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Ga as an additive in the As_2Te_3 glass

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Results of measurements of the mean atomic volume (V), the glass transition temperature (T_g), the activation energy for glass transition (E_t) and the d. c. electrical conductivity (σ) are reported and discussed for ten glass compositions of the Ga–As–Te system. The glasses studied can be represented as $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, with the additive Ga ranging from 0 to 12 atomic percent (at.%) in the parent As_2Te_3 glass. In the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, changes in slope are observed in the V, T_g, E_t, σ and other electronic properties, at the composition with a Ga content of 2 at.%. The results are compared with those obtained on introduction of Ag and Cu to the As_2Te_3 and the [$0.5As_2Te_3$–$0.5As_2Se_3$] glasses. Analysis of the data suggest formation of GaAs, Ga_2Te_3 and excess Te structural units (s.u.) in lieu of some of the original As_2Te_3 s.u., for addition of Ga up to 2 at.% to the parent As_2Te_3 glass; for higher Ga contents, formation of GaAs, GaTe and excess Te s.u. are indicated.

1. Introduction

Initial work on the effect of metallic 'additives' to chalcogenide glasses were somewhat confined to studies on the role of several metals in affecting σ of the As_2Se_3 glass [1–6]. In general, the additive in a multicomponent glass can affect its spatial, structural, chemical and electronic properties. Therefore, their effect can also be probed by a careful characterisation and analysis of properties such as V, T_g, E_t, σ, and the activation energy for electrical conductivity (ΔE).

With this in view, the role of Ag and Cu as additives in modifying the V, T_g, E_t, σ and ΔE of the As_2Te_3 and the [$0.5As_2Te_3$–$0.5As_2Se_3$] glasses were investigated, and the results of these studies are reported in our earlier communications [7–13]. The effects of addition of Cu to the [$0.5GeSe_2$–$0.5As_2Se_3$] glass were also studied [14]. In the variations of V, T_g, E_t and other electronic properties with composition, changes in slopes were observed at compositions containing ∼1 to ∼3 at.% (depending on the system and the additive) of the metallic additive. The σ of glasses up to incorporation of ∼3 at.% of the metallic additive, were lower than that of the parent glass, with their ΔE being close to that of the parent glass; the σ of glasses with higher metallic contents were higher than that of the parent glass [8, 10, 11].

The following conclusions were arrived at [7–10, 13] from the analysis of these results. (i) in small concentrations (generally ∼1 to ∼3 at.%), the metal atoms do not drastically alter the structure of the parent glass, as they do not modify either the medium range or the short range ordering of the parent glass (ii) assuming a uniform distribution of the metallic additive in the matrix of the parent glass, the distance between the clusters of metallic atoms turns out to be greater than the range for medium range ordering (which is typically ∼1.6 to 1.8 nm for chalcogenide glasses) for additive concentrations of ∼3 at.% (iii) for higher concentrations, the metallic atoms affect the medium and short range ordering of the parent glass by forming bonds with the elements of the parent glass (iv) the properties of the resulting glasses can be explained by assuming formation of various s.u. of the metal with the elements of the parent glass (e.g. formation of Ag_2Te s.u. in the Ag–As–Te system, of Cu_2Te s.u. in the Cu–As–Te system, of $CuAsSe_2$ and the CuAsTe s.u. in the Cu–As–Se–Te system, and of Ag_2Te and Ag_3AsSe_3 s.u. in the Ag–As–Se–Te system) (v) the studies also indicated the necessity of generating the corresponding E_t-composition data, for inferring the true T_g-composition dependencies in many systems.

As a continuation of the work of this nature, the role of Ga as an additive in the As_2Te_3 glass was investigated in the present study. In terms of the at.% proportions of the elements, the compositions studied (Table I) can be represented as $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, with each glass identified in terms of x, its Ga content in at.%.

2. Experimental

The standard melt–quenching method was adopted to synthesise the glasses; appropriate at.% quantities (2 to 3 g total per batch) of high purity (99.999%) elements (Ga and As from Johnson Matthey, UK and Te from Atomergic Chemmetals, USA) were weighed into 12 mm diameter fused silica ampoules, which were then sealed under a pressure of 10^{-5} Torr. The ampoules were first heated gradually to 900°C and were continuously rotated along their axis during melting (for homogenisation). After an hour, the ampoule temperature was reduced to 800°C and maintained under continuous rotation for about eight to ten hours. The melt temperature was then reduced to ∼450°C and the ampoule with the viscous melt dropped in ice cooled water. This procedure was found to yield bright, shiny and pore free

TABLE I Data on d, V, T_g, E_t (kcal/mole), σ ($\text{ohm}^{-1}\text{cm}^{-1}$), ΔE and C ($\text{ohm}^{-1}\text{cm}^{-1}$) of $\text{Ga}_x(\text{As}_{0.4}\text{Te}_{0.6})_{100-x}$ glasses

x	d (gcm^{-3})	V (cc)	T_g (K), at various heating rates in (K/min)					E_t	$-\log\sigma$ at various temperatures (K)			ΔE (eV)	$\log C$
			2.5	5	10	20	40		180	200	220		
0	5.535	19.247	377.0	381.5	386.5	391.0	396.0	41.5	7.93	6.90	6.00	0.40	3.00
0.3	5.537	19.220	380.5	384.0	387.9	392.0	396.3	50.8	7.40	6.57	5.83	0.32	1.51
0.6	5.538	19.196	382.2	385.6	389.0	392.7	396.6	55.4	6.97	6.23	5.53	0.28	0.84
1	5.537	19.173	383.2	386.4	389.5	393.5	396.9	59.0	6.67	6.00	5.36	0.26	0.57
2	5.525	19.148	386.1	389.8	391.9	395.2	398.3	60.8	6.37	5.77	5.17	0.24	0.32
3.5	5.526	19.045	389.7	394.0	396.5	400.5	403.0	61.3	6.40	5.80	5.20	0.23	0.28
5	5.526	18.945	394.1	397.7	401.3	404.5	407.5	61.5	6.37	5.75	5.20	0.23	0.29
7.5	5.508	18.840	400.8	404.3	407.7	411.0	414.5	61.4	6.40	5.80	5.30	0.24	0.30
10	5.485	18.751	–	–	–	–	–	–	6.38	5.78	5.25	0.24	0.29
12	5.453	18.726	414.1	417.8	422.0	425.8	429.0	61.6	6.40	5.85	5.30	0.24	0.29

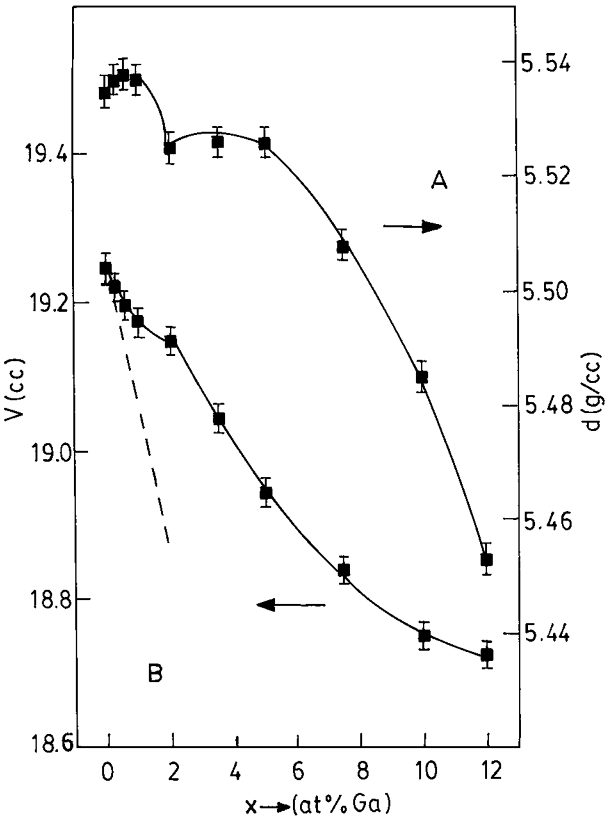

Figure 1 (A) Experimental d vs. x data and (B) Experimental V vs. x data for the $\text{Ga}_x(\text{As}_{0.4}\text{Te}_{0.6})_{100-x}$ glasses. The broken line is the V evaluated assuming interlayer occupancy for Ga up to 2 at.% (see text for details). The curves are drawn as a guide to the eye.

glasses. Samples, whose glassy state were confirmed from their x-ray powder diffractograms, were used in the measurements.

As already described in detail [7, 9, 10, 13, 15], the densities were measured by pyknometry (with deionised water as the immersion fluid), using an analytical balance (Sartorius, model A 200S). Care was exercised to prevent the formation of air bubbles around the samples which can affect the accuracy of the measured densities. Densities, listed in Table I, measured to an accuracy of better than 0.04%, are typical values for the various compositions. Scatters in the density values ranged from 0.1% to 0.2% for any specified composition, as inferred from the data on multiple (three or four) batch preparations of several compositions. These scatters are indicated in the density and V data of Fig. 1.

The T_g's of the glasses were measured using a differential scanning calorimeter (Perkin Elmer DSC7). Typically, ~30 mg of the powdered glass, crimped in the standard aluminium pan was used in the measurement. An empty crimped aluminium pan was used as the reference specimen and high purity dry nitrogen was used as the purge gas. Samples were annealed *in situ* by holding them for 15 minutes at a temperature of about 5°C higher than the corresponding T_g and then cooling them to room temperature. The annealed samples were used in the determination of T_g at various heating rates. Other details pertaining to the measurement and identification of T_g, the precautions taken and the method of estimating the E_t (from the slopes of the linear $\log T_g^2/\alpha$ vs. $1/T_g$ data, where α is the heating rate adopted to measure T_g) are already outlined in detail [7, 9, 10, 12, 13] and are therefore not elaborated here. In the present study, the T_g's of the various compositions were measured at five heating rates from 2.5 K to 40 K/min. For a specified composition and heating rate, differences of 0.5 K in T_g were observed from measurements on three or four samples. Specified compositions from three or four parallel batch preparations indicated a scatter of ~1 K in the T_g values at any given heating rate. The scatters in the T_g and the E_t data are indicated in the respective figures.

As in our earlier measurements [8, 10, 11, 16], the samples for the σ measurements were flat, typically 0.8 to 1.2 mm in thick, with the opposite surfaces rendered parallel to within 0.002 cm. The contacts from the sample to the electrodes were effected through silver paste. A chromel–alumel thermocouple situated close to the sample was used to register the temperature. Low temperature (140 to 300 K) measurements were performed in a cryostat using liquid nitrogen under reduced pressure as the refrigerant; to prevent condensation of moisture on the sample at these temperatures, the sample chamber was evacuated during the low temperature runs. High temperature (300 to 400 K) runs were performed by introducing the sample holder into an appropriate tubular furnace. A d. c. voltage of 5 volts was applied to the sample and the current through the sample measured using an appropriate picoammeter (Keithley, model 410A) for measurements at low temperatures; for temperatures above 250 K, the current through the sample was evaluated from the voltage drop across a precision 1 Ω resistor in series with the sample.

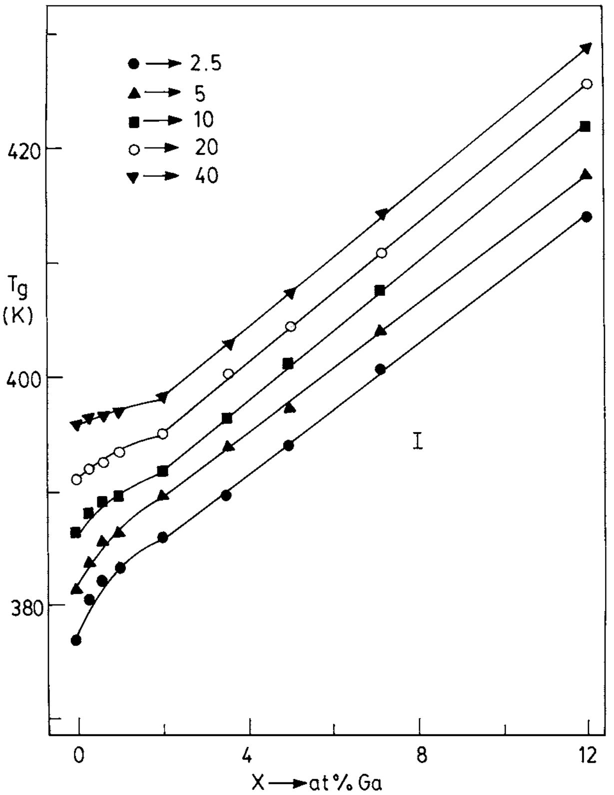

Figure 2 T_g vs. x data for the $\mathrm{Ga}_x(\mathrm{As}_{0.4}\mathrm{Te}_{0.6})_{100-x}$ glasses at heating rates of 2.5 (●), 5 (▲), 10 (■), 20 (○) and 40 (▼) K/min. The lines are drawn as a guide to the eyes.

3. Results

Figs 1 to 8 and Table I summarise the results of the present study. The density values obtained for the compositions with $x = 5$ and $x = 10$ (Table I), compare well with the reported values of 5.53 and 5.48 gcm^{-3} respectively [17] for these compositions. A kink is observed at $x = 2$ in the density–x data of the $\mathrm{Ga}_x(\mathrm{As}_{0.4}\mathrm{Te}_{0.6})_{100-x}$ glasses (Fig. 1a). This feature is also reflected in the V–x data (Fig. 1b) of these glasses; though the kink at $x = 2$ in the V–x data is small, the conclusion about its presence at $x = 2$ is strengthened by the observation that several other properties such as d, T_g, E_t, σ, ΔE (discussed later) also show clear changes in slope at $x = 2$.

In the T_g–x data of these glasses (Fig. 2), a kink or a change in slope is observed at $x = 2$; this effect is more pronounced at higher heating rates. For the composition with $x = 10$, the V and the σ data (up to 375 K) have been displayed in Figs 1 and 7, but the T_g of this composition is not depicted in Fig. 2, as this composition was found to undergo a thermally induced microphase separation when heated beyond 380 K. Figs 3 and 4 display the linear log (T_g^2/α) vs. $(1/T_g)$ data of these glasses, which were used to estimate the E_t of the glasses. The E_t of these glasses (Fig. 5) shows a sharp increase with x for x from 0 to 2 and then levels off at higher x values.

The absence of any time dependent effects in the σ values of these samples indicates that the conduction is essentially electronic in nature. The observed linearity of the $\log\sigma$ vs. $1/T$ data, shown in Figs 6 and 7 (for the temperature range from 140 K to 370 K), indicate that the σ follows the standard dependence, namely,

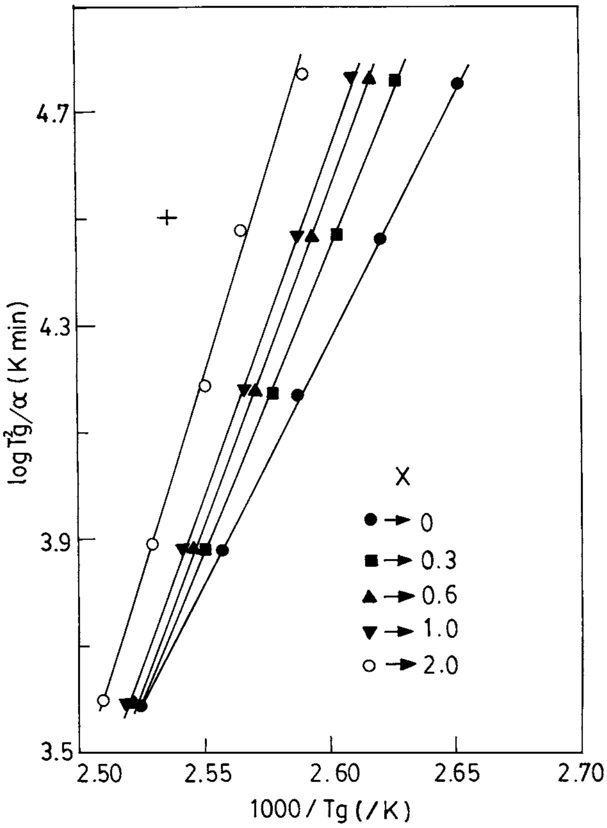

Figure 3 log (T_g^2/α) vs. $(1000/T_g)$ data for the $\mathrm{Ga}_x(\mathrm{As}_{0.4}\mathrm{Te}_{0.6})_{100-x}$ glasses with $x = 0$ (●), 0.3 (■), 0.6 (▲), 1 (▼) and 2 (○). The + symbol indicates the error bars in the ordinate and abscissa values.

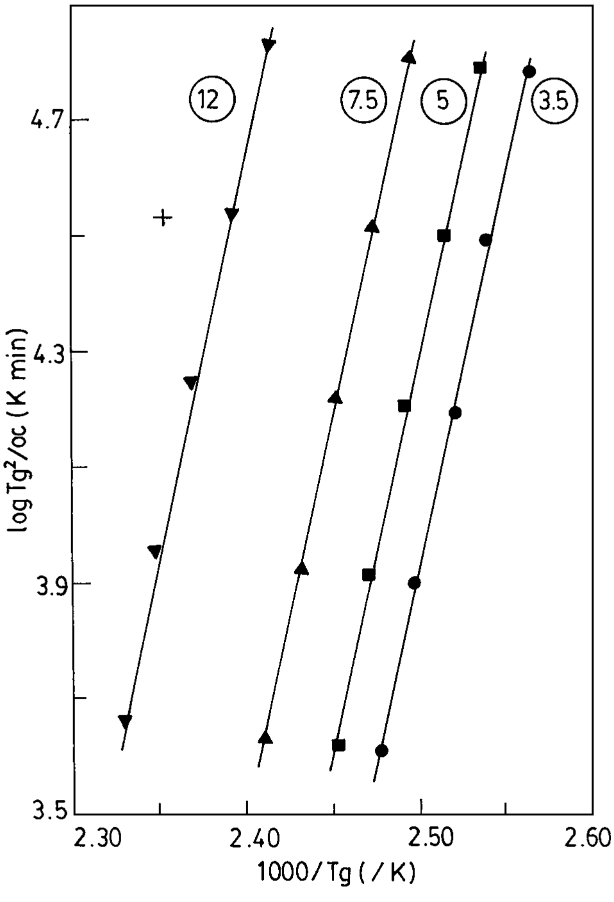

Figure 4 log (T_g^2/α) vs. $(1000/T_g)$ data for the $\mathrm{Ga}_x(\mathrm{As}_{0.4}\mathrm{Te}_{0.6})_{100-x}$ glasses with $x = 3.5$ (●), 5 (■), 7.5 (▲), and 12 (▼). The + symbol indicates the error bars in the ordinate and abscissa values.

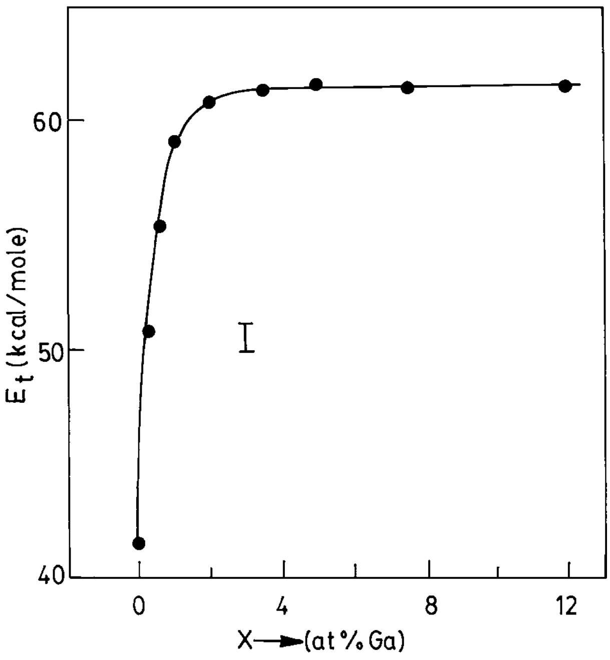

Figure 5 E_t vs. x data for the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses.

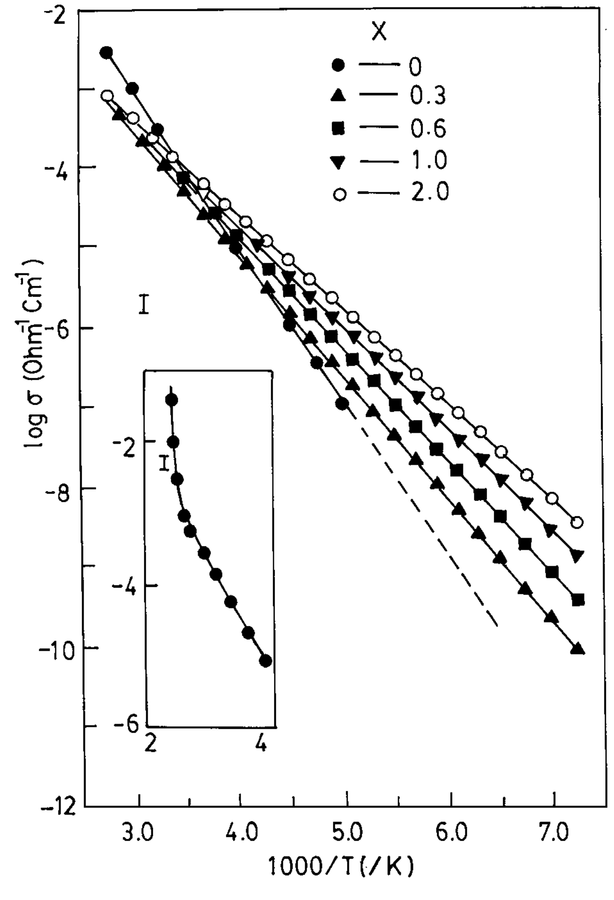

Figure 6 $\log \sigma$ vs. $1/T$ data for the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses with x values of 0 (●), 0.3 (▲), 0.6 (■), 1 (▼) and 2 (○). The data for the composition with $x = 0$ is from reference [2]. The inset shows the data for the composition with $x = 0.3$ for $T > 250$ K.

$\sigma = C \exp(-\Delta E/kT)$; here C is the pre exponential factor. For temperatures higher than ~380 K, a steep increase in σ is observed (as shown in the insets of the Figs 6 and 7 for two samples) even though the temperature as registered by the thermocouple (which is in the vicinity of the sample) is lower than the T_g of these glasses. This is due to a local self heating effect of these

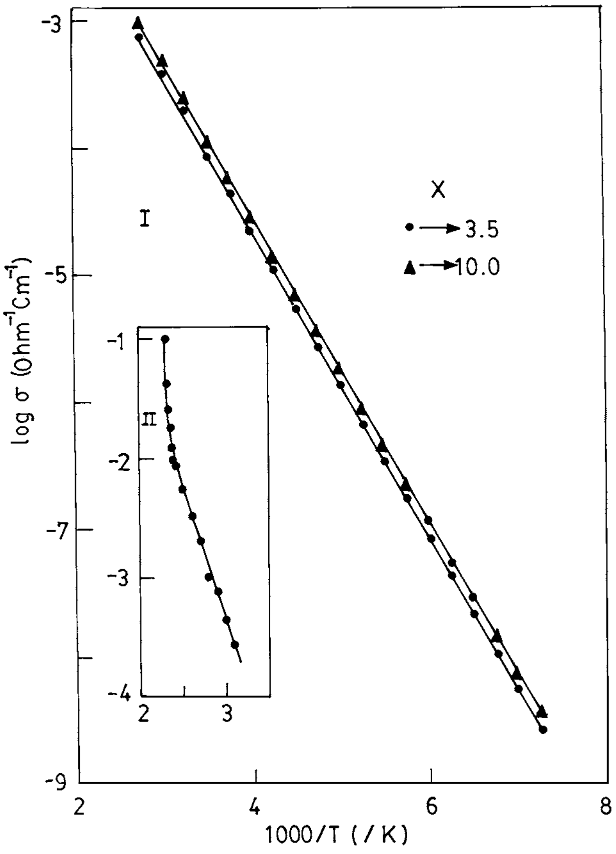

Figure 7 $\log \sigma$ vs. $1/T$ data for the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses with x values of 3.5 (●) and 10 (▲). The data for the compositions with x of 5, 7.5 and 12 lie in the narrow range between the data for $x = 3.5$ and 10 and have therefore not been depicted in the Figure. The inset shows the data for the composition with $x = 3.5$ for $T > 330$ K

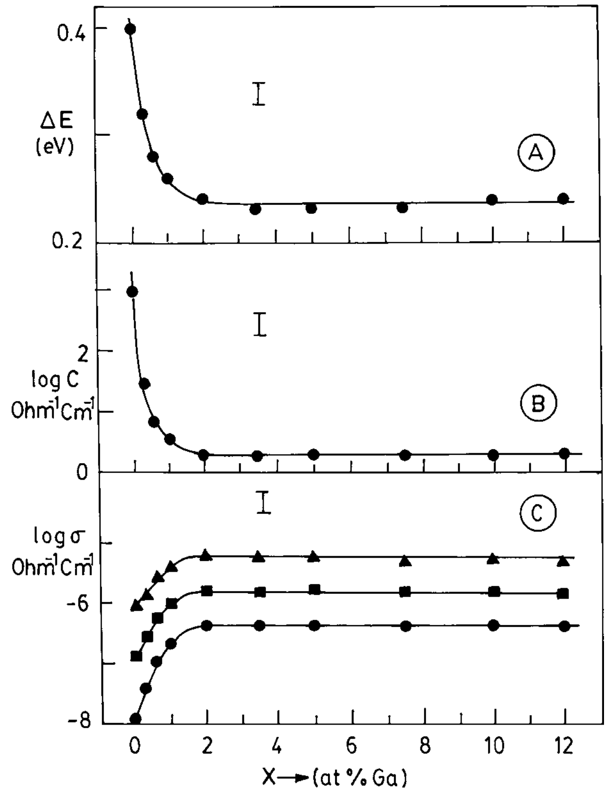

Figure 8 Variation of (A) ΔE, (B) $\log C$ and (C) $\log \sigma$ [at 180 K (●), 200 K (■), and 220 K (▲)] with Ga content for $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses.

samples (see appendix) under the experimental conditions used. The high temperature data for only two of the compositions are depicted in the insets of Figs 6 and 7; the high temperature data for other compositions are similar to these data.

Fig. 8 depicts the variations of ΔE, C and σ of these glasses with x. These properties also exhibit changes in slopes at the composition with $x = 2$. Though the values of C obtained by extrapolating the $\log \sigma$ versus $1/T$ data to $1/T = 0$ are not considered very accurate, this method is widely adopted to infer the composition dependence of C, rather than its absolute value.

4. Discussion

The results are first qualitatively discussed using some conclusions regarding (i) the general structure of chalcogenide glasses [18–23] and (ii) the features observed on addition of metallic additives to other chalcogenide glasses [7–13].

It is known [18–23] that chalcogenide glasses [including ($As_{0.4}Se_{0.6}$), ($As_{0.4}S_{0.6}$), [$As_{0.4}(Se,Te)_{0.6}$], ($As_{0.4}Te_{0.6}$) etc.,] generally have a corrugated layer structure, with finite layer thickness. The short range ordering in these materials corresponds to the formation of the respective s.u. and their interconnection; the interconnection extends along a layer, the interlayer separation being typically ~0.4 to ~0.5 nm. The s.u. generally correspond to those of the stable chemical compounds of the system. The medium range ordering (also called the intermediate range ordering) in these glasses extends to four or five correlated layers, i.e. ~1.6 to ~1.8 nm.

A cursory look at the data of the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses indicates that they are similar to those of the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$, and $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses [7–11, 13, 14], in the sense that, the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses also exhibit changes in slope in the property–composition data, at an x value between ~1 and ~3. However, a closer examination of the data, indicate the differences [(i) to (iii)] discussed below, for low concentrations of the metallic additive.

(i) In the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$, and $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, T_g is either constant (as in the $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$, glasses) or T_g shows an apparent decrease [as in the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$ and $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses)], as x changes from 0 to ~3; for higher x values, T_g increases with increasing x. In the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses however, an increase of T_g with increasing x is observed not only for $x \geq 2$, but also for x values between 0 and 2 (Fig. 2). The E_t–x data of the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses (Fig. 5) are similar to those obtained [7, 13] for the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$ and $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses. The decrease of T_g with x for x up to 2 at.% in the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$ and $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses was found to be only apparent [7, 13] and an artefact of the steep increase in E_t with x of these glasses over the same range of x from 0 to 2 at.%; in these systems, the true T_g values are invariant with x for x up to 2 at.%. In the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, an increase of T_g with x (for x from 0 to 2) occurs even though the corresponding E_t has also registered a steep increase with x for x from 0 to 2. This indicates that the observed increase of T_g with x in the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses is a true increase, and not an artefact of the E_t–x dependence of these glasses.

(ii) In the $Cu_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, for additions of Cu up to 3 at.%, Cu atoms occupy interlayer positions between the uncorrelated layers in the layered network of the parent ($As_{0.4}Te_{0.6}$) glass [10]; due to this, the V values evaluated as $V = mV_{As_{0.4}Te_{0.6}}$, [where m is the mole fraction of ($As_{0.4}Te_{0.6}$) type s.u. in the various compositions] agree well [10] with the experimental data. In the $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ and $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses also, for x up to 1 (or 2), the clusters of Cu (or Ag) atoms occupy interlayer positions between the uncorrelated layers in the matrix of the parent $As_{0.4}Se_{0.3}Te_{0.3}$ glass [9, 13]. The V of these glasses, evaluated as $V = nV_{As_{0.4}Se_{0.3}Te_{0.3}}$, [where n is the mole fraction of the ($As_{0.4}Se_{0.3}Te_{0.3}$) type s.u. in the various compositions], give values close to the experimental data [9, 13]. On the other hand, the V of the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$, glasses, calculated as, $V = mV_{As_{0.4}Te_{0.6}}$ [assuming interlayer occupancy of Ga up to 2 at.% in the matrix of the parent ($As_{0.4}Te_{0.6}$) glass], give V values [Fig. 1b, broken line] which are in disagreement with the experimental data.

(iii) In the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, and $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, the σ of glasses for $x \leq \sim 3$ are lower than that of the corresponding parent glass and their ΔE values are not very different from that of the parent glass [8, 10, 11]. In the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses however, the σ of glasses (up to 250 K) for x from 0.3 to 2, are higher than that of the parent glass (Fig. 6); further, their ΔE and C values show a steep decrease as x changes from 0 to 2 (Fig. 8).

In the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$, $Ag_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, up to ~3 at.%, clusters of Ag (or Cu) atoms are located beyond the range of the medium and short range ordering of the parent glass [7, 9, 10, 13]. They, therefore do not alter the interlayer attractive or repulsive forces and therefore the T_g of glasses with up to ~3 at.% of the metallic additive (Ag or Cu), are the same as that of the parent glass [7, 9, 10, 13]. Up to this stage, the clusters of Ag or Cu atoms occupy interlayer positions between the uncorrelated layers (i.e. the layers which are beyond the purview of medium range ordering) of the parent glass network, as inferred from the V–x and T_g–x data of these glasses [7, 9, 10, 13]. The σ measurements indicate that, up to this stage, clusters of Ag or Cu atoms act as neutral scattering centres in these materials, thereby resulting in a small decrease of the σ of these glasses compared to that of the parent glass [8, 10, 11]. These conclusions indicated the existence of a weak, but important force operative beyond the correlation length of medium range ordering in these materials [7, 9, 10, 13, 24].

On the other hand, the presently observed increase of T_g on addition of Ga from 0.3 up to 2 at.% to the As_2Te_3 glass indicates an increase in the interlayer attractive forces between the correlated layers, which come within the purview of the medium range and short range ordering in these glasses. This indicates formation of bonds between Ga and the elements of the parent glass, namely As and Te, even for low Ga contents of ~0.3 at.% or higher. Also, (a) the disagreement of the V calculated assuming interlayer occupancy for Ga up to 2 at.% in the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$, with the experimental values and (b) the observed increase of σ (and the decrease of C and ΔE) on addition of up to 2 at.% of Ga (Fig. 8), in contrast to the decrease in σ observed [8, 10, 11] for low additive concentrations in the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}Te_{0.6})_{100-x}$, and $Cu_x(As_{0.4}Se_{0.3}Te_{0.3})_{100-x}$ glasses, further strengthen the conclusion (arrived at from their T_g–x data) that Ga forms bonds with As and Te even for low Ga concentrations and alters perceptibly the structural arrangement of the parent glass even for additions of ~0.3 at.% Ga or higher. The reason as to why Ga behaves differently from those of Ag or Cu in the As_2Te_3 glass is not clear at present, though it is interesting to note that Ga forms compounds both with As and Te, while Ag and Cu form compounds only with Te and not with As.

From the aforesaid considerations, it can be concluded that in the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, Ga forms bonds with As and Te atoms which are within the correlated layers of the parent glass for $Ga \geq 0.3$ at.%. Further, the changes in slope observed at $x = 2$ in the various property–composition data (Figs 1, 2, 5, 8), indicate a change in the type of structural units for compositions with $x < 2$ compared to those present for compositions with $x \geq 2$.

For any further discussion of the results, structural data on Ga–As–Te glasses are needed and this data is not yet available. However, using the following results (a) to (c) on these materials, a plausible structural model has been attempted here to understand the experimental features. (a) It is known that no ternary compound is formed in the Ga–As–Te system [17]. (b) Ga forms one compound, GaAs, (of density 5.31 gcm^{-3} [25]) with As and two compounds GaTe and Ga_2Te_3 (with densities of 5.44 and 5.57 gcm^{-3} [25] respectively) with Te. (c) The bond energies of the Ga–As and the Ga–Te bonds (evaluated as per reference [26], using the homopolar bond energies and electro negativities of As, Ga and Te) are respectively equal to 53.71 and 42.36 kcal/mole.

Corresponding to the compounds of Ga with As and Te, formation of s.u. of GaAs, GaTe and Ga_2Te_3 are considered in addition to the parent As_2Te_3 s.u. in the various glass compositions of the Ga–As–Te system. In one of the methods (say, model I), with progressive increase in the Ga content, formation of GaAs, Ga_2Te_3 and excess Te s.u. are considered in lieu of some of the original As_2Te_3 structural units of the parent glass. In any composition, the ratio of the GaAs and GaTe bonds formed is taken to be in the ratio 1.268 of their bond energies. Thus, one has

$$\begin{aligned} Ga_x(As_{0.4}Te_{0.6})_{100-x}\text{---}\rightarrow\ &(0.5591x)\mathrm{GaAs} \\ &+(0.2205x)Ga_2Te_3+(20-0.4795x)As_2Te_3 \\ &+(0.1772x)\mathrm{Te}, \\ =\ &(0.5591x)\mathrm{A}+(0.2205x)\mathrm{B}+(20-0.4795x)\mathrm{C} \\ &+(0.1772x)\mathrm{D}, \end{aligned}$$

where A, B, C and D correspond respectively to the GaAs, Ga_2Te_3, As_2Te_3 and Te s.u. The corresponding V is given as

$$\begin{aligned} V = (1/M)[&(0.5591x)V_\mathrm{A}+(0.2205x)V_\mathrm{B} \\ &+(20-0.4795x)V_\mathrm{C}+(0.1772x)V_\mathrm{D} \rightarrow \text{(I)} \end{aligned}$$

here, $M = (20 + 0.4773x)$ and V_A to V_D are the volumes of the s.u. A to D. In another method of calculation (model II), with progressive increase of Ga, formation of GaAs, GaTe and excess Te s.u. are considered in lieu of some of the original As_2Te_3 s.u. of the parent glass. In this case.,

$$\begin{aligned} &Ga_x(As_{0.4}Te_{0.6})_{100-x}\text{---}\rightarrow (0.5591x)\mathrm{A} \\ &+(0.4409x)\mathrm{E}+(20-0.4795x)\mathrm{C}+(0.3978x)\mathrm{D}, \end{aligned}$$

where E corresponds to the GaTe s.u. The corresponding V is given as

$$\begin{aligned} V = (1/N)[&(0.5591x)V_\mathrm{A}+(0.4409x)V_\mathrm{E} \\ &+(20-0.4795x)V_\mathrm{C}+(0.3978x)V_\mathrm{D} \rightarrow \text{(II)} \end{aligned}$$

here, $N = (20 + 0.9183x)$ and V_E is the volume of the GaTe s.u.

An increase of volume by ~10% generally occurs for chalcogenide glasses on going over to the glassy state from their corresponding crystalline state; for metallic glasses, the increase in volume on going over to the glassy state from its crystalline state is ~2%. For s.u. which have both the metal and the chalcogenide therefore, an increase of volume by ~6% has been taken for evaluating the V of the various glasses. V_A, V_B and V_E thus have values of 14.44, 19.88, and 19.23 cc respectively; V_c and V_D have values of 19.25 [1], and 21.27 cc (based on the density value of 6.0 gcm^{-3} for amorphous Te [27]).

The data of Fig. 9 indicate that both the models I and II show good agreement between the calculated and experimental V for x up to ~2; for $x \geq 2$, the model II gives V values which are in better agreement with the experimental values. These results, along with the requirement of a change in the type of s.u. for compositions with $x \geq 2$, therefore suggest the following structural arrangement in these glasses. For addition of Ga up to 2 at.%, formation of GaAs, Ga_2Te_3, As_2Te_3 and excess Te s.u. take place in lieu of the original As_2Te_3 s.u. of the parent glass; for $Ga \geq 2$ at.%, formation of GaAs, GaTe, As_2Te_3 and excess Te s.u are indicated. Structural studies on these glasses, when available, will help to substantiate this conjecture.

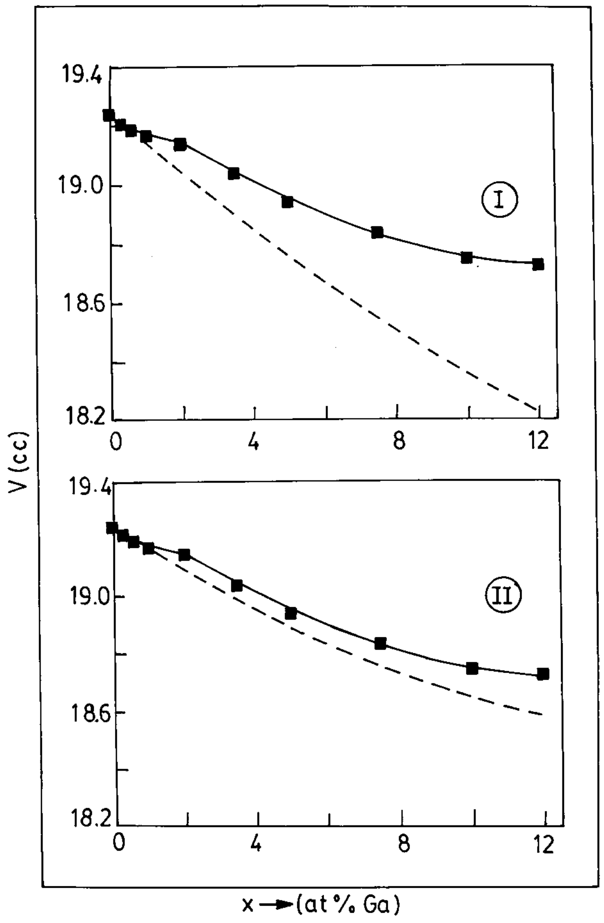

Figure 9 (I) Experimental (curve through the data points) and calculated (broken curve) V for the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, using model I described in the text. (II) Experimental (curve through the data points) and calculated (broken curve) V for the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, using model II described in the text.

The bond energies of Ga–As and Ga–Te bonds are higher than that of the As–Se bond (which has a value of 40.9 kcal/mole). Also, both GaAs and GaTe are tetrahedrally bonded (and are therefore stronger than pyramidal s.u.). Both these factors account for the observed increase of T_g (Fig. 2) with increasing Ga content.

On addition up to 2 at.% of Ga to the parent glass, both C and ΔE show a decrease and the overall σ registers an increase with increasing Ga content (Fig. 8). C is related to the density of localised states [28] and a decrease of C indicates an increase in the density of localised states. There is thus an increase in the randomness of the network on introduction of Ga to As_2Te_3.

Fig. 10a is the schematic of the energy band diagram of the parent glass. In this figure, the Fermi level E_F is shown at the centre of the mobility gap because of the large density of localised states in the gap. As chalcogenide glasses are generally p–type, the ΔE (of 0.4 eV) of the parent glass corresponds to the energy difference between E_F and the top of the valence band [Fig. 10a]; also shown are the acceptor-like (C_1^-) and the donor-like (C_3^+) localised states.

The observed decrease of ΔE on introduction of Ga can be brought about either by a downward shift of the Fermi Level or an upward shift of the valence band edge E_v [29, 30]. The former case is realised if the additive acts as acceptor in the glass and the latter case is realised if the additive brings about ordering in the structure of the glass. In the present case however, introduction of Ga has increased the randomness, as inferred above from the values of C. The decrease of ΔE is therefore due to a downward shift of E_F brought about by a decrease in the C_1^- charge centres. In chalcogenides, the formation of charged defects according to $2C_2^0 \rightarrow C_3^+ + C_1^-$ is favoured; as in the usual notation, the subscript denotes the coordination and the superscript the charge state. In the Ga–As–Te system, addition of Ga to As–Te results in the formation of negatively charged Ga_4 from the neutral Ga_3 state according to $Ga_3^0 + C_1^- \rightarrow Ga_4^- + C_2^0$, which, with the earlier equation above gives $Ga_3^0 + C_2^0 \rightarrow Ga_4^- C_3^+$. Formation of Ga_4^- centers on the introduction of Ga is achieved by reducing the concentration of the acceptor like C_1^- centers. This leads to a shift of the Fermi Level towards the valence band as shown schematically for a composition with $x = 0.6$ in Fig. 10b. The behaviour is similar to those of In and Tl in Ge–Se glasses [31, 32]. The insensitivity of the electronic properties for $x > 2$ is probably due to a saturation in the reduction of the acceptor like states, brought about by structural changes taking place in these compositions.

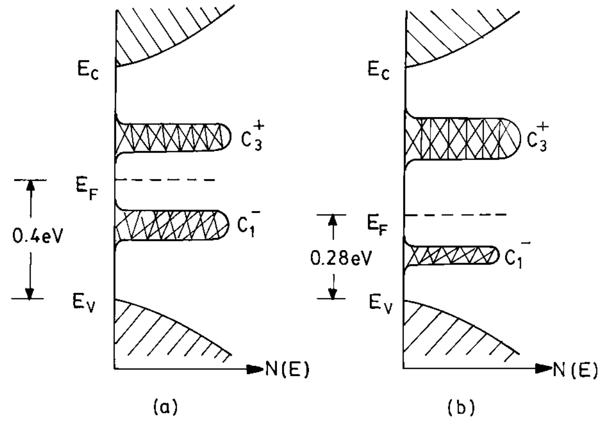

Figure 10 (a) Schematic of the energy band diagram of the parent glass. (b) Schematic of the energy band diagram for the composition with a Ga content of 0.6 at.%.

5. Conclusions

In the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses, changes in slopes (or a kink) are observed in the d, V, T_g, E_t, σ, C and ΔE data at the composition with a Ga content of 2 at.% Examination of the data indicates that at low concentrations, Ga in the As_2Te_3 glass behaves differently from Ag and Cu in the As_2Te_3 glass. While T_g of the parent As_2Te_3 glass is invariant up to additions of ~3 at.% of Ag or Cu, the T_g of the As_2Te_3 glass increases on addition of even small amounts of Ga of ~0.3 at.%. or more.

In the $Ag_x(As_{0.4}Te_{0.6})_{100-x}$, $Cu_x(As_{0.4}\ Te_{0.6})_{100-x}$ and the $Cu_x(As_{0.4}Se_{0.3}Te_{0.6})_{100-x}$ glasses, the σ of glasses for additions of up to ~3 at.% of Ag or Cu are lower than that of the As_2Te_3 glass, but, the σ of parent glass increases even for small additions of Ga in the $Ga_x(As_{0.4}Te_{0.6})_{100-x}$ glasses.

Introduction of low concentrations (~2 to 3 at.%) of Ag or Cu does not affect the medium or the short range ordering of the parent As_2Te_3 glass; but Ga begins to form bonds with As and Te within the correlated layers, even for Ga concentrations ≥0.3 at.%. Analysis of the data suggest formation of GaAs, Ga_2Te_3 and excess Te s.u. in lieu of some of the original As_2Te_3 s.u. for additions of Ga up to 2 at.% For Ga $\geq$ 2 at.%, formation of GaAs, GaTe and excess Te s.u. are indicated.

Appendix

In the present σ measurements on Ga–As–Te glasses, and in our earlier σ measurements [16, 33–36] on glasses of the Ge–Sb–Se, Ge–Se–Te, As–Se–Te, As–Sb–Se and other systems, a d. c. voltage of 5V is applied across the sample and the current in the circuit measured with an appropriate picoammeter. In the Ge–Sb–Se and Ge–Se–Te systems, the sample resistances at high temperatures (in the region of their T_g) are in the range of $5 \times 10^5 \Omega$, while, in the As–Se–Te and As–Sb–Se systems, they are in the range of $5 \times 10^4 \Omega$ [13, 33–36]. For the resulting typical currents of 10 to 100 μA therefore, the I^2R heating in these samples is very small. It is therefore possible to record the σ data through the glass transition region in these systems [13, 33–36]. In the Ga–As–Te glasses studied presently, the sample resistances are in the range of 20 to 50 Ω for temperatures ~370 K. The resulting current of 100 to 200 mA causes an I^2R heating of 0.6 to 1 watt or say, typically 0.8 joules/sec. The temperature rise per second in these samples (ΔT), due to this self heating effect can be estimated by equating 0.8 joules/sec to $4.186(ms\Delta T)$, where m is the mass and s, the heat capacity of the sample. For sample thickness of ~0.8 mm, area of ~0.08 cm^2 and glass density of ~5.5 $gcm.^{-3}$, m has a value of ~0.035 g. The specific heat, s, of the glasses below their T_g is ~6.2 cals/gm/K [37]. From these values, ΔT turns out to be ~0.8 to 1 K/sec.

For typical experimental times of ~2 to 3 minutes (in the high temperature region), local temperature rises in the range of ~100 to ~160 K can be expected for the samples due to this self heating effect. If, instead of 5 V, a voltage of 1 V is used in the measurement of σ, then the region of increasing σ (regions I and II in the Figs 6 and 7) can be shifted to higher temperature ranges.

Glasses of the Ga–As–Te system are known to have high crystallising ability; for the As and Te contents in the glasses studied, the differences between the crystallisation temperature and the glass transition temperature lie in the range of 60 to 90 K [17]. The observed increase in σ of the Ga–As–Te glasses for $T > 370$ K is therefore due to regions of local crystallisation in the samples, brought about due to a local self heating of the samples. The samples, after temperature excursions (through the regions I and II indicated in the insets of Figs 6 and 7), indeed exhibited portions which had turned 'dull' (as examined by the naked eye and under a 25 × magnifier) in the regions where they had crystallised; further, the sample resistances did not return to the original values at room temperature after this high temperature cycling. If the temperature is restricted to less than ~350 K, the samples did reproduce the original σ–$1/T$ data on subsequent temperature recycling.

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