Density and $T_g$ of glasses of the As–Al–Te system

S. MAHAD EVAN, GIRIDHAR
Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

Results of measurement of the density and the glass transition temperature ($T_g$) on 25 glass compositions of the As-Al-Te system are reported and discussed. A linear increase of density and a decrease of $T_g$ are seen with increasing As content across the As$_{15}$Te$_{85-x}$–As$_2$Te$_3$ tie-line compositions. In the density-composition and mean atomic volume-composition dependences for the As$_{15}$Al$_{10}$Te$_{85-x}$, As$_{15}$Al$_{10}$Te$_{92-x}$, and As$_{15}$Al$_{12}$Te$_{88-x}$ glasses, a change in slope is seen at the respective tie-line compositions, indicating chemical ordering in these glasses. When the dependence of density on the average coordination number $Z$ are considered, the effects of chemical ordering are obscured; instead, the effects of topological nature emerge, with changes in slope at the topological thresholds of $Z \approx 2.40$ and $Z \approx 2.67$. The results further indicate that the dependence of mean atomic volume $\nu$ on $Z$ is controlled by the Te content in these glasses. Due to this, the generally observed features in the dependence of $\nu$ on $Z$ for chalcogenide glasses, namely a minimum in $\nu$ for $Z \approx 2.40$, a peak in $\nu$ for $Z \approx 2.67$ and a decrease of $\nu$ for $Z > 2.67$, are suppressed.

1. Introduction
The As-Al-Te glass system is important due to the switching effect observed in bulk glasses of this system [1]. The glass formation in this system extends [2] up to about 20 at % Al and 35-75 at % Te, the rest being As (Fig. 1a). Though characterization studies on several random compositions [3] and structural data on some glasses [4, 5] have been reported, systematic variation of the properties with composition has not been investigated for this system.

The compositions of the glasses prepared for the present study are indicated in Fig. 1b and listed in Table I. Based on the existence of the ternary compound As$_{15}$Te$_{84}$ [6], which is also easily obtained in the glassy state, six of the compositions studied presently were chosen along the As$_{15}$Te$_{85-x}$–As$_2$Te$_3$ tie-line. The study also covered glasses of families with Al at 5, 8, 10, 12 and 16.67 at %. One glass composition from each of these families is also a member of the As$_{15}$Te$_{85-x}$–As$_2$Te$_3$ tie-line and thus forms the so-called "stoichiometric" or tie-line composition of the corresponding family. With the tie-line composition of each family as reference, glasses with As content higher than that of the corresponding tie-line composition can be referred to as the As-rich compositions, and glasses with As content lower than that of the corresponding tie-line composition as the Te-rich compositions of the respective families.

In this communication, the results of measurement of the density and glass transition temperature ($T_g$) of these glasses are presented; the observed features in the composition dependence of these properties are understood on the basis of the existing models [7-15] for network glasses.

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Appropriate quantities (6-8 g total) of pure elements (99.999%, As and Te obtained from Atomergic Chemmetals Corp., USA and Al from Johnson Matthey, USA) were weighed and sealed under a vacuum of 10^-3 torr. The ampoules were then heated in a rotary furnace (for purposes of homogenization) at 800 °C for 8 h and quenched in iced water to obtain the glasses. The amorphous nature of the various compositions was confirmed by recording their powder X-ray diffractograms (CuKα).

Densities were determined by the hydrostatic method using the density kit supplied along with the microanalytical balance used (Sartorius, model A 200 S). Deionized water was used as the immersion fluid and utmost care was exercised to avoid formation of any air bubbles around the sample which can affect the measured density. The error in measurement was further reduced by choosing large (typically 1 g) samples for measurement. Densities were measured on four to six samples from each batch preparation; the mean value obtained for these samples is indicated in Table I along with the experimentally observed scatter for the various compositions. The maximum scatter in the density value for different samples of any given composition ranged from 0.02 to 0.2% for most of the compositions and up to 0.4% in a few cases (Table I).

A scatter of similar magnitude was observed from measurements on different batch preparations of specified compositions.

After the routine calibration, a Perkin Elmer DSC-2 differential scanning calorimeter (DSC) was used for recording the thermograms to determine \( T_g \). Using the standard procedure [16], \( T_g \) was identified as the temperature corresponding to the intersection of the two linear portions adjoining the transition elbow of the DSC trace. The \( T_g \) values indicated (Table I) are those obtained at a heating rate of 10 K min^-1, on samples which were annealed (by holding at temperature of about 10 K higher than the respective \( T_g \) for 15 min) and then cooled through the transition region at a rate of 10 K min^-1.

### 3. Results

The densities of the various compositions along with the observed scatter and their mean atomic volume \( v \) are all listed in Table I. The mean value of \( d \) has been used for evaluating \( v \) for the various compositions.

Fig. 2 shows the variation of density with composition. A linear increase of density with increasing As (i.e., As\_3Te\_2) content is seen for the tie-line compositions (line AA through filled circles in Fig. 2). A change in slope is seen from the fit of 5.725 ± 0.005, so it is described as an A2 phase.

For the glasses of composition 62.09 g Al with Te from 5.86 g to 64.91 g, a linear increase is observed in the composition series.
in slope in the dependence of density on composition is seen at the corresponding tie-line composition for the families investigated.

The linear dependence of the density of the Te-rich glasses of the various families, when extrapolated to the corresponding Te (100 at %) point, give a value of 5.725 ± 0.005 g cm⁻³ for the density of glassy Te. Amorphous Te cannot be obtained in bulk form and so its density value is not available. The present value of 5.725 g cm⁻³, assuming a generally observed increase of about 10% in density on crystallization of many chalcogenide glasses, gives a value of 6.29 g cm⁻³ for crystalline Te, in good agreement with the value of 6.24 g cm⁻³ for Te. A value of 5.86 g cm⁻³ has been inferred for the density of glassy Te from data on the As-Te system [17].

A similar extrapolation of the density of As-rich glasses to the pure As (100 at %) end shows some interesting features. The density data points of the As₅Al₃Te₈₋ₓ, family, when extrapolated to the pure As end (broken line extension to 100 at % of As, Fig. 2) gives a value of 4.695 g cm⁻³ for the density of amorphous As, which is in excellent agreement with the reported value of 4.70 g cm⁻³ [18] for amorphous As. For the As₅Al₃Te₈₋ₓ, family (filled squares in fig. 2), the density data of As-rich glasses up to about 37 at % As fall along the line joining the density of the corresponding tie-line composition with the density of As. For the As₅Al₃Te₈₋ₓ, glasses (open triangles), the deviation sets in around the composition As₃₀Al₁₀Te₆₀. Thus for families with a progressive increase in Al content (i.e. as one moves from top to bottom along the line AA), there is a reduction in the As content of the compositions up to which the density data fall along the line joining the density of the corresponding tie-line composition with that of As.

For the tie-line compositions (Fig. 3a), a linear decrease of ρ is indicated with increasing As content. The data for ρ of the individual families (Fig. 3b) reflect the dependence of the densities of these glasses (Fig. 2). A change in slope is seen at the respective tie-line compositions of the various families, followed by another change in slope for the families with Al at 8, 10 and 12 at % at compositions which have As at 37, 30 and 28 at %.

In the Tₜ-composition data (Fig. 4a), a linear decrease of Tₜ with increasing As content is seen for the As₅Al₃Te₈₋ₓ, glasses; this dependence, when extrapolated to 40 at % As, agrees well with the reported [17, 19, 20] Tₜ of As₅Te₈. For the individual families, an increase of Tₜ with increasing As content is observed.

4. Discussion

4.1. Existing models and expected features

In this section, salient features of existing models [15], which are helpful in understanding the observed features, are briefly summarized. Earlier attempts at understanding the features seen in the composition dependence of various properties of chalcogenide glasses were based on the chemically ordered Network Model (CONM) [7, 8, 21–23]. In the CONM, the formation of heteropolar bonds is favoured over the formation of homopolar bonds; the glass structure is pictured to be made up of cross-linked structural units of stable chemical compounds.
The variation of $d$ and $v$ with composition

For analysing $d$ and $v$ in terms of the topological models, the $Z$ values of these glasses were evaluated using the standard procedure [24]. The coordination of As, Al and Te used in the evaluation of $Z$ were obtained from the results of structural data on these glasses [4, 5] and also on glasses of the related Al-Te [1] and As-Te [25] systems. The following conclusions have been drawn from these studies.

(i) Al has tetrahedral coordination in all these glasses.

(ii) Based on the low value of Al-Te bond energy and the low atomic percentage of Al in these glasses, the formation of Al-Te bonds is negligible.

(iii) In the bonding scheme, each Al atom takes one electron from one of the As or Te atoms which surrounds it. This results in a tetrahedral vertex for the Al atom in a prismatic structure.

(iv) Apart from the As-Te bonds which have the highest coordination, the bonds are less strong above 0.45 at% of Te in these glasses.

(v) Based on similar reasoning, the Al-As and Al-Te bonds in the Al-Te glasses are 3-dimensional structures.

Table I lists the $Z$ values evaluated using X-ray diffraction data [15]. In these systems, the overall dependence is a function of the specific properties of the glasses. In these systems, the overall dependence is a function of the specific properties of the glasses. In these systems, the overall dependence is a function of the specific properties of the glasses. In these systems, the overall dependence is a function of the specific properties of the glasses. In these systems, the overall dependence is a function of the specific properties of the glasses.

4.4. Variation of $d$ with $Z$

The $d$ and $Z$ data show that there is no relationship between any $Z$, and $d$. This is indeed true. However, the correlation between $d$ and $Z$ is very high, reaching a value of $Z = 2.67$ at $d = 4.0$. A more detailed analysis, with the help of the X-ray diffraction data, is provided in Fig. 6. A more detailed analysis, with the help of the X-ray diffraction data, is provided in Fig. 6. A more detailed analysis, with the help of the X-ray diffraction data, is provided in Fig. 6. A more detailed analysis, with the help of the X-ray diffraction data, is provided in Fig. 6. A more detailed analysis, with the help of the X-ray diffraction data, is provided in Fig. 6. A more detailed analysis, with the help of the X-ray diffraction data, is provided in Fig. 6.
surrounds it. The atom which gives the electron becomes fourfold or threefold coordinated depending on whether it is an As or a Te atom; every atom in the tetrahedra vertex provides 1/4th of an electron to the Al atom in a probabilistic sense.

(iv) Apart from those Te atoms bound to Al atoms which have threefold coordination, an additional fraction of about 0.2 % x, where x is the atomic percentage of Te in the glass, is also found in threefold coordination.

(v) Based on the approximately equal values of the Al-As and Al-Te bond energies, the numbers of Al-As and Al-Te bonds are proportional to the relative concentrations of As and Te in the corresponding glass composition.

Table I lists the Z values of the various compositions, evaluated using the conclusions summarized above. Fig. 5 shows the d-Z data for these glasses, in which extensions to the d of Te at Z = 2 and to that of As at Z = 3 are also indicated. The data of Fig. 5 indicate a change in slope at Z = 2.67. With the limited data available at low Z, a change of slope is seen at Z = 2.43 also. However, generating data points at lower values of Z between 2.0 and 2.4 was precluded in this system by the boundary of the glass-forming region. The change in slope occurring at the topological thresholds of Z ~ 2.40 and Z ~ 2.67 are due respectively to the floppy-to-rigid transition and the "structural transition" occurring in network glasses which are summarized in section 4.1. In the d-Z data, the effects of chemical ordering (which was seen as a change in the slope of the tie-line compositions in the d-composition data of Fig. 2) is obscured. Corresponding to this transition at Z ~ 2.67 (Fig. 4), changes in slope were seen in the d-composition data (Fig. 2) also at the compositions which have Z values of 2.67 (Table I).

4.4. Variation of \( \nu \) with Z

The \( \nu \)-Z data for the As-Al-Te glasses are shown in Fig. 6. Due to the large scatter in the data points at any Z, it is not possible to infer any regular dependence of \( \nu \) on Z. At any specified Z, compositions with higher Te content have larger volumes, suggesting a correlation between the \( \nu \) and the Te content. That \( \nu \) is indeed the case is seen from the data in the inset of Fig. 6. A monotonic increase of \( \nu \) with Te content is seen, with the dependence extrapolating well to the \( \nu \) of Te at 100 % Te and to the \( \nu \) of As at 0 % Te.

In the systems whose \( \nu \)-Z dependences were discussed in section 4.1, the atomic radii of the constituent atoms As, Se, Ge (0.122, 0.117 and 0.126 nm, respectively) are approximately the same at 0.122 nm. In the As-Al-Te system studied presently, the Te atoms have large radii (0.138 nm) compared to those of As and Al (0.125 nm). In the structural transitions already discussed in section 4.1, in the region of Z between 2.40 and 2.67, \( \nu \) is determined by the interlayer separation of the two-dimensional layer structure proposed for these glasses. The larger Te atoms which determine the interlayer separation thus control the resultant volume. The features of a minimum in \( \nu \) at Z ~ 2.40 and the peak in \( \nu \) at Z ~ 2.67 in the \( \nu \)-Z dependence, seen in systems whose constituent atoms have approximately the same radii, are thus suppressed in this system in which the constituent atoms differ largely in atomic radii.
4.5. Dependence of $T_g$ on composition and $Z$. It is known that several complicating factors determine the $T_g$ of a glass [24]. Using the empirical $T_g - E - C$ correlation [26] (where $E$ and $C$ are the optical gap and the connectedness, respectively) it is generally used to understand the $T_g$ behaviour of chalcogenide glasses, it is possible to qualitatively rationalize the observed (Fig. 4) dependence of $T_g$ on composition and $Z$.

In the $T_g - E - C$ correlation an increase of $T_g$ is indicated with increase of connectedness, i.e. average coordination number $Z$. In chalcogenide glass systems, the optical band gap is twice the activation energy of electrical conductivity, $\Delta E$ [27]. Conductivity data on several As–Al–Te glasses indicate [28] that $2\Delta E$ does not drastically alter for these glasses, in the overall observed change in this parameter from 0.70 to 0.90 eV, $\Delta E$ decreases with increasing Al content. The $Z$ of these glasses increases with increasing As content (Table I). The observed increase of $T_g$ with increasing Al content for the tie-line compositions (closed circles in Fig. 4a) can be qualitatively traced to the larger effect of $Z$ on $T_g$ than that due to the change in $\Delta E$. For the individual families, the increase of $T_g$ with increase of As content is traceable to the increase of $Z$ (Fig. 4b).

5. Conclusions
The results of measurement of the density and $T_g$ of 25 glass compositions of the As–Al–Te system are reported and discussed. A linear increase in density and a decrease in $T_g$ are seen with increasing As content across the AsAlTe$_2$–As$_2$Te$_3$ tie-line compositions.

When examined as a function of composition, the density and $T_g$ of the various families of glasses indicate a change in slope at the respective tie-line compositions due to chemical ordering. There is another change in slope at the respective tie-line compositions due to chemical ordering are obscured and those due to the topological transition occurring at this value of $Z$.

When examined as a function of $Z$, the effects of chemical ordering are obscure and those due to the topological nature of the networks emerge. In the $d$–Z data changes in slope are seen for $Z = 2.43$ and $Z = 2.67$ which are respectively due to the floppy-to-rigid transition and the "structural transition" occurring in network glasses.

The results further indicate that the dependence of $v$ on $Z$ is determined by the Te content in these glasses due to the larger atomic radius of Te. Because of this some expected features at $Z = 2.40$ and $Z = 2.67$ in the dependence of $v$ on $Z$ are suppressed.

The $T_g$ behaviours of these glasses are rationalized on the basis of their band gap and $Z$ values.

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References
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