

Thermal diffusivities and molar volumes of ternary $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ alloy glasses: evidence of self-organization

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Abstract

Thermal diffusivities (α) and molar volumes (V_m) of bulk $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ alloy glasses in the composition range $0 \leq x \leq 35$ are examined. The results reveal a broad maximum in α and a broad minimum in V_m in the $15 < x < 25$ range. Earlier temperature modulated differential scanning calorimetric measurements on these glasses have revealed the non-reversing heat flow to show a global minimum (reversibility window) in the same composition range. Taken together these results suggest that present glasses in the $15 < x < 25$ range are self-organized. The thermal diffusivity maximum observed near $x=20$ is consistent with a minimal scattering of thermal waves in the homogeneous and stress-free glass composition residing in the center of the self-organized phase.

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1. Introduction

1.1. Electrical switching in chalcogenide glasses

Electrical switching refers to an abrupt field induced transition in a material from a high resistance OFF state to a low resistance ON state, which can be reversible (threshold type) or irreversible (memory type) [1].

The origin of switching in both memory and threshold switching chalcogenide glasses is the same and is electronic

in nature. The initiation of switching takes place when the charged defect traps are filled by the field injected charge carriers and the lifetime of the charge carriers increases sharply from a low value to a value higher than that required to cross the sample thickness. The samples exhibit memory or threshold behavior subsequently, depending on their nature.

Memory switching is usually seen in chalcogenide glasses, which are more amenable to devitrification. In these samples, the Joule heating, due to the excited current carriers, leads to the formation of a crystalline filamentary conducting path that spans the sample thickness [1–3]. Threshold samples do not exhibit crystallization when they switch [3].

The motivation for this work was to understand the role played by the thermal diffusivity in the switching behavior of $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses which have been found earlier to exhibit a composition dependent change in the switching behavior (memory to threshold) [3]. Further, the effect of network topological thresholds on the composition

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dependence of thermal diffusivity of these glasses has also been studied.

1.2. A photopyroelectric technique to measure thermal diffusivity of solids

Fig. 1 shows the schematic of the photopyroelectric (PPE) method used in the present thermal diffusivity measurements. Here, it is assumed that the optical absorption of the sample is high, so that the intensity modulated light impinging the sample is completely absorbed at the surface. Non-radiative de-excitation of the absorbed optical energy causes thermal waves to be launched into the sample. These are detected at the rear face of the sample using a pyroelectric detector. The thermal diffusion length (μ) is given by Ref. [4]:

$$\mu = \sqrt{\frac{\alpha}{\pi f}} \quad (1)$$

Where α is the thermal diffusivity of the sample and f is the modulation frequency. Eq. (1) indicates that the penetration depth of thermal waves is variable with modulation frequency. At higher frequencies, it may be the case that the diffusion length (μ) is restricted inside the sample thickness (l_s), i.e. $\mu < l_s$. In such a case, the sample is considered to be ‘thermally thick’. At lower frequencies it may be possible that $\mu > l_s$ and the sample is ‘thermally thin’. In a typical experiment, the sample thickness (l_s) and the modulation frequency range may be so chosen that a transition occurs from thermally thick to thermally thin regime at a critical frequency (f_c), when f is progressively reduced from a high to a low value. This transition can easily be observed, as the frequency dependence of the PPE signal voltage is known to be different in the two regimes.

In the present study, PPE experiments have been performed on samples with the set-up described in the following section, measuring the frequency dependent magnitude of the PPE signal. It has been observed that as f was progressively reduced from a high value, there appeared a breakaway from the initial linear dependence, through an oscillatory pattern, into a linear region with a higher slope.

Fig. 2 shows the variation of the magnitude of the PPE signal with frequency for a representative $\text{Al}_{20}\text{As}_{20}\text{Te}_{60}$ sample, indicating the thermally thick and thermally thin

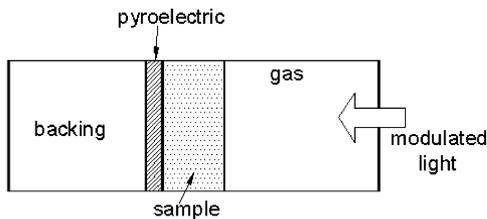


Fig. 1. Schematic of a standard photopyroelectric (PPE) experiment.

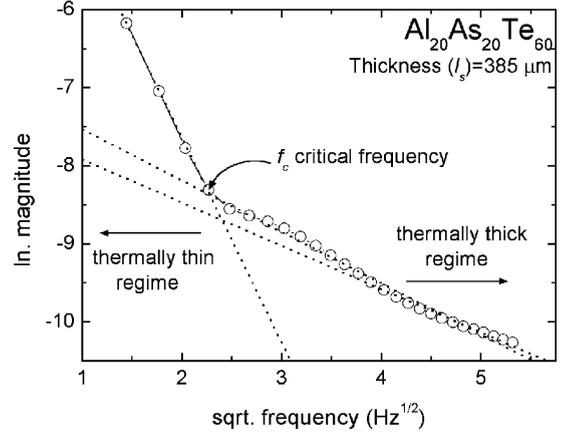


Fig. 2. Logarithm of the PPE amplitude versus square root of the chopping frequency, for a representative $\text{Al}_{20}\text{As}_{20}\text{Te}_{60}$ glass. The critical frequency is identified as the frequency (f_c) at which the slope changes sharply.

regions and the crossover frequency (f_c). Once f_c has been identified as above, the thermal diffusivity α is calculated from Eq. (1).

2. Experimental details

Bulk $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses ($0 \leq x \leq 35$) were prepared by traditional melt quenching. X-ray diffraction and differential scanning calorimetry were used to confirm the glassy nature of the samples. Specimens typically about 5–8 mm in diameter and about 400 μm in thickness were obtained by polishing bulk pieces with emery paper of 800 and 1000 grades. Sample thicknesses were measured using a screw gauge. Samples were cleaned with methyl alcohol and painted with a thin layer ($< 1 \mu\text{m}$) of watercolor based black paint.

Photopyroelectric studies were performed using a lab-made system [5]. The pyroelectric sensor is a 28- μm thick metallized polyvinylidene fluoride (PVDF) film. Samples were mounted on the PVDF sensor with a fine layer of Apiezon-M thermal conducting grease in between to ensure a good thermal contact with slight pressure being brought to bear using a spring-loaded copper wire (250 μm diameter). Care was taken to see that the impinging laser beam was at least 2–3 mm from the tip of the copper wire. The light source was a 5 mW He–Ne laser operating at 632.8 nm; intensity modulation was achieved using a mechanical chopper. The experiments were conducted on a minimum of three specimens for each composition. Every specimen and its mounting including the amount of thermal grease used, was optimized to obtain frequency dependences as seen in Fig. 2, with negligible oscillation as the transition region is traversed. Once the critical frequencies marking the crossover from thermally thick to thermally thin, are

identified experimentally, the thermal diffusivity (α) was estimated from Eq. (1), knowing the sample thickness (l_s).

Measurements of density were undertaken using a Sartorius micro-analytical balance and the density kit accessory; xylene was used as the immersion liquid. Densities were measured for three samples for each composition on specimens that weighed between 25 and 50 mg. From the density (D) and the molecular weight (M), the molar volumes (V_m) were estimated.

Measurements of the DC resistivity of the glasses were also undertaken, by the two-probe technique using thin strips ($2 \times 1 \times 0.2 \text{ mm}^3$) of samples with their parallel surfaces coated with Ag electrodes.

3. Results

The composition dependence of α of $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses is shown in Fig. 3(A). The error bars indicate the scatter obtained in measured values about the average. Thermal diffusivity is seen to increase sharply with increasing arsenic content (x); a subtle slope change is seen in the composition dependence of α around $x=15$ with maximum around 20 at.% of arsenic. A decrease is seen in thermal diffusivity above $x=20$, which continues up to $x=25$. Beyond this, an increase is seen again in the thermal diffusivity.

A plot of the molar volume versus the composition is also shown in Fig. 3(A), which indicates that there is a minimum in molar volume around $x=20$. The variation in glass transition temperature (T_g) of $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses

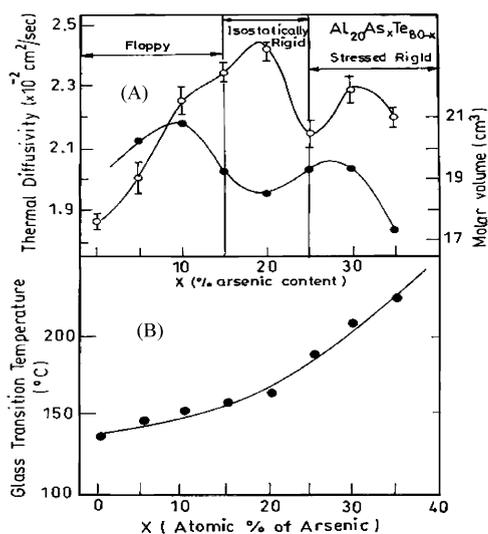


Fig. 3. (A) Composition dependence of thermal diffusivity and molar volume of $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses. The compositions corresponding the onset and completion of rigidity percolation, are shown in the figure. (B) The variation with composition of glass transition temperature of $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses.

with composition is shown in Fig. 3(B), which indicates that the T_g of these glasses increases monotonically with arsenic content. Fig. 4 shows the composition dependence of electrical resistivity (ρ) of the $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$ glasses, indicating that at lower arsenic contents the resistivity is lower compared with that at higher arsenic contents.

4. Discussion

4.1. Thermal diffusivity, electrical resistivity and electrical switching

Under the influence of a high electric field in electrical switching studies, [3,6] the current carried between the electrodes in glass specimens with lower arsenic proportions is high, since the resistivity at these compositions is low (Fig. 4). The Joule (I^2R) heating will thus be higher. Also, at lower arsenic contents, the samples exhibit lower thermal diffusivity (α). This implies higher impedance to the flow of the diffusing thermal waves; the rate at which heat is dissipated within the glass, away from the current carrying channel is low. A consequence of these two effects is to cause a rise in temperature sufficiently high to trigger the phase transformation, which causes memory switching.

With increasing arsenic content, there is a progressive replacement of the weaker Te-Te bonds with stronger As-Te and As-As bonds, leading to an increase in resistivity. The situation with regard to switching is now reversed. Higher resistivity implies a lower current, and a lower I^2R heating. In conjunction with the higher thermal diffusivity α , this may preclude a high enough temperature rise in the current carrying region to cause a structural phase transformation. In this case, an irreversible switching does not occur and threshold behavior is seen.

Qualitatively thus, in conjunction with electrical resistivity trends, the thermal diffusivity values obtained in the present study, can be correlated with the nature of switching in these glasses.

4.2. The extrema at specific compositions

The most interesting outcome of the present experiments is the specific features seen in the composition dependence of thermal diffusivity and molar volumes, at compositions $x=15, 20, 25$. We attribute these effects to the network topological thresholds in the glassy system.

The rigidity percolation threshold (RPT), also known as the stiffness/mechanical threshold, deals with the structural rigidity of the glassy network. In chalcogenide glasses, the structural rigidity increases with the addition of higher coordinated atoms and at a critical composition, known as the RPT, the material undergoes a transition from a floppy polymeric glass to a rigid amorphous solid [7,8].

It has been recently pointed out that in certain glassy systems, the rigidity percolation may span over a range of

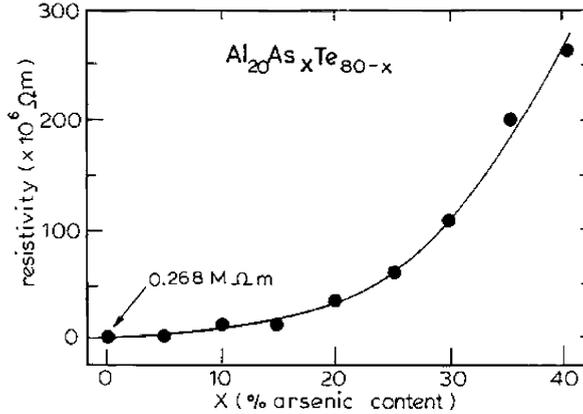


Fig. 4. Composition dependence of electrical resistivity of $Al_{20}As_xTe_{80-x}$ glasses.

compositions. These systems are characterized by three different phases namely, the floppy, the intermediate and the rigid phases. There are two distinct transitions in such glasses, namely from the floppy to isostatically rigid state and from the isostatically rigid to the stressed rigid state [9]. Glass compositions residing between the floppy and the stressed rigid phases constitute the intermediate phase, forming space-filling networks with lower molar volumes [9]. The presence of an intermediate phase in certain chalcogenide glassy systems has first been seen in modulated differential scanning calorimetric (MDSC) studies; the intermediate phase is characterized by a vanishing of non-reversing heat flow, which suggests it is configurationally closer to its liquid counterpart and can be considered to be self-organized [9].

The recent MDSC investigations by Cai et al. [10], reveal that in $Al_{20}As_xTe_{80-x}$ glasses there exists a thermally reversing window in the composition range $15 < x < 25$ with the compositions $x=15, 25$ corresponding to the onset and completion of an extended rigidity percolation and the composition $x=20$ being the centroid of the thermally reversing window. Glasses in the composition range $15 < x < 25$ correspond to the intermediate phase.

The present thermal diffusivity and density measurements provide a supporting evidence for the existence of a self-organized intermediate phase in $Al_{20}As_xTe_{80-x}$ glasses, in the composition range $15 < x < 25$, suggested by Cai et al. [10]; specific signatures are seen in the composition dependence of thermal diffusivity at compositions $x=15, 25$ and a maximum is observed in α at $x=20$. The maximum in thermal diffusivity around $x=20$ is consistent with the idea of the self-organized intermediate phase, as around this composition the glassy network is homogeneous and stress free and the scattering of the thermal waves is minimal. Further, the minimum is seen in the molar volume of these glasses around $x=20$, also supports the idea of space filling self-organized networks.

In this context it is interesting to look at the variation of glass transition temperature with composition shown in Fig.

3(B). The monotonic increase in T_g with composition is suggestive of a smooth increase in global connectivity with arsenic content and none of the observed anomalies in thermal diffusivity or molar volume can be related to nanoscale phase separation in $Al_{20}As_xTe_{80-x}$ glasses.

5. Conclusions

The thermal diffusivity (α) and the molar volume (V_m) measurements on $Al_{20}As_xTe_{80-x}$ ($0 \leq x \leq 35$) glasses provide an evidence for the existence of a self-organized intermediate phase in $Al_{20}As_xTe_{80-x}$ glasses in the composition range $15 < x < 25$. The maximum seen in thermal diffusivity around $x=20$ (the centroid composition) indicates that the glassy network is homogeneous and stress free and the scattering of the thermal waves is minimal. The present studies also reveal that there is a qualitative correlation between the thermal diffusivity and the nature of switching exhibited by these glasses.

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