

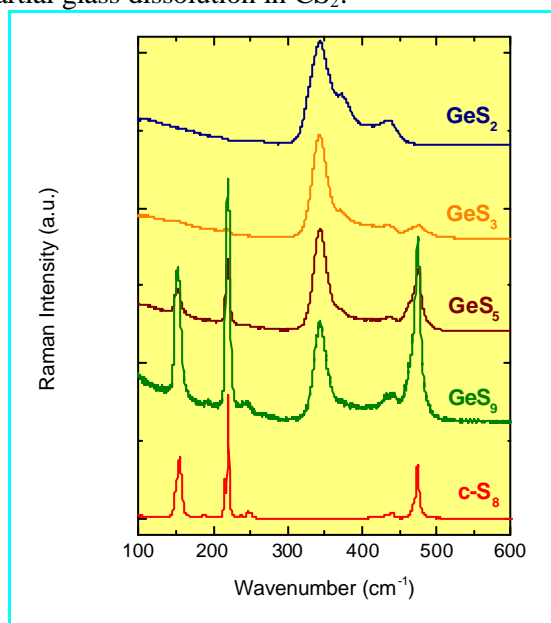
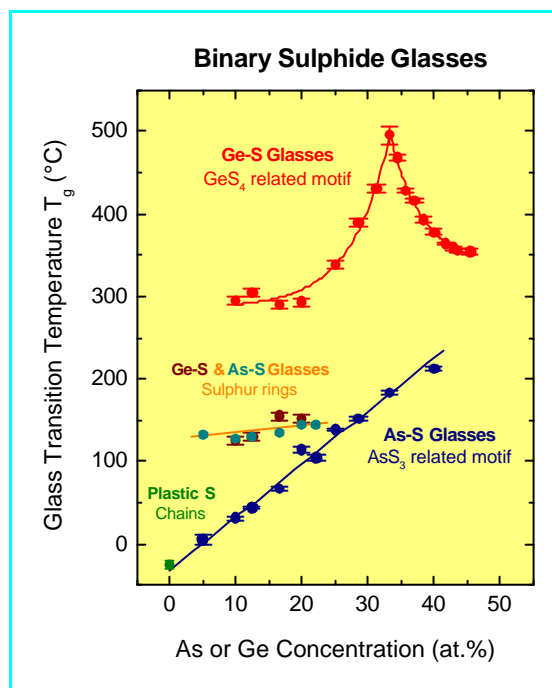


STRUCTURAL CHANGES IN SULPHUR-RICH BINARY GLASSES

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Small-angle neutron scattering, Raman spectroscopy and DSC were used to study structural changes for sulphur-rich AsS_x ($x \geq 1.5$) and GeS_x ($x \geq 2$) glasses. Two structural regions were found in the both systems. (1) Between stoichiometric (As_2S_3 and GeS_2) and ‘saturated’ ($\text{AsS}_{2.3}$ and $\text{GeS}_{2.7}$) compositions, excessive sulphur atoms form sulphur dimers and/or short chains, replacing bridging sulphur in corner-sharing $\text{AsS}_{3/2}$ and $\text{GeS}_{4/2}$ units. (2) Above the ‘saturated’ compositions at $[\text{As}] < 30.5$ at.% and $[\text{Ge}] < 27$ at.%, sulphur rings and longer sulphur chains (especially in the AsS_x system) appear in the glass network. The glasses become phase-separated with the domains of 20 to 50 Å, presumably enriched with sulphur rings. The longer chains S_n are not stable and crystallise to c- S_8 on ageing of a few days to several months, depending on composition.

Kawamoto et al. [1] were the first who observed two types of sulphur in S-rich GeS_x glasses: (i) insoluble in CS_2 species (sulphur chains), and (ii) soluble in CS_2 species (sulphur rings). Many research groups identified sulphur rings as S_8 using Raman spectroscopy (see, for example, [2]). A simple model was proposed to account for these results. (1) Excessive sulphur atoms, added to the stoichiometric glass (As_2S_3 or GeS_2), transform bridging sulphur into S_2 dimers. At a ‘saturated’ composition AsS_3 or GeS_4 , all structural units ($\text{AsS}_{3/2}$ pyramids or $\text{GeS}_{4/2}$ tetrahedra) become isolated, i.e., they do not share any longer their corners separated by three (AsS_3) or four (GeS_4) sulphur dimers. (2) Above the ‘saturated’ compositions at $x > 3$ (AsS_x) or $x > 4$ (GeS_x), the S_8 rings appear in the glass network, evidenced by characteristic vibrations in the Raman spectra and partial glass dissolution in CS_2 .

Figure 1. Raman spectra of sulphur-rich GeS_x glasses.Figure 2. Glass transition temperatures for sulphur-rich GeS_x and AsS_x glasses.

Our Raman spectroscopy results do not support the simple model; in particular, the ‘saturated’ compositions are clearly different from the predicted ones, AsS_3 and GeS_4 . In the AsS_x system, the characteristic vibrations of sulphur rings at 152 and 220 cm^{-1} appear at $x \geq \approx 2.5$. For their germanium counterparts GeS_x , they become visible at $x \geq \approx 3$ (Fig. 1). Nevertheless, the existence of the two suggested composition domains seems to be evident. Only a broad feature at 475 cm^{-1} appears in the spectra of GeS_x in the domain (1) in addition to A_1 , A_{1c} and other Raman lines in the 300–450 cm^{-1} range, attributed to Ge-S vibrations in the corner-sharing CS - and edge-sharing $\text{ES-GeS}_{4/2}$ tetrahedra [2,3]. The 475 cm^{-1} feature is common to S-S vibrations in all forms of



sulphur from chains to rings, and in the absence of characteristic ring vibrations indicates a chain-like bonding of sulphur species.

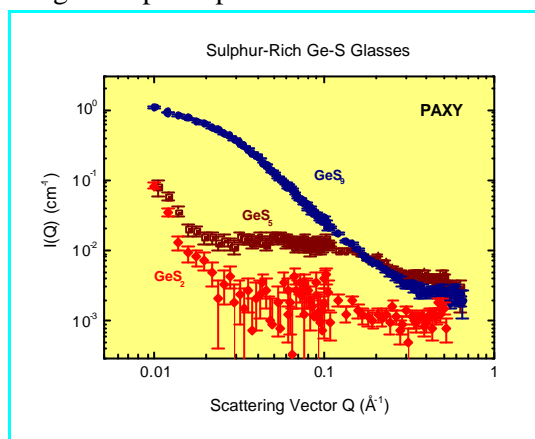


Figure 3. Typical SANS functions for selected GeS_x glasses.

A single glass transition in the domain (1) and a bimodal shape of the DSC traces in the domain (2) for the two binary systems suggests the phase separation. The composition dependence of the glass transition temperatures, T_g , shows also remarkable similarities and differences between the As-S and Ge-S vitreous alloys (Fig. 2). In both cases, the $T_g(1)$ corresponding to either $\text{GeS}_{4/2}$ or $\text{AsS}_{3/2}$ structural motif decreases with increasing sulphur content but the initial decrease in the domain (1) for the GeS_x glasses ends by a flattening in the domain (2). In contrast, freshly prepared AsS_x alloys exhibit a nearly linear decrease of $T_g(1)$, which extrapolates to -30°C for pure sulphur, a value characteristic of plastic sulphur, whose metastable structure is a mixture of chains and rings [4,5]. The values of $T_g(2)$ are similar and nearly constant in the both systems. Apparently, they correspond to a glassy phase mostly consisting of sulphur rings. The $T_g(2)$ fraction increases with increasing sulphur content. Typical small-angle neutron scattering functions $I(Q)$ for the selected Ge-S glasses are given in Fig. 3. Homogeneous GeS_2 glass is a weak scatterer, especially at $Q > 0.01 \text{ \AA}^{-1}$. The SANS intensity changes are small in the domain (1). The appearance of the sulphur rings in the domain (2) is accompanied by a characteristic and systematic change in the $I(Q)$. Correspondingly, the SANS intensity increases by two to three orders of magnitude between 0.01 and 0.1 \AA^{-1} with

increasing S concentration. A typical size of the second glassy phase varies between 20 and 50 \AA . The AsS_x glasses exhibit similar trends, but the structural changes on mesoscopic scale are much less pronounced compared to GeS_x . The stoichiometric glass compositions As_2S_3 and GeS_2 do not show any time-dependent phenomena. Nevertheless, glasses from the domain (2) in the both systems exhibit well-documented ageing. The phase separation becomes more pronounced (Fig. 4), and the T_g increases with time for the S-richer As-S glass compositions. This behaviour needs to be studied in more details.

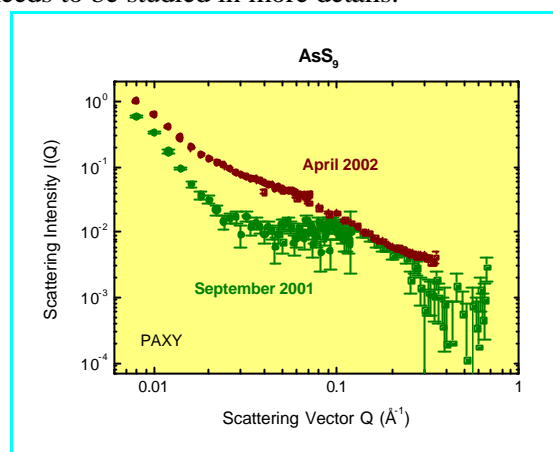


Figure 4. Time-dependent phenomena in the mesoscopic structure for binary glasses in the domain (2).

Quantitative analysis of the Raman data, SANS and DSC indicate that the AsS_x glasses in the domain (2) contain sulphur chains. The above conclusion can explain many observed phenomena. In contrast to the sulphur rings, the S_n chains, where n increases with the S content, are supposed to be inserted in the glass network between the $\text{AsS}_{3/2}$ pyramidal units, thus decreasing the network rigidity and T_g in a monotonic manner (Fig. 2). A smaller fraction of the sulphur rings in the AsS_x phase-separated glasses means the reduced SANS intensity, also consistent with the experimental findings. The sulphur chains are not stable neither in crystalline nor in glassy form. Consequently, they would be transformed into the stable c-S_8 form on ageing, giving rise to a number of time-dependent phenomena on mesoscopic (confirmed by SANS) and macroscopic scale (DSC), e.g., a T_g increase caused by the loss or decreasing in length of the inserted S_n fragments.

References

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