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Development of technique for preparation of As_2S_3 glass preforms for hollow core microstructured optical fibers

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For the first time, the preforms for drawing negative curvature hollow core fibers (NCHCF) based on As_2S_3 glass, promising to achieve ultra low optical losses and expansion of transmission range in the mid-infrared, have been manufactured. The theoretical minimum optical losses in proposed ideal NCHCFs are estimated to be lower than 1 dB/km. The temperature dependence of work of adhesion of As_2S_3 glass to silica glass was investigated, as well as the optimal temperature conditions for obtaining preforms were determined. The fiber preforms were manufactured by the “stack and draw” technique from substrate tubes and 8 or 10 capillaries with a designated geometry and thickness of the walls, arranged in a specific configuration for hollow core photonic crystal structure. Substrate tubes were obtained by centrifugal casting, and capillaries were fabricated by melt extraction from a double crucible.

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1. Introduction

Microstructured optical fibers (MOFs) [1] possess a number of unusual properties, such as the realization of endless region of single-mode light propagation, a specified effective mode area, a mode with zero dispersion at any wavelength, the ability to generate a supercontinuum, possibility of light propagation through hollow core; therefore they are attractive to create a variety of fiber-optic devices. Hollow core MOFs (HC-MOF) that guide radiation by Bragg diffraction have attracted a considerable amount of attention, because this kind of fibers has lower Rayleigh scattering, lower nonlinearity and potentially lower transmission loss as compared to conventional fibers. The theoretical losses in HC-MOFs can be very low, because the material absorption and Rayleigh scattering in the air are negligible compared to glass [2]. Special potential is accorded to HC-MOFs, whose core has a negative curvature of refractive index. Experiments on silica fibers of that type show not only the possibility of achieving low optical losses, but also a considerable extension of the transmission region to longer wavelengths in comparison with conventional optical fibers [2,3].

In recent years, great attention has been paid to development of the mid-infrared (IR) region, which is due to numerous potential applications in analytical IR spectroscopy, pyrometers and transmission of IR lasers. Among the wide variety of IR glasses, for mid-IR MOFs chalcogenide glasses have the best prospects. They are characterized by a number of significant advantages, such as a wide transmittance range (1-12 μm), low intrinsic losses in the mid-IR, low phonon energy, and the absence of free-carrier effects [4].

The development of chalcogenide MOFs with a hollow core (HC-MOF) is an important and urgent task because of the theoretical possibility to achieve optical losses, which are lower than material losses, an expansion of transmission range, as well as to transmit high-power CO and CO_2 laser radiation. Therefore, after the first publication on MOF of Ga-La-S system in 1998 [5], an interest in the world in the preparation and study of such fibers of different chalcogenide glasses, as a solid-core and hollow-core MOFs, has increased significantly. Published data on chalcogenide MOFs, especially with a hollow core, is limited because the production of such fibers is a rather difficult technical challenge.

In published papers on preparing chalcogenide MOFs with a solid core, the following techniques of preform manufacturing have been used: “stack and draw” (assembly of capillaries inside the substrate tube) [5-7], molding (with use of silica glass pattern of the specified photonic crystal design) [8,9], and drilling [10]. Usually the thin capillaries are drawn from the chalcogenide glass tube prepared by centrifugal casting. However, the additional heat treatment can provoke crystallization of the glass and increase the excess optical loss in the resulting fibers. The disadvantages of the drilling method to make holes in the substrate chalcogenide glass tube are the formation of broken surface layers of the holes and the need for an additional stage of glass heating.

The first production of chalcogenide HC-MOF was reported in paper [11]. This MOF was made of $Te_{20}As_{30}Se_{50}$ glass by the “stack and draw” technique and consisted of six rings of capillaries, but, unfortunately, was non-transparent. We have previously made NCHCF with relatively simple single-layer photonic crystal structure of high-purity As-Se-Te [12] and As-S-Se [13] glasses, which were transparent in the mid-IR region.

All of the known papers on chalcogenide MOFs, except those made by the drilling method, describe their preparation as based on As-Se, Ge-Se, As-Se-Te, Ge-Sb-S glass systems. The MOFs of As_2S_3 glass have not been produced previously, probably due to the high adhesion of arsenic sulfide to silica glass, which hinders production of quality tubes. The properties of As_2S_3 glass have been studied sufficiently, the methods of its preparation in a special pure state have been developed [4,14], which has made possible the production of fibers with optical losses of 12-14 dB/km at 3.0 and 4.8 μm [15]. The low tendency to crystallize of As_2S_3 glass allows multi-step heat treatment, which is especially important to prepare MOFs.

An interest in As_2S_3 glass as a material for manufacturing MOFs is caused by its high transparency in the middle IR range, low tendency to crystallize, and a relatively low linear refractive index among chalcogenide glasses (n=2.395 at 3 μm wavelength). The complicating technical issue is its high adhesion to silica glass. Therefore, the development of a technique for preparation of preforms for As_2S_3 glass HC-MOFs is urgent.

2. Fiber modeling

As a model HC-MOF, glassy arsenic sulfide was taken and a relatively simple design of photonic crystal structure developed, as tested previously for silica glass [3] and $As_{30}Se_{50}Te_{20}$ glass [12]. These HC-MOFs with a negative curvature of the core boundary belongs to the type of HC-MOFs that do not support photonic band gaps (NCHCF). Such NCHCFs have relatively high transmission losses in comparison with photonic band gap HC-MOFs, but possess a larger bandwidth. The latter is due to the fact, that the air-core localized modes are coupled only weakly with the cladding modes in the low loss wavelength regions. The high loss wavelengths in the transmission spectrum correspond to the avoided crossing of the air-core modes and the cladding modes.

Fig.1 illustrates a structure of 8 capillaries within the substrate tube with air core diameter D_{core} of 223 μm, the outer diameter of capillaries of 178 μm, the ratio of the inner and outer diameters of the capillaries of 0.8). To model the optimal design of the NCHCF, we used the FemLab 3.1 software. The values of linear refractive index of As_2S_3 glass were taken from paper [16]. By means of the finite element method, we calculated the loss level of the fundamental HE_{11} air-core mode in the spectral range of 2-16 μm. Fig. 2 gives the theoretical losses of the fundamental HE_{11} air-core mode for As_2S_3 glass fiber for the structure illustrated in Fig. 1 in comparison with $As_{30}Se_{50}Te_{20}$ glass fiber. It can be seen that the spectrum of ideal fiber with negative curvature of the hollow core is irregular, the optical losses change in the transmission windows from a minimum value of 0.001 dB/m to a maximum value of 100 dB/m. Such irregular behavior of optical losses, even in very narrow spectral ranges, is due to the weak coupling of the core modes with the dielectric modes having a high azimuthal dependence (modes with a high azimuthal index), the cut-off wavelengths of which fall in these spectral regions.

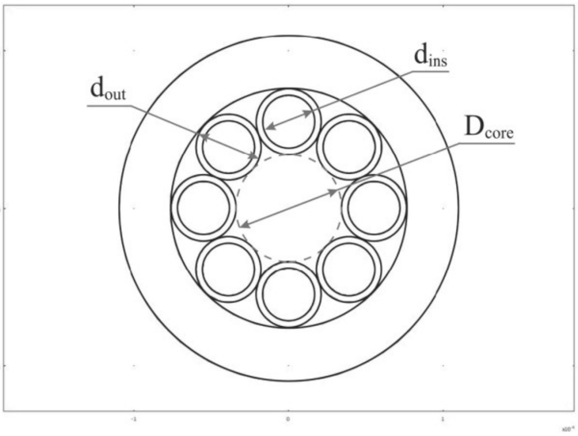

Fig. 1. HC-MOF with negative curvature of the core with cladding consisting of one row of capillaries.

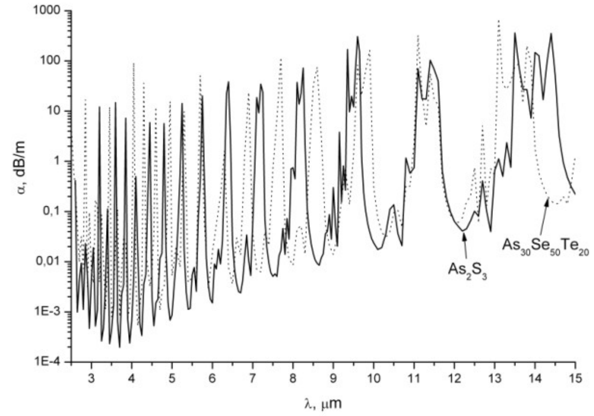

Fig. 2. The calculated transmission bands for ideal NCHCF (8 capillaries; D_{core} = 223 μm, d_{in}/d_{out} = 0.8) for As_2S_3 (solid line) and $As_{30}Se_{50}Te_{20}$ (dotted line) glasses.

Theoretical spectra of optical losses in ideal As_2S_3 and $As_{30}Se_{50}Te_{20}$ NCHCFs are similar, but transmittance bands for As_2S_3 are wider. Also, the calculated bending losses for fiber of arsenic sulfide is about 3-4 times lower as compared with $As_{30}Se_{50}Te_{20}$ (Fig. 3). The losses of the fundamental HE_{11} air-core mode for small bending radii are characterized by the resonance behavior, as has been shown previously [12].

The theoretical losses in As_2S_3 NCHCF in the field of CO_2 laser radiation at a wavelength of 10.6 μm were about 0.1 dB/m. Also, according to this finite element method, the optical losses in real arsenic sulfide glass NCHCFs were calculated (see Discussion).

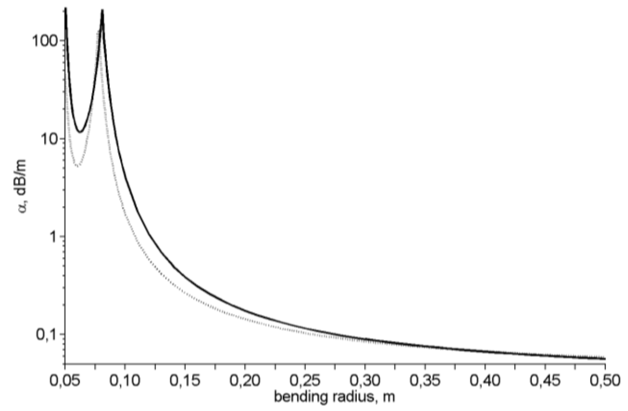

Fig. 3. Calculated dependence of the bending losses of the fundamental HE_{11} air-core mode on bending radius at $\lambda = 10.3$ μm for As_2S_3 (dotted line) and $As_{30}Se_{50}Te_{20}$ (solid line) glasses.

3. Experimental

3.1. Glass synthesis

As_2S_3 glass was produced by cooling the melt obtained by vacuum charge melting from arsenic monosulfide and elementary sulfur in a sealed silica ampoule [17]. The initial substances were purified by chemical and distillation methods. The charge weighing 0.5 kg was heated at 750^{0}C for 10 h with melt mixing. A series of additional operations was used to decrease the content of oxygen impurity and heterophase impurity inclusions. The melt was cooled under conditions excluding convective flows, with a subsequent annealing of glass to remove mechanical stress. The high-purity As_2S_3 glasses were obtained in the form of a monolithic rod with a diameter of 40 mm (weight was ~ 250 g) to draw the fine holed thin tubes (capillaries), and as rods with a diameter of 15 mm to form the substrate tubes by centrifugal casting.

The glass samples were characterized for metal impurities and silicon content by atomic-emission spectroscopy; for oxygen, hydrogen and carbon content by IR spectroscopy and for the content of heterophase inclusions of a submicron size by laser ultramicroscopy. The content of limiting impurities was as follows: carbon - <0.1 ppm wt, hydrogen as SH group - <0.5 ppm wt, silicon - ≤0.5 ppm wt, metals - < 0.1 ppm wt.

3.2. Microstructured preform preparation

Adhesion study

Preliminary experiments have shown that the formed As_2S_3 tubes cannot be separated from the inner surface of the silica ampoules without destruction unacceptably often. Therefore, the temperature dependence of arsenic sulfide adhesion to silica glass in the temperature range of 125-165^{0}C was investigated to determine the optimum conditions for manufacturing perfect substrate tubes. The adhesion value was determined experimentally by a steady detachment method [18] using a dynamometer machine with a limit of breaking force of 180 N. The measured experimental temperature dependence of work of adhesion for As_2S_3 glass is shown in Fig.4. Adhesion was higher than 180 N at the temperature above 170^{0}C, and it was below 10 N at the temperature below 120^{0}C.

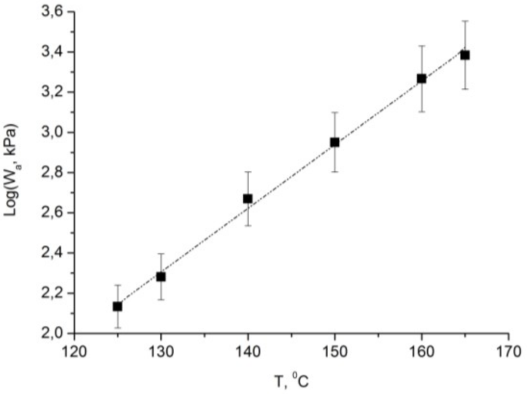

Fig. 4. Temperature dependence of work of adhesion (W_a) for As_2S_3 glass to silica glass.

Adhesion, which increases with rising temperature, is the critical parameter during the annealing of the samples in the form of rods and tubes near the glass transition temperature (185^{0}C). To prevent the destruction of preforms during the cooling process, it is useful to introduce separation step of the surface of the sulfide-arsenic glass sample from the walls of the silica ampoule, executing a forced local cooling of interface of chalcogenide and silica glasses. The “separating front” is created using directional narrow cool airflow. To avoid repeat sticking, the annealing temperature should not exceed the value of 170-180^{0}C.

Preparation of microstructured As-S preforms

Substrate As-S tubes were prepared by centrifugal casting of molten chalcogenide glass. The procedure involved the following sequential steps: 1) loading arsenic sulfide as glass rods into Heraeus silica glass ampoule (with OH-groups content of 2 ppm) having an inner diameter of 16 mm; 2) evacuation and sealing of silica ampoule with arsenic sulfide; 3) melting chalcogenide glass using a gas burner or a muffle furnace at 500^{0}C; 4) rotation of the silica glass ampoule, containing the with molten chalcogenide glass, around its axis at a speed of 800 rev/min for 1 minute in cooling mode; 5) "separation" of the surface of chalcogenide glass from the walls of silica ampoule; 6) annealing at T = 180^{0}C for two hours and 7) slow cooling the tube to room temperature in a muffle furnace. Fig. 5 a shows the photographs of the obtained chalcogenide glass tubes (outside diameter was 16 mm, internal diameter was 11 mm, length was up to 165 mm).

Capillaries of 2.6-3.2 mm diameter were manufactured from the As_2S_3 chalcogenide glass melt using double crucible technique as follows [3]. The As_2S_3 ingot was placed into the void for cladding glass, and the empty volume for core glass was pressurized with argon to 100 Pa. The cross-sections of the capillaries had a coaxial geometry with a ratio of internal and outside diameters of 0.8-0.9. Concentricity of obtained capillaries was over 80%. The fiber preforms were manufactured using the “stack and draw” technique with substrate tubes and 8 or 10 capillaries, of defined geometry and thickness of the walls, arranged in a specific configuration to achieve the hollow core photonic crystal design (Fig. 5b).

3.3. Microstructured optical fibers and their properties

The prepared preforms were used to draw NCHCFs. For this, the overpressure of dry inert gas (argon) was established in each capillary and inside of the substrate tube. The preform with an outside diameter of 16 mm was drawn in fiber with diameter of 700-900 µm. To prepare a defined structure of NCHCF, the conditions of fiber drawing (the temperature, the drawing rate, the excess argon pressure in capillaries and substrate tube) were determined by experiment. At high temperature of fiber drawing (low viscosity glass), the capillaries inside the substrate tube were distributed randomly (Fig.6 a-c). The NCHCF had a structure close to the defined one, at a drawing temperature of 310 ^{0}C. As shown in Fig.6 d,e, the capillary rings had no discontinuities, and the capillaries themselves had deviations from the original spherical shape due to conditions of fiber drawing.

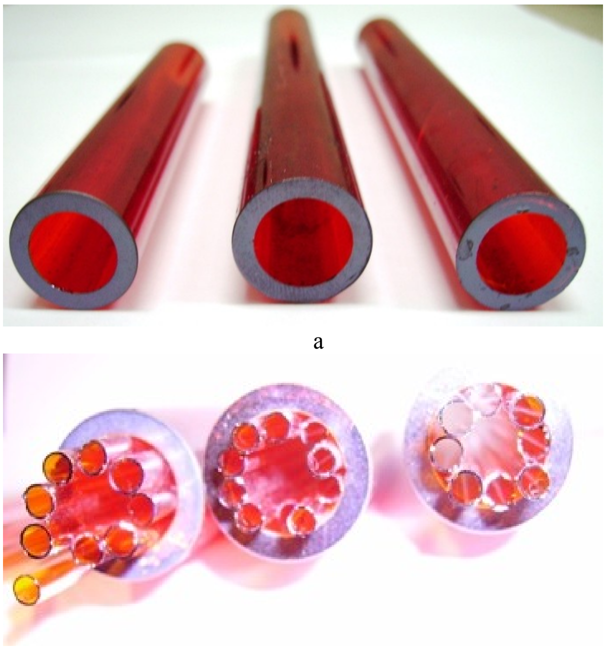

Fig. 5. (a) Substrate chalcogenide tubes; (b) HC-MOF preforms.

More than 10 meters of NCHCFs were drawn, and their optical transmittance was measured using the conventional cut-back technique. The measured length of optical fibers was about 1.5 m. To remove the influence of cladding modes, the surface of input and output ends of fiber was recoated by liquid gallium-indium alloy. The spectra of optical losses of prepared As_2S_3 NCHCFs with diameter of 700 µm illustrated in Fig. 6 (d and e) are given in Fig. 7. The optical losses in fibers without Ga-In immersion were higher than in Ga-In immersed fibers. Our best fiber (illustrated in Fig. 6e) was transparent in the 1.5-8.2 µm wavelength range and has minimum loss about 3 dB/m at 4.8 µm. Unfortunately, the obtained MOFs contained impurity bands appropriated for arsenic sulfide. There are some bands due to S-H bonds at 6.8; 4.1; 3.7; 3.1 µm; due to CO_2 impurity at 4.31 and 4.34 µm; due to OH groups at 2.92 µm; due to COS at 4.9 µm, and due to molecular H_2O at 6.33 µm.

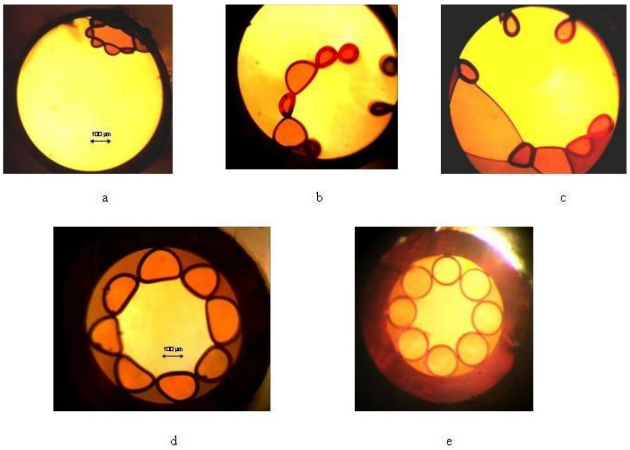

Fig. 6. The cross sections of As_2S_3 MOFs obtained under different drawing conditions. The temperature: a, b, c - 330-340^{0}C, d - 320^{0}C, d - 310^{0}C. The excess argon pressure in capillaries: a – 0, b – 100 Pa, c – 600 Pa, d - 1000 Pa, e - 4000 Pa.

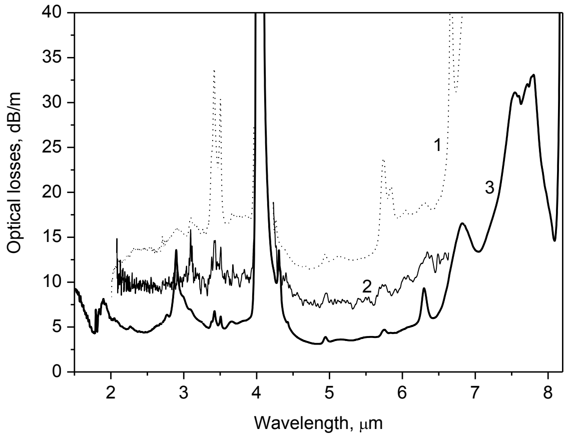

Fig. 7. The spectra of optical losses in prepared As_2S_3 MOFs with diameter of 700 µm: 1 – fiber illustrated in Fig.6d without Ga immersion; 2 - fiber illustrated in Fig.6d with Ga-In immersion; 3 - fiber illustrated in Fig. 6e with Ga-In immersion.

4. Discussion

The calculation of the structural design of As_2S_3 NCHCF, with a hollow core, by numerical experiment has shown the possibility of achieving optical losses less than 0.1 dB/m at a wavelength of 10.6 μm and 0.2-10 dB/km in the windows of transparency in the spectral region of 2-8 μm. However, a necessary condition for achieving this transmittance level is not only high purity of glass on limiting impurities and its optical homogeneity, but also the high accuracy of the geometrical dimensions of a given photonic crystal structure. The technique of preform production for NCHCFs, developed in this paper, is less labour-consuming as compared with the alternative method of drilling and avoids contamination of the inner surface of formed tube preforms.

One of the challenges of developing this technique is the preparation of “perfect” chalcogenide glass tubes of sufficient length (80-160 mm) as a support for the assembly of the preform. The realization of the centrifugal casting method of chalcogenide melt inside a silica ampoule is associated with the need to determine the time-temperature conditions to obtain the perfect substrate tube. However, it was found that the substrate arsenic sulfide tubes are fractured due to the strong adhesion of chalcogenide glass to silica glass at annealing temperatures. The temperature dependence of the work of adhesion of As_2S_3 glass to silica glass shows its exponential increase with temperature. The required breaking force is greater than 180 N at the Tg of As_2S_3 glass, near the annealing glass temperature. This underscores the necessity of the deliberate separation step of arsenic sulfide glass from the base silica ampoule using a local forced-cooling and annealing at temperatures below Tg to prevent re-adhesion. To produce a perfect As_2S_3 tube, controlling the temperature-time conditions of the glass cooling and separation stages are essential, because over-cooling of arsenic sulfide preform causes its fracture. Uncracked tubes were obtained, when the duration of centrifugation and separation was about 1 minute. Reducing the centrifugation time caused sagging of tubes, but increasing centrifugation time caused their fracture.

Preparation of arsenic sulfide capillaries by extrusion from a double crucible, in contrast to capillary drawing of a tubular preform, commonly used and reported in the literature [4-6], eliminates the additional step of heat treatment of the sample to reduce the crystallization and to obtain the smooth outer and inner surfaces of the capillaries.

Homogeneity of glass composition of chalcogenide glass substrate tubes and capillaries is among the most important criteria. Melting the chalcogenide glass inside a silica ampoule in a muffle furnace at a temperature of 500^0C before the centrifugation led to the preparation of a sufficiently homogeneous tube not containing gas bubbles not striae in the bulk, confirmed by optical microscopy and laser ultra-microscopy. Heating the glass melt using a gas burner led to inhomogeneity of the resulting glass, and the presence of striae and bubbles due to uneven heating of the glass. Optical fibers produced from such imperfect substrate tubes were uniform in diameter but partially crystallized.

The prepared NCHCFs of arsenic sulfide were suitable for the mid-IR radiation transmission, although the optical losses were higher than the theoretically predicted level. According to theoretical estimates, the ideal NCHCF can transmit more than 95% of the input power. However, our experimental NCHCFs were found to support radiation transmitting in the glass cladding of >5%, which was confirmed by the presence of SH vibrational absorption bands in the spectra of the optical loss. The decrease of optical loss in immersed fibers indicates that the radiation propagates primarily inside of the hollow core, rather than in the glass clad. Minimum optical losses in the fibers were 3 dB/m at 4.8 μm.

Real As_2S_3 NCHCFs have higher optical losses as compared with the calculated values for the ideal NCHCF, which is probably due to the inhomogeneity of fiber length and geometric imperfection of the photonic crystal structure, resulting in leakage modes in the cladding. Therefore, we calculated the optical losses of real As_2S_3 NCHCF using their cross-section as micrographs with imperfections and deviations from the ideal at 5-10 μm. The calculation of optical losses in real NCHCF in the wavelength range below 5 μm was complicated by technical reasons to estimate it. The comparison of the measured and calculated values of optical losses in real NCHCF has shown their good agreement (Fig. 8).

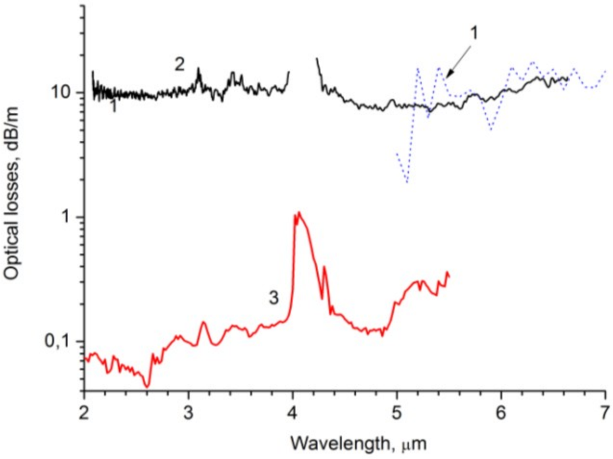

Fig. 8. The comparison of the calculated (1) and measured (2) values of optical losses in real experimental HC-MOF, and the optical losses in classic As_2S_3 glass fiber (3).

As_2S_3 HC-MOFs have not been previously described in the literature. Unfortunately, the optical losses obtained in our fabricated As_2S_3 NCHCFs exhibited excess loss compared to classic step index fibers, due to different mechanisms of radiation propagation and imperfect fiber (Fig. 8). As compared to manufacturing the $As_{30}Se_{50}Te_{20}$ glass NCHCFs of the same design, which we have previously reported in [12], the preparation of As_2S_3 glass

NCHCFs was associated with the difficulty of formation of high quality tubular preforms. As compared with quartz NCHCFs [3], the preparation of As_2S_3 NCHCFs has fundamental differences that lead to significant technological difficulties: 1) the strong dependence of viscosity of arsnic sulfide on temperature in comparison with quartz glass (more stringent requirements on the temperature gradients at fiber drawing); 2) the large refractive index increases accuracy requirements for capillary thickness (e.g., if the optical thickness is different by 10% it is necessary that the geometrical thickness differed by < 7.6% at n = 1.45 and 4.6% at n = 2.4); 3) the quality of As_2S_3 capillaries, obtained by the double crucible, is not good enough in comparison with quartz glass capillaries extending from commercial tubes. NCHCFs with a hollow core are promising especially for the transmission of high optical power, and the achievement of optical losses close to the theoretically calculated level is possible in the case of geometrically correct photonic crystal structure.

Thus, to prepare the hollow core microstructured fibers with low optical losses in the mid-IR range (special interest in fibers transmitted at wavelengths of 5-6 μm and 9.3-10.6 μm), further optimization of their design and fiber drawing conditions is required to prevent the deformation of their photonic crystal structure, which is also one of the reasons for the increase in optical losses.

5. Conclusions

The technique for manufacture of arsenic sulfide glass tubes for HC-MOFs was developed. The conditions for As_2S_3 melting, centrifugation and cooling, for separation of arsenic sulfide tube from the walls of silica ampoule, which provide the production of homogeneous substrate tubes with smooth inner and outer surfaces, with the same thickness of tube walls in diameter and in length, have been determined. A technique for the manufacture of microstructured preforms was developed, which was the assembly of the substrate glass tube and 8-10 capillaries. To improve the optical transmission of chalcogenide NCHCF, the further optimization of the design and improvement of geometric perfection during fabrication are needed.

Acknowledgments

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