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Preparation of low-loss core–clad As–Se glass fibers

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ABSTRACT

Arsenic selenide glass with the low content of residual impurities (hydrogen ⩽0.02 ppm wt, oxygen <0.1 ppm wt, carbon <0.5 ppm wt, silicon ⩽0.1 ppm wt, and metals 0.01–0.1 ppm wt) is prepared. The effect of the method for producing arsenic selenide on the content of limited impurities and the optical transmission in the mid-IR range is investigated. Optical fibers of high-purity $As_{30}Se_{70}$–$As_{40}Se_{60}$ glass compositions are drawn. The minimum optical loss in unclad $As_{35}Se_{65}$ glass fiber of diameter 200 μm is 70 dB/km at wavelengths of 2.7 and 3.8 μm. The minimum optical loss in core–clad $As_{40}Se_{60}$/$As_{38}Se_{62}$ glass fiber is 67 dB/km in the 6–6.5 μm spectral range, which is the best result for the core–clad As–Se glass fibers.

1. Introduction

The preparation of high-purity As–Se glasses and low-loss optical fibers is stimulated by prospects of creation of various telecommunication systems for laser radiation delivery, remote temperature pyrometer, fiber sensors and lasers of the mid-IR range [1–3]. Depending on the functional application, there are IR optical fibers of different types: unclad fibers – for chemical sensors, multi-mode ones – for transmission of infrared radiation, single-mode ones – for creating fiber lasers, supercontinuum generators and spatial filters of mid-infrared.

The main parameters of optical fibers that determine their practical application are optical losses and the spectral transmission range. According to estimates [4,5], the minimum optical losses in glassy arsenic selenide are 0.08–0.1 dB/km at a wavelength of 6.1 μm.

The typical optical losses in arsenic selenide fibers are significantly higher and have the values of 0.2–0.8 dB/m. Commercially available As–Se fibers with optical losses of 0.5–1 dB/m in the range of 1.5–6.5 μm had been producing by the Amorphous Materials Inc [6] over the past twenty years. According to [7], the unclad optical fiber from the $As_{35}Se_{65}$ glass, prepared by direct synthesis of high purity arsenic and selenium, was drawn from the crucible and had the minimum optical losses of 76–80 dB/km in the transmission windows at a wavelength of 4 μm and less than 100 dB/km in the range of 3.6–6 μm. According to [8], the core–clad $As_{39}Se_{61}$/$As_{37}Se_{63}$ glass fiber had optical losses of 490 dB/km at a wavelength of 7.42 μm. Currently, the CorActive High Tech, Inc [9] proposes As–Se glass fibers with optical losses of 200–400 dB/km.

This level of optical losses in arsenic selenide fibers is sufficient for their use for development and creation of remote pyrometers and nonlinear optical devices [1,2,10,11]. However, the presence of impurity absorption bands in the spectra of optical fibers due to Se–H, OH, As–O impurity bonds [11], which overlap important spectral intervals and increase optical losses, limits the areas of application, for example, such as chemical sensors, fiber lasers and long-distance systems for transmission of infrared radiation. In the case of full realization of potential properties of material, i.e. when real optical losses in fibers will be close to theoretical level in the spectral range of 1–11 μm, the application areas of arsenic selenide optical fibers can be greatly expanded.

The main mechanisms of excess optical losses in arsenic selenide optical fibers are extrinsic absorption of oxygen, hydrogen, carbon and silicon impurities dissolved in the glass matrix and scattering by heterophase inclusions and crystals. To achieve the optical losses in the As_2Se_3 glass fiber at the level of intrinsic losses, the content of impurities of oxygen, carbon and silicon should not exceed 0.1 ppm wt, and hydrogen – 1 ppb wt [11]. The content of these limited impurities in typical glasses is 5–20 times higher. To improve the chemical and phase purity of glass for the manufacture of optical fibers with optical losses, close to intrinsic level, the further development of methods for producing high purity glasses and fibers is necessary. For this, the following problems should be resolved: the choice of optimal macro-compositions of glasses with low tendency to crystallization and micro-separation; comparison of chemical purity of glasses prepared by different variants;

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establishment of the possibility of known methods and procedures for preparation of high pure samples; development of new methods for glass synthesis.

Generally, the production of As–Se glasses was carried out as a direct melting the initial elements in an evacuated silica-glass ampoule and subsequent quenching glass-forming melt [7,11,12]. The disadvantage of this method is the high content of impurities of light elements. One of the effective ways to improve the purity of As–Se glasses is an addition to the traditional scheme of procedure of chemical distillation purification of glass-forming melt with chemical getters, such as Al, Mg [11,12], $TeCl_4$, $SeCl_4$ or $AlCl_3$ [8,13,14].

The aim of this work was a preparation of As–Se glass samples with the lowest content of gas-forming impurities (oxygen – less than 0.1 ppm wt, hydrogen – less than 0.02 ppm wt), and manufacturing unclad and core–clad glass fibers with optical losses less than 100 dB/km.

2. Experimental

The glass samples of As_xSe_{100-x} (x = 30–40) compositions were prepared by direct melting of as-received specially pure starting elements in an evacuated silica-glass ampoule in a rocking furnace. The difference in macro-composition was caused by a search of glasses with low tendency to crystallization and phase separation and selection of pairs of glasses for the manufacture of core–clad optical fibers.

The starting substances (with purity 6 N) in the form of pieces with an addition of chemical getters of impurities (Al and/or $TeCl_4$) were batched in an inert atmosphere box into a silica-glass ampoule, which then was evacuated and sealed off. The charge in the evacuated silica ampoule was melted in a rocking furnace at a temperature 800 °C for 8–12 h. During melting, the impurity oxygen reacting with Al formed a non-volatile Al_2O_3, and chlorine from $TeCl_4$ reacted with impurity hydrogen to form volatile HCl. Then, it was carried out the purification of the As–Se melt from these limited impurities by multiple vacuum distillation, with subsequent homogenization of distillate at 750 °C for 6 h; quenching in air; annealing at 175 °C for 1 h, and cooling to room temperature.

The glass compositions after the final distillation and homogenization were examined by energy-dispersive X-ray microanalysis using a scanning electron microscope SEM-515 (Philips, Netherlands) equipped with an energy dispersive analyzer EDAX-9900 (EDAX, USA). Thermal analysis of the glass samples (differential scanning calorimetry (DSC)) was carried out using a synchronous Netzsch STA 409 PC Luxx analyzer with sensitivity of 1 μV/mW and accuracy with respect to temperature ±1 K, at the heating rate 10 K/min in the temperature range 50–500 °C.

The content of impurity metals and silicon in prepared glasses was determined by means of laser mass-spectrometry. The impurity content (oxygen, hydrogen, carbon) was determined by means of absorption spectra using the known extinction coefficients [11]. Glasses were analyzed using IR-spectroscopy (Fourier transform IR spectrometer IRP Prestige–21, Shimadzu, Japan).

Optical fibers were produced from a melt from a single or double crucible [11]. The core and clad glasses were placed in appropriate containers of double crucible and heated to a plastic state. Inert gas (Ar) pressure was used to create the necessary melt flows through the coaxial circular and annular channels of the die. The core–clad optical fiber with a required outer diameter and a ratio of core/clad diameters was drawn. The fibers were coated with a protective fluoroplastic F-42 layer. The fiber diameter was from 200 to 500 μm, depending on the drawing rate and the overpressure of the inert gas above the melt.

The optical losses in fibers were measured using the conventional cut-back technique. An error of measurement was 4% and 8% at the level of optical losses 1 and 0.1 dB/m, respectively. To reduce cladding modes, the Ga–In alloy immersion of input and output fiber surface was applied.

3. Results

The prepared glass samples were in the form of rods of diameter 10–30 mm and length 50–200 mm.

Fig. 1 gives absorption spectra of As–Se glass samples of optical path-length 115 mm prepared by melting with Al and $TeCl_4$ getters. The intensity of impurity absorption bands does not exceed 0.02 cm^{-1}, that is an evidence of high efficiency of used purification technique. The content of main impurities in arsenic selenide samples, according to IR-spectroscopy and mass-spectrometry data, is given in Table 1. Fig. 2 shows the DSC curves of As–Se glasses of different compositions.

Fig. 3 gives optical loss spectra of unclad As–Se glass fibers. Fiber 1 was manufactured from the As_2Se_3 glass prepared by direct synthesis from high purity As and Se batched into a silica-glass ampoule by vacuum distillation from intermediate ampoules. This fiber of diameter 350 μm was drawn from a rod at the temperature of 340 °C. The minimum optical losses in this fiber were 150 dB/km at a wavelength of 6.7 μm.

Unclad fiber 2 (Fig. 3) was manufactured from the $As_{35}Se_{65}$ glass sample prepared using chemical and distillation purification with 500 ppm wt Al getter, with subsequent double distillation and homogenization at 750 °C. The fiber was drawn from a single crucible at the temperature of 280 °C, at a drawing rate of 3 m/min. It was prepared more than 100 m of the fiber of diameter 200 μm. The minimum optical losses in this unclad As–Se 200 μm fiber, measured on several 15 m pieces, were 70 dB/km at wavelengths of 3.8 μm and 2.68 μm.

Fig. 4 gives the spectrum of core–clad fiber (core diameter is 250 μm, clad diameter is 400 μm) manufactured from pair of high-purity $As_{40}Se_{60}/As_{38}Se_{62}$ glasses prepared using double chemical distillation purification with 750 ppm wt Al and 2000 ppm wt $TeCl_4$ getters. This core–clad glass fiber having a protective F-42 fluoroplastive coating was drawn by double crucible technique. The optical losses were measured on several fiber pierces of 30 m length. To remove the influence of cladding modes, the surface of input and output ends of fiber was immersed by liquid Ga–In alloy. Minimum optical losses in the fiber were 67–70 dB/km at wavelengths of 6–6.5 μm. Numerical aperture measured at a wavelength of 2 μm was 0.28.

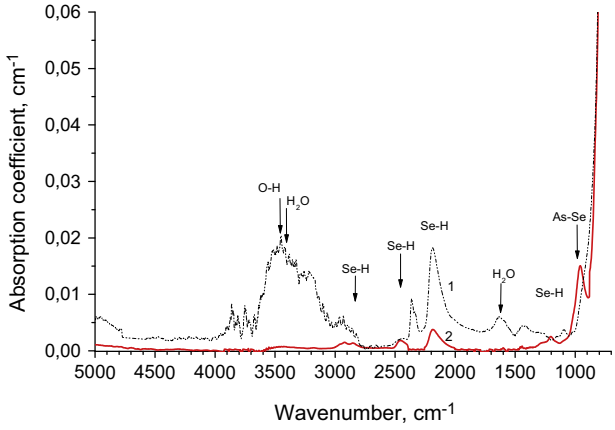

Fig. 1. Absorption spectra of arsenic selenide glasses prepared with adding 500 ppm wt Al (curve 1), and 750 ppm wt Al + 2000 ppm wt $TeCl_4$ (curve 2).