Composition dependence of the energy gap and thermal diffusivity in bulk As–Se glasses

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Abstract. We have measured the composition dependence of the optical energy gap and thermal diffusivity in bulk $As_x Se_{1-x}$ ($0.10 \leqslant x \leqslant 0.50$) glasses using photoacoustic technique. The energy gap shows a threshold minimum value and thermal diffusivity has a threshold maximum value at the stoichiometric composition $As_2 Se_3$ corresponding to $x = 0.40$. The decrease in energy gap is explained on the basis of chemical bonding. It is argued that the threshold percolation of rigidity in the random network is responsible for the peaking of the thermal diffusivity at the stoichiometric composition.

1. Introduction

There has been a great deal of interest in understanding the structural, optical and electronic properties of semiconducting chalcogenide glasses. The chemical bonding and topology of chalcogenide alloys are important as they are the best representatives of covalent glassy materials. Of the glass-forming alloys of the group $A_x^V B_{1-x}^{VI}$, $As_x Se_{1-x}$ family is perhaps the most studied one. A number of papers have appeared in literature reporting various properties of amorphous As–Se alloys both in the bulk and thin film forms (Nemanich *et al* 1978; Street *et al* 1978; Lucovsky *et al* 1977). Composition-dependent studies on the physical properties of chalcogenide glasses belonging to the groups $A_x^{IV} B_{1-x}^{VI}$ and $A_x^V B_{1-x}^{VI}$ give evidence for the existence of mechanical and chemical thresholds at certain compositions in these materials (Phillips 1982). The composition dependence of acoustic attenuation and velocity in $Ge_x Se_{1-x}$ and $Ge_x S_{1-x}$ glasses measured by Gilroy and Phillips (1983) exhibit a low-temperature peak in the attenuation for $x = 0.20$ and $x = 0.33$ which are the compositions corresponding to mechanical and chemical thresholds respectively in these systems. Murase *et al* (1983) measured the composition dependence of several narrow Raman bands in $Ge_x Se_{1-x}$ glasses. They have reported a discontinuity near $x = 0.20$ composition corresponding to $\delta\omega \approx 3\,\mathrm{cm}^{-1}$. The infrared transverse and longitudinal optic spectra of $Ge_x Se_{1-x}$ glasses reported by Murase and Fukunaga (1984) indicate a softening of the longitudinal optic peak with a threshold at $x = 0.20$. In $As_x Se_{1-x}$ glasses which belong to $A_x^V B_{1-x}^{VI}$ group the mechanical and chemical thresholds coincides at $x = 0.40$. The composition dependence of glass transition temperature T_g in this system indicates that T_g is maximum at $x = 0.40$ (Myers and

Felty 1967). A deep minimum in the glass transition width in temperature in the specific heat curve has been observed at this composition (Chaudhuri *et al* 1966; Blachnik and Hoppe 1979).

To explain the observed phenomena most of the authors have sought the help of the constraints theory (Phillips 1979, 1980, 1981) and the idea of rigidity percolation (Thorpe 1983; Phillips and Thorpe 1985). According to constraints theory the valence force fields between atoms play a crucial role in glass formation and the glass forming composition is optimized mechanically by equating the number of force field constraints N_c, which are intact at the $T = T_g$, with the number of atomic degrees of freedom N_d. It is now generally accepted that in the range of glass forming compositions, the system contains both overconstrained (rigid) regions with $N_c > N_d$ and underconstrained (floppy) regions with $N_c < N_d$. As the average coordination number m increases the rigid regions increase in volume until at $m = m_p$ a percolation transition takes place to a rigid network. Mean field theory predicts that $m_p = 2\cdot4$ (Thorpe 1983; Dohler *et al* 1980). Arguments based on constraints theory and rigidity percolation (Thorpe 1983; Phillips and Thorpe 1985; Phillips 1985) show that at the critical composition corresponding to $m = 2\cdot4$, where the valence force field constraints is balanced by the vector degrees of freedom, the system is mechanically most stable. Correspondingly, the number of zero-frequency vibrational modes in the network, which is the difference between the number of degrees of freedom and the number of linearly independent force field constraints, is minimum.

We have carried out measurements of the optical energy gap and thermal diffusivity of bulk As_xSe_{1-x} semiconducting glasses using photoacoustic (PA) technique to find out whether these parameters exhibit any extrema near the critical composition corresponding to $m = 2\cdot4$.

2. Experimental details

Bulk As_xSe_{1-x} $(0\cdot10 \leqslant x \leqslant 0\cdot50)$ glasses were prepared by the usual melt quenching technique. To prepare a particular composition appropriate quantities of five nine purity constituent elements sealed in evacuated quartz ampoule were melted in a rotary furnace at about 1000 K. The ampoules were rotated continuously at a speed of 10 rpm for 24 h to ensure thorough mixing of the constituents. The ampoules were then quenched in ice water. The amorphous nature of the samples was checked by X-ray diffractometry.

A PA spectrometer in which the cell has provisions to change the backing medium of the sample was used to measure optical absorption and thermal diffusivity. A powerful Xe lamp, a monochromator, a mechanical chopper and a lock-in amplifier were the other modules of the experimental set-up. A sensitive electret microphone was used to detect the PA signals. The details of the set-up were reported earlier (Madhusoodanan *et al* 1988). Circular samples having thickness $\approx 100\,\mu m$ were used for thermal diffusivity measurements. Samples of thickness $\approx 100\,\mu m$ were prepared from the bulk glass by hand lapping and polishing. The optical energy gap E_o was determined by measuring the normalized PA signal amplitude as a function of wavelength of the incident radiation. Optical absorption coefficient is directly proportional to the PA signal amplitude and from the amplitude-wavelength plot, of the type shown in figure 1 for three samples, one can determine the energy gap as the
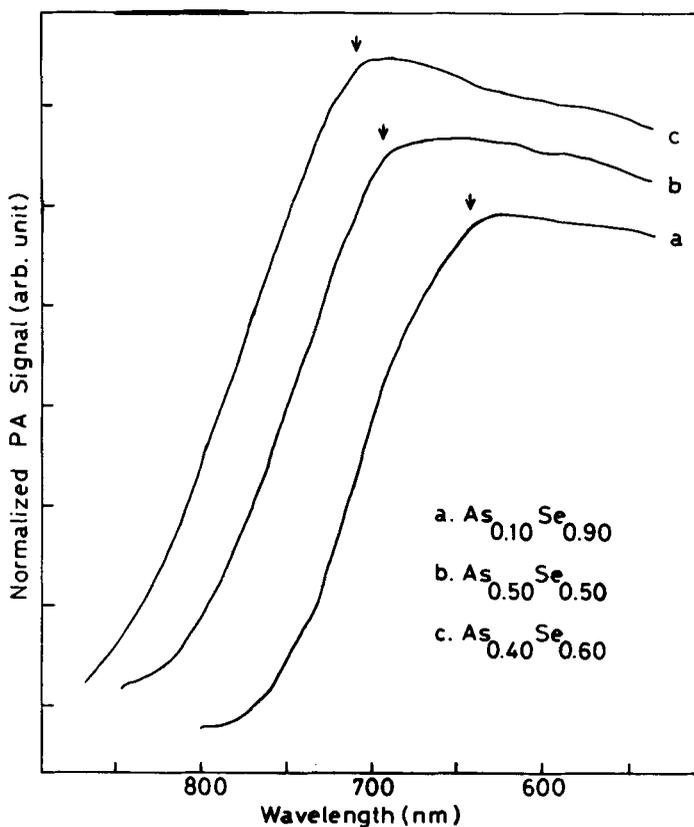
Figure 1. Normalized PA spectra of $As_x Se_{1-x}$ samples.

photon eneryg corresponding to the wavelength at which the normalized PA signal amplitude saturates. The uncertainty in the accuracy of the measurement is within $\pm 2\%$. The PA spectra were plotted for five more compositions and not all of them are shown in figure 1 as the plots are similar to those shown.

The thermal diffusivity α was determined by measuring the PA signal amplitude as well as phase, at a wavelength below E_o, as a function of the chopping frequency f. A thermally thick medium such as copper was used as the backing medium for the sample. The thickness of the sample, was so chosen that it is thermally thin for $f < f_c$, the characteristic frequency, and thermally thick for $f > f_c$ (Charpentier *et al* 1982; Lachaine and Poulet 1984). The PA amplitude vs chopping frequency plot for three samples along-with that for the thermally thick reference sample are shown in figure 2. Again these plots are shown only for three samples. The slope of the plot sharply changes at $f = f_c$ and one can determine the thermal diffusivity using the relation $\alpha = f_c l^2$ where l is the sample thickness (Charpentier *et al* 1982; Lachaine and Poulet 1984). At f_c the sample goes from a thermally thin regime to a thermally thick regime and above f_c the PA signal is independent of the thermal properties of the backing medium.

The measurements of optical energy gap and thermal diffusivity were carried out on a number of samples of the family $As_x Se_{1-x}$, with x lying in the glass forming range $0.10 \leqslant x \leqslant 0.50$, at room temperature.
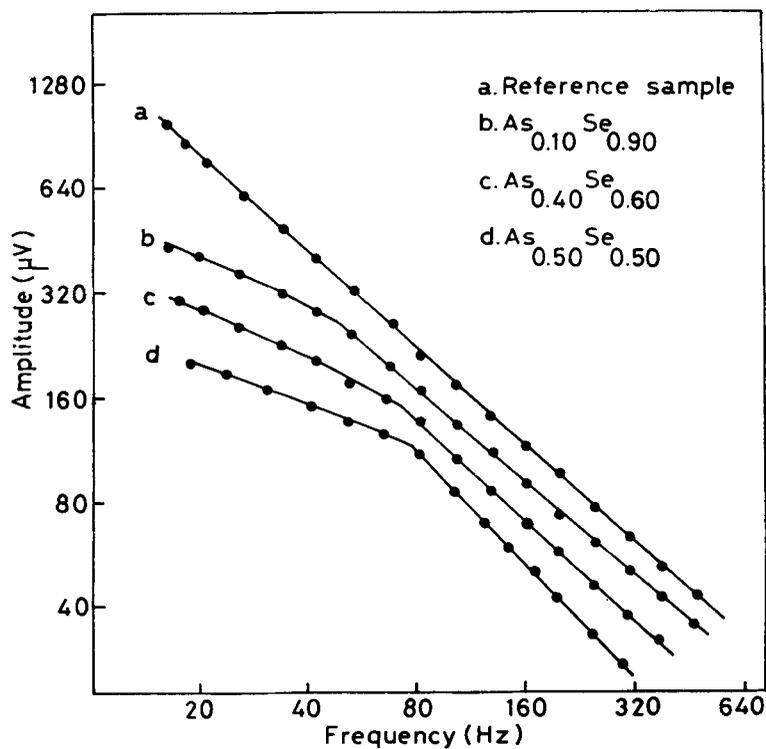
Figure 2. Log-log plots of the variation of PA signal amplitude with chopping frequency.

3. Results

The variation of the measured optical energy gap E_o as a function of composition parameter x in $As_x Se_{1-x}$ glasses with $0.10 \leqslant x \leqslant 0.50$ is shown in figure 3. The value of x was determined from the starting composition in the melt. The optical energy gap data, determined from the absorption measurements using spectrophotometer, are available on several composition of bulk samples in the range $0.20 \leqslant x \leqslant 0.50$ (Street *et al* 1978). The E_o values determined using the PA technique have been compared with these results and the agreement is found to be very good. It can be seen that E_o has a threshold minimum value at $x = 0.40$ which corresponds to the alloy composition $As_{0.40} Se_{0.60}$. This is the stoichiometric composition $As_2 Se_3$ for this family.

The variation of the thermal diffusivity plotted as a function of the composition parameter x is shown in figure 4. A direct comparison could not be made as thermal diffusivity or conductivity data on these glasses in the bulk form are not available in literature. But the accuracy of the technique was tested on some polymers and Ge–Te glasses (Madhusoodanan *et al* 1987, 1988) and the agreement with thermal conductivity values measured using other methods on those samples is very good. In figure 4 we notice that thermal diffusivity has a threshold maximum value at the
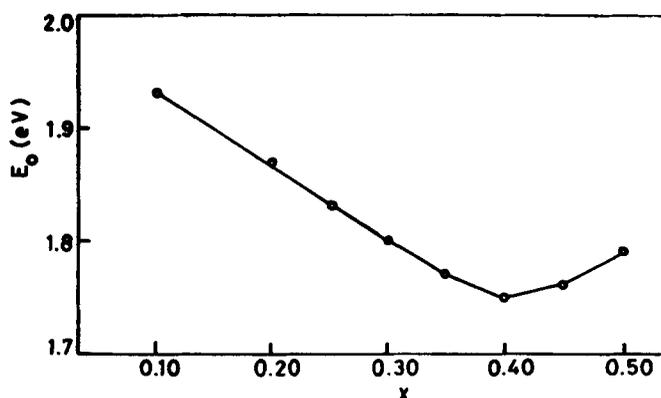
Figure 3. Variation of optical energy gap E_0 with composition parameter x for As_xSe_{1-x} glasses.
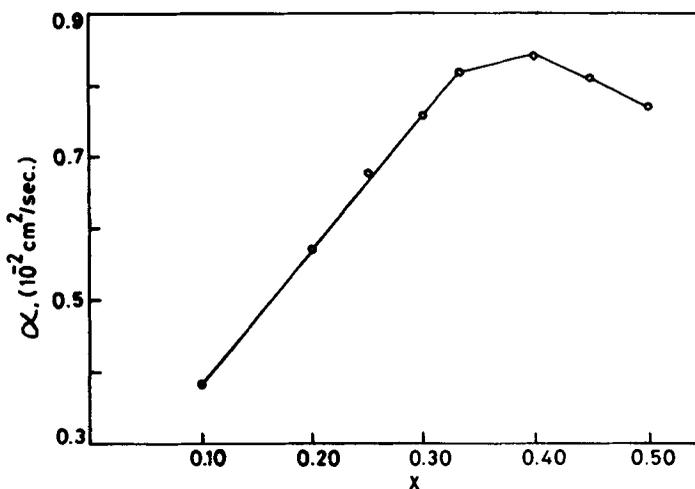

Figure 4. Variation of thermal diffusivity α with composition parameter x for As_xSe_{1-x} glasses.

composition for which $x = 0.40$ which again is the stoichiometric composition As_2Se_3.

4. Chemical bonding and rigidity percolation

Figure 3 indicates that the value of E_0 is close to that of amorphous Se for small As concentrations as expected and decreases as x increases. It has a minimum value at $x = 0.40$ composition corresponding to the formation of the stoichiometric compound As_2Se_3. At this composition the network is formed by fully connected $As(Se_{1/2})_3$ pyramidal structural units with minimum number of homopolar bonds (Lucovsky and Hayes 1979). In Se-rich glasses the network is dominated by Se atom chains and addition of As atoms leads to the formation of branching chains on 3-fold

coordination of As atoms into the basic Se structural units. The two-coordinated Se atoms form $(Se)_n$ chains or $(Se)_8$ rings and the addition of three coordinated As atoms break these chains or rings to satisfy its coordination number and form a large complex atomic group structure in the glass.

The energy gap and related optical properties are closely related to the nature of the chemical bond between atoms and the short-range order existing in the system. The electronic band structure is formed by the supperposition of the molecular orbital states of the constituent bonds. In chalcogenide glasses, in the chalcogen-rich composition range, the lone pair nonbonding band of the chalcogen forms the valence band and the antibonding band constitutes the conduction band. The average coordination number m is an important parameter in determining the composition dependence of various physical properties and the topological description of the glass-forming tendency. If N_{As} and N_{Se} are the coordination numbers of As and Se atoms respectively then

$$m = xN_{As} + (1 - x)N_{Se}$$

Taking $N_{As} = 3$ and $N_{Se} = 2$, for the compositions we have studied, m lies in the range $2 \cdot 10 \leqslant m \leqslant 2 \cdot 50$ with $m = 2 \cdot 4$ for As_2Se_3 with $x = 0 \cdot 40$. Since the existence of energy gap in glass is directly related to the chemical bonding nature (Kastner 1972), the change in the distribution of different bond types and the average bond energy as the composition is varied can be expected to give explanation for the variation of E_o with x (Madhusoodanan et al 1988). According to the chemically ordered network (CON) model (Lucovsky and Hayes 1979) the As_xSe_{1-x} system contains only fully coordinated As–Se bonds at $x = 0 \cdot 40$. For composition with $x < 0 \cdot 40$ the system contains As–Se and Se–Se bonds and for $x > 0 \cdot 40$, As–Se and As–As bonds are present. The bond energies of As–As, As–Se and Se–Se bonds are 43·40, 44·46 and 44 kcal mol^{-1} respectively (Sanderson 1971). Since these values are very close to one another we cannot expect a considerable change in the average bond energy in the system as the composition is varied. Therefore it is rather difficult to explain the observed variation of E_o with x in As–Se system from the point of view of bond energy. It appears that the increase in network disorder associated with the deviation from the stoichiometry has the effect of increasing E_o by pushing the mobility edge further into the bands. The lone pair electrons of the constituent elements have an important influence on the properties of chalcogenide glasses. In As–Se glasses, since As and Se both have lone pair electrons, the optical energy gap across the entire composition range is associated with lone pair to antibonding transitions. In the Se-rich region the bottom of the conduction band is driven upward in energy due to the Se lone pairs. As the As concentration increases the As–Se lone pair interaction increases which results in the widening of the valence band and correspondingly the energy gap is reduced. This effect is maximum at the stoichiometric composition where the minimum in E_o occurs. Band structure calculations, based on similar arguments, done by White (1974) using relatively small number of tight binding matrix elements for As–Se glasses yield a relative minimum in E_o at the compound composition.

The number of wrong bonds at the stoichiometric composition in the system may not be zero as proposed by the CON model. However such bonds are minimum at this composition. Griffiths et al (1982) suggested a model based on the formation of partially polymerized clusters for describing the structure of covalent network glasses.

According to this molecular cluster network model the cluster surface plays an integral role in determining the glass forming tendency and the final structure. The chemical order of the network is intrinsically broken while clusters are formed and this allows a minimum number of wrong bonds at the stoichiometric composition in the partially polymerized cluster (PPC) model.

From the description of covalent glasses on the basis of constraints theory (Phillips 1979) and percolation model (Thorpe 1983; Phillips and Thorpe 1985) we can see that in As_xSe_{1-x} at $x = 0.40$, where the average coordination number is 2·4, the number of valence force field constraints are equal to the number of atomic degrees of freedom if bond-stretching and bond-bending constraints are taken into account. The composition at which $m = 2.4$ is a threshold composition for this system where a percolation transition takes place from a polymeric glass to a rigid network or amorphous solid. The rigidity is associated with extended finite frequency modes whereas floppiness is associated with localized zero frequency modes. Using mean-field theory it has been shown (Thorpe 1983) that the number of zero frequency modes is zero when the average coordination number $m \geqslant 2.4$. The threshold behaviour in thermal conduction exhibited by the As_xSe_{1-x} glasses can be attributed to the mechanical stiffening of the glass network at the critical composition $x = 0.40$ due to the threshold percolation of rigidity and the corresponding threshold in the internal stress.

For the $A^V B^{VI}$ glasses like As_xSe_{1-x}, the ideal glass composition is the one for which $x = 0.40$ and the number of zero frequency modes would be minimum at this composition. At this composition the network offers minimum resistance to propagating thermal waves and consequently, thermal diffusivity has a maximum value. Our experimental results agree with this idea which has resulted from the idea of rigidity percolation in covalent network.

Acknowledgements

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