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Preparation and investigation of $[GeSe_4]_{100-x}I_x$ glasses as promising materials for infrared fiber sensors

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ABSTRACT

The glasses of $[GeSe_4]_{100-x}I_x$ (x = 1, 3, 5, 8, 10) compositions are prepared; their thermal properties, transparency in the mid-IR range and stability against crystallization are investigated. The glass transition temperature (T_g) in this system decreases monotonically with increasing iodine content from the value of T_g = 176 °C at x = 1 to T_g = 129 °C at x = 10. It has been determined by X-ray diffraction method that the addition of iodine reduces the volume fraction of the crystalline phase in glasses after annealing at 350 °C. Using a single crucible technique, the rod of $[GeSe_4]_{95}I_5$ glass was drawn into a single-index fiber of 300 μm diameter and 10 m length. The optical losses were 2–3 dB/m in the spectral range 2.5–8 μm; the minimum optical losses were 1.7 dB/m at a wavelength of 5.5 μm. The content of impurity hydrogen in the form of Se-H in the fiber was about 3.6 ppm(wt), impurity oxygen in the form of Ge-O is 1 ppm(wt). The possibility of use of such $[GeSe_4]_{95}I_5$ glass single-index fiber for infrared analysis of liquids by example of crude oil and water solutions of acetone has been demonstrated.

1. Introduction

A promising area of application of chalcogenide glasses is IR spectroscopy using fiber-optic sensors for the analysis of liquids and gases [1]. Glasses for such fiber sensors must have a wide range of transparency in the mid-IR region and a high stability against crystallization, which provides the possibility to draw the optical fiber. Currently, the As - Se - Te, Ge - Se, Ge - Se - Te and Ge - As - Se - Te glass fibers are used as materials for IR sensors [1–3]. An advantage of optical fibers based on telluride glasses is their transparency in the range of 2–12 μm, where there are the selective absorption bands of most organic substances. However, the tendency to crystallization of these glasses hinders the preparation of low-loss optical fibers, which reduces the sensitivity of the sensors. The obtained background optical losses in chalcogenide fibers in the spectral range 6–9 μm, which depends on the glass composition and impurity content, are as following: <0.6 dB/m (minimum is 0.1 dB/m at a wavelength of 6.5 μm) for $GeSe_4$ glass [4], 1 dB/m for $Ge_{30}As_{10}Se_{30}Te_{30}$ glass [5], 1–5 dB/m for $Ge_{27}Se_{18}Te_{55}$ glass, 10 dB/m for $Ge_{21}Se_3Te_{76}$ glass [6], <1 dB/m for $As_{30}Se_{50}Te_{20}$ glass [7]. Due to the low optical losses, the Ge - Se glass fiber sensors may be very sensitive to determine the substances that absorb IR radiation up to 9 μm wavelength (saturated, unsaturated and aromatic hydrocarbons, ketones, aldehydes, etc.). At present, the prospect of sensors based on $GeSe_4$ glass fibers to determine carbon dioxide is shown in paper [8].

Despite the relatively high stability of $GeSe_4$ glass against crystallization, its long-term heating during the fiber drawing process leads to the formation of the crystalline phase [9]. It is known that the addition of iodine to Ge-Se-based glasses increases their stability against crystallization and transparency in the mid-IR range, but at the same time reduces the glass transition temperature [10]. Based on this, it can be expected that the incorporation of iodine atoms in the Ge-Se glass matrix will improve the properties of Ge - Se glass fibers for optical sensors. At present, the properties of Ge - Se - I glasses were studied not enough to establish properly compositions which are suitable for drawing optical fibers by crucible method. The aim of this study was to prepare the glasses of $[GeSe_4]_{100-x}I_x$ (x = 1, 3, 5, 8, 10) compositions, to investigate their optical, thermal properties, stability against crystallization and to show the possibility in principle to fabricate the optical fibers. The choice of compositions is caused by the fact that in the Ge - Se system the $GeSe_4$ glass composition has the greatest stability against crystallization [4]. Adding more than 10 at.% of iodine can significantly reduce the thermal and chemical stability of chalcogenide glasses.

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2. Experimental

To prepare $[GeSe_4]_{100-x}I_x$ glasses, germanium of purity 6N, selenium of purity 6N additionally purified by double vacuum distillation, and the germanium(IV) iodide synthesized from specially pure elements and purified by triple vacuum distillation were used. According to the atomic-emission spectrometry with inductively coupled plasma, the sum content of 28 metal impurities in the obtained germanium(IV) iodide does not exceed 5 ppm(wt). The reagents were weighed and loaded into silica-glass ampoules to produce 15 g of glass:

$$0.25x\mathrm{GeI_4} + (20 - 0.45x)\mathrm{Ge} + (80 - 0.8x)\mathrm{Se} = [\mathrm{GeSe_4}]_{100-x}\mathrm{I}_x. \quad (1)$$

The ampoules with the charges were evacuated to 10^{-6} Torr (~10^{-4} Pa) and sealed off from the vacuum system. To prepare low impurity content glasses, the germanium(IV) iodide and selenium were loaded into a silica-glass reactor with a batch of germanium by vacuum evaporation from intermediate ampoules. Preparation and homogenization of the glass-forming melt were carried out in a rocking muffle furnace at the temperature 750 °C for two hs. The glass samples were prepared by quenching the melt in water with subsequent annealing near the expected glass transition temperature and slow cooling to room temperature.

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 50–450°C. The accuracy of temperature measurement was within the limits of ±0.5 °C. The glass stability against crystallization was additionally studied by X-ray diffraction (XRD) method using an X-ray diffractometer XRD-6000 Shimadzu (CuK_α-radiation). To this, the glass samples were annealed in evacuated silica-glass ampoules for 5 hs at 350 °C (by 50–70 °C above the fiber drawing temperature). The samples cooled to a room temperature were then triturated into powder and investigated by XRD in the range of $2\theta = 10–60°$. The optical transmission of prepared glasses in the range of 2–18 μm was investigated by means of IR-spectroscopy (Fourier transform IR-spectrometer Tensor 27, Bruker). To measure the optical transmission, the glass samples were in the form of rods (discs) of diameter 10 mm and length: 2–40 mm with parallel-plate polished surface plates.

The obtained glass samples were used to produce single-index optical fibers. The fibers were drawn from a single crucible at a temperature of thermostat of 280–300 °C depending on the glass composition. About 10 m of 300–400 μm diameter single-index fibers of different glass compositions was manufactured. The optical losses in fibers were measured using the conventional cut-back technique.

The prepared single-index $[GeSe_4]_{95}I_5$ glass fiber was tested to verify the suitability of Ge - Se - I glasses as an infrared sensor materials. For this purpose, the transmission spectrum of the optical fiber of 1 m long and 300 μm in diameter was recorded in air. The optical fiber section of 15 cm length was then immersed into the analyzed liquid (solution of acetone in water or crude oil), and the transmission spectrum of this immersed fiber was recorded as well. The absorption spectrum of the analyzed liquid was calculated by the Lambert-Beer's equation:

$$A(\lambda) = -\log\left(\frac{I_s}{I_{ref}}\right), \quad (2)$$

where A(λ) is absorbance at a wavelength λ; I_{ref} and I_s are intensities of radiation passed through the fiber in air and after its immersion into the analyzed liquid, respectively.

3. Results

The DSC heating curves of prepared samples show the characteristic glass transition interval and do not show crystallization exothermic signals. Table 1 gives the values of the glass transition temperature (T_g) of the samples of different chemical composition. The glass transition temperature in $[GeSe_4]_{100-x}I_x$ glasses decreases monotonically with increasing iodine content from the value of $T_g = 176$ °C at $x = 1$ to $T_g = 129$ °C at $x = 10$. According to the TGA, the weight loss at a heating up to 450 °C does not exceed 0.5 wt% indicating their thermal stability at temperatures of drawing optical fibers (280–300 °C).

Fig. 1 shows the XRF patterns of glass samples annealed at 350 °C for 5 hs and crystallized germanium(IV) selenide prepared by melting of simple special pure substances (corresponds to the card PDF no.71-0117 [11]). The XRF pattern of $[GeSe_4]_{99}I_1$ glass exhibits low-intensity diffraction reflections from crystallographic planes at 14.5° and near 30°, which are characteristic for $GeSe_2$. The volume fraction of the crystalline phase in the sample, estimated as the relative integrated intensity of the reflections, was 3%. The sample of the same glass, annealed for 5 hs at T_g, did not crystallized. Other glass samples after annealing at 350 °C were X-ray amorphous; thus, the content of the crystalline phase in them was less than 1 vol%. The obtained results show that the addition of 3 at.% of iodine to the $GeSe_4$ glass significantly increases its stability against crystallization.

Absorption spectra of $[GeSe_4]_{100-x}I_x$ glasses in the spectral range of 2–17 μm are shown in Fig. 2(a). The sample "$x(2) = 5$" was prepared by melting of charge elements loaded in the synthesis reactor by vacuum evaporation from intermediate ampoules. The chemical components of other glass samples were loaded in air. The spectra of glasses show selective absorption bands of water impurity (2.79 μm, 6.3 μm), Se-H (4.51 μm, 3.50 μm), Ge-O (7.9 μm, 12.6 μm), Se - O (10.8 μm) bands and intrinsic absorption bands of Se-Se (13.2 μm) [12]. The integrated intensity of the absorption of Se-H band (4.51 μm) decreases monotonically with increasing iodine content in glass (reduction of selenium content). The intensity of impurity bands in the spectrum of glass "$x(2) = 5$" is significantly lower than that in the spectra of other samples. Increase of iodine content in glasses from 1 to 10 at.% causes a slight displacement of the fundamental edge of transmission to a side of longer wavelengths (Fig. 2(b)). This is due to the increase in reduced mass of glass matrix after the replacement of selenium atoms by iodine. The values of wavelengths corresponding to the absorption coefficient of $\alpha = 2$ cm^{-1} (1% transmittance for a sample with optical path length of 1 cm) for $[GeSe_4]_{100-x}I_x$ glasses are given in Table 1.

Fig. 3 shows the spectrum of total optical losses of the 300 μm diameter single index $[GeSe_4]_{95}I_5$ glass fiber. In the spectral range of 2–9 μm, there are impurity absorption bands of water, Se-H and Ge-O. The optical losses due to hydrogen impurity in the form of Se-H (4.51 mm) are 4 dB/m. The minimum optical losses in the fiber were 1.7 dB/m at a wavelength of 5.5 μm. The absorption spectra of this fiber immersed in a solution of acetone in water and in a crude oil are shown in Figs. 4 and 5. The most intense bands in the spectra of water solutions of acetone at 5.87 μm and 2.95 μm correspond to vibrations of carbonyl and stretching vibrations of water. With increasing the acetone concentration in the water solution, the intensity of its absorption bands (5.87 μm, 7.02 μm, 7.32 μm, 8.11 μm) increases, and the intensity of the absorption bands of water (2.95 μm, 6.08 μm) naturally decreases. In the spectrum of crude oil, the absorption bands of long-chain saturated hydrocarbons of normal and isomeric structure (3.46 μm, 6.95 μm, 7.36 μm);