Letter to the Editor

Mean atomic volume and $T_g$ of Cu–Ge–As–Se glasses

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Abstract

Results of measurements of the mean atomic volume ($V$), the glass transition temperature ($T_g$) and the activation energy for glass transition ($E_t$) are reported for 11 glass compositions of the Cu–Ge–As–Se system. The compositions studied can be represented as $\text{Cu}_x(\text{Ge}_{0.125}\text{As}_{0.25}\text{Se}_{0.625})_{100-x}$ glasses. In the $V$--$x$, $T_g$--$x$ and the $E_t$--$x$ data of these glasses, changes in slope are observed at an $x$ value of $\sim 2$. The results are consistent with a picture wherein, up to $\sim 2$ at.% of Cu atoms occupy interlayer positions between the uncorrelated layers of the parent glass matrix without affecting either the medium or the short range ordering of the parent glass. The results also suggest that up to $\sim 2$ at.% of Cu atoms act as ‘plasticisers’ in the parent glass matrix, reducing its $T_g$. © 2000 Elsevier Science B.V. All rights reserved.

The role of metallic additives, namely, of Ag and Cu in modifying the mean atomic volume ($V$), the glass transition temperature ($T_g$) and electrical conductivity ($\sigma$) of the $\text{As}_2\text{Te}_3$ and the $[\text{0.5As}_2\text{Se}_3-0.5\text{As}_2\text{Te}_3]$ glasses were reported in our earlier communications [1–6]. Changes in slope in the property--composition data were observed at the composition with $\sim 2$ to 3 at.% of the metallic additive. Analysis of the data indicated [1–6] that small amounts of the metallic additive do not affect the short range or the medium range ordering of the parent (host) glass and therefore do not drastically alter the structure of the parent glass. For higher concentrations of the additive (generally greater than $\sim 2$ to 3 at.%), formation of bonds between the metallic atoms and the elements of the parent glass were indicated. The observed property dependence was rationalised by considering the formation of structural units (s.u.) of the metal with the elements of the parent glass. The studies also indicated [1–6] the necessity of generating the corresponding $E_t$-composition data for inferring the true $T_g$-composition dependencies in many systems.

In order to study some Ge-based chalcogenide glass systems, we tried to synthesise the GeSe$_2$ glass with Cu and Ag as additives, but were unsuccessful in synthesising these glasses. We were, however, successful in synthesising the $[0.5\text{GeSe}_2-0.5\text{As}_2\text{Se}_3]$ glass with an addition of up to 10 at.% of Cu by using the two-stage quenching method [1,3,4,7]. In this communication, the results of measurements of the $V$ and $T_g$ of the parent glass $[0.5\text{GeSe}_2-0.5\text{As}_2\text{Se}_3]$ and of 10 glass compositions, with Cu ranging from 0.3 to 10 at.%, are reported. The compositions of the glasses are hereafter referred to in terms of the at.% proportions of the elements. Accordingly, with the parent glass $[0.5\text{GeSe}_2-0.5\text{As}_2\text{Se}_3]$ denoted as Ge$_{12.5}$As$_{25}$Se$_{62.5}$, the glasses studied (Table 1) can...
be represented as \( \text{Cu}_{x}(\text{Ge}_{0.125}\text{As}_{0.25}\text{Se}_{0.625})_{100-x} \), with each glass being specified in terms of \( x \), its Cu content in at.\%.

The details of the synthesis of the glasses, the methods and the set up adopted for measuring the density and \( T_g \), the evaluation of the activation energy \( E_t \) of glass transition [from the slope of the linear \( \log(T_g^2/T)/\alpha \) vs. \( 1/T_g \) data], along with the precautions necessary are all already described in detail elsewhere [1,3,4,6,8]; only the results are presented here.

Figs. 1–3 and Table 1 summarise the data of the present study. In the \( V-x \) data (Fig. 1), a change in slope is observed at \( x \sim 2 \); this slope change is clearer in the inset of the Fig. 1 in which the range of \( x \) has been restricted. In the \( T_g-x \) data (Fig. 2) of these glasses, an initial decrease of \( T_g \) with \( x \), for \( x \) values up to \( \sim 2 \) is followed by a marginal increase of \( T_g \) with \( x \) for \( x > 2 \).

\[ E_t = \frac{1}{T_g} \text{in K at various heating rates (K min}^{-1}) \]

\[
\begin{array}{ccccccc}
 x & d & V & V' & E_t & T_g \\
 \text{cm}^{-3} & \text{cm}^3 & \text{cal} \text{ cm}^3 & \text{K} & 2.5 & 5 & 10 & 20 & 40 \\
 0 & 4.447 \pm 0.005 & 17.35 & 17.350 & 83.7 & 488.0 & 491.5 & 495.5 & 499.3 & 503.7 \\
 0.3 & 4.456 \pm 0.002 & 17.30 & 17.298 & 77.7 & 480.5 & 484.7 & 488.8 & 492.6 & 497.5 \\
 0.6 & 4.467 \pm 0.002 & 17.25 & 17.246 & 70.8 & 478.0 & 482.7 & 486.7 & 491.2 & 496.7 \\
 1.0 & 4.483 \pm 0.004 & 17.18 & 17.177 & 69.0 & 477.7 & 482.2 & 486.5 & 490.8 & 496.0 \\
 2.0 & 4.514 \pm 0.005 & 17.03 & 17.003 & 68.0 & 477.5 & 482.2 & 486.0 & 490.6 & 495.8 \\
 2.5 & 4.534 \pm 0.004 & 16.94 & 16.81 & 68.0 & 477.5 & 482.3 & 486.5 & 491.2 & 496.0 \\
 3.5 & 4.562 \pm 0.006 & 16.61 & 16.18 & 70.7 & 477.9 & 482.5 & 486.7 & 491.0 & 496.1 \\
 5.0 & 4.607 \pm 0.004 & 16.60 & 16.38 & 73.0 & 479.2 & 482.7 & 486.7 & 491.9 & 496.2 \\
 6.5 & 4.656 \pm 0.002 & 16.38 & 16.38 & 74.6 & 479.8 & 483.3 & 487.2 & 493.0 & 496.6 \\
 8.0 & 4.698 \pm 0.002 & 16.19 & 16.19 & 76.0 & 480.6 & 483.9 & 487.6 & 493.4 & 497.3 \\
 10.0 & 4.761 \pm 0.003 & 15.92 & 15.92 & 77.0 & 480.9 & 484.3 & 489.2 & 493.4 & 497.2 \\
\end{array}
\]

The results are discussed by adopting: (i) the general picture already used for understanding the properties of \( \text{As}_{40}\text{Te}_{60} \) and \( \text{As}_{40}\text{Se}_{30}\text{Te}_{30} \) glasses on introduction of Ag and Cu [1–6]; (ii) the gross general structure of chalcogenide glasses [9–14]; chalcogenide glasses have a corrugated layer.

![Fig. 1. V-x data for the Cu(\text{Ge}_{0.125}\text{As}_{0.25}\text{Se}_{0.625})_{100-x} glasses. The change in slope at \( x \sim 2 \) is rendered clearer in the inset. The lines are drawn as a guide to the eye.](image)
structure with finite layer thickness. The short range ordering in these materials corresponds to the formation of the respective structural units and their interconnection. The interconnection extends along a layer, the interlayer separation being typically 0.4 to 0.5 nm. The medium range ordering (also called the intermediate range ordering) in these glasses extends to generally about four correlated layers, i.e. 1.6 to 1.8 nm [9–14].

A cursory examination of the $V-x$, and $T_g-x$ data obtained presently indicates that these results are qualitatively similar to those observed [1,3,4,6] upon introduction of Cu and Ag to the As$_{80}$Te$_{60}$ and the As$_{80}$Se$_{60}$Te$_{10}$ glasses; the data [1,3,4,6] of 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$_{0.3}$)$_{100-x}$ and the Ag$_x$(As$_{0.4}$Se$_{0.3}$Te$_{0.3}$)$_{100-x}$ glasses have been reproduced in the Figs. 4 and 5 for purposes of ready reference. In these systems (Figs. 4 and 5), changes in slope are observed in the $V-x$ and $T_g-x$ data at $x$ values between 1 to 3 for the various systems. The following conclusions were arrived at [1–6] from these studies. (i) In small concentrations, generally from ~1 to 3 at.%, the metal atoms do not drastically affect the basic structure of the parent glass. (ii) Assuming a uniform distribution of the metal in the matrix of the parent glass, the distance between the clusters of metallic atoms turns out to be greater than that of the range for medium range ordering, (which is typically ~1.6 to 1.8 nm for chalcogenide glasses) for $x$ from ~1 to 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 rationalised by considering the formation of various structural units of the metal with the elements of the parent glass (e.g. formation of Ag$_2$Te structural units in the As–Ag–Te system, of the Cu$_2$Te structural units in the As–Cu–Te system, of the CuAsSe$_2$ and the CuAsTe structural units in the As–Cu–Se–Te system, and the Ag$_2$Te and...
Ag₃AsSe₃ structural units in the As–Ag–Se–Te system).

Based on these general conclusions [1–6], it can be concluded that in the Cu–Ge–As–Se glasses studied presently also, the Cu atoms up to ~2 at.％ do not alter the basic structure of the parent glass as they lie outside the purview of medium range ordering. In the Cuₓ(As₀.₄Te₀.₆)₁₀₀₋ₓ and Cuₓ(As₀.₄Se₀.₃Te₀.₃)₁₀₀₋ₓ glasses it is found that Cu atoms, for concentrations less than ~3 at.％, occupy interlayer positions between the uncorrelated layers in the layered network of the parent glass [3,4]. If a similar picture is assumed for Cu in the Ge₁₂.₅As₂₅Se₆₂.₅ glasses also, then the Cu atoms, per se, do not contribute to the total V because of their interlayer occupancy; the resulting V of the Cuₓ(Ge₀.₁₂₅As₀.₃₇₅Se₀.₆₂₅)₁₀₀₋ₓ glasses (for addition of Cu up to 2 at.％) is evaluated as $V = mV_{Ge_{12.5}As_{25}Se_{62.5}}$, where $m$ is the mole fraction of Ge₁₂.₅As₂₅Se₆₂.₅ in that composition. The V values thus calculated [V(cal)], using a value of 17.35 cm⁻³ for the V of Ge₁₂.₅As₂₅Se₆₂.₅ glass, are in good agreement with the experimental data (Table 1).

Fig. 4. $V$–$x$ data [1,3,4,6] for the Agₓ(As₀.₄Te₀.₆)₁₀₀₋ₓ, Cuₓ(As₀.₄Te₀.₆)₁₀₀₋ₓ, Cuₓ(As₀.₄Se₀.₃Te₀.₃)₁₀₀₋ₓ, and the Agₓ(As₀.₆Se₀.₄Te₀.₁)₁₀₀₋ₓ glasses.

Fig. 5. $T_g$–$x$ data [1,3,4,6] for the Agₓ(As₀.₄Te₀.₆)₁₀₀₋ₓ, Cuₓ(As₀.₄Te₀.₆)₁₀₀₋ₓ, Cuₓ(As₀.₄Se₀.₃Te₀.₃)₁₀₀₋ₓ, and the Agₓ(As₀.₆Se₀.₄Te₀.₁)₁₀₀₋ₓ glasses.
parent glass and facilitate cluster movements, thereby acting as a plasticiser, leading to softening of the parent matrix and thus reducing its $T_g$. However, further work is needed to support this conclusion. Also of interest in the context of the results obtained presently are the data [18] on $[\text{As}_2\text{Se}_3-\text{CuI}]$ glasses. Structural studies on these glasses have indicated [18] that addition of CuI to $\text{As}_2\text{S}_3$ glass does not alter the maximum position of the First Sharp Diffraction Peak (which is determined by some repetitive characteristic distance between the structural units) but alters only its width (which is related to the correlation length, which represents the scale of the medium range ordering). It is concluded [18] that there are no strong interactions between the $\text{As}_2\text{S}_3$ and CuI structural units but the disturbance caused by the CuI molecules located between the layers of the $\text{As}_2\text{S}_3$ network that introduce additional disorder and have effects on the correlation length.

For Cu > 2 at.%, medium range correlation gets modified, with the Cu atoms affecting the short and medium range ordering of the parent glass by forming bonds with the elements of the parent glass. Apart from the well-known ternary compound $\text{CuAsSe}_2$, formation of several binary compounds of Cu with As (such as $\text{Cu}_3\text{As}$, $\text{Cu}_3\text{As}_2$) and with Se (such as $\text{Cu}_2\text{Se}$, $\text{Cu}_4\text{Se}_3$) are indicated in the literature [19]. An examination of the results necessitates knowledge as to which of these structural units are formed in the various compositions of the Cu–Ge–As–Se system. Structural studies on Cu–Ge–As–Se glasses are not yet available for examining these results.

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References