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Reversibility window in as-quenched Ge–As–S glasses

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Abstract

Thermoanalytical characteristics and Raman scattering of high purity sulfur and ternary bulk glasses $Ge_xAs_xS_{(100-2x)}$ for $x=4$–22 at. % were studied. The intermediate phase characterized by vanishing of non-reversing heat flow ΔH_{nr}, i.e. so-called the thermally reversing window was found between mean coordination number $\langle r\rangle \sim 2.28$–2.47. Separated phase of non-crystalline cycloocta-S, manifesting itself by λ-transition at ~155 °C, was found for glasses with sulfur content higher than ~80 at.%. Raman spectra of studied Ge–As–S glasses showed different shapes in three different areas according to three distinct phases of network glasses-floppy, intermediate, rigid.

Keywords: A. Chalcogenides; C. Differential scanning calorimetry (DSC); Raman spectroscopy; D. Thermodynamic properties

1. Introduction

The discovery of thermally reversing window [1] in chalcogenide glasses represents development in glass science. It has led to the recognition of self-organization in disordered network [2,3]. It has been in several binary and ternary systems that the glass transition becomes almost completely thermally reversing in character over a range of chemical compositions, for example [4–7]. The non-reversing enthalpy associated with the glass transition accessed from temperature-modulated differential scanning calorimetry (MDSC) was found to nearly vanish for these compositions. Furthermore these thermal measurements completed by Raman scattering have revealed that thermal reversing windows usually open for example [5,8] between mechanically floppy and stressed-rigid phases of glasses. Glass compositions in these windows define intermediate phases [1–3] that are thought to represent stress-free (self-organized) phases of disordered networks. In selected glassy systems the window collapses to a solitary composition and it was observed a sharp floppy to stressed rigid transition near a mean coordination number $\langle r\rangle = 2.34$ [4,6]. The later observation is in good agreement with the Phillips-Thorpe rigidity transition [9,10].

The new results on elastic phase transitions in network glasses have again opened a related issue, the microscopic origin of anomalies observed in glasses near a mean coordination number $\langle r\rangle = 2.60$. Several years ago Tanaka [11] suggested that anomalies in physical properties (including glass transition temperature, T_g) of chalcogenide glasses near $\langle r\rangle = 2.60$ may result from a floppy to rigid transition involving a change of network dimensionality.

The subject of the present paper is the study of chalcogenide glassy system $Ge_xAs_xS_{(100-2x)}$ for $x=4$–22 at. %. These glasses are of interest [12] because they include wide range of the mean coordination numbers $\langle r\rangle$~2.12–2.66. Because of sulfur overstoichiometry in studied glasses with $x<18$ at.%, one can expect that sulfur will play significant role in properties of glasses. Relevant MDSC or StepScan DSC data dealing with high purity sulfur was not available and so our attention was also focused on this one.

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2. Experimental

High purity sulfur was additionally refined by Wartenberg method and twice distilled in quartz apparatus under the argon atmosphere.

Ten chalcogenide glasses of $Ge_xAs_xS_{(100-2x)}$ system with nominal composition varying from $x=4$–22 at.%, were prepared from refined sulfur and high purity (5N) Ge and As. All elements (total weight 5 g) were weighed into quartz ampoules, evacuated (5×10^{-7} Torr), sealed and consequently heated in rocking furnace at temperature 850 °C for 24 h. Melts were cooled on air except samples of $x=4$, 6, 8, 10 at.% quenched into cold water. We would like to point out that glasses with $x>18$ at.% are sulfur uderstoichimetric, $x=18$ at.% is very close to stoichiometry. Glasses with $x<18$ at.% are sulfur overstoichiometric.

X-ray analysis of all glasses prepared was used to check their amorphous character.

Powdered samples were measured with a D8 Advance X-ray diffractometer (Bruker AXS, Germany).

All samples were analyzed by the electron scanning microscope JEOL JSM-5500LV with energy-dispersive X-ray microanalyser-IXRF Systems (detector GRESHAM Sirius 10). The accelerating voltage of the primary electron beam was 20 kV.

Raman spectra of glasses under study were taken with triple monochromator T 64000 (Jobin Yvon) in back-scattering configuration using Kr^+ laser (647.1 nm excitation line), and laser power 3 mW at a sample and spectral resolution of 1 cm^{-1}, flux density was 3 mW/μm^2. Spectra were acquired at 1 cm^{-1} resolution.

Temperature modulated DSC (MDSC) measurements were carried out using a model 2920 (TA Instruments) at a scan rate 3 °C/min and a modulation rate 1/100 s.

StepScan DSC measured on Pyris 1 (Perkin–Elmer) was used with temperature step 1 °C, step heating rate 100 °C/min, isothermal step duration approx. 1 min with maximum heat flow deviation $\pm5\times10^{-4}$ mW before next step.

3. Results and discussion

3.1. X-ray measurements and sample analysis

X-ray diffraction has shown no traces of any crystalline phase and confirmed glassy nature of all prepared samples.

The results of energy-dispersive X-ray microanalysis showed actual chemical composition of all glasses. Results are collected in Table 1. From this one it is obvious however, that the content of both germanium and arsenic differs each other in some cases. It is why the sulfur content must be taken for samples labeling. To calculate mean coordination number $\langle r\rangle$ the coordination numbers of Ge, As, and S of four, three and two were taken according to 8-N rule along with their actual content in glasses, Table 1.

Table 1
The results of energy-dispersive X-ray microanalysis and actual mean coordination number

Nominal composition	Actual composition			Actual mean coordination number ($\langle r\rangle$)
$Ge_xAs_xS_{(100-2x)}$	Ge (at.%)	As (at.%)	S (at.%)	
$Ge_4As_4S_{92}$	4.5	4.3	91.2	2.12
$Ge_6As_6S_{88}$	6.2	6.0	87.8	2.18
$Ge_8As_8S_{84}$	8.5	8.3	83.2	2.25
$Ge_{10}As_{10}S_{80}$	9.3	9.7	81.0	2.27
$Ge_{12}As_{12}S_{76}$	9.2	10.7	80.1	2.28
$Ge_{14}As_{14}S_{72}$	14.0	14.3	71.7	2.41
$Ge_{16}As_{16}S_{68}$	15.5	16.8	67.7	2.47
$Ge_{18}As_{18}S_{64}$	17.7	18.8	63.5	2.53
$Ge_{20}As_{20}S_{60}$	19.0	21.0	60.0	2.58
$Ge_{22}As_{22}S_{56}$	19.4	21.5	59.1	2.61

3.2. Temperature modulated DSC and StepScan DSC

Thermal properties of high-purity sulfur were studied because of its overstoichiometry in the glasses with $(100-2x)>64$. The characteristic temperatures of sulfur are connected with conversion of the orthorhombic α-S to monoclinic β-S modification, both of them based on the packing of crown-like S_8 rings, taking place at the temperature little bit higher than 95 °C, and with melting of monoclinic sulfur having onset at temperature close to 115 °C, [13,14]. Melting sulfur forms a pale-yellow liquid, with the structure consisting mainly of S_8 rings and preserves this structure up to the so-called lambda transition started at $T_\lambda\sim155$ °C. This temperature is connected with endothermic effect of molten sulfur polymerization, i.e. with S_8 rings opening and creation of polymeric S_n chains [6,15,16]. Heating rate independent temperatures of all above mentioned effects were found on pure sulfur using

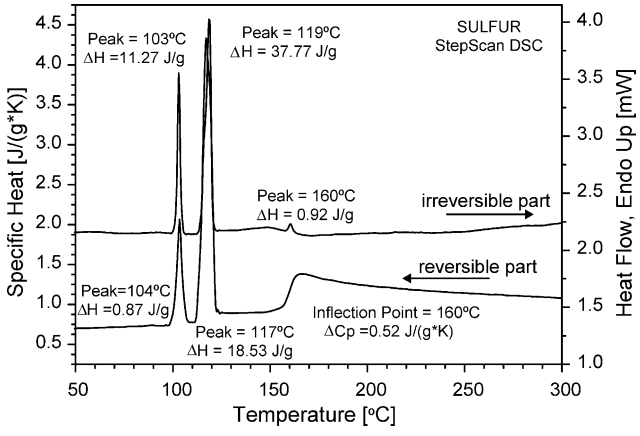

Fig. 1. StepScan DSC measurement of high-purity sulfur.

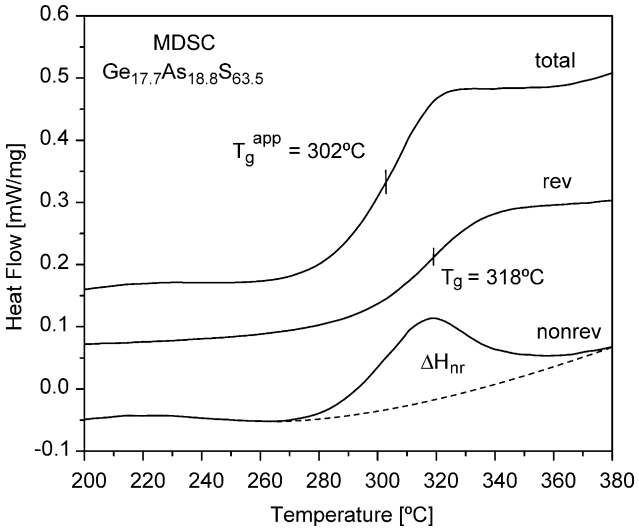

Fig. 2. Typical MDSC of glass. Total heat flow (total) and its reversing (rev) and non-reversing (nonrev) components.

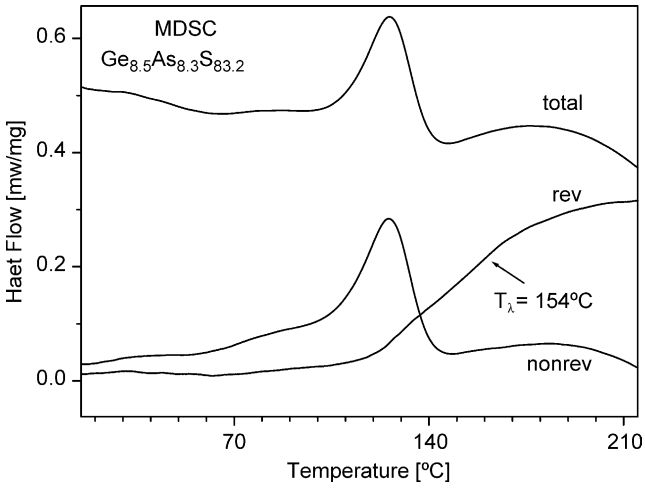

Fig. 4. The λ-transition in MDSC of $Ge_{8.5}As_{8.3}S_{83.2}$ glass. Confront with reversible part in Fig. 1.

StepScan DSC, $T_p(\alpha \rightarrow \beta) = 104$ °C, $T_p(\beta$ melting$) = 117$ °C, T_λ(inflection point) = 160 °C, see reversible part in Fig. 1.

Typical result obtained by temperature modulated differential scanning calorimetry (MDSC) for the glasses under study is shown in Fig. 2. Thermoanalytical features of studied glasses are summarized in Figs. 3–5.

From the compositional dependence of non-reversing component of MDSC it is clearly seen, that non-reversing heat flow, ΔH_{nr}, shows global minimum where ΔH_{nr} almost vanishes for glasses $Ge_xAs_xS_{(100-2x)}$ with actual sulfur content in the range ~68–80 at.%, Fig. 3. In agreement with Boolchand's concept [1] it means that thermally reversing window was found in these glasses.

From reversing component of MDSC it was found that, the glass transition temperature, T_g, decreases continuously depending on increasing of sulfur content. The monotonous decrease of T_g continues even for compositions falling into range of thermally reversing window, Fig. 3. When increasing sulfur content exceeds ~80 at.%, the glass transition temperature decreases more sharply. This effect can be caused by phase separation of sulfur, because for glasses with sulfur content higher than ~80 at.% an endothermic effect close to the temperature ~155 °C was found on reversing component of MDSC data, Fig. 4. Comparing this one with data of pure sulfur, Fig. 1, shows that this effect is λ-transition of sulfur. However, melting of sulfur was not observed at the same time and so we can conclude in accord with X-ray analysis that separated sulfur forms non-crystalline phase consisting mainly of S_8 rings.

Contrary to the compositional dependence of T_g, that 'does not see' thermally reversing window, the same dependence of the isobaric specific heat capacity difference at glass transition (changes of vibrational amplitudes), ΔC_P, reaches maximum for compositions corresponding to the thermally reversing window. The dependence of both the isobaric specific heat capacity difference in the glass transition area, ΔC_P, and non-reversing heat flow variation, ΔH_{nr}, on mean coordination number $\langle r \rangle$ is seen in Fig. 5. In the $\langle r \rangle$ scale the thermally reversing window corresponds

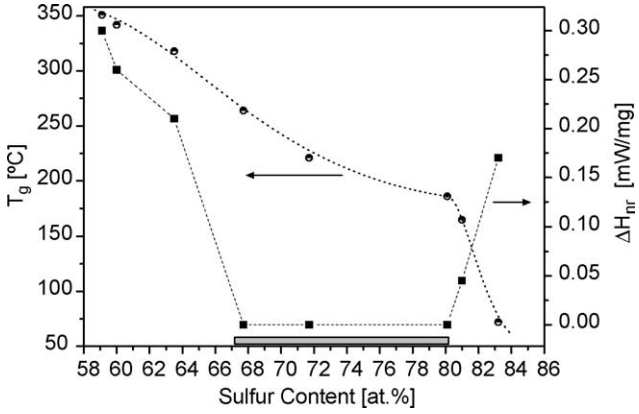

Fig. 3. Compositional dependence of the glass transition temperature, T_g, and non-reversing heat flow, ΔH_{nr}, for glasses $Ge_xAs_xS_{(100-2x)}$, $x = 4$–22 at.%.

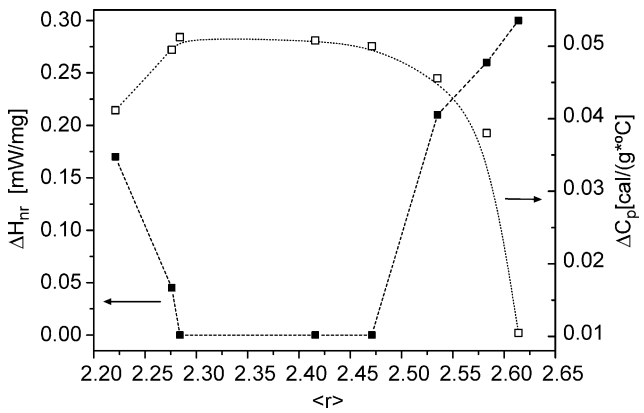

Fig. 5. The dependence of both non-reversing heat flow, ΔH_{nr}, and heat capacity difference, ΔC_P, on mean coordination number $\langle r \rangle$ for Ge_xAs_x-$S_{(100-2x)}$ glasses, $x = 4$–22 at.%.

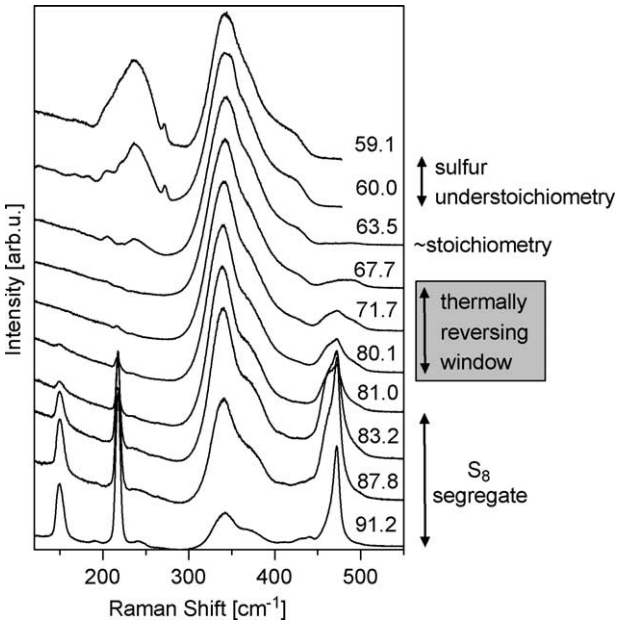

Fig. 6. Raman spectra of $Ge_xAs_xS_{(100-2x)}$ glasses, $x=4$–22 at.% (excitation energy 647.1 nm). The sulfur content (in at.%) is labeled on right-hand side.

to $\langle r\rangle \sim 2.28$–2.47, fairly well close to Phillips-Thorpe rigidity transition at $\langle r\rangle = 2.4$. The wider interval of $\langle r\rangle$ found for the glasses under study is very probably caused by the fact that one can only hardly expect implicit validity of the $8-N$ rule in disordered systems.

3.3. Raman scattering

Raman spectra of glasses under study are collected in Fig. 6 and labeled by actual sulfur content, Table 1. In the Raman spectra, it is possible to find three different series of curves according to three distinct phases of network glasses: floppy, intermediate, rigid. The first one for glasses with high sulfur overstoichiometry (sulfur content over 80.1 at.%), the second one for glasses with sulfur content 80.1–67.7 at.%, and the third one for nearly stoichiometric (63.5 at.% S) and sulfur deficient (understoichiometric) glasses (sulfur content lower than 63.5 at.%).

Five principal groups of bands were found, i.e. 150, 216, 238, 340 and 470 cm^{-1}. For glasses labeled 91.2–80.1 bands at energy 150, 216, 340 and 470 cm^{-1} are clearly seen. The intensity of the bands at 150, 216 and of 470 cm^{-1} decrease with decreasing sulfur content and bands at 150, 216 cm^{-1} practically vanish for sulfur content lower than 81.0 at.%. For glass labeled 63.5 the band at energy 470 cm^{-1} disappears and new bands broadening with increasing of sulfur understoichiometry appear with maximum at approx. 238 cm^{-1}. Maximum of 340 cm^{-1} group shifts up to 370 cm^{-1} at the same time. In this region should appear vibrations of corner-sharing and edge-sharing tetrahedra $Ge(S_{1/2})_4$ as well as $As(S_{1/2})_3$ pyramids or As_4S_4 molecules. The shift can be caused by change of their ratio. Detailed analysis of Raman spectra of ternary Ge–As–S glasses was published recently in [17].

Starting from highly sulfur overstoichiometric glasses when sulfur content decreases the characteristic Raman spectral features from S_8 segregated phase vanish. Going through compositions of thermally reversing window, the spectral features change to ones of nearly stoichiometric and sulfur deficient glasses, Fig. 6. Low intensive bands of Ge–Ge vibrations seen in spectrum of nearly stoichiometric glass in region ~200–240 cm^{-1} denote the low over-stoichiometry of germanium, see also Table 1. Sulfur deficient glasses are characterized by increasing of broad structureless band at 238 cm^{-1}. This one probably bears mainly on distorted rock salt $Ge(S_{1/6})_6$ units (Ge–Ge vibration in so-called ethan-like units) [18]. On the other hand, with decreasing content of sulfur increases intensity of band with maximum of about 340 cm^{-1} in all three above mentioned groups. Because with decreasing content of sulfur increases mean coordination number $\langle r\rangle$, i.e. increases connectivity and structure changes from floppy to isostatically rigid it is possible to connect this broad band with progressive cross-liking in glasses under study.

4. Conclusions

Thermoanalytical characteristics and Raman scattering of high purity sulfur and ternary bulk glasses $Ge_xAs_xS_{(100-2x)}$ with 59.1–91.2 at.% of sulfur were studied. Compositions change from sulfur understoichiometric to sulfur overstoichiometric glasses. Separated phase of non-crystalline cycloocta-S, manifesting itself by λ-transition at ~155 °C, was found for glasses with sulfur content higher than ~80 at.%.

The thermally reversing window was found in the range of mean coordination $\langle r\rangle \sim 2.28$–2.47 (66.7–80.1 at.% S). Glass compositions in this window defined intermediate phase which represent stress-free (self-organized) phases of disordered network [1–3]. In the thermally reversing window, heat capacity change, ΔC_P, reaches maximum, contrary to T_g's dependence which decreases with increasing concentration of sulfur over the whole composition region.

Raman spectra of Ge–As–S glasses showed that for glasses in composition region of thermally reversing window no 'wrong' bonds (homopolar bonds of As–As, Ge–Ge and S–S) are detectable in the sensitive limit of Raman spectroscopy. Nevertheless, the glasses with composition falling into the thermally reversing window are not stoichiometric and so one can conclude that $8-N$ rule is not satisfied at all in disordered system under study.

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