HOMOGENEITY THRESHOLD IN SULPHUR RICH Ge-S GLASSES

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The glassy Ge-S system was analysed on the basis of Raman spectra with the aim to find the compositional dependence of cyclo-octo-sulphur and polycatena sulphur.

1. Introduction

Ge_xS_{1-x} glasses have been intensively studied for many years. Great effort was paid to the study of short-range order (SRO) in these materials. Several structural models have been proposed to describe SRO: random-covalent-network model (RCNM), generalised chain crossing model (CCM) [1,2] and Philipp's model [3]. All these models were used by Lucovsky and co-workers [4] for interpretation of Raman spectra of Ge-S glasses. For glasses with sulphur overstoichiometry authors have found that analysis of IR and Raman spectra supports CCM model rather than a RCNM model. Based on these results authors [4] supposed that mostly two atoms of sulphur link Ge atoms and that the excess of sulphur separates as new phase. But this approach led to discrepancy between computed and experimental data for increasing overstoichiometry of sulphur. The SRO models based only on statistics of chemical bonds don't seem to be good approximation and they don't successfully correlate the properties of materials with their structure. For that reason authors [5] proposed the SRO-model for Ge-S glasses which is based on the assumption that atom in excess of the stoichiometric composition GeS_2 is considered to be the central atom of the respective structural units in this system. The homopolar bonds between atoms in understoichiometry don't originate. For sulphur rich glasses of Ge-S system the sulphur is central atom of structural units and thus Ge-Ge bonds don't exist. It means that germanium can only takes part in $GeS_{4/2}$ units. Three basic structural units may be considered: (Ge-S-Ge), (Ge-S-S) and (S-S-S). Their ratio bears on the properties of the material. From the dependence of relative population of above mentioned structural units on decreasing atomic fraction of germanium, x, the equivalent relative concentration of all kinds of structural units is reached for x = 0.2 and for x < 0.2 only the content of (S-S-S) units increases [5]. One can expect, in accordance with [4,6], that properties of Ge-S system could differ in regions x < 0.2 and x > 0.2. The main aim of this paper is analysis of Raman spectra of glassy Ge-S system with sulphur overstoichiometry with respect to compositional dependence of cycloocta-sulphur and polycathena-sulphur and testing of SRO-model [5] applicability.

2. Experimental

Bulk samples were prepared by direct synthesis from high purity elements in evacuated quartz ampoules in a rocking furnace. The melt was quenched in water (glasses with x > 0.20), respectively in air (x = 0.20 and 0.15). Chemical composition of glasses was checked by X-ray microprobe (Kevex). Raman spectra of glasses and both sulphur allotropes were measured under laboratory temperature in the back scattering geometry using FT spectrometr (Bruker IFS-55 with FRA-106). The excitation line 1064 nm (Nd:YAG laser) and Ge detector cooled with liquid nitrogen were used. Specific density of bulk glasses was measured by conventional pycnometric method.

Polycathena-sulphur S_n was obtained as a rest after dissolving the cycloocta-sulphur from high purity sulphur (5N) in distilled carbon disulphide. Soxhlett's extraction apparatus was used.
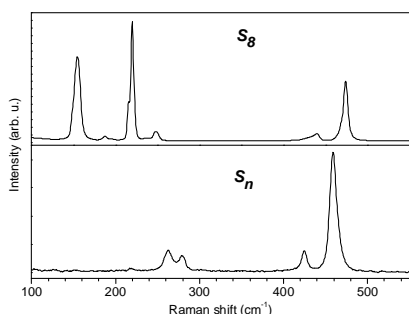
Fig. 1. Raman spectra of S_8 and S_n sulphur.
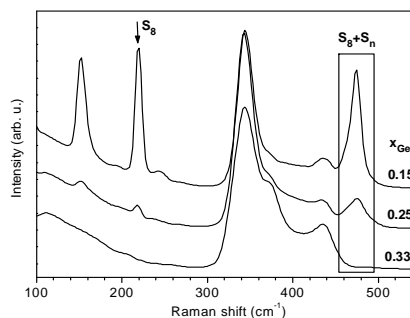
Fig. 2. Reduced Raman spectra of Ge_xS_{1-x}
glasses. Labelled bands were used for
the study.

3. Results

Lucovsky at al. [4] identified two species in Raman spectra, a network structure based on a local $GeS_{4/2}$ configuration and molecular species S_8. We assumed that indispensable concentration of linear chains S_n could be also present in the glass, especially when the glass is quickly quenched. To confirm this assumption we measured the Raman spectrum of sulphur S_n, because its spectrum was not available in literature. Raman spectra of S_n and S_8 sulphur are shown in Fig. 1. Spectrum of S_n consists of four well-resolved bands (263, 279, 424 and 459 cm^{-1}). At the spectra of Ge-S glasses only the most intensive band of S_n at 459 cm^{-1} can be identified as a shoulder on 473 cm^{-1} band of cycloocta-sulphur, see part labelled 'S_8+S_n' in Fig. 2.

Raman spectra of Ge_xS_{1-x} glasses were measured for x = 0.15, 0.20, 0.25, 0.30 and 0.333. Obtained spectra are shown in Fig.2. Raman bands labelled in this figure were used for our study from following reasons:

i) S_8 sulphur band at ~ 220 cm^{-1} is very intensive and has not considerable overlap with surrounding bands,

ii) in the region ~ 460 – 490 cm^{-1} both sulphur S_n and S_8 bands are found and can be easily separated.

All Raman spectra obtained were computer separated into bands. Integral intensities of labelled bands (Fig. 2) were normalised to the strength of Raman band at 343 cm^{-1} to provide a measure of their compositional dependence, analogously to [4]. This relative normalisation is based on an assumption that this mode is associated with the vibrations of Ge-S bonds and its strength scales as x. Compositional dependence of normalised integral intensities was compared with compositional dependence of (S-S-S) species of the SRO-model [5], see Fig. 3.
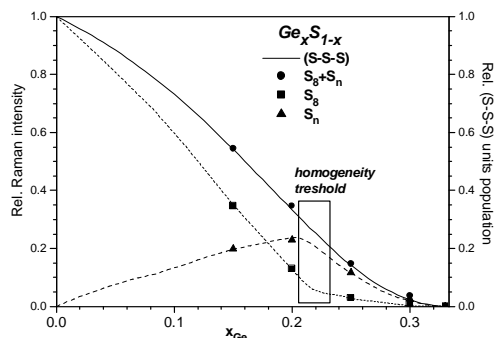Specific densities of studied glasses are in Fig. 4.

Fig. 3. Compositional dependence of obtained Raman relative intensities of monitored
sulphur bands and (S-S-S) species population computed according to the SRO-model [5].

4. Discussion

We found the lower values of normalised relative intensities in the case of S_8 in comparison with [4] probably bears on the fact that authors [4] replaced integral intensities of bands by their heights. The good agreement was achieved between compositional dependence of general S_8 and S_n content in glasses with its theoretical prediction based on the SRO-model [5], Fig. 3. Obtained dependence shows that there is considerable concentration of S_n chains in the glasses with sulphur overstoichiometry. For x = 0.2 their content reaches ~ 66% of total (S-S-S) units population, see Fig. 3. In contrast to S_8 molecules, which have to separate, it isn't possible, however, to determine if the S_n chains are separated into individual phase or if they are built in any structure containing germanium.
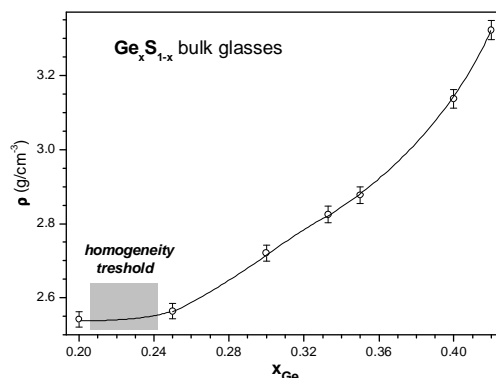

Fig. 4. Specific densities of Ge_xS_{1-x} glasses.

From the compositional dependencies, Fig. 3, it results that with increasing overstoichiometry of sulphur in glasses Ge_xS_{1-x}, approximately over 76 at.% S, the concentration of S_8 sulphur increases very quickly to the detriment of S_n sulphur. Thus if glasses with sulphur content more than 80 at.% (x < 0.20) are prepared the cooling rate has to be risen up sufficiently to prevent $S_n \rightarrow S_8$ transition and its following separation into microcrystalline phase. This assumption is in agreement with DSC results [7]. It is known that increasing overstoichiometry of chalcogen over ~ 80 at.% is accompanied with decrease of glass-forming ability of Ge-X melts, see e.g. [8].

On basis of these results we conclude that glassy system Ge_xS_{1-x} seems to be microheterogeneous for x less than approx. 23 at. % Ge. Its structure is built up by $GeS_{4/2}$ tetrahedra partly linked with S_n chains, and by microcrystalline sulphur S_8. This concept corresponds well with gradual break of compositional dependence of density near x ~ 0.23, Fig. 4. The lower volume of microcrystalline sulphur contrary to amorphous sulphur can be good explanation of this break. Our homogeneity threshold at x ~ 0.23 corresponds also with rigidity transition threshold near x = 0.23 of Ge_xSe_{1-x} glasses found by Boolchand [9].

5. Conclusions

The analysis of Raman spectra of Ge_xS_{1-x} glassy system has shown, that in the region $0.20 \leq x < 0.33$ the S_n chains are present and the concentration of co-existing cycloocta-sulphur S_8 is very low. S_n chains probably act as linkage of $GeS_{4/2}$ units and they are stabilised by this way. With increase overstoichiometry of sulphur, however, the number of such kind of structures decreases and thus the content of free sulphur increases and sulphur chains can phase-separate. In this phase of polycathena-sulphur the transition of the $S_n \rightarrow S_8$ occurs and the microcrystalline S_8 phase creates. It is demonstrate that the SRO-model [5] describes well compositional dependence of relative population of (S-S-S) units. It is shown that these units are parts of S_8 molecules as well as of S_n chains.

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