Thermal properties across threshold compositions in Ge-As-Se glasses

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The Ge-As-Se chalcogenide glasses is an interesting system to test the validity of different constraint models proposed for these materials, in view of the fact that this system has a wide glass forming range which makes it possible to measure composition dependent properties over ranges covering most predicted thresholds. We have measured the thermal parameters—thermal diffusivity, thermal effusivity, thermal conductivity and heat capacity—of Ge-As-Se glasses covering composition range in which thresholds in physical properties have been predicted for covalent glasses employing a modified photopyroelectric technique. Our results show that this system exhibits a minimum in heat capacity at an average coordination number $Z = 2.4$ corresponding to a 3-D network as per the Phillips-Thorpe model, whereas thermal conductivity exhibits a threshold maximum at $Z = 2.67$ which is in agreement with the Tanaka model. © *2003 Kluwer Academic Publishers*

1. Introduction

Systematic studies on the variation of different 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 three dimensional glass formation in these materials is,

$$N_c = N_d \qquad (1)$$

where N_c is the number of constraints on each atom and N_d is the number of degrees of freedom per atom. The constraints are defined in the sense of Lagrangian mechanics and are due to the directional covalent bonds distributed in the network. The total number of constraints on an atom for covalent glasses is given by [9],

$$N_c = \frac{Z}{2} + (2Z - 3) \qquad (2)$$

where Z is the average coordination number for the network. For a 3-dimensional network $N_d = 3$ so that we get,

$$3 = \left(\frac{Z}{2}\right) + (2Z - 3) \qquad (3)$$

or $Z = 2.4$. This is a rather surprising result in the sense that 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,

$$3 = \left(\frac{Z}{2}\right) + (Z - 1) \qquad (4)$$

This expression gives a value $Z = 2.67$, i.e., the average coordination number of glasses having a stable layer structure embedded in a 3-D network works out to be 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 at 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 concepts presented above. 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 take place in the system forming $GeSe_{4/2}$ and $AsSe_{3/2}$ structural units. Simultaneously, formation of complex structural units like $As_2Ge_{4/2}Se_{4/2}$ also occurs. Approximate thermo-chemical calculations indicate that in the three component Ge-As-Se system, there can be several

regions with varying contents of different 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 $Z = 2.4$ as well as at $Z = 2.67$. Elastic constants of Ge-As-Se glasses show a threshold behaviour at $Z = 2.4$ [15], but the data does not match with a previous report [16]. A study of the Z dependence of ΔC_p measured at glass transition temperature T_g shows a minimum at 2.4. However, 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 feature 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]. It has been reported that the ternary Ge-Sb-Se glass system exhibits thresholds at $Z = 2.67$ in several physical properties, while a few exhibit thresholds at $Z = 2.4$. The relations between thresholds in these properties and the glass structure have been established and discussed by earlier workers [19, 20].

In this paper we report the variation of the thermal parameters, thermal diffusivity, thermal effusivity, thermal conductivity and heat capacity, measured as a function of the average coordination number Z for the $Ge_x As_{25} Se_{75-x}$ ($2.5 < x < 27.5$) system of glasses using a modified photopyroelectric technique [21]. The compositions have been chosen to produce an average atomic coordination Z ranging from 2.30 to 2.75. Average coordination number Z of a ternary glass of the form $A_x B_y C_{100-x-y}$ is given by

$$Z = [x N_A + y N_B + (100 - x - y) N_C]/100 \quad (5)$$

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 glass network.

2. Experimental

Glass samples with the general formula, $Ge_x As_{25} Se_{75-x}$ ($2.5 \leq x \leq 27.5$) have been prepared by the melt quenching technique. Appropriate quantities of high purity constituents are taken in quartz ampoules and are evacuated and sealed. The ampoules are kept in an electrical furnace and slowly heated to 1000°C. They are kept at 1000°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 employing the photopyroelectric (PPE) technique [21]. Thin slices of samples with thickness of the order of 0.5 mm and area of the order of 3×3 mm^2 have been cut with a slow speed diamond wheel saw, and then hand lapped and polished for the measure-

ments. In the PPE technique, a thermally thick pyroelectric film, acting as the heat sensor, is attached to one side of the sample, which is also thermally thick, and the combination is mounted on a thermally thick backing medium. The other side of the sample is illuminated by a beam of light, modulated in intensity, which gives rise to periodic temperature variations by optical absorption. The thermal waves so generated propagate through the sample and are detected by the pyroelectric detector. A mechanical chopper (Model SR 540) has been used to modulate the light beam and the signal is measured using a dual phase lock-in amplifier (Model SR 830). A 120 mW He-Cd laser of wavelength 442 nm has been used as the radiation source and a polyvinylidene difluoride (PVDF) film of thickness 28 μm, both sides coated with Ni-Cr film, as the pyroelectric detector in these experiments.

A careful calibration of the experimental setup and procedure has been done prior to carry out the measurements. The thermal thickness of the PPE detector at the used modulation frequency has been ensured by plotting the PPE signal amplitude and phase with frequency with the detector itself acting as the sample. Similarly, the thermal thickness of the samples are also ensured. A modulation frequency of 40 Hz has been used for the determination of thermal parameters of the samples, which ensures the thermal thickness of the sample, detector and the backing medium. Measurement of PPE signal phase and amplitude enables one to determine thermal diffusivity ($\alpha = K/\rho c_p$, where K is the thermal conductivity, c_p is the specific heat and ρ is the density) and thermal effusivity ($e = \sqrt{K \rho c_p}$) respectively of the sample under investigation. Once the density of the sample is known, thermal conductivity and heat capacity of the sample can be calculated. Measurement on each sample has been repeated many times. It is found that the variations of output signal (PPE amplitude and phase) between sample mountings are very small (less than 1%).

3. Results and discussion

Thermal diffusivity (α) of each sample is determined from the corresponding PPE signal phase and thermal effusivity (e) from PPE signal amplitude. The variations of α and e with average coordination number Z are shown in Fig. 1.

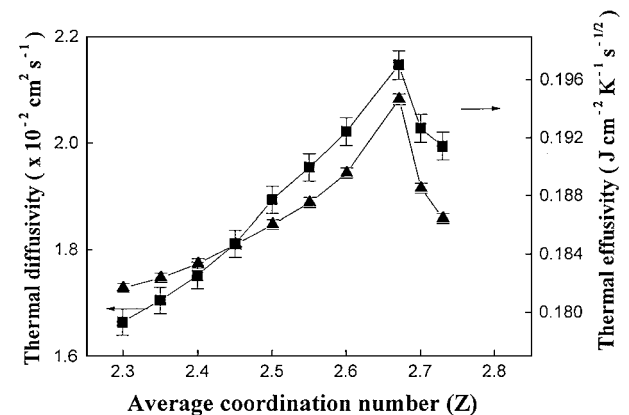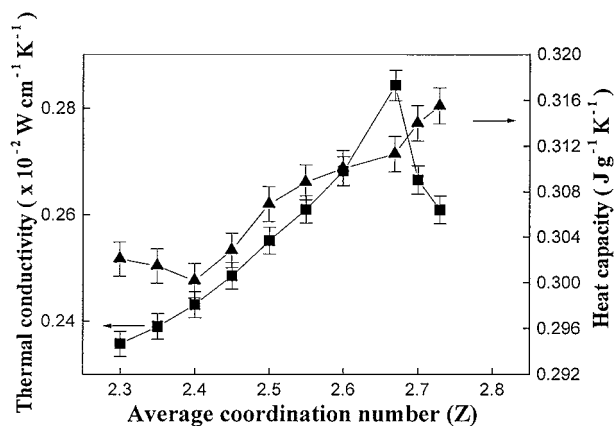*Figure 1* Variation of thermal diffusivity and thermal effusivity of $Ge_x As_{25} Se_{75-x}$ glasses with average coordination number.

Figure 2 Variation of thermal conductivity and heat capacity of $Ge_xAs_{25}Se_{75-x}$ glasses with average coordination number.

Sample mass densities have been determined using the Archimedean principle with liquid paraffin used as the densiometric fluid. Then, thermal conductivity (K) and heat capacity (c_p) of the samples can be determined using the relations,

$$K = e\sqrt{\alpha} \tag{6}$$

$$c_p = \frac{e}{\rho\sqrt{\alpha}} \tag{7}$$

Variations of K and c_p with Z are shown in Fig. 2. From the results presented in Figs 1 and 2, it can be seen that thermal diffusivity and thermal effusivity show threshold maxima around $Z = 2.67$. Thermal conductivity also shows a maximum at $Z = 2.67$, while heat capacity shows a minimum around $Z = 2.4$.

These results are in qualitative agreement with the results reported on the Ge-Sb-Se ternary glass system by U. Senapati *el al*. [19, 20]. These authors have reported thresholds in thermal properties such as minimum in heat capacity at $Z = 2.4$ and maximum in thermal expansion at $Z = 2.67$ in this system.

The occurrence of threshold maxima in α and K values round $Z = 2.67$ can be explained in terms of the changes in network topology and dimensionality of the system. 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, value of Z increases and cross-linking of the Se atom chains occurs. As a result, the flexibility of the network glass gets reduced or the system becomes rigid. 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 defects present in the three-dimensional structure. The fact that the system forms rigid structure at $Z = 2.4$ (Phillips-Thorpe model) accounts for the minimum in heat capacity at this composition.

4. Conclusions

Thermal parameters of the $Ge_xAs_{25}Se_{75-x}$ ($x = 2.5$–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 α and K around $Z = 2.67$ indicate that medium range interactions have an important role in determining the network topology in these glasses.

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