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Photo-thermal deflection and electrical switching studies on Ge–Te–I chalcogenide glasses

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Abstract

Measurements on thermal diffusivity (α) and electrical switching studies have been undertaken on bulk, melt-quenched $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ ($3 \leq x \leq 10$) chalcogenide glasses. The thermal diffusivity values of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses lie in the range $0.09\text{--}0.02 \text{ cm}^2 \text{ s}^{-1}$, and are found to decrease with increase in iodine content. The variation of α with composition has been understood on the basis of fragmentation of the Ge–Te network with the addition of iodine. The composition $x = 5$ ($\bar{r}_c = 2.39$), at which a cusp is seen in the composition dependence of thermal diffusivity, has been identified to be the inverse rigidity percolation threshold of the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system at which the network connectivity is completely lost.

Further, $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses are found to exhibit memory-type electrical switching. At lower iodine concentrations, a decrease is seen in switching voltages with an increase in iodine content, in comparison with the switching voltage of the $\text{Ge}_{22}\text{Te}_{78}$ base glass. The observed initial decrease in the switching voltages with the addition of iodine is due to the decrease in network connectivity. An increase is seen in switching voltages of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses at higher iodine contents, which suggests the domination of the metallicity factor of the additive atoms on the switching voltages at higher iodine proportions. It is also interesting to note that the composition dependence of the threshold voltages shows a slope change at $x = 5$, the inverse rigidity percolation threshold of the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system.

1. Introduction

Chalcogenide glasses have been the subject of a renewed interest in recent times owing to their potential application in phase change memories [1–3], which work on the principle of memory-type electrical switching. The memory switching involves an amorphous–crystalline transition

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(phase change) in the current carrying path due to Joule heating. The thermal diffusivity of a glass plays a major role in the memory switching behaviour, as it decides the rate at which heat can be dissipated away from the conducting crystalline channel. It has been recently pointed out that there is a strong correlation between the thermal diffusivity and the switching behaviour of chalcogenide glasses [4]; glasses with low thermal diffusivity are likely to exhibit memory behaviour and those with higher values of thermal diffusivity may show threshold-type switching. Hence, the measurement of thermal diffusivity of switching glasses is important for identifying suitable materials for phase change memory applications.

Though the phenomenon of electrical switching has been mostly observed in chalcogenide glasses, the chalcogen halide glasses have also been found to exhibit electrical switching. The chalcogen halide glasses are formed by adding halide elements or halide salts to the chalcogens. The addition of halogens to the chalcogens results in a breakup of the three-dimensional amorphous network, and this has a pronounced effect on their electrical and thermal behaviour [5–9].

The present work deals with the thermal diffusivity measurements on $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses ($3 \leq x \leq 10$), using photo-thermal deflection spectroscopy (PDS), which has the highest sensitivity at room temperature in comparison with other thermal wave techniques [10, 11]. Electrical switching studies have also been undertaken on these samples to explore the correlation between thermal diffusivity and switching voltages.

2. Experiment

Bulk $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses ($3 \leq x \leq 10$) were prepared by the traditional melt quenching method. Calculated quantities of high purity (99.8%) Ge, Te and I lumps were used as starting materials. The materials were reacted in evacuated ($\sim 10^{-5}$ Torr) fused quartz ampoules of 5 mm inner diameter and 1 mm wall thickness. The starting materials were slowly taken up to 1223 K, and the melts were homogenized for an extended period (24 h) in a rotating furnace at that temperature. Subsequently, the ampoules were quenched in an ice water + NaOH mixture (1 l:1 g) at a temperature around 270 K. X-ray diffraction and differential scanning calorimetry (DSC) were used to confirm the glassy nature of the samples.

The thermal diffusivity experiments were conducted using a custom-built PDS system (figure 1), with an intensity modulated (using a mechanical chopper) Ar ion laser (10 mW @ 514 nm) as the pump beam. The sample was kept immersed in a CCl_4 liquid medium, contained in a sample cell. Here, CCl_4 was used as the deflection medium, as it absorbs mainly below 250 nm and has a high refractive index change with temperature.

Optical excitation with an intensity modulated light and the subsequent non-radiative recombination process produce a thermal wave in the sample [12], which is propagated into the surrounding CCl_4 medium creating a refractive index variation in it [13, 14]. This refractive index variation causes a deflection in a probe He–Ne laser beam (5 mW @ 632 nm) skimming the surface of the sample, which is detected by a position-sensitive quadrant detector and a lock-in amplifier (figure 1). In the present experiment, the amplitude of the PDS signal was measured as above for different chopping frequencies in the range 0–200 Hz.

The value of thermal diffusivity (α) is determined from the slope of the plot of logarithm of the PDS signal versus the square root of the chopping frequency, knowing the sample thickness l (~ 0.50 mm) and using the relation [13]

$$\alpha = \pi \left(\frac{l}{\text{slope}} \right)^2. \quad (1)$$

Studies on current–voltage characteristics and switching behaviour of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$

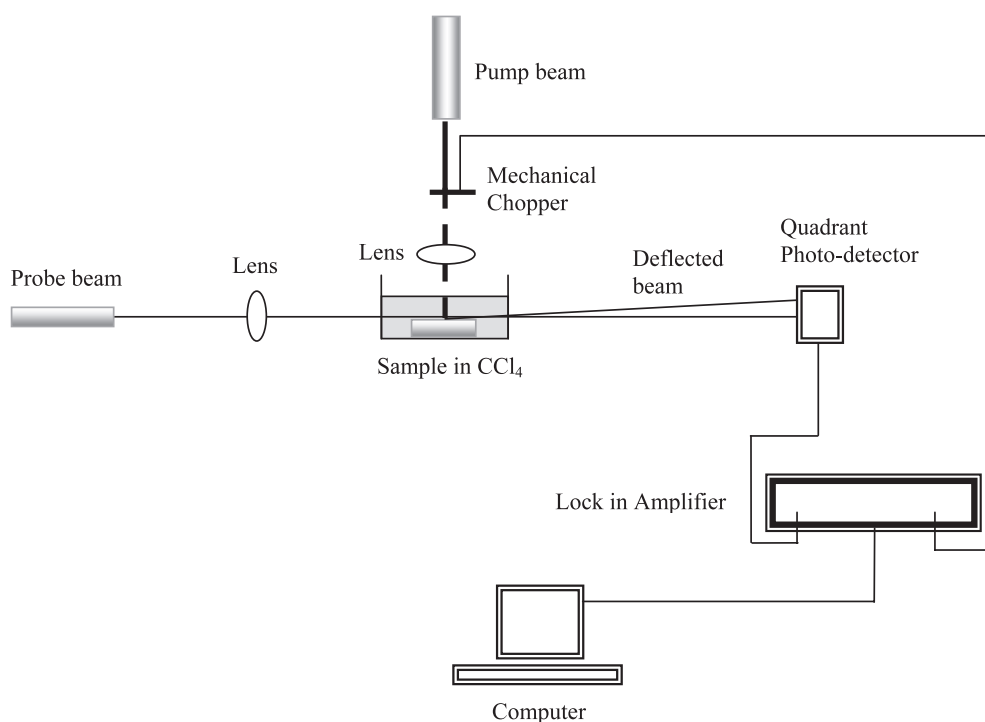


Figure 1. Schematic diagram of the photo-thermal deflection spectroscopy (PDS) setup.

glasses were undertaken by employing an electrical switching analysis system, developed in the laboratory. Here, the sample (~ 0.35 mm thickness) was held between a point contact top electrode and a flat plate bottom electrode, both made of brass. Variable current (0–1 mA) was passed through the sample and the voltage developed across was measured.

3. Results and discussion

Figure 2 shows the plot of the log of the PDS signal amplitude against the square root of the chopping frequency for a representative sample $\text{Ge}_{22}\text{Te}_{74}\text{I}_4$, which is a straight line. The thermal diffusivity (α) of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses determined from the slope of the straight lines (using equation (1)) lie in the range $0.09\text{--}0.02$ $\text{cm}^2 \text{s}^{-1}$, depending on the iodine content. It is interesting to note that the thermal diffusivity of the $\text{Ge}_{22}\text{Te}_{78}$ base glass is around 0.03 $\text{cm}^2 \text{s}^{-1}$ [15].

The variation of thermal diffusivity of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses ($3 \leq x \leq 10$) with composition/average coordination number is shown in figure 3; the average coordination number has been estimated using the coordination numbers of 4 for Ge, 2 for Se and 1 for I, conforming with Mott's ($8 - N$) rule [16, 17].

The connectivity as well as its rigidity of a glassy network is determined by the average coordination number. In the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system, both the network connectivity and rigidity decrease with the addition of iodine, as the average coordination number, \bar{r} , decreases with the addition of iodine. The decrease in α values of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses in the composition range $3 \leq x < 5$ ($2.42 \leq \bar{r} < 2.39$) (figure 3) is associated with a decrease in \bar{r} . It has been found

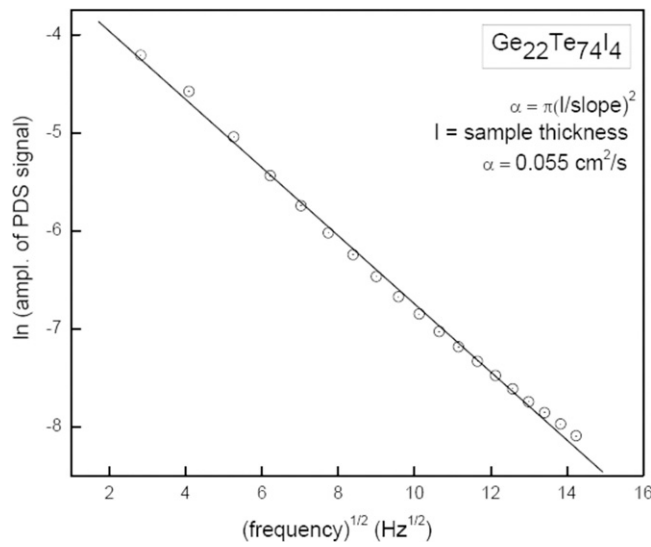


Figure 2. A representative plot of the log of PDS signal amplitude against the square root of the chopping frequency for the sample Ge₂₂Te₇₄I₄.

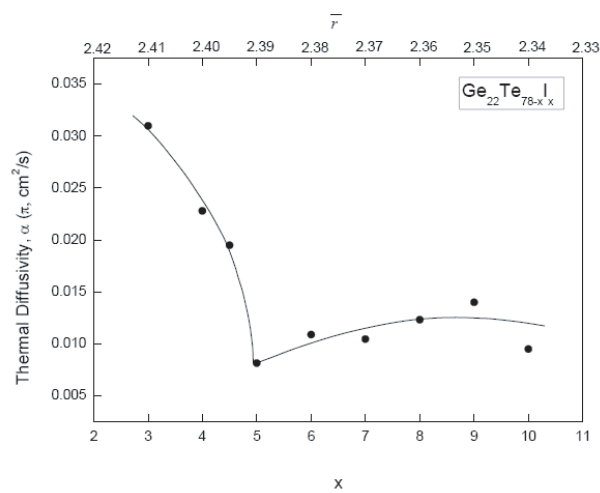


Figure 3. The composition dependence of thermal diffusivity of Ge₂₂Te_{78-x}I_x ($3 \leq x \leq 10$) glasses.

earlier that in several glassy systems such as Ge–Te [15], Si–Te [15], Al–As–Te [4], etc, the thermal diffusivity increases with an increase in \bar{r} , which supports this conjecture.

It can also be seen from figure 3 that the thermal diffusivity of Ge₂₂Te_{78-x}I_x glasses exhibits a cusp around $x = 5$ ($\bar{r}_c = 2.39$) and that there is only a marginal change in thermal diffusivity above this composition. We propose that the effect seen in the composition dependence of thermal diffusivity around 5 atom% of iodine is associated with the inverse rigidity percolation of the system at which the fragmentation of the covalent network takes place. The composition $x = 5$ has been referred to here as an inverse rigidity percolation

threshold, as at this composition the system undergoes a transformation from a rigid amorphous solid to a floppy polymeric glass. On the other hand, at the normal rigidity percolation threshold of a glassy system, the transformation occurs from a floppy polymeric glass to a rigid amorphous solid.

The percolation of network rigidity with an increase in structural cross linking was first proposed by Philips and Thorpe [18, 19]. According to them, a mechanical critical point occurs in covalently bonded networks constrained by bond-stretching (α) and bond-bending (β) forces, when the number of constraints per atom n_c equals the number of degrees of freedom n_d of the network ($n_c = n_d$) [18, 19]. Specifically, it was shown that for covalent networks in which all the atoms chemically bond with coordination numbers r greater than or equal to 2, the number of zero-frequency modes vanishes when the average coordination number \bar{r} equals 2.40 ($\bar{r} = \bar{r}_c = 2.40$). At $\bar{r}_c = 2.40$, the system undergoes a percolative transition from a floppy polymeric glass to a rigid amorphous solid.

Recently, the constraint theory was extended for chalcogenide systems containing one-fold coordinated atoms (OFC atoms) by Boolchand and Thorpe [20–22]. In these systems, the OFC atoms are considered not to contribute to network connectivity and so are percolatively ineffective. For such networks, the condition $n_c = n_d$ is realized when

$$\bar{r}_c = 2.4 - 0.4 \left(\frac{n_1}{n} \right) \quad (2)$$

where $\left(\frac{n_1}{n} \right)$ represents the fraction of OFC atoms in the glassy network. Thus, we find that in systems containing OFC atoms, the rigidity percolation threshold is shifted to lower \bar{r} values, compared to the mean-field estimation of $\bar{r} = 2.4$. For the present $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system of glasses, the percolative transition can be predicted to occur at $\bar{r}_c = 2.373$ ($x = 6.66$).

In $\text{Ge}_x\text{Te}_{100-x}$ glasses, the network connectivity and rigidity increase with the addition of higher-coordinated Ge atoms (at the expense of Te) and it is known that, at the composition $x = 20$ (corresponding to $\bar{r}_c = 2.40$), the system exhibits the rigidity percolation transition [15, 23]. It is therefore obvious that in the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system, the composition of the base glass ($\text{Ge}_{22}\text{Te}_{78}$) is above the rigidity percolation threshold and the glassy network is already over-constrained and rigid. As mentioned earlier, the addition of one-fold coordinated iodine (at the expense of either Ge or Te) reduces the connectivity and network rigidity; the iodine atoms serve to randomly terminate the corner and edge-sharing tetrahedral network of $\text{Ge}(\text{Te}_{1/2})_4$ units prevailing in the base glass. Consequently, the network gets progressively fragmented with the addition of iodine atoms and the difficulty in the propagation of thermal waves with the fragmentation of the glassy network leads to the decrease in thermal diffusivity. Further, the composition $x = 5$ ($\bar{r}_c = 2.39$), at which a cusp is seen in the composition dependence of thermal diffusivity, corresponds to the inverse rigidity percolation threshold of the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system at which the network connectivity is completely lost.

It is interesting to note here that the average coordination number corresponding to the percolation threshold ($\bar{r}_c = 2.39$) in the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system is slightly higher than the theoretical estimate ($\bar{r}_c = 2.373$). The possible reason for the higher value of \bar{r}_c is that not all the iodine atoms enter the network as chain terminators.

It is also interesting to note that $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses exhibit memory-type electrical switching (figure 4). Usually, chalcogenide glasses which have higher thermal diffusivity (α) exhibit threshold-type electrical switching and those which have a lower α show memory behaviour. The comparatively lower thermal diffusivity values of Ge–Te–I glasses is consistent with their memory behaviour.

Figure 5 shows the composition dependence of the switching voltages (V_t) of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses. Generally, the composition dependence of switching voltages of chalcogenide glasses is determined by two important factors, namely the metallicity of the additive and the variation

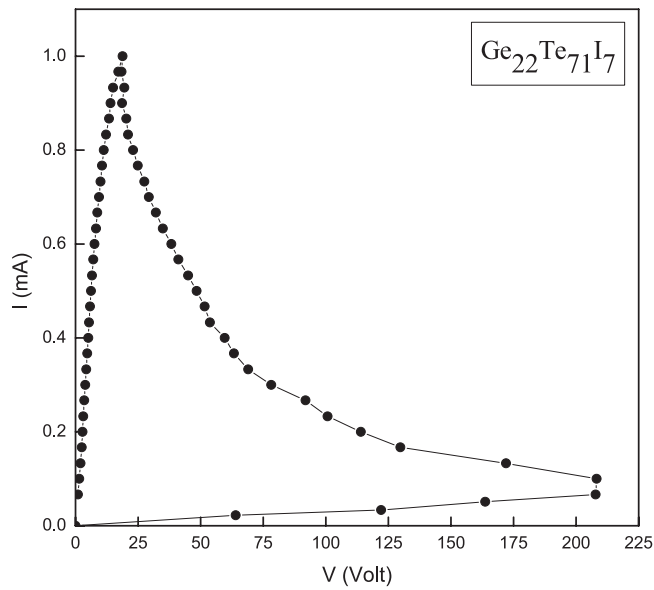


Figure 4. The I - V characteristics of a representative $\text{Ge}_{22}\text{Te}_{71}\text{I}_7$ glass indicating memory switching behaviour.

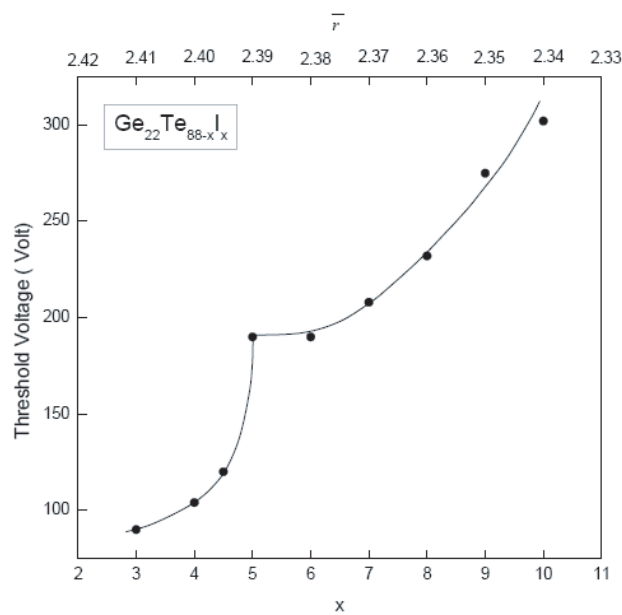


Figure 5. The composition dependence of threshold voltages of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ ($3 \leq x \leq 10$) glasses.

in network connectivity/rigidity. The addition of less-metallic additives and increase in network connectivity/rigidity are known to increase the switching voltages [24].

In the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system, an increase in V_t is expected with the addition of iodine based on the metallicity factor ($\rho_{\text{iodine}} > 10^7 \Omega \text{ m}$ and $\rho_{\text{Te}} \approx 10^{-4} \Omega \text{ m}$). However, on the basis of network connectivity/rigidity, a decrease in V_t is expected with the addition of iodine. The initial decrease in V_t with iodine content (figure 5), in comparison with the $\text{Ge}_{22}\text{Te}_{78}$ base glass [25], indicates that the network factor dominates at lower iodine concentrations. The increase seen in switching voltages of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses at higher iodine concentrations (figure 5) suggests that the influence of the metallicity factor on the switching voltages is stronger than the effect of network connectivity at higher iodine proportions.

Further, the variation with composition of the electrical switching voltages shows a pronounced slope change at $x = 5$, the inverse rigidity percolation threshold, identified based on the thermal diffusivity variations.

4. Conclusions

The composition dependence of thermal diffusivities (α) and electrical switching voltages (V_t) of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ chalcogenide glasses ($3 \leq x \leq 10$) has been studied. It is found that the thermal diffusivity of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses decreases with increase in iodine content, which has been understood on the basis of fragmentation of the Ge-Te network with the addition of iodine. Also, a cusp is seen in the composition dependence of thermal diffusivity at the composition $x = 5$ (average coordination number, $\bar{r} = 2.39$), which has been identified to be the inverse rigidity percolation threshold of the system at which the network connectivity is lost.

Further, $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses are found to exhibit memory-type electrical switching. At lower iodine concentrations, a decrease is seen in switching voltages with an increase in iodine content (in comparison with the $\text{Ge}_{22}\text{Te}_{78}$ base glass), which is due to the decrease in network connectivity. The increase seen in switching voltages of $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ glasses at higher iodine contents suggests that the influence of the metallicity factor on the switching voltages is stronger at higher iodine proportions. It is also interesting to note that the composition dependence of the threshold voltages shows a slope change at $x = 5$, the inverse rigidity percolation threshold of the $\text{Ge}_{22}\text{Te}_{78-x}\text{I}_x$ system.

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