

Photoacoustic spectra of As_2S_3 — As_2Se_3 glasses^{*}

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Abstract. Photoacoustic spectra of As-S, As-Se glasses as well as the $As_2(S,Se)_3$ glasses have been investigated. Photoacoustic spectra of powdered samples give results comparable to those obtained from transmission spectra, the latter studies requiring preparation of thin films. Temperature-dependent studies of the As_2S_3 glass have been carried out. Optical behaviour of these glasses has been interpreted in terms of homoatomic bonding defects.

Keywords. Arsenic chalcogenide glasses; homoatomic bonding defects; optical absorption edge; photoacoustic spectroscopy.

1. Introduction

It has been recognized (Ganguly and Rao 1981) that photoacoustic spectroscopy (PAS) is a sensitive method for studying solids which are difficult to study by normal transmission or reflectance spectroscopic techniques. Arsenic chalcogenide glasses which exhibit absorption edges in the visible region (Tanaka 1976) possess high extinction coefficients and are highly reflecting and thin films of the material have to be taken for studying their optical behaviour. Arsenic sulphide, As_2S_3 and arsenic selenide, As_2Se_3 glasses also exhibit interesting photo-structural effects (Treacy *et al* 1980; De Neufville 1976). We therefore consider it instructive to investigate the PAS of As_2S_3 and As_2Se_3 glasses and extend the previous preliminary study of Ganguly and Rao (1981) to other systems. In view of the many investigations reported about these glasses by Mohan (1981), it should be possible to assess the viability of PAS as a useful investigative tool to study glasses. We show in this investigation that the absorption edges are indeed easily located and that many useful inferences about the behaviour of chalcogenide glasses may be drawn from PAS studies.

2. Experimental

As_2S_3 , As_2Se_3 and three different $As_2(S,Se)_3$ glasses were prepared from 5N purity elements (Koch-light). Proper mixtures of the elements were melted in quartz ampoules sealed under low pressure of argon. The melts were agitated in a rotary furnace for over 8 hours at 1000°C and quenched in water. Powders of these glasses suitable for PAS studies were prepared by grinding the glass thus obtained.

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PA spectra were recorded with a spectrometer consisting of a 250 W tungsten halogen lamp; schoeffel 1/4m G250 monochromator, 163 PAR chopper and 124 A PAR lock in amplifier. The details of the PAS cell have been described elsewhere by Ganguly and Rao (1981). Low temperature measurements were made in a cell described earlier by Ganguly and Rao (1981). The normalised PA spectra were obtained by dividing by carbon black power spectrum. The resolution chosen was 5 nm and the spectra were recorded at a drive of 50 nm/min with a time constant of 1 sec.

3. Results and discussion

PA spectra of As_2S_3 , As_2Se_3 glasses and of crystalline samples are shown in figure 1. PA spectra of the three $As_2(S,Se)_3$ glasses are shown in figure 2. These results are essentially independent of chopping frequencies.

PA spectrum of As_2S_3 glass indicates a steep rise in photoabsorption between 500 and 600 nm. In conventional absorption spectroscopy this absorption region is observed only with thin samples (Young 1971). Reported values of absorption edge wavelengths in As_2S_3 and As_2Se_3 glasses corresponding to extinction coefficients, α , of $\approx 10^3 \text{ cm}^{-1}$ are 510 and 670 nm respectively (Treacy *et al* 1980). These wavelengths correspond to 90% of realizable PAS intensity for these glasses. Since the absorption edge in our PAS study is at shorter wavelength compared to normal transmission studies using thin films, we feel that the position of the absorption edge in our PA spectra is not much affected by saturation effects. These results therefore clearly indicate the suitability of PAS for the study of such glasses. The absolute value of PAS intensities are difficult to interpret in view of their dependence on many other factors (Ganguly and Rao 1981 and references therein). Absorption band edges are fixed, in

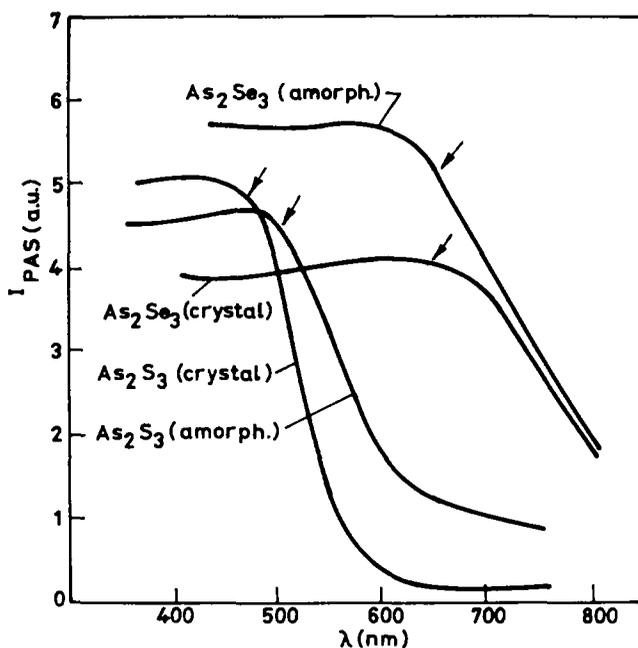


Figure 1. Normalised PA spectra of amorphous and crystalline As_2S_3 and As_2Se_3 .

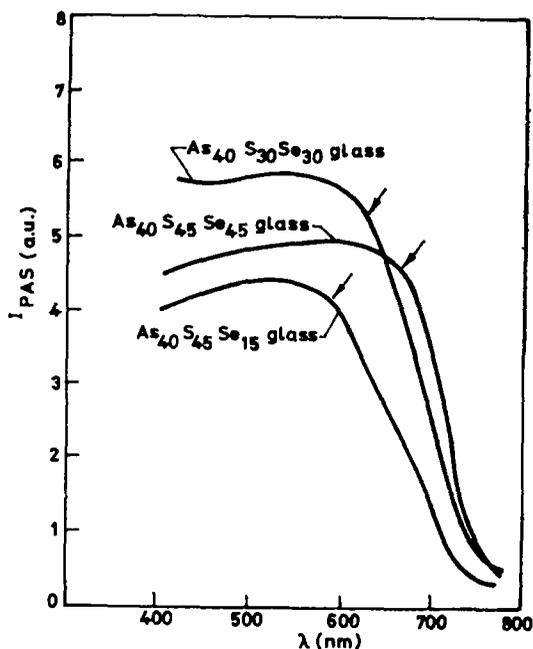


Figure 2. Normalised PA spectra of various $As_2(S,Se)_3$ glasses.

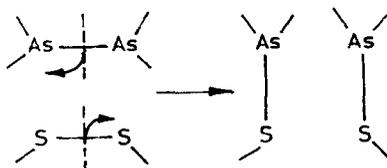
Table 1. Absorption band edges from PAS.

Compound	Absorption band edges from PAS ^(a) ± 5 nm
As_2S_3 (crystalline)	470
As_2Se_3 (crystalline)	670
As_2S_3 glass	520
$As_{40}S_{45}Se_{15}$ glass	620
$As_{40}S_{30}Se_{30}$ glass	655
$As_{40}S_{15}Se_{45}$ glass	675
As_2Se_3 glass	680

(a) 90% of the normalised saturation intensity.

certain cases, by taking the intersection of the extrapolated absorption edge and the saturation curve (Bhatnagar and Subrahmanyam 1982). To make a reference point with respect to the reported band edge wavelengths we have chosen 90% maximum normalised PAS intensity for the band edge. The absorption edges thus determined by PAS are given in table 1. In both As_2S_3 and As_2Se_3 we notice that the band edges are higher for crystalline than for glassy states. Young (1971) suggested that this difference arose from the generally higher atomic spacing (lower density) in the vitreous state. However this implies that the rather large difference in the energies between vitreous and crystalline states of As_2S_3 with identical first shell of neighbours is almost entirely from density-dependent bond energy differences. An alternative explanation which

we believe more appropriate is that the loose packing inherent to disordered chalcogenides gives rise to a greater spread of the non-bonding levels originating from chalcogens and these levels are known to constitute the top of the valence band (Kastner 1972). Hence a decrease in the optical gap in vitreous state ensures from such spread of valence band levels. In the case of vitreous As_2S_3 the large difference in the densities of crystalline and glassy states (3.49 and 3.16 gm/cc respectively) may arise at least in considerable part from realgar-like structures (Nemanich *et al* 1978) involving $>\text{As}-\text{As}<$ and, $-\text{S}-\text{S}-$ linkages. Indeed the antibonding levels corresponding to $>\text{As}-\text{As}<$ bonds should constitute the bottom of the conduction band. Populating these levels by optical excitation weakens the $>\text{As}-\text{As}<$ linkages and bond rearrangements of the type, shown in scheme 1,



Scheme 1

are facilitated. We feel that such rearrangements constitute the likely steps in the large ('giant') photo structural changes (Singh *et al* 1980) in amorphous As_2S_3 . Presence of such homoatomic bonds in As_2S_3 glass and glasses rich in As_2S_3 has been inferred from structural studies by Parthasarathy *et al* (1982) using EXAFS. It is a surprising coincidence that the energy released in such rearrangements is 0.2 eV (energies of As-As, S-S, As-S bonds are respectively 2.07, 2.69 and 2.48 eV (Rao and Mohan 1981) and the difference in the energies of the absorption band edges between crystalline and glassy states of As_2S_3 is about 0.26 eV. The agreement is quite close and suggests that band edge energies of perfectly annealed, defect-free As_2S_3 glass and As_2S_3 crystals should not be different by more than 0.06 eV ($\sim 500 \text{ cm}^{-1}$).

As_2Se_3 glass has been shown to possess a chemically ordered structure through a number of investigations. Density differences between As_2Se_3 glass (4.58 g/cc) and As_2Se_3 crystals (4.75 g/cc) is 0.33 g/cc which is just about 3.6% as compared to 10% difference in the case of As_2S_3 . This again indicates in comparison with As_2S_3 that As_2S_3 glasses involve considerable homoatomic bonding defects. In As_2Se_3 glass, therefore, we expect little difference in the absorption band edge though the edge itself is expected to be more 'smeared' out in the glass.

The temperature dependance of the PA spectra of the As_2S_3 glass presented in figure 3 indicates a red shift consistent with the observation of Young (1971). Edge energies are plotted in the inset of figure 3 and the choice of the PAS edges is indicated by arrows. The thermal coefficient of band edge energy is $7.1 \times 10^{-4} \text{ eV dg}^{-1}$ in rather good agreement with the reported literature value ($7.0 \times 10^{-4} \text{ eV dg}^{-1}$).

Band edge energies of intermediate compositions $\text{As}_2(\text{S}_{1-f}\text{Se}_f)_3$ decrease as the selenium content in the glass increases as shown in figure 4. Assuming a simple Kastner (1972)-type band picture wherein the band widths are proportional to the concentration of the bond species, substitution of sulphur by selenium should result in a fairly linear decrease in band gap (the decrease being proportional to f , the mole fraction of As_2Se_3 referred to in figure 4). However, the variation is rather steep in the

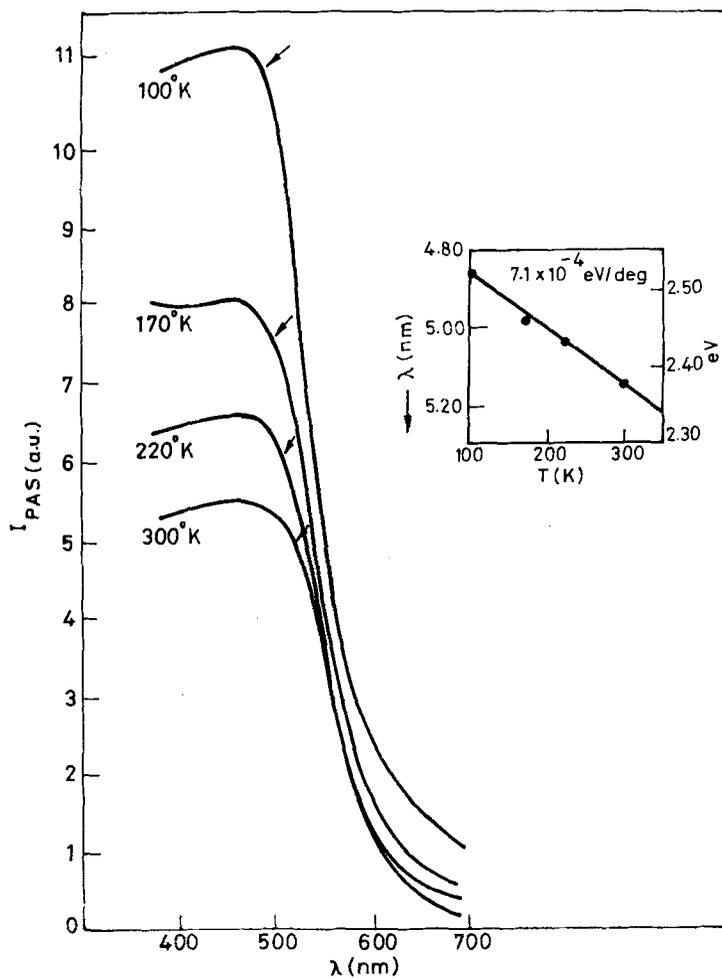


Figure 3. Temperature dependence of PA spectra of As_2S_3 glass. Inset shows the variation of band edge energies. The band edges are marked by arrows.

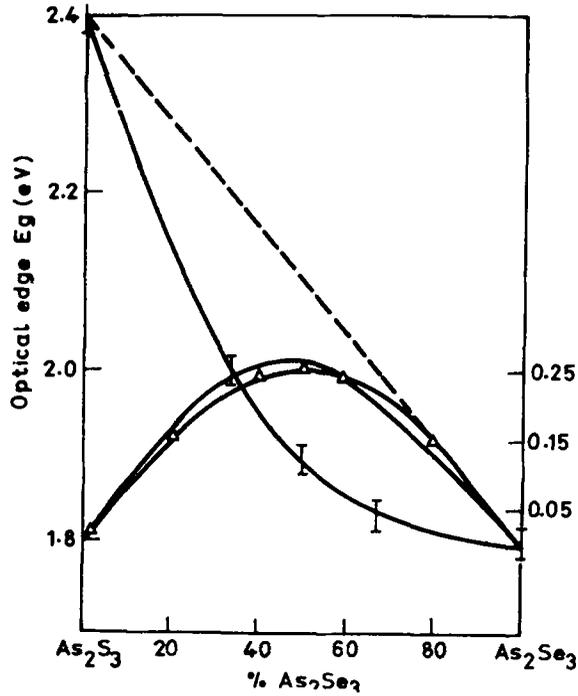
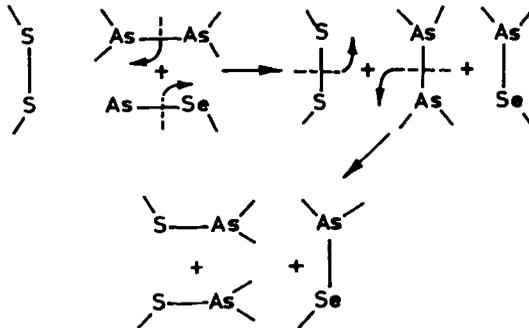


Figure 4. Variation of band edge energies as a function of composition. The dotted straight line is the hypothetical linear variation. The full line dome represents the difference between straight line and actual edge energies. The triangles and thin lines correspond to $f(1-f)$ function, the scale of which is given on the right ordinate.

initial stages of substitution. The difference between the linear (shown as broken line) and actual variation is also plotted in figure 4 (dotted line). The dome shape of the dotted line suggests that the additional decrease of band gap responsible for the nonlinearity has the form of $(f(1-f))$ function (shown as Δ marks on an adjusted scale). This, we believe, is due to the elimination of homoatom bonds upon As_2Se_3 substitution which therefore involves participation of As-Se bonds as intermediate steps. Such steps are essential for reorienting $>\text{As}-\text{As}<$ and $-\text{S}-\text{S}-$ linkages in the vitreous phases. One may visualize such a step through scheme 2:



Scheme 2

The reaction mechanism thus requires participation of $>As-Se$ -linkages and hence the process itself is dependent on the concentrations of both As_2S_3 (f) (which determines $>As-As<$ and $-S-S$ -linkages) and As_2Se_3 ($1-f$), (which determines concentration of $As-Se$ links).

4. Conclusions

The present investigation shows that, (a) photoacoustic spectroscopy can be effectively used to investigate spectroscopic behaviour of glasses and (b) As_2S_3 and As_2Se_3 rich glasses contain homoatomic bonding defects which determine their optical behaviour.

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