Fiber sensor on the basis of Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$ glass for FEWS analysis

A.P. Velmuzhov, V.S. Shiryaev[*], M.V. Sukhanov, T.V. Kotereva, M.F. Churbanov,
N.S. Zernova, A.D. Plekhovich

G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinin Str., Nizhny Novgorod, 603950, Russia

ARTICLE INFO

ABSTRACT

The high-purity Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$ glass sample was prepared by chemical distillation purification method. This glass is characterized by high value of glass transition temperature (263°C), high optical transparency in the spectral range of 2—10 μm, and low content of residual impurities. The Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$ glass rods were drawn into single-index fibers using the "rod" method and the single crucible technique. The optical losses in the 400 μm diameter fiber, fabricated by the "rod" method, were within 0.3—1 dB/m in the spectral range 5.2—9.3 μm. The minimum optical losses in the 320 μm diameter fiber, fabricated by the "crucible" technique, were 1.6—1.7 dB/m in the spectral range 6—8.5 μm. Using these Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$ glass fibers as a sensor, the aqueous solutions of acetone (0—20 mol.%) and ethanol (0 —90 mol.%) were analyzed by fiber evanescent wave spectroscopy. Peculiarities in the change of the integrated intensity and spectral position of absorption bands of these organic substances in dependence on the analyte composition and the length of the sensitive zone were established.

1. Introduction

The fiber evanescent wave spectroscopy (FEWS) is a rapidly developing method of analysis. To date, this method is used to study the mixtures of organic and inorganic substances, petroleum and petroleum products, biomaterials, food, to determine the content of toxic impurities in water, etc. [1,2]. The main advantage of the FEWS method is the possibility of remote testing of samples outside a spectrometer that allows carrying out the analysis of substances directly in the system without additional sampling.

The main materials for the production of middle infrared (mid-IR) fiber sensors are chalcogenide glasses and crystalline halides of silver and thallium [3]. Among chalcogenide glasses, the glasses in As-Se, As-Se-Te, Ge-Se-(I), Ge-Te-(Se or AgI) and Ge-As-Se-Te systems are most promising for mid-IR sensory analisis [1,2,4—6]. Unfortunately, the glass transition temperature of As-Se [7], As-Se-Te [8], Ge-Se-(I) [9] and Ge-Te-(Se or AgI) [10,11] glasses is lower than 185 °C, which reduces the number of applications of such fibers. In addition, the glasses in Ge-Se and Ge-Te-(Se or AgI) systems have low stability against crystallization. The advantages of the quaternary Ge-As-Se-Te glass system are high glass-forming ability

due to the presence of arsenic in the composition, wide transparency area in the mid-IR range due to heavy tellurium atoms (and absence of sulfur), and good stability against crystallization [6,12,13]. The increase in the germanium content in the Ge-As-Se-Te system promotes high T$_g$ value [12], which is important, when the glass fiber sensor is used for the study of high-temperature processes [3]. As an example, the authors of [6] have fabricated the Ge$_{30}$As$_{10}$Se$_{30}$Te$_{30}$ glass fiber sensor (T$_g$ = 265 °C) and have shown its promising opportunities to study toxic organic substances (chloroform, methanol, hexane, etc.).

In this work, we propose Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$ glass as a material for fabrication of the FEWS sensor. The choice of this composition was caused by increase in glass-forming ability due to the increased arsenic content as compared with Ge$_{30}$As$_{10}$Se$_{30}$Te$_{30}$ glass and by shift of the transmission edge to longer wavelengths due to high content of tellurium. A sufficiently high glass transition temperature is achieved by increasing the total concentration of the cationic components with respect to the anionic ones [13] (40/60 = 0.67 for Ge$_{30}$As$_{10}$Se$_{30}$Te$_{30}$ glass and 43/57 = 0.75 for Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$).

The aim of the paper was to produce a single-index optical fiber of high-purity Ge$_{26}$As$_{17}$Se$_{25}$Te$_{32}$ glass and to show the prospects of its use as a fiber sensor for the study of liquid solutions by FEWS. Aqueous solutions of acetone and ethanol, having strong absorption bands in the spectral range 3—10 μm, were chosen as model systems. The investigation of these solutions is necessary for a

* Corresponding author.
    E-mail address: shiryaev@ihps.nnov.ru (V.S. Shiryaev).

variety of processes of food and chemical industry, environmental monitoring, and medical applications [1].

2. Experimental

To prepare high pure $Ge_{26}As_{17}Se_{25}Te_{32}$ glass, the initial special purity substances (Ge of purity 6N; As of purity 5N; Se of purity 5N; tellurium of purity 6N) were used. The volatile components of the charge (arsenic, selenium and tellurium) were additionally purified by double vacuum distillation to remove the oxygen impurity and water. The process of preparation of high purity $Ge_{26}As_{17}Se_{25}Te_{32}$ glass was described in detail in papers [14–17]. A general basic approach is the chemical distillation purification of the glass melt using the getters of impurities. For binding the impurities of oxygen and hydrogen, 500 ppm(wt) of pure aluminum and 700 ppm(wt) of pure $TeCl_4$ were added to the glass charge. The melting process of the batch was carried out in an evacuated silica-glass ampoule at 850 °C for 7 h in a rocking muffle furnace. To remove the products of reaction of chemical getters and impurities from the melt, a multi-stage vacuum distillation was performed. To keep the required glass composition, this process was carried out in the closed system with a low rate of evaporation and without a cube residue. The purified glass melt was then homogenized at 750 °C for 5 h in the muffle rocking furnace and quenched in air. The final glass sample was annealed at 250°C for 30 min with subsequent cooling to room temperature. The prepared glass rod was 14 mm in diameter and 150 mm in length.

The composition of the glass sample after distillation was determined by energy dispersion X-ray microanalysis using a scanning microscope SEM-515 (Philips, Netherlands). Thermal scanning calorimetric analysis (DSC) and thermal gravimetric analysis (TGA) of the glass sample were carried out using a synchronous Netzsch STA 409 PC Luxx analyzer with sensitivity of 1 μV/mW and accuracy with respect to temperature ±0.5°C, at the heating rate 10 K/min in the temperature range 50–450 °C. The glass transition temperature (Tg) was determined from the DSC heating curve as the intersection point of tangents in the initial region of thermal event [8,12]. The transmission of the as-prepared glass was determined using IR-spectroscopy (Fourier transform IR spectrometer Tensor 27 (Bruker)) in the spectral range 2–12 μm. To measure the optical transmission, the glass samples were cut in the form of rods with diameter of 14 mm and lengths of 32 and 80 mm with parallel-plate polished surface plates. To fabricate single-index fibers, two methods were used: a well-known "rod" method and a single crucible technique. The 80 mm long $Ge_{26}As_{17}Se_{25}Te_{32}$ glass rod was drawn into a single-index fiber with diameter of 400 μm and length of 30 m. Using a single crucible technique, the $Ge_{26}As_{17}Se_{25}Te_{32}$ glass rod of 32 mm length was drawn into a single-index fiber with diameter of 320 μm and length of 35 m. The optical losses of as-prepared fibers were measured using the conventional cut-back technique by means of FTIR spectrometer IFS-113 (Bruker).

The 70 cm long fiber pieces were used as optical sensors, which were placed in the U-shaped glass tube filled with a precise volume of the test liquid mixture. The transmission spectra with a resolution of 8 cm^{-1} were obtained by averaging 32 scans. The absorption spectrum of the analyzed liquid was calculated by the equation:

$$A(\lambda) = -\log\left(\frac{I_s}{I_{ref}}\right),$$ (1)

where A (λ) is the absorption at wavelength λ; I_{ref} is the intensity of radiation passing through the optical fiber without the liquid analyte; and I_s is the intensity of radiation passing through the fiber

immersed into the analyzing liquid. The length of the fiber part contacting with a solution was varied from 8 to 22.5 cm by adding an appropriate volume of liquid to the measuring cell. For measurements, the aqueous solutions of acetone with the concentration of 1, 5, 10, 15, 20 mol.% and aqueous solutions of ethanol with the concentration of 10, 30, 50, 70, 90 mol.% were prepared. Before each series of measurements, the fiber was washed with deionized water and purged with a stream of hot air to remove traces of analytes.

3. Results

The results of synchronous thermal analysis of $Ge_{26}As_{17}Se_{25}Te_{32}$ glass are shown in Fig. 1. The DSC heating curve of this obtained sample is characterized by one endothermic event connected with the glass transition temperature (T_g). The T_g for the $Ge_{26}As_{17}Se_{25}Te_{32}$ glass is 263 °C; it is one of the highest values among selenide glasses used as materials for optical fiber sensors (Table 1). The DSC heating curve does not exhibit crystallization exothermic signals up to 500 °C at the heating rates of 2.5 and 10 K/min that demonstrates the low tendency to crystallize. According to TGA, the weight loss at a heating up to 500 °C does not exceed 0.12 wt%.

The absorption coefficient spectrum of $Ge_{26}As_{17}Se_{25}Te_{32}$ glass sample of optical path-length 32 mm in the spectral range 2–12 μm is shown in Fig. 2 (the insert). The absorption spectrum exhibits weak bands due to selective impurity absorption of Se-H (2190 cm^{-1}) and Ge-H (2000 cm^{-1}) [19]. The concentrations of impurity hydrogen in the form of Se-H and oxygen in the form of Ge-O, estimated using the known extinction coefficients [19–22], were 0.04 ppm(wt) and <0.03 ppm(wt), respectively. The presence of C-H bonds (weak absorption bands at 2850 and 2920 cm^{-1}) in the glass spectrum is likely to be due to surface contamination. The total optical loss spectra of the fibers fabricated by two different drawing methods (Fig. 2, curves 1 and 2) exhibit the same impurity absorption bands as for bulk glass sample, have similar shapes, but various level of baseline losses. The optical losses in the 400 μm diameter fiber, fabricated by the "rod" method, were within 0.3–1 dB/m in the spectral range 5.2–9.3 μm. The minimum optical losses in the 320 μm diameter fiber, fabricated by the "crucible" technique, were 1.6–1.7 dB/m in the spectral range 6–8.5 μm. The increase in optical losses of fiber drawn from crucible was likely to be due to particular glass crystallization during drawing process. The content of hydrogen impurity in the form of Se-H groups and oxygen impurity in the form of Ge-O, calculated from the optical loss spectrum of the fiber, was 0.03 ppm(wt). Therefore, the fiber drawing process does not cause any significant additional
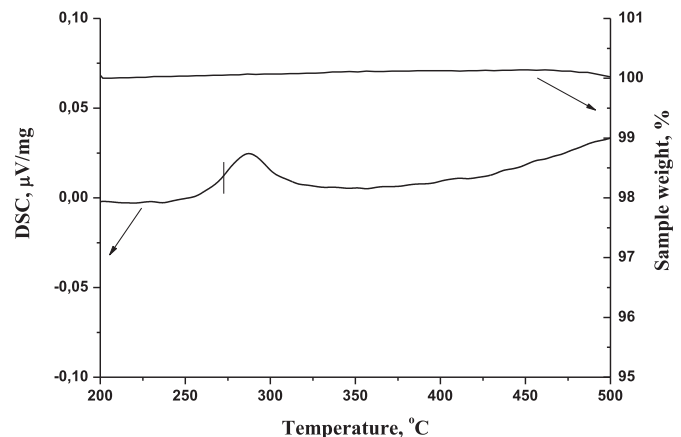

Fig. 1. DSC and TGA heating curves of the as-prepared $Ge_{26}As_{17}Se_{25}Te_{32}$ glass.