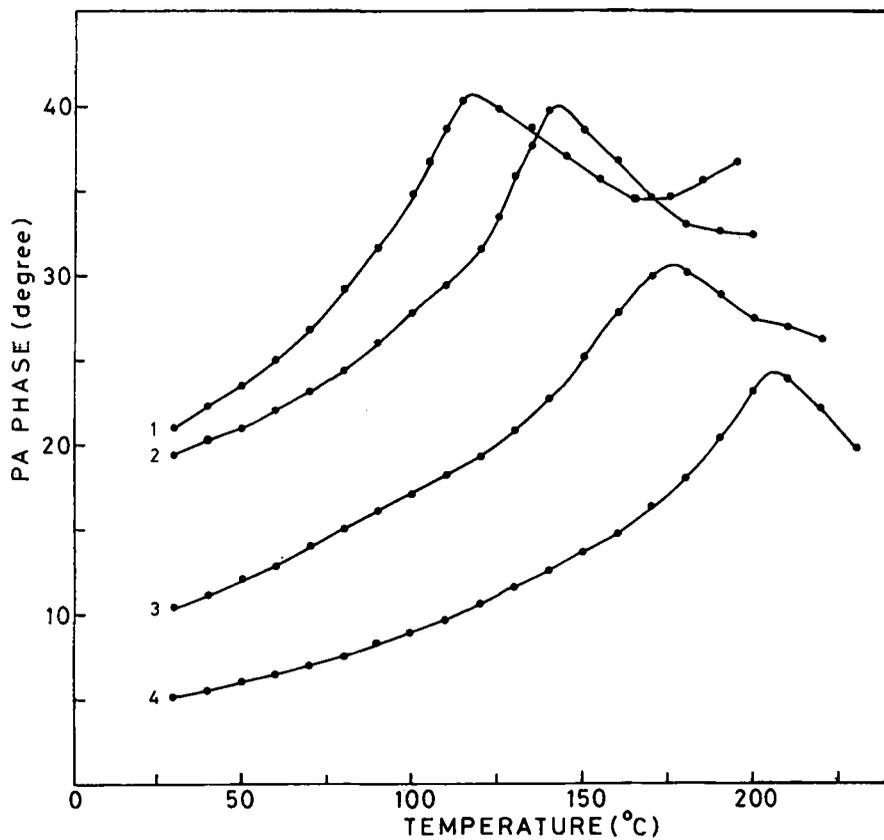
Figure 1. Variation of PA signal amplitude with temperature.

(1)  $\text{Ge}_{0.10}\text{Se}_{0.90}$ , (2)  $\text{Ge}_{0.15}\text{Se}_{0.85}$ , (3)  $\text{Ge}_{0.20}\text{Se}_{0.80}$ , (4)  $\text{Ge}_{0.25}\text{Se}_{0.75}$ .

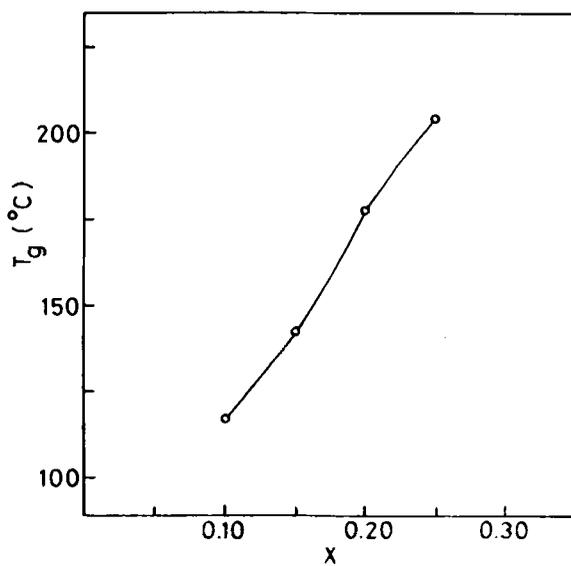
length of the sample, is proportional to the thermal diffusion length  $\mu$  of the sample given by

$$\mu = \left( \frac{\alpha}{\Lambda f} \right)^{1/2} = \left( \frac{k}{\Lambda \rho C_p f} \right)^{1/2}. \quad (1)$$

Here  $k$  is the thermal conductivity,  $\rho$  is the density,  $C_p$  is the specific heat,  $f$  is the chopping frequency and  $\alpha = k/\rho C_p$  is the thermal diffusivity of the sample. At the glass transition temperature the specific heat shows a maximum which in turn is reflected



**Figure 2.** Variation of PA signal phase with temperature.  
 (1)  $\text{Ge}_{0.10}\text{Se}_{0.90}$ , (2)  $\text{Ge}_{0.15}\text{Se}_{0.85}$ , (3)  $\text{Ge}_{0.20}\text{Se}_{0.80}$ , (4)  $\text{Ge}_{0.25}\text{Se}_{0.75}$ .



**Figure 3.** Variation of glass transition temperature with composition parameter  $x$ .

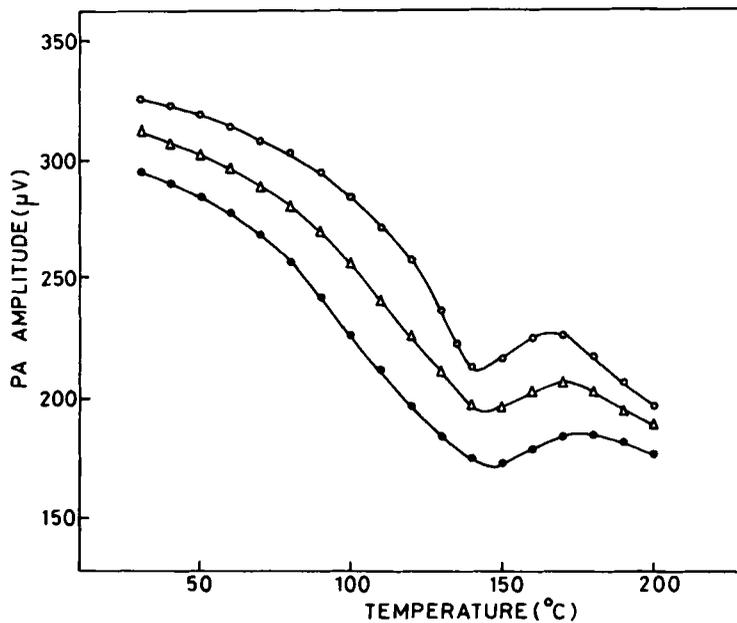


Figure 4. PA amplitude as a function of temperature for  $\text{Ge}_{0.15}\text{Se}_{0.85}$  sample at three different chopping frequencies. (○) 22 Hz (△) 180 Hz (●) 330 Hz

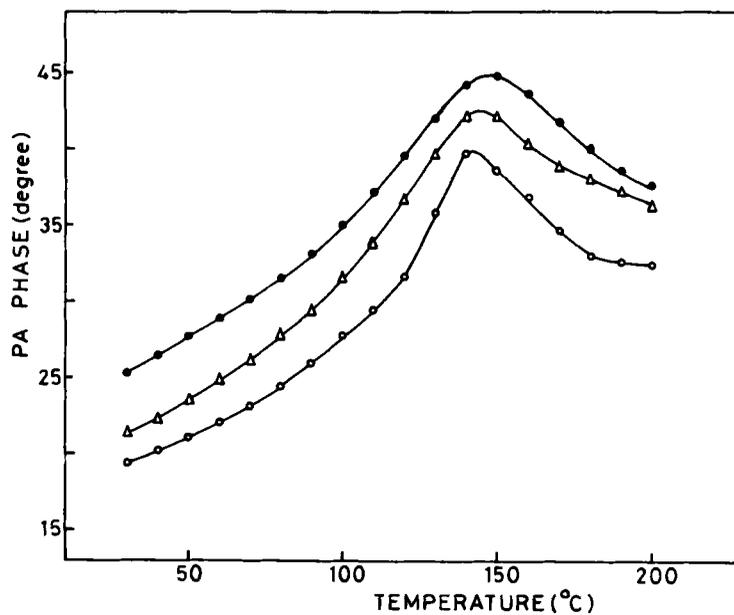


Figure 5. PA phase as a function of temperature for  $\text{Ge}_{0.15}\text{Se}_{0.85}$  at three different chopping frequencies. (○) 22 Hz (△) 180 Hz (●) 330 Hz

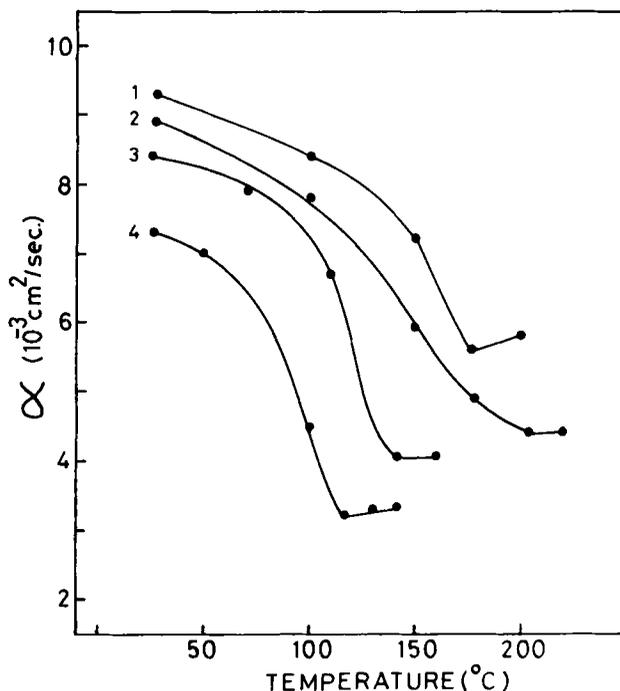


Figure 6. Variation of thermal diffusivity with temperature.

(1)  $\text{Ge}_{0.20}\text{Se}_{0.80}$ , (2)  $\text{Ge}_{0.25}\text{Se}_{0.75}$ , (3)  $\text{Ge}_{0.15}\text{Se}_{0.85}$ , (4)  $\text{Ge}_{0.10}\text{Se}_{0.90}$ .

in the PA signal amplitude as well which shows a minimum value at  $T_g$ . The fact that PA amplitude has minimum value at  $T_g$  indicates that the sample has minimum thermal diffusivity, as has been experimentally observed and shown in figure 6, or maximum thermal resistance at  $T_g$ . As a result of this the thermal waves generated when chopped light beam falls on the sample takes longer time to travel through the sample and get converted into pressure waves in the surrounding gas medium. Therefore the corresponding phase delay is maximum at  $T_g$ . As the temperature increases there will be a decrease in the mean free path due to increase in phonon collision rates which reduces thermal conductivity. As  $T_g$ , which is a softening temperature for the glass, is approached the mean free path is decreased substantially which in turn retards the thermal transport to the maximum extent as is evident from figure 6. The anomalous increase in specific heat taking place at  $T_g$  will also be contributing to cause a decrease in thermal diffusivity. Both these effects in fact work in the same direction.

The PA spectra recorded as a function of incident wavelength at various temperatures for  $\text{Ge}_{0.10}\text{Se}_{0.90}$  sample are shown in figure 7. Similar spectra have been recorded on other compositions as well. It is observed that the exponential absorption edge region (Tauc 1974) of the spectrum broadens as the temperature is increased and the rate of this broadening is more for temperatures larger than  $T_g$ . It can be inferred that the disorder induced potential fluctuations increase as temperature increases and this is getting reflected in the optical absorption spectrum. The optical energy gap  $E_0$  at various temperatures has been determined for  $\text{Ge}_x\text{Se}_{1-x}$  glasses

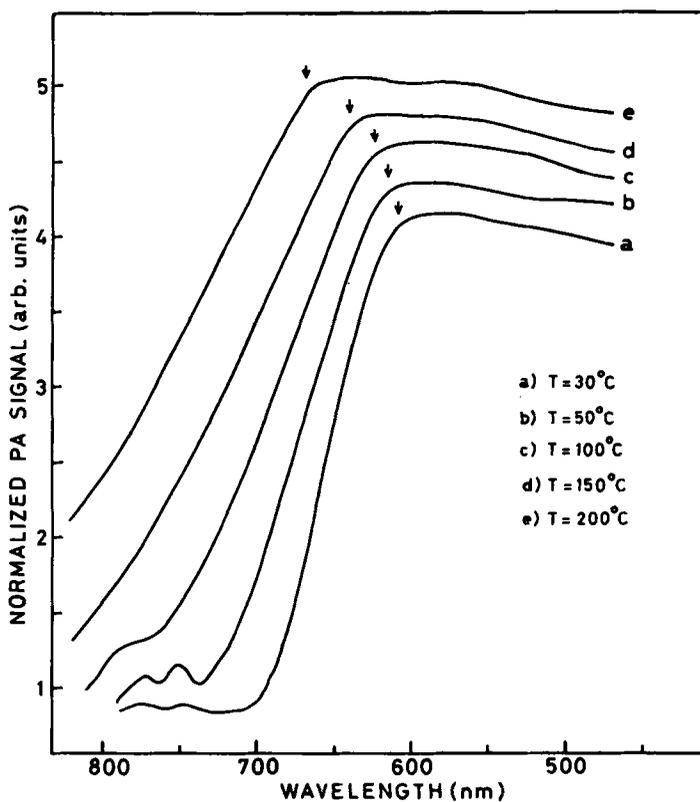


Figure 7. PA spectra of  $\text{Ge}_{0.10}\text{Se}_{0.90}$  glass at different temperatures.

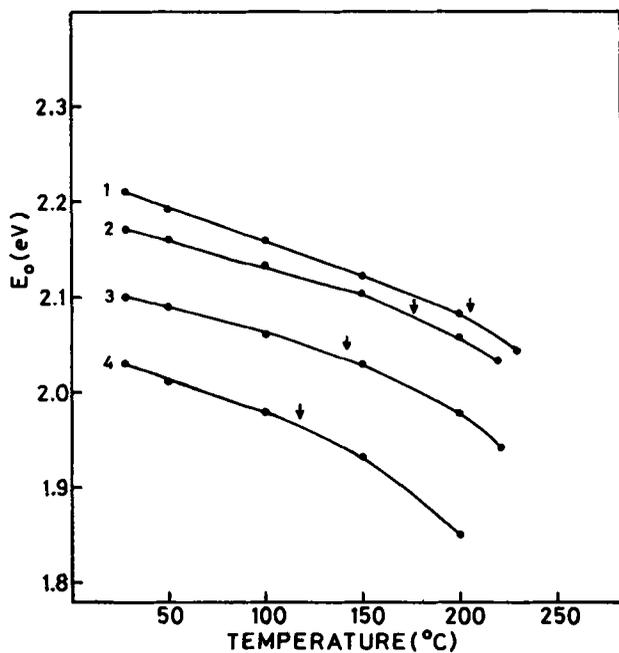


Figure 8. Variation of optical energy gap as a function of temperature. The arrows indicate glass transition temperature.

(1)  $\text{Ge}_{0.25}\text{Se}_{0.75}$ , (2)  $\text{Ge}_{0.20}\text{Se}_{0.80}$ , (3)  $\text{Ge}_{0.15}\text{Se}_{0.85}$ , (4)  $\text{Ge}_{0.10}\text{Se}_{0.90}$ .

with  $0.1 \leq x \leq 0.25$  from the PA spectra as the photon energy above which the spectra saturate (Madhusoodanan and Philip 1988). In figure 8 the variation of  $E_0$  with temperature is plotted. It may be noticed that  $E_0$  decreases with increase in temperature and the rate of change of  $E_0$  with temperature is larger for  $T > T_g$ . As the temperature is increased the covalent bond weakens and consequently there is a decrease in the average bond energy in the system. This in turn reduces the optical energy gap. The absence of any sharp change in  $E_0$  at  $T_g$  indicates that glass transition and optical absorption are not directly related.

#### 4. Conclusions

The PA technique is found to be very effective for investigating the features of glass transitions in chalcogenide glasses. This is because the PA signal depends greatly upon the thermal properties such as thermal conductivity, specific heat etc. of the samples. These parameters undergo discontinuous changes at  $T_g$  indicating that glass transition is second order in nature. So at  $T_g$  the PA signal also undergoes anomalous changes. As has been demonstrated in this work it is also possible to determine the thermal and optical properties of radiation absorbing glasses near glass transition temperatures. Moreover we have been able to determine the temperature dependence of the thermal diffusivity which in turn gives thermal conductivity in selected compositions of Ge–Se alloys. It is interesting to note that this dependence is similar in all the compositions investigated.

As has been shown by us in a previous work (Philip and Madhusoodanan 1988), in  $A_x^{IV}B_{1-x}^{VI}$  chalcogenide alloys such as  $Ge_xSe_{1-x}$  the thermal diffusivity exhibits a threshold peak at the critical composition  $x_c = 0.2$  which corresponds to the average coordination  $m_p = 2.4$ . This corresponds to the formation of stable  $AB_4$  tetrahedra. The above observation has been attributed to the mechanical stiffening of the network at the critical composition due to the threshold percolation of rigidity and the corresponding threshold in the internal stress. Our results indicate that the critical composition remains the same and the network rigidity is kept intact at all temperatures below glass transition.

#### Acknowledgements

This work has been supported by Department of Atomic Energy (BRNS), Government of India under grant No. 37/4/85-G. One of us (KNM) also thank CSIR for a fellowship.

#### References

- Bechthold P S, Campagna M and Schober T 1980 *Solid State Commun.* **36** 225
- Bresser W, Boolchand P and Suranyi P 1986 *Phys. Rev. Lett.* **56** 2493
- Büchner B and Korpiun P 1987 *Appl. Phys.* **B43** 29
- Charpentier P, Lepoutre F and Bertrand L 1982 *J. Appl. Phys.* **53** 608
- Etxebarria J, Uriarte S, Fernandez J, Tello M J and Cuevas A G 1984 *J. Phys.* **C17** 6601
- Feltz A, Aust H and Blayer A 1983 *J. Non-Cryst. Solids* **55** 179
- Gilroy K S and Phillips W A 1983 *Philos. Mag.* **B47** 655

- Korpiun P and Tilgner R 1980 *J. Appl. Phys.* **51** 6115  
Lachain A and Poulet P 1984 *Appl. Phys. Lett.* **45** 953  
Madhusoodanan K N and Philip J 1988 *Phys. Status Solidi* **108** 775  
Madhusoodanan K N, Philip J, Parthasarathy G, Asokan S and Gopal E S R 1988 *Philos. Mag.* **B58** 123  
Murase K, Fukunaga T, Yakushiji K, Yoshimi T and Yunoki I 1983 *J. Non-Cryst. Solids* **59–60** 883  
Philip J and Madhusoodanan K N 1988 *Phys. Rev.* **B38** 4127  
Phillips J C 1979 *J. Non-Cryst. Solids* **34** 153  
Phillips J C 1980 *Phys. Status Solidi* **B101** 473  
Phillips J C 1981 *J. Non-Cryst. Solids* **43** 37  
Phillips J C 1982 *Phys. Today* **35** 27  
Phillips J C 1985 *Phys. Rev.* **B31** 8157  
Phillips J C and Thorpe M F 1985 *Solid State Commun.* **53** 699  
Rosencwaig A 1980 *Photoacoustics and photoacoustic spectroscopy* (New York: Wiley)  
Rosencwaig A and Gersho A 1976 *J. Appl. Phys.* **47** 64  
Somasundaram T, Ganguly P and Rao C N R 1986 *J. Phys.* **C19** 2137  
Thorpe M F 1983 *J. Non-Cryst. Solids* **57** 355  
Tauc J 1974 *Amorphous and liquid semiconductors* (ed.) J Tauc (New York: Plenum Press) Ch. 4