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Preparation and investigation of Ge–S–I glasses for infrared fiber optics

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ABSTRACT

Glass samples of $[GeS_x]_{90}I_{10}$ (x = 1.5, 1.7, 2.0, 2.3, 2.45, 2.6) compositions were prepared, and some their thermal, optical properties as well as tendency to crystallization were investigated. The compositional dependences of glass transition temperature, volume fraction of crystallized phase and activation energy of glass formation (E_g) have nonmonotonic character with a maximum for $[GeS_{2.0}]_{90}I_{10}$ glass. Glasses of $85.8GeS_2$–$14.2GeI_4$ and $[GeS_{1.5}]_{90}I_{10}$ compositions are identified as promising for preparation of optical fiber. For the first time, Ge–S–I glass fibers were produced. Minimum optical losses in $85.8GeS_2$–$14.2GeI_4$ glass fiber were 2.7 dB/m at a wavelength of 5.1 μm, and that in $[GeS_{1.5}]_{90}I_{10}$ glass fiber were 14.5 dB/m at 5.5 μm.

1. Introduction

During the last few years the Ge–S–I glasses are considered as a promising material for the production of optical fiber amplifiers and lasers of near and mid-infrared ranges [1,2]. They are characterized by high transparency in the spectral area of 0.5–10 μm, a significant ability to dissolve rare earth elements, a high quantum efficiency of photoluminescence [3,4]. However, Ge–S–I glass fibers and their optical losses have not been previously described in the literature.

Earlier, it was found [5] that in the $yGeS_2$–$(100 - y)GeI_4$ system the tendency to crystallization decreases with increasing iodine content from 5 to 15 at.%. The glasses were crystallized when trying to draw fibers by crucible method. Based on extrapolation of the experimental compositional dependence of the fraction of the crystalline phase after annealing of glasses, it has been suggested that the $85.8GeS_2$–$14.2GeI_4$ glass composition with 17.3 at.% of iodine will not show an appreciable crystallization during the fiber drawing. The authors of paper [6], on the basis of investigation of the thermal properties of glasses, have offered polymeric materials of $[GeS_x]_{100-y}I_y$ (x = 1.5–1.7, y = 5–25) compositions for the fiber cladding, but have nothing reported about the fiber drawing.

The goal of the work was the investigation of thermal and optical properties, the tendency to crystallization of $[GeS_x]_{90}I_{10}$ (x = 1.5, 1.7, 2.0, 2.3, 2.45, 2.6) glasses as well as the choice of the glass composition which is suitable for the fiber drawing by a crucible technique.

2. Experimental

To prepare Ge–S–I glasses, the germanium(IV) iodide synthesized from specially pure elements, germanium of purity 6N and sulfur of purity 5N purified by chemical thermal technique and vacuum distillation were used. The technique for preparation of Ge–S–I glasses has been described in paper [5]. The maximum temperature of synthesis was 750 °C. To prepare glasses with low content of optically active impurities, the batches of germanium (IV) and sulfur were loaded into the synthesis silica-glass reactor, which contained metallic germanium, by vacuum distillation from intermediate ampoules. The prepared glass samples were in the form of rods of diameter 10 mm and length: 40–60 mm.

The glass samples were investigated by a method of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using a synchrotronous Netzsch STA 409 PC Luxx analyzer at the heating rate of 10 K/min in the temperature range of 100–550 °C. Preliminary calibration of the calorimeter provided the accuracy of temperature within the limits of ±0.5 °C. The glass stability against crystallization was studied by X-ray diffraction (XRD) method using an X-ray diffractometer XRD-6000 Shimadzu (Cu

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Kα-radiation) after heating samples up to 650 °C at the rate of 10 K/min. The optical transmission of prepared glasses was investigated by means of IR-spectroscopy (Fourier transform IR-spectrometer Tensor 27) in the range of 2–12 μm. The transmission of the glasses in the spectral range of 450–800 nm was measured be means of spectrometer UV-3600 (Shimadzu, Japan). To measure the optical transmission, the glass samples were in the form of rods (discs) of diameter 10 and length: 2–40 mm with parallel-plate polished surface plates. The micrographs of bulk glass samples were obtained using an electron scanning microscope (JSM-5910LV, JEOL) in scattered electrons in the Z-contrast mode.

The optical fibers were produced by drawing from the melt (the single crucible method) in the inert atmosphere of specially pure argon gas at the temperature of 510 °C ($[GeS_{1.5}]_{90}I_{10}$ glass) and 590 °C ($85.8GeS_2$–$14.2GeI_4$ glass). The drawing rate was 1.5–2 m/min. More than 25 m of unclad fibers of each glass were drawn, and their optical losses were measured using the conventional cut-back technique.

3. Results

Fig. 1 shows the glass transition temperatures of prepared samples. Variation in T_g for $[GeS_x]_{90}I_{10}$ glasses, in contrast to $yGeS_2$–$(100-y)GeI_4$ glasses, is nonmonotonic. The maximum value of T_g corresponds to the glass composition of $[GeS_{2.0}]_{90}I_{10}$. DSC heating curves of all the $[GeS_x]_{90}I_{10}$ samples do not show crystallization exothermic signals up to a temperature of 550 °C. According to the TGA, the mass loss at 550 °C was 0.41% for the $[GeS_{2.6}]_{90}I_{10}$ sample, 0.28% – for $[GeS_{2.45}]_{90}I_{10}$, and <0.1% – for all other samples.

The XRD patterns of $[GeS_x]_{90}I_{10}$ glasses after their poly-thermal annealing up to 650 °C at the rate of 10 K/min are given in Fig. 2. Samples of $[GeS_x]_{90}I_{10}$ composition with $x = 1.7$, 2.0, 2.3 and 2.45 were visually opaque, their XRD patterns manifested diffraction peaks which are characteristic for orthorhombic germanium(IV) sulfide (PDF No. 75-1978) [7]. Samples with $x = 1.5$ and 2.6 did not manifest diffraction peaks and were transparent without observable crystallization. Fig. 3 shows the results of determination of the volume fraction of crystallized phase in glasses after their poly-thermal annealing. The calculation was performed by the method described in [5] using the X-ray pattern of crystalline GeS_2 synthesized from simple substances. The maximum fraction

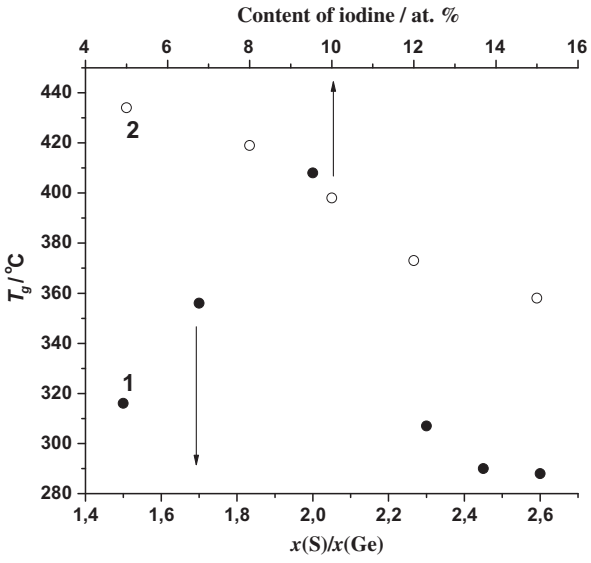

Fig. 1. Variations in T_g for (1) $[GeS_x]_{90}I_{10}$ and (2) $yGeS_2$–$(100-y)GeI_4$ glasses.

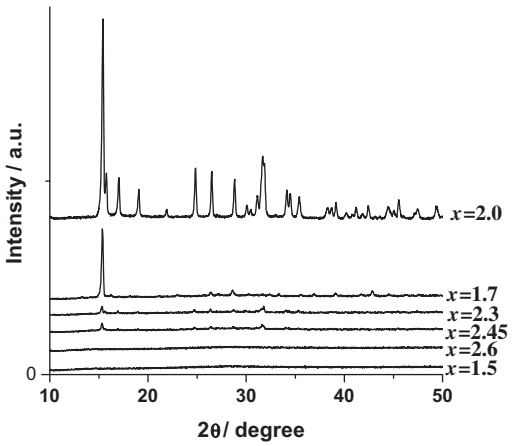

Fig. 2. XRD patterns of $[GeS_x]_{90}I_{10}$ glasses after poly-thermal annealing up to 650 °C.

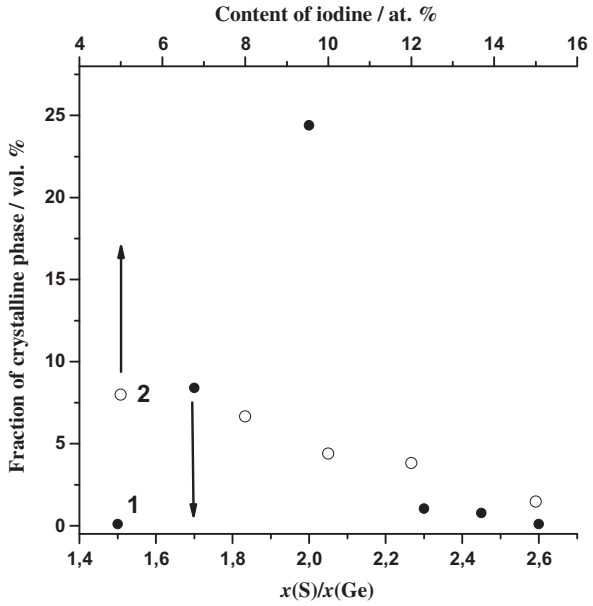

Fig. 3. Dependence of volume fraction of crystalline phase on glass composition: 1 – $[GeS_x]_{90}I_{10}$ system; 2 – $yGeS_2$–$(100-y)GeI_4$ system.

of crystalline phase (24 vol.%) corresponds to $[GeS_{2.0}]_{90}I_{10}$ glass. The calculated fraction of crystalline phase for $[GeS_{1.5}]_{90}I_{10}$ and $[GeS_{2.6}]_{90}I_{10}$ glass compositions did not exceed 1 vol.% (the limit of detection for the used XRD methodology).

The absorption spectra of $[GeS_x]_{90}I_{10}$ glasses in the spectral range of 450–800 nm are given in Fig. 4. The position of the short-wave absorption edge of samples depends on glass composition nonmonotonically. Using the spectra obtained by the standard procedure [8] in the coordinates $(\alpha h\nu)^{1/2} = f(h\nu)$, the values of the band gap energy of glasses have been calculated (Fig. 5). The maximum value E_g (2.47 eV) corresponds to $[GeS_{2.0}]_{90}I_{10}$ glass. The values of the glass transition temperature and the band gap energy are given in Table 1.

Transmission of glasses in the spectral range of 2–10 μm was 75–85% for samples with thickness up to 10 mm. The absorption spectra of the samples (Fig. 6) exhibited impurity bands of hydrogen and oxygen in the form of S–H (4.0, 3.1 μm), Ge–H (4.9 μm), Ge–O (7.9 μm) bonds, H_2O (6.32, 2.85 μm), COS (4.92 μm), CS_2 (6.68 μm), H_2S (4.31 μm) molecules and the broad bands of intrin-