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High purity arsenic-sulfide glasses and fibers with minimum attenuation of 12 dB/km

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A vitreous As_2S_3 has been produced and characterized with the impurity content of OH-groups 0.1-0.3 ppb wt, CO_2 ~ 1 ppb mole, SH-groups - 0.5-1 ppm mole, scattering centers with the diameter of ≤100 nm - $<10^4$ cm^{-3}, and transition metals - ≤0.5 ppm wt. The optical fibers made from this glass have record low optical losses of 12 ± 2 dB/km at 3.0 μm and 14 ± 2 dB/km at 4.8 μm, the average bending strength of 0.52 GPa, and the numerical aperture of 0.21 at 1.55 μm.

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1. Introduction

Chalcogenide glasses of As-S system are the most promising materials for fiber optics in the middle IR-range. This is due to their high transparency in the near and middle IR-range, low optical losses, stability to crystallization and to the effect of environment. As_2S_3 glass is the most stable to crystallization among all chalcogenide glasses. Its critical cooling rate is estimated as 2.4×10^{-6} K/s and is comparable with that for silica glass [1].

The transparency region of As_2S_3 glass with the attenuation level lower then 1 cm^{-1} covers the wavelength range of 0.8 – 11.5 μm [2] with theoretical estimation of the minimum optical losses of 0.05 dB/km near 4.3 μm [3]. Up to now the minimum optical losses in optical fibers produced from As_2S_3 were equal to 23±4 dB/km at 2.3 μm [4]. A great difference between the theoretical and experimental values is mainly explained by absorbing impurities both incorporated into the glass network and present in the form of solid and gaseous inclusions.

The level of optical losses in the region of maximum transparency of As_2S_3 glass is determined by impurities in the form of compounds of carbon, oxygen, hydrogen and by heterophase impurity inclusions of a sub-micron size. Their content in the best glass samples is 1 – 0.1 ppm wt. To achieve the intrinsic optical losses the content of limiting impurities should be lowered by 1-3 orders of magnitude accounting for the experimental values of extinction coefficients for the main absorbing impurities [5]. In this connection the main goal of the present work is to produce As_2S_3 glass with a higher purity degree as compared to the earlier achieved, and to fabricate low-loss optical fibers.

2. Experimental

As-S glass for the core and cladding of optical fibers was produced by cooling the melts obtained by vacuum charge fusion from arsenic monosulfide and elementary sulfur in the sealed silica ampoule [6]. The initial substances were purified by chemical and distillation methods. The charge weighting 0.5 – 0.6 kg was fused at 750^{O}C with melt mixing. The melt was cooled in the conditions excluding the convective flows with a subsequent annealing of glass to remove mechanical stress. In contrast to the previous technique of glass production, a series of additional operations was used to decrease the content of oxygen impurity and heterophase impurity inclusions.

$As_{40}S_{60}$ and $As_{38.7}S_{61.3}$ glasses were produced for fiber core and cladding in accordance with the dependence of refractive index upon glass composition [7]. The glass samples were characterized for the content of impurities of metals and silicon by atomic-emission spectroscopy, for the content of oxygen, hydrogen and carbon by IR spectroscopy, and for the content of heterophase inclusions of a submicron size by laser ultramicroscopy. The content of impurities of transition metals was less than $1\cdot10^{-5}$ mass %, the content of silicon was $\leq5\cdot10^{-5}$ mass %. The optical fibers with the diameter of core and cladding 500 and 550 μm, respectively, were drawn by double-crucible method. Deviations in fiber diameter did not exceed ±5 μm. Optical fibers had the primary coating from fluoroplastic F-42 and the secondary coating from polyvinylchloride. Optical losses in fibers up to 100 m long were measured in 1.5 – 6.5 μm spectral range by the well-known cut-back method [8]. The numerical aperture [9] was measured by the far-field method at 1.55 μm. The mechanical bending strength was determined by the method of approaching plates [10].

The breaking stress (σ) of optical fiber samples was calculated by equation $\sigma = E \cdot \varepsilon$, where E is the Young's modulus for glass, ε is the relative elongation equal to

$$\varepsilon = 1.198\ \frac{2r}{D-d},$$

where r is the radius of uncoated optical fiber, d is the total fiber diameter, D is the distance between plates at the break. The value of Young's modulus for arsenic-sulfide glass of $As_{40}S_{60}$ composition was taken equal to 16.7 GPa.

3. Results and discussion

Fig. 1 gives the absorption spectrum of 120 mm thick glass samples. The impurity bands in absorption spectrum are due to hydrogen in the form of SH-groups (4.01 µm), carbon dioxide (4.33 µm). The absorption bands of hydroxyl groups were absent at 2.3 µm and 2.9 µm. The content of scattering centers in glasses with the diameter more than 100 nm was less than 1×10^{4} cm^{-3}.

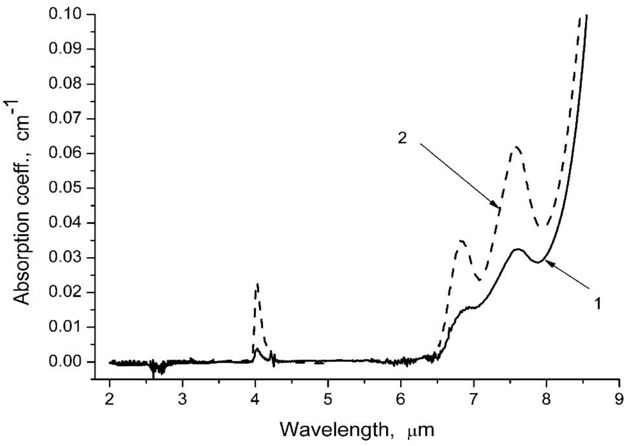

Fig. 1. Middle IR absorption spectra of arsenic-sulfide glasses for optical fibers: 1 – core glass of $As_{40}S_{60}$, 2 – cladding glass of $As_{38.7}S_{61.3}$.

Fig. 2 presents the total optical loss spectra of fibers produced by the method described in [6] (curve 1) and in the present paper (curve 2). Fig. 3 shows the measuring results of bending strength test of optical fiber in the form of Weibull diagram. The breaking stress at lnln[1/(1-F)]=0 (breaking probability F=63%) has made 0.52 GPa.The measured transmission spectra prove that the produced bulk glass samples and optical fibers are the purest ones with respect to oxygen impurity as compared to the previously produced samples.

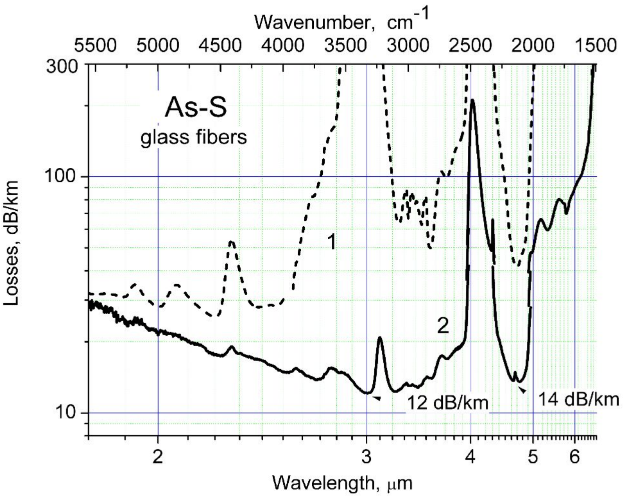

Fig. 2. Optical loss spectra of As-S fibers (see description in the text).

Calculation of the oxygen content by intensity of OH-group band in optical fibers and extinction coefficient $(5\text{-}10)\times10^{3}$ dB/km ppm, adopted for OH-groups in silica and fluoride glasses [11,12], gives the value of 0.1-0.2 ppb wt. The band intensity with the maximum at 4.33 µm corresponds to the content of carbon dioxide equal to 0.7 ppb mole. In the total optical loss spectrum of optical fiber the bands are observed due to SH-groups, i.e., 4.01; 3.17 µm with intensity of 190 and 8 dB/km, respectively. This corresponds to the hydrogen content of ~0.7 ppm·mole. The low-intensity band with the maximum at 4.65 µm is due to carbon disulfide impurity, and the bands at 5.17 and 5.56 µm are the intrinsic bands. Low oxygen impurity content has predetermined the bonding of impurity hydrogen with sulfur atoms and, as a result, the low content of OH-groups and low intensity of the corresponding absorption bands. In our opinion, the optical loss level of 12 ± 2 dB/km at 3.0 µm and of 14 ± 2 dB/km at 4.8 µm is the lowest one among all the results published on chalcogenide glasses and optical fibers on their basis. Previously, the minimum of optical losses of 23 dB/km in arsenic-sulfide glass fibers was observed at 2.3 µm between the overtones of OH- and SH-groups [4]. Lowering the content of oxygen impurity down to the level, at which the main band of stretching bands of OH-groups in glass at 2.9 µm is actually not observed, shifted the experimental position of the optical loss minimum to the long-wave range more close to the theoretically predicted wavelength $\lambda_{min.}$ = 4.3 µm and 4.8 µm, according to [3] and [13], respectively. As is seen from the Fig. 2, the loss level within 1 - 3.5 µm is determined not only by the selective impurity absorption, but also by "weak" absorption related to the tails of the density of states in the energy gap of disordered materials with the exponential dropping into the long-wave range. Extrapolation of experimental dependencies of the edges of weak and multiphonon absorption to their intersection indicates that lowering the content of hydrogen impurity in the form of SH- and OH-groups can lead to optical losses less than 10 dB/km at 3-5 µm.

4. Conclusions

Vitreous As_2S_3 has been produced with low content of oxygen impurity in the form of OH-groups and carbon dioxide. The minimum optical losses in optical fiber produced from this glass were 12 ± 2 dB/km at 3 μm and 14 ± 2 dB/km at 4.8 μm. The position of minimum optical losses in the purest glass, as compared with the known data, is shifted toward the long-wave range and coincides with that predicted theoretically.

Optical fibers with the lowered optical loss level are promising for IR-pyrometry, thermal imaging, analytical and other special applications.

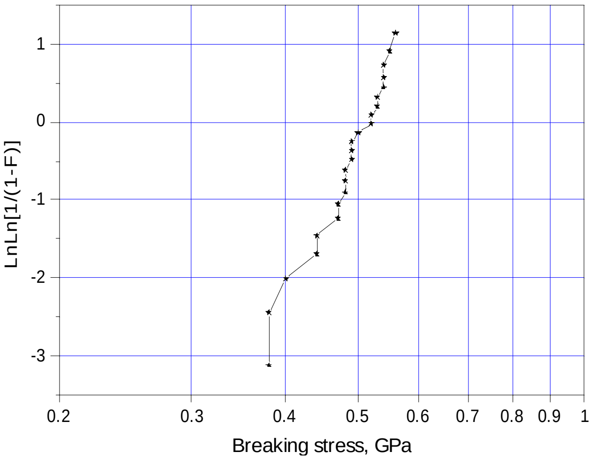

Fig. 3. Weibull distribution for breaking probability of optical fiber from $As_{40.1}S_{59.9}$ *(core) and* $As_{38.7}S_{61.3}$ *(cladding) with fluoroplastic F42 coating. The core diameter is 500 μm and the total diameter is 550 μm.*

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