CHAPTER 7

Thermal properties across thresholds in Ge-As-Se glasses

7.1 Introduction

Systematic studies on the variation of various mechanical, optical, chemical, thermal and elastic properties [1-7] of chalcogenide glasses with average coordination number have gained considerable interest among solid state physicists, in view of their many potential applications in solid state devices. According to Phillips' constraints theory [8], the optimum condition for glass formation is,

\[ N_c = N_d \]  \tag{7.1}

where \( N_c \) and \( N_d \) are the constraints and the degrees of freedom per atom respectively. The constraints are in the sense of Lagrangian mechanics [9] and are due to the directional covalent bonds. As already stated in Chapter 1 of the thesis, the total number of constraints on an atom is,

\[ N_c = \frac{Z}{2} + (2Z - 3) \]  \tag{7.2}

for covalent glasses. For 3-dimensional network, \( N_d = 3 \) and we get,

\[ 3 = \left( \frac{Z}{2} \right) + (2Z - 3) \]  \tag{7.3}

or \( Z = 2.4 \). This is a surprising result because it is not material specific and there are no adjustable parameters involved in the calculation [8].
Later, Tanaka extended Phillips' ideas to 2-dimensional glass structures [10, 11]. Assuming a hypothetical material having a plane lattice laid in 3-D space, the constraints balancing equations for the layer material gets modified as.

\[ 3 = \left( \frac{Z}{2} \right) + (Z - 1) \]  

(7.4)

This expression gives a value \( Z = 2.67 \), i.e., the average coordination number of glasses having a stable layer structure is 2.67.

Transition from an under constrained to an over constrained network has been interpreted by Thorpe [12, 13] in terms of percolation of rigidity in an inhomogeneous medium containing both rigid and floppy regions. Anomalous features in many physical properties have been reported around \( Z = 2.4 \) and \( Z = 2.67 \) as well as the chemical threshold in several systems.

The ternary glass system Ge-As-Se has got one of the largest glass forming regions among chalcogenide glasses. Therefore, it is particularly well suited to test the validity of the above concepts. Germanium, arsenic and selenium are elements of groups IV, V, and VI respectively of the same period. This brings about the covalent character of the interaction between their atoms and results in a broad glass-forming region. In the three component Ge-As-Se system, selenium will react with germanium and produce structural units of GeSe_{4/2}. When germanium is introduced into arsenic selenides, gradual composition changes takes place in the system forming GeSe_{4/2} and AsSe_{3/2} structural units. Also, formation of complex structural units like As_{2}Ge_{4/2}Se_{4/2} occurs. Approximate thermo chemical calculations indicate that in the three component Ge-As-Se system, there can be several sections with
different contents of structural units, and consequently, with different physical and chemical properties. There can be sections in which the structure is determined mainly by bonds of the selenium type [14].

The composition dependence of many physical properties of Ge-As-Se system of glasses show anomalous variations at \( Z = 2.4 \) and \( Z = 2.67 \). Elastic constants of Ge-As-Se glasses show a threshold behaviour at \( Z = 2.4 \) [15], but the data do not match with a previous report [16]. A study of the \( Z \) dependence of \( \Delta C_p \) measured at \( T_g \) shows a minimum at 2.4. But the persistent infrared spectral hole burning studies of the effect of network topology on low temperature relaxation in Ge-As-Se system of glasses do not show any indication of a rigidity transition or any other unusual features at \( Z = 2.4 \) [17]. On the other hand, the composition dependence of optical band gap and thermal diffusivity show threshold maxima at \( Z = 2.67 \) [18].

In this chapter, we report the variation of thermal parameters, viz., thermal diffusivity, thermal effusivity, thermal conductivity and heat capacity as a function of the average coordination number \( Z \) for Ge\(_x\)As\(_{2.5}\)Se\(_{75-x}\) system of glasses. The photopyroelectric technique described in Chapter 2 has been used for the determination of the above thermal parameters. The compositions have been chosen to produce an average atomic coordination \( Z \) ranging from 2.30 to 2.80. Average coordination number \( Z \) of a ternary glass of the form \( A_xB_yC_{100-x-y} \) is given by

\[
Z = \left[ x N_A + y N_B + (100-x-y) N_C \right] / 100
\]

(7.5)

where, \( N_A, N_B \) and \( N_C \) are the coordination numbers of the elements A, B and C respectively and \( x \) and \( y \) are the atomic weight percentages of the elements A and B respectively in the network glass.
7.2 Sample preparation and experimental details

Glass samples with the general formula, Ge$_x$As$_{2.5}$Se$_{7.5}$-$_x$ (2.5 $\leq x \leq$ 27.5) have been prepared by the melt quenching technique. Appropriate quantities of high purity constituents are taken in quartz ampoules, which are evacuated and sealed. The ampoules are kept in an electrical furnace and slowly heated to 1000$^\circ$C. They are kept at 1000$^\circ$C for nearly 24 hours with intermittent rotation of the ampoules for homogeneous mixing of the constituents. Then the ampoules are quenched in ice water to obtain the glassy samples. The amorphous natures of the samples are confirmed by X-ray diffraction technique.

Thermal parameters of the samples have been determined using the photopyroelectric (PPE) technique described in earlier chapters. Samples of thickness $\approx 0.5$ mm have been used for the measurements. A He-Cd laser ($\lambda = 442$ nm) has been used as the source of radiation and a PVDF film of thickness 28 $\mu$m, both sides coated with Ni-Cr as the detector. Light modulation is achieved using a mechanical chopper (Model SR540). PPE signal is measured using a dual phase lock-in amplifier (Model SR830).

7.3 Results and discussion

Thermal thicknesses of the samples are confirmed by plotting the PPE signal amplitude and phase as a function of modulation frequency. These plots are shown in Figs. 7.1 and 7.2.
Fig. 7.1 Frequency dependence of PPE amplitude for different compositions of Ge$_x$As$_{25}$Se$_{75-x}$ glasses.

Fig. 7.2 Frequency dependence of PPE phase for different compositions of Ge$_x$As$_{25}$Se$_{75-x}$ glasses.
Thermal diffusivity ($\alpha$) of the samples is determined from the corresponding PPE signal phases and thermal effusivity ($e$) from PPE signal amplitudes. The variations of $\alpha$ and $e$ with average coordination number $Z$ are shown in Fig. 7.3.

Sample mass densities have been determined using the Archimedian principle with liquid paraffin used as the densiometric fluid. Fig. 7.4 shows the $Z$ dependence of density. Thermal conductivity ($K$) and heat capacity ($c_p$) of the samples can be determined using the relations.

$$K = e \sqrt{\alpha} \quad (7.6)$$

$$c_p = \frac{e}{\rho \sqrt{\alpha}} \quad (7.7)$$

Variations of $K$ and $c_p$ with $Z$ are shown in Fig. 7.5.

From the composition dependence studies, it is seen that thermal diffusivity and thermal effusivity show maxima around $Z = 2.67$. Thermal conductivity also shows a maximum at $Z = 2.67$, while heat capacity shows a minimum around $Z = 2.4$.

The occurrence of threshold maxima in $\alpha$ and $K$ values round $Z = 2.67$ can be explained in terms of the change in network topology and dimensionality. In Se-rich glasses of the Ge-As-Se system, the two-fold coordinated Se will form flexible chains of Se in the glass network. The addition of four-fold coordinated germanium results in branching and cross-linking of these chains. These configurational changes result in the formation of a two-dimensional structure, which is stabilized by the medium range intermolecular interactions. Thus, as the Ge concentration increases, the value of $Z$ increases and cross-linking of the Se atom chains occurs. As a result, the
Fig. 7.3 Variation of thermal diffusivity and thermal effusivity of Ge$_x$As$_{25}$Se$_{75-x}$ glasses with average coordination number.

Fig. 7.4 Variation of density with average coordination number for Ge$_x$As$_{25}$Se$_{75-x}$ glasses.
Fig. 7.5 Variation of thermal conductivity and heat capacity of Ge₅As₂₅Se₇₅₋ₓ glasses with average coordination number

Flexibility of the network glass gets reduced. This results in an increase in the value of α. At Z = 2.67, the medium range order fully gets developed and a layered structure is formed. This results in a maximum value for α. At this composition, the system goes over to a rigid 3-D structure and the system will be rigid beyond this composition.

In these glassy materials, thermal conductivity depends crucially on the phonon mean free path in the system. The threshold maximum of K around Z = 2.67 can be explained on the basis of the development of a more ordered and rigid structure at this composition. The slight decrease in the value of K beyond this composition may be due to the large number of defect present in the three-dimensional structure.
7.4 Conclusions

Thermal parameters of the Ge$_x$As$_{25}$Se$_{75-x}$ ($x = 2.5\text{-}27.5$) system of glasses have been measured using the photopyroelectric technique. From the average coordination number dependence studies, it is seen that anomalous variations occur at threshold compositions. The results are explained on the basis of the various structural models for chalcogenide glasses. The observed maxima in the values of $\alpha$ and $K$ around $Z = 2.67$ indicate that medium range interactions have an important role in determining the network topology in these glasses.
References

15. B. L. Halfpap and S. M. Lindsay, Phys. Rev. Lett. 57 (1986) 847