THERMAL PROPERTIES OF As-S GLASSES IN THE GLASS TRANSITION REGION

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The compositional dependence of $T_g$, $C_p$ and relaxation enthalpy in the glassy system As-S was investigated. The observed modifications are related to the change of coordination polyhedra.

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1. Introduction

Glass transition is usually characterized by a phenomenological value $T_g$ and by a width of so-called glass transition region. In this region the diffusive motion of the melt begins to freeze in, before a glassy structure is achieved with viscosity values typical of solids $10^{13}$ Ns m$^{-2}$. Glasses are metastable solid materials without long range order. They lack translation and rotation symmetry. The nature of glass transition is complex and even today remains poorly understand. Numerous studies have been devoted to measurements and understanding of the glass transition temperature $T_g$ which is influenced by experimental conditions. There is not consensus yet if structural or thermodynamic factor are responsible for determining of $T_g$.

2. Experimental

The glasses of the $\text{As}_x\text{S}_{(100-x)}$ system, where $x = 33 - 42$ at.%, were prepared by direct synthesis from the pure elements. The differential scanning calorimetry (DSC) experiments in the heating regime were performed using DSC Pyris 1 (Perkin-Elmer). The StepScan software (Perkin-Elmer) was used to separate steady state thermodynamic and kinetic processes in the glass transition region.

3. Results

Using the StepScan method the glass transition temperatures, $T_g$, were obtained. Main benefit of method used is ability to separate the heat capacity, $C_p$, representing the changes associated with the rapid molecular motion in the material in the time scale of experiment and enthalpy changes (thermodynamic component), $\Delta H_{T_g}$, associated with slow irreversible processes (kinetic component) in the glass transition region. The quantities characterizing thermodynamic part of the glass transition are plotted in Fig.1. The dependencies of the specific heat capacity difference in the glass transition region, $\Delta C_{p,T_g}$, of the configurational entropy difference in the glass transition region, $\Delta S_{T_g}$, and of the Gibbs free energy difference in the glass transition region, $\Delta G_{T_g}$, on arsenic content were calculated from experimental DSC data.
Fig. 1. The dependence of the thermodynamic component of the glass transition ($T_g$, $\Delta C_{p,T_g}$) on arsenic concentration. In the insert: the compositional dependence of $C_{p,g}$ at the temperature 140°C is shown. The curves are only for eye guidance.

The entropy difference in the glass transition region $\Delta S_{T_g}$ was calculated from the measured temperature dependence of $C_p$ for all prepared glasses according to relation:

$$\Delta S = S_{T_1} - S_{T_2} = \int_{T_1}^{T_2} C_p \, dT,$$

(1)
temperature $T_1$ corresponds to the temperature of the beginning of the glass transition and $T_2$ temperature is the temperature of the melt at the end on the transformation. For result see Fig. 2.

Gibbs free energy difference in the glass transition region, $\Delta G_{T_g}$, for all prepared samples was calculated:

$$\Delta G_{T_g} = \Delta H_{T_g} + T_{T_g} \Delta S_{T_g},$$

(2)
$\Delta H_{T_g}$ corresponds to so-called relaxation overshoot (the kinetic component). Gibbs free energy differences in the glass transition region, $\Delta G_{T_g}$, for studied glasses are in Fig. 3. The strong discontinuity for glasses with 35–38 at.% of arsenic is found for both dependencies.

Fig. 2. The dependence of the configuration entropy difference, $\Delta S_{T_g}$, in the glass transition region on the arsenic content.

Fig. 3. The dependence of Gibbs free energy difference in the glass transition region $\Delta G_{T_g}$ on the concentration of arsenic.

Similarly strong change was observed by Borisova [1] for composition dependence of the thermal expansion coefficient $\alpha$, see Fig. 4.
All results obtained were also plotted as functions of the mean coordination number \( <r> \), Fig. 5.

**Fig. 4.** The temperature dependence of the thermal expansion coefficient \( \alpha \) on the concentration of arsenic. Inset shows the dependence of viscous-flow activation entropy on arsenic content [1].

**Fig. 5.** The dependence of obtained thermodynamic quantities in the glass transition region as function of \( <r> \) for 3-fold arsenic.

### 4. Discussion

The glass transition temperatures were determined from measured \( C_p(T) \) dependencies, Fig. 1. It was found that \( T_g \) reaches maximal value for stoichiometric composition \( \text{As}_5\text{S}_3 \). The calculated dependence of the heat capacity difference at \( T_g \), \( \Delta C_{p,T_g} \), reaches maximum for \( \text{As}_5\text{S}_3 \) as well as in the case of As-Se glasses, see [2]. The concentration dependence of \( C_{p,g} \) at 140 \(^\circ\)C, i.e. at temperature lower than onset of the glass transformation temperature, is shown in the inset into Fig. 1. It is obvious that for chemical compositions close to \( \text{As}_5\text{S}_6 \) the strong change of the slope of dependence of \( C_{p,g} \) on As concentration takes place. From the compositional dependence of the configuration entropy difference, \( \Delta S_{T_g} \), in the glass transition region (Fig. 2) it is possible to conclude that the change of the basic structural units probably takes place in the studied glasses.

Borisova [1] supposes for 28.57 at.% of arsenic existence of quasi-tetrahedral units which correspond to \( \text{As}_2\text{S}_3 \) glass composition, and pyramidal units \( \text{AsS}_2 \) for the stoichiometric \( \text{As}_5\text{S}_3 \) composition. In the region between these two limit compositions the transformation of quasi-tetrahedral units into pyramidal units takes place, a vice versa. On going from \( \text{As}_5\text{S}_3 \) to \( \text{As}_2\text{S}_3 \) the value of viscous-flow activation entropy \( S_o \) increases which represents, according to [1], a transition from tetrahedral to trigonal coordination of arsenic in As-S glasses (see Fig.4, inset). Studied glasses predominantly fall in this transformation region. X-ray and neutron diffraction measurements shown that structure of As-S and As-Se glasses are very similar in the range of compositions \( x = 0 \rightarrow 70 \), [3]. On the base of changes of \( T_g \) slope on concentration of arsenic it is concluded [4] that two fractions of chemical composition could coexist in this region of chemical compositions. Authors [4] suppose that two possible oxidation states of arsenic can exist in the studied covalent glasses, i.e. \( \text{As}^V \) and \( \text{As}^{VI} \). One fraction of the above mentioned glasses can be created by 4-fold coordinated \( \text{As}^V \) with quasi-tetrahedral local configuration with three bridging Se atoms and one double bonded Se. In the second one there are preliminary units with 3-fold coordinated \( \text{As}^{III} \) in pyramidal configuration. The change of \( C_{p,g} \) slope on composition for \( x = 35 \text{ at.}\% \) As was observed, see Fig. 1, inset. We suppose structural units changing close this composition. Providing that all arsenic is 3-fold coordinated (\( \text{As}^{III} \)) the mean coordination number \( <r> = 2.35 \). If all arsenic is 4-fold coordinated (\( \text{As}^V \)) the mean coordination number \( <r> \) would be 2.7. It is necessary to point out that these two limited values are very close to the values for so-called chemical and/or topological transitions i.e. \( <r> = 2.4 \) or 2.65 [5,6]. According to the constraint theory it is suggested [5] that valence forces (bond-stretching and bond-bending) can serve as the atomic constrains in the covalent network. It is supposed that glass formation would be optimal (ideal mechanical stability) when the number of constrains per atom equals 3 (3 degrees of
freedom per atom in 3D network). These ideas lead to the recognition that glass network becomes for \( \langle r \rangle = 2.4 \) elastically rigid. The rigid clusters can percolate and a phase transition (so-called rigidity transition) can take place. The feature observed at \( \langle r \rangle = 2.67 \) was understood using the structural transition model as well [6]. It was established by topological consideration using medium-range structures and it is attributed to the transition from essentially layered structure to 3D network arrangement due to the cross-linking. The dependence of obtained thermodynamic quantities in the glass transition region as function of \( \langle r \rangle \) is shown in Fig. 5. There are shown studied dependencies for the case when only pyramidal structural units are present in the glasses. Strong discontinuities are evident again. Pyramids are also supposed to be main structural units in As-Se glasses with \( x \leq 40 \) at.% As, [7].

It is not possible to prepare crystalline analogs of As-S glasses, except of As\(_2\)S\(_3\) [8] and so it is necessary to bear on indirect data only for their analysis, unfortunately.

5. Conclusions

Compositional dependence for As\(_x\)S\(_{(100-x)}\) (\( x = 33 \) – 42 at.% As) of \( T_p \), \( C_p \) and relaxation enthalpy in the glass transition region were measured. Obtained data show that the changes of oxidation state and associated changes of the coordination number of arsenic take place very probably in the studied region of chemical compositions. Changes in the studied quantities reflect the changes of coordination polyhedra (short-range order change). Observed changes are in good agreement with published structural studies dealing with the above mentioned glasses.

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References