Investigation of chemical and mechanical extrema in Ge-In-Se glasses using a photoacoustic technique

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Abstract. Twelve glass compositions, belonging to the $Ge_xIn_5Se_{95-x}$ family of semiconducting chalcogenides are prepared from high-purity constituent elements by a melt quenching technique. The variation of the optical band gap (E_g) and thermal diffusivity (α) with average coordination number (Z) are investigated using a photoacoustic (PA) technique. The E_g values obtained from PA measurements have been compared with the values obtained from UV–Vis–NIR absorption spectra. Extrema are seen in the α against Z curves at Z values of 2.41 and 2.67, which correspond to the topological thresholds, and a maximum in the E_g against Z curve is found at $Z = 2.73$, corresponding to the chemical threshold of this system of glasses. These results are interpreted in terms of the Phillips–Thorpe model of rigidity percolation based on constraints theory, Tanaka's model of dimensional transition and the chemically ordered covalent network model for tetrahedrally-bonded glasses.

1. Introduction

Systematic studies on the variation of various physical and chemical properties [1–7] of chalcogenide glasses with average coordination number have recently gained considerable attention due to their potential technological applications in solid-state devices. The features observed in the composition dependence of various physical properties of chalcogenide glasses are explained, in general, on the basis of the chemically ordered covalent network (COCN) model [8, 9], topological models based on constraints theory [10–14] and structural dimensionality considerations [15–18]. Phillips, Thorpe and others [10–14], equated the total number of interatomic force field constraints per atom N_c to the number of degrees of freedom per atom N_d. Phillips [10], through a constraint counting analysis and considering only short-range order, demonstrated that a covalent random network structure has maximum stability at $Z = 2.4$. He obtained this number based on the intuitive argument that interatomic bonds in stable glasses have three degrees of freedom. The relation connecting Z and N_d can be expressed by

$$N_d = Z/2 + (2Z - 3) \qquad (1)$$

where $Z/2$ is the number of bond stretching and $(2Z - 3)$ is the bond bending constraints for the system with Z number of bonds. For a three-dimensional system, a topological transition at the critical value $Z = 2.4$ is predicted at which the network changes over from a floppy (underconstrained) to a rigid (overconstrained) type. Glasses with $Z < 2.4$ are considered underconstrained (or floppy) and those with $Z > 2.4$ are overconstrained (rigid). Several experimental evidences have been reported for this composition driven phase transition in

many binary and pseudobinary chalcogenide glasses. In the underconstrained glass the bond bending and bond stretching constraints give rise to a finite number of low-frequency modes (zero-frequency modes theoretically), the fraction of which is given by

$$f = 2 - 5Z/6. \tag{2}$$

The number of such low-frequency modes goes to zero as Z tends to 2.4. This has been verified experimentally from inelastic neutron scattering and ultrasonic measurements in selected systems [13]. As Z exceeds 2.4 for the network, the elastic constants build up very quickly and, correspondingly, the network supports the allowed phonon modes arising from the vibration of the atomic species.

Tanaka [15–18] modified the ideas of Phillips and Thorpe by arguing that medium-range order also should be considered in the constraint balancing condition as evidenced by characteristic signatures in the composition dependence of certain physical properties at $Z = 2.67$. Tanaka demonstrated that the features observed at this composition can be related to the formation of stable layer structures in the network. If one assumes a hypothetical network having a plain lattice laid in a three-dimensional space, the angular term and the constraint balancing equation get modified. Including this feature, the bond bending term $(2Z - 3)$ in (1) reduces to $(Z - 1)$ because, for a planar cluster in the $x–y$ plane, an atom bonded to another at the origin has freedom over the angle θ alone. Hence (1) is modified to

$$N_d = Z/2 + (Z - 1) \tag{3}$$

predicting another composition-driven structural phase transition at $Z = 2.67$. Two-dimensional layered structures are fully evolved at this critical composition and for higher values of Z, due to the increase in the number of the cross-linked sites, the network undergoes a structural phase transition to a three-dimensional structure.

According to the COCN model, heteropolar bonding is maximized, thereby favouring chemical order, which also results in features such as extremum or a change of slope in the composition dependence of physical properties at the stoichiometric compositions of these glasses. Raman, x-ray and Mossbauer studies on some chalcogenide glasses confirm the formation of structural units which generally correspond to those of the stable chemical compounds of the system.

Anomalous features in many physical properties [19–22] have been reported around $Z = 2.4$ and $Z = 2.67$, as well as at the chemical threshold composition corresponding to stoichiometry in several systems, which have helped in verifying the validity of the above models in different systems of glasses.

In most of the glasses containing IV–VI or V–VI elements, the chemical thresholds are seen to coincide with the mechanical thresholds, making it difficult to isolate the effects of chemical ordering from those of topological origin in such systems. From phase diagrams it is known that $Ge_x In_5 Se_{95-x}$ glasses with $12 < x < 32$, giving rise to Z values ranging from 2.39 to 2.79, form bulk glasses in the entire range covering the mechanical and chemical threshold compositions. Moreover, in Ge–In–Se glasses these occur at different Z values, making this system an ideal one to test the validity of the above two-constraint counting arguments. Even though $Ge_x In_5 Se_{95-x}$ are ternary in the strict sense, they can be considered as forming binary $Ge_x Se_{85-x}$ glasses with In dispersed in them, or the system can be considered as a pseudobinary one.

In order to get an insight into the variation of electronic and vibrational properties around different extrema, we report the results of our investigations on the variation of the optical band gap E_g and thermal diffusivity α with average coordination number Z n bulk $Ge_x In_5 Se_{95-x}$ glasses using a photoacoustic (PA) technique [23]. Thermal diffusivity measurements are often preferred over conductivity measurements due to its insensitivity to radiative heat losses.

Details of the experimental method, results obtained and discussions of the results are given in the following sections.

2. Experimental method

Bulk $Ge_x In_5 Se_{95-x}$ glasses ($12 < x < 32$) were prepared from 5N purity chemical by the well established melt quenching method at a cooling rate of approximately $100\,°C\,s^{-1}$. The amorphous nature of the samples are inferred from their powder x-ray diffractograms. $Ge_x In_5 Se_{95-x}$ glasses with Z values ranging from 2.39 to 2.85 can be prepared in the bulk form by the above method [24]. The Z values of the compositions $Ge_x In_y Se_z$ ($x + y + z = 1$) are evaluated by $Z = 8 - 4x - 3y - 6z$ [24–27]. Table 1 lists the compositions prepared along with their Z values.

Table 1. Average coordination number Z, optical band gap E_g and thermal diffusivity α of Ge–In–Se glasses.

Composition (mol%)				E_g (eV)		
Ge	In	Se	Z	PA technique	UV–Vis–NIR method	α (10^{-2} cm^2 s^{-1})
12	5	83	2.39	1.67	1.66	0.76 ± 0.009
13	5	82	2.41	1.70	1.67	1.41 ± 0.008
16	5	79	2.47	1.75	1.80	1.21 ± 0.02
18	5	77	2.51	1.92	1.85	0.99 ± 0.01
20	5	75	2.55	2.04	1.98	0.88 ± 0.02
22	5	73	2.59	2.11	2.08	0.95 ± 0.02
25	5	70	2.65	2.23	2.21	1.48 ± 0.004
26	5	69	2.67	2.28	2.26	1.63 ± 0.01
28	5	67	2.70	2.33	2.32	1.48 ± 0.007
29.17	5	65.83	2.73	2.40	2.37	1.18 ± 0.004
30	5	65	2.75	2.22	2.26	0.95 ± 0.02
32	5	63	2.79	2.08	2.13	0.69 ± 0.005

Measurement of the optical band gap E_g and thermal diffusivity α on these samples have been carried out using the PA technique. For this, a PA spectrometer comprising of a 1 kW xenon arc lamp, a monochromator, a mechanical chopper, a non-resonant PA cell enclosing the sample and a dual phase lock-in amplifier are used [28]. The PA spectrum for each sample is normalized using the PA spectrum obtained with a highly-absorbing carbon black sample. The normalized PA signal increases from the higher-wavelength side and reaches a saturation level for photon energies $h\nu > E_g$. As explained by Tauc [29], there are three different regions in the optical absorption curve for an amorphous semiconductor giving rise to three different ranges of absorption coefficients. In the first region the absorption is weak with the absorption coefficient $\beta < 1$ cm^{-1}. The second region corresponds to absorption in the range 1 cm$^{-1} < \beta < 10^4$ cm^{-1}. The absorption in this region depends exponentially on photon energy according to the relation

$$\beta(h\nu) = \beta_0 \exp(h\nu/E) \tag{4}$$

where E characterizes the slope of the exponential absorption region. This dependence corresponds to the region where the normalized PA signal increases with $h\nu$ as in figure 1. The high value for the absorption coefficient ($\beta > 10^4$) marks the third region, corresponding to saturation [23, 30, 31] in the PA spectrum. A comparison between the PA spectrum and the optical absorption spectrum obtained using UV–Vis–NIR spectrophotometer shows that the
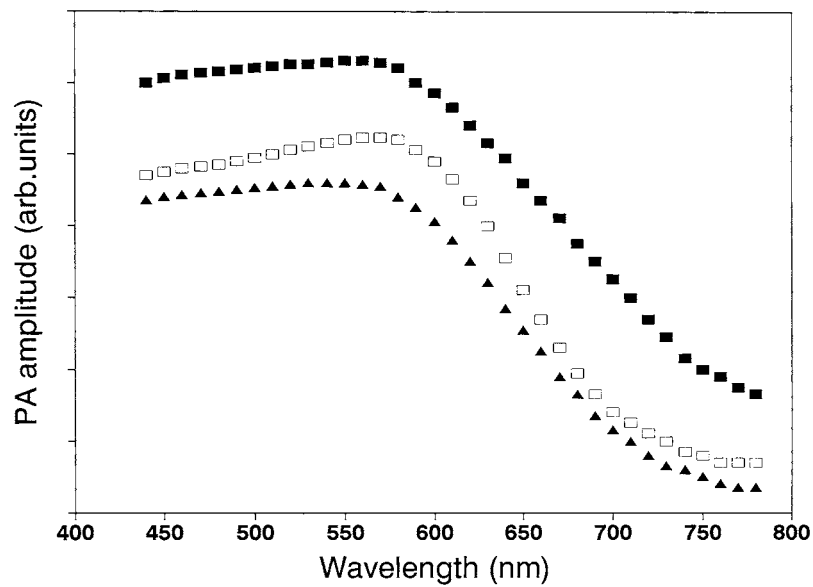
Figure 1. Normalized PA spectra of Ge$_x$In$_5$Se$_{95-x}$ glasses: $x = 29.5$ ($\blacksquare$), $x = 30$ ($\square$) and $x = 32$ ($\blacktriangle$).

two match very well and the quantitative correlation between them is very good in the three absorption regions.

The PA technique offers a powerful tool for determining thermal diffusivity α of solid samples since the periodic component of the surface temperature of the sample can be determined indirectly with high sensitivity. The basic principle involved in measuring the thermal diffusivity employing a PA technique are well known [32]. In order to measure the thermal diffusivity of Ge–In–Se glasses, we employed a modified dual-beam technique which is quite similar to that proposed by Pessoa *et al* [33] for bulk samples having large optical absorption coefficients. In this method, the relative phase lag, $\psi_F - \psi_R = \Delta\psi$, of the generated PA signal between the front and rear surfaces of illumination when the sample is irradiated by a single light beam is determined by rotating the PA cell freely by 180° about a vertical axis [34]. This reduces the inherent complexities and uncertainties involved in the dual-beam set-up developed by Pessoa *et al* [33]. In this method thermal diffusivity is determined using the relation

$$\tan(\Delta\psi) = \tanh(a_s l_s) / \tan(a_s l_s) \tag{5}$$

where $a_s = (\pi f / \alpha)^{1/2}$ is the thermal diffusion coefficient of the samples and f is the chopping frequency. The advantages of this modified technique are that it can be used with thermally thick as well as thin samples and that measurements can be carried out at a single chopping frequency. The estimated error in the thermal diffusivity values obtained using this technique is lower than 5%. Bulk samples of thickness approximately 0.5 mm and diameter 5 mm are used to carry out the measurements reported in this work.

3. Results

The PA absorption spectra obtained for three Ge$_x$In$_5$Se$_{95-x}$ samples are shown in figure 1. Similar curves have been obtained for other samples. The variation of E_g with average
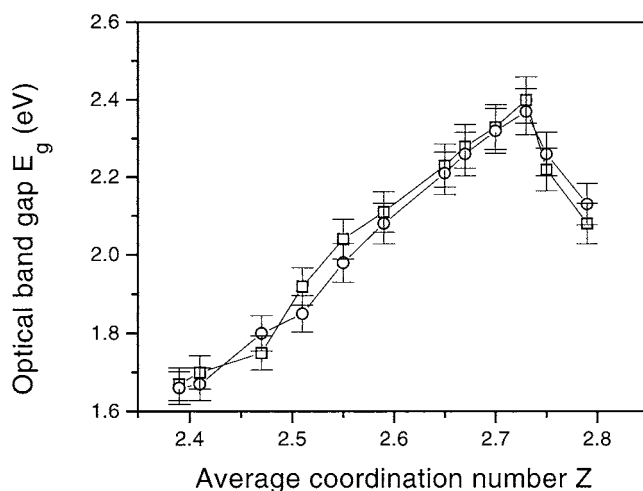
Figure 2. Variation of the optical band gap E_g with average coordination number Z for the Ge$_x$In$_5$Se$_{95-x}$ glasses using the PA technique ($\square$) and using UV–Vis–NIR absorption technique (O).
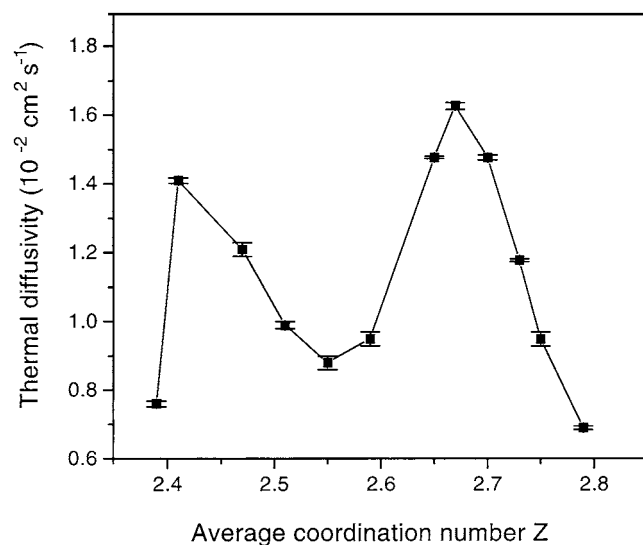

Figure 3. Variation of thermal diffusivity α with average coordination number Z for Ge$_x$In$_5$Se$_{95-x}$ glasses.

coordination number Z in these glasses using PA as well as UV–Vis–NIR absorption method are shown in figure 2. The measured values of E_g using both these techniques are tabulated in table 1. The uncertainty in the values of E_g determined by this method is of the order of 2%. It is seen that E_g increases with increasing Ge content up to the stoichiometric composition ($Z = 2.73$) and decreases thereafter for Ge-rich glasses. The measured values of thermal diffusivity are also tabulated in table 1. The variation of α with Z is shown in figure 3. Extrema in α values at the two topological thresholds $Z = 2.41$ and $Z = 2.67$ are clearly seen in the experimental data in this system of glasses.

4. Discussion

The peak in the values of E_g occurring at the chemical threshold corresponding to $Z = 2.73$ can be attributed to the chemical ordering taking place in these glasses. This composition is referred to as the tie-line composition where the glass structure is made up of completely cross-linked $GeSe_2$ and In_2Se_3 structural units which consists of only energetically favoured heteropolar bonds, with neither Ge nor Se in excess. If the tie-line composition is taken as the reference, glasses with a Se content greater than those on the tie-line are referred to as Se-rich compositions and those with less Se content as Ge-rich glasses. The COCN model views the glass structure to be composed of three-dimensional cross-linked $GeSe_2$ and In_2Se_3 structural units and excess of Ge or Se, if any. The decrease in E_g for Se-rich compositions can be attributed to the replacement of strong heteropolar Ge–Se bonds having bond energy 55.4 kcal mol^{-1}, by weak, homopolar Se–Se bonds with a bond energy of 44 kcal mol^{-1}. The bond energies were calculated by standard procedure using listed electronegativities of elements [35]. Similarly, the decrease in E_g for Ge-rich compositions is rationalized on the basis that more and more Ge–Se bonds are replaced by weaker Ge–Ge bonds with bond energy 49.1 kcal mol^{-1}. The energy gap values of Ge–In–Se glasses reported from data on activation energy for electrical conductivity also show an increase with Ge content up to the tie-line composition and decreases thereafter for Ge-rich glasses [36]. The variations of the glass transition temperature T_g with Z also exhibit a maximum at $Z = 2.73$ [24].

The composition-dependent thermal diffusivity of these glasses show extrema at $Z = 2.41$ and $Z = 2.67$. The peak at $Z = 2.41$ can be attributed to criticality in the system corresponding to mechanical threshold at this composition owing to the constraint balancing condition being satisfied, as predicted by the Phillips–Thorpe model [37]. The undercontrained glass with $N_c < N_d$ or $Z < 2.4$ contain large, floppy regions with a few rigid inclusions, whereas overconstrained glasses with $N_c > N_d$ or $Z > 2.4$ contain rigid regions having percolated to form a rigid interconnected network extending into the whole solid with a few floppy inclusions in it. The network with $N_c = N_d$ or $Z = 2.4$ is the percolation threshold where the network undergoes transformation from floppy to rigid type, driven by the average coordination number. As has been stated earlier, experimental results on elastic constants [38] and neutron scattering [39] support this model. In order to explain the peak in thermal diffusivity at $Z = 2.41$, one has to invoke the role played by low-frequency modes in the undercontrained glass. As Z tends to 2.4, the network becomes more and more rigid and the number of low-frequency modes correspondingly decrease. Scattering of propagating thermal waves by the low-frequency modes limit the thermal diffusivity for $Z < 2.4$. As Z approaches 2.4, the number of low-frequency modes approach zero, resulting in a corresponding enhancement in thermal diffusivity. As Z increases beyond 2.4, the elastic forces quickly build up, giving rise to an increase in the values of elastic constants. Calculations based on mean field theory and elastic constant measurements in glasses support this argument. Correspondingly, the allowed vibrational modes characteristic of a rigid elastic network become established. Scattering of thermal waves by these modes lead to a reduction in thermal diffusivity for $Z > 2.4$. It may be noted that there is a correspondence between the increase in the values of the elastic constants with the average coordination number and a decrease in the thermal diffusivity with the average coordination number for $Z > 2.4$.

The presence of an extremum in the value of α at 2.67 may be considered as due to a topological transition from a two- to a three-dimensional structure of the system, as predicted by Tanaka's model [15–18]. We believe that this system essentially consists of a Ge–Se network with In–Se bonds dispersed in it. For values of Z less than 2.67, In–Se bonds form a two-dimensional interconnected network laid in the three-dimensional Ge–Se network. Even

though $Ge_x In_5 Se_{95-x}$ is a ternary system, the low concentration of In make it, essentially, a pseudobinary one. The layer structure of the In–Se lattice is fully evolved at $Z = 2.67$ at which the constraint balancing equation (equation (3)) is satisfied and the network undergoes a transition from a two- to a three-dimensional structure at this composition. For $Z < 2.67$, the In–Se layers form a lattice misfit and act as scattering regions for propagating thermal waves resulting in a reduced thermal diffusivity. As Z approaches 2.67, the lattice misfit decreases and a uniform three-dimensional structure is evolved at $Z = 2.67$. However, at this transition composition the elastic forces involving the In–Se lattice are not fully developed and hence the vibrational modes are not fully evolved. This results in the observed maximum in thermal diffusivity at this composition. As Z exceeds 2.67, the network becomes a uniform three-dimensional one with elastic forces characteristic of three-dimensional glassy solids. The vibrational modes correspondingly become established and they scatter the propagating thermal waves causing a further reduction in the thermal diffusivity for $Z > 2.67$. Careful neutron scattering and elastic constant measurements can throw more light on these arguments. Finally, at $Z = 2.73$, corresponding to the chemical threshold, the system forms a stoichiometric glass.

5. Conclusions

Effects due to chemical ordering in this glass system are marked by a maximum in E_g at $Z = 2.73$ in the variation of optical band gap with composition. Topological extrema at $Z = 2.41$ and 2.67, due to a floppy to rigid transition and a two- to three-dimensional structural transition respectively in these glasses are registered by maxima in the composition dependence of thermal diffusivity investigated using the PA technique. Results indicate that the three extrema occur at three different average coordination numbers in the glass-forming range of this system, making this a good system for experimentation. Arguments such as occurrence of a two-dimensional layered structure dispersed in a three-dimensional network which is mechanically rigid, are still controversial and need to be resolved with more experiments.

Acknowledgments

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