



# Arsenic-sulfide glasses with low content of hydrogen impurity for fiber optics

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## ARTICLE INFO

### Article history:

Received 26 November 2017

Received in revised form

13 January 2018

Accepted 16 January 2018

### Keywords:

Arsenic-sulfide glasses

Optical losses

High-purity substances

Hydrogen impurity

## ABSTRACT

The article discusses the problem of preparing arsenic-sulfide glasses for fiber optics with a low content of impurity hydrogen which determines the level of optical absorption loss in the range of 2–6  $\mu\text{m}$ . The sources of impurity hydrogen in the form of SH-groups with its content of 1–100 ppb wt, their relative contribution and the effect on the transparency of bulk samples of glasses and optical fibers are considered. The results of studies of the contaminating effect of the apparatus material and the environment in the preparation of arsenic-sulfide glasses and optical fibers on their basis with low optical losses are presented.

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## 1. Introduction

As-S glass systems refer to the efficient materials for fiber optics of the middle IR range. The range of their transparency lies between 0.6 and 10  $\mu\text{m}$  at a transmission level of 0.001  $\text{cm}^{-1}$ . The theoretical estimate of the minimum optical losses in  $\text{As}_2\text{S}_3$  glass gives the value from 0.08 to several dB/km in the range of 5–6  $\mu\text{m}$  depending on the models of the glass structure used and the interaction of the light flux with the optical medium [1,2]. The advantages of these glasses also include high non-linearity of optical properties, laser and mechanical strength, resistance to environmental effects. Properties of glasses can be changed in a rather wide range of values changing the ratio of the content of macro components.

Optical fibers from  $\text{As}_2\text{S}_3$  with low optical losses are in demand for the creation of new optical and optoelectronic devices using middle IR radiation [3]. The typical losses in optical fibers from  $\text{As}_2\text{S}_3$  attained up to the present time are 50–150 dB/km in the range 2–6  $\mu\text{m}$  and in the best of the prepared samples they are 12–14 dB/km at 3.1 and 4.8  $\mu\text{m}$  [4,5]. This is by two orders of magnitude higher than theoretically predicted and by an order of magnitude higher than those required for some practical problems.

The excessive absorption losses in the 2.5–5  $\mu\text{m}$  range in the transparency window of the atmosphere (1.9–2.4; 3.4–4.2  $\mu\text{m}$ ) are due to the impurities of hydrogen, oxygen and carbon which are chemically related to each other and to the macro-components of the glass. Hydrogen in the form of SH-groups has absorption bands with maxima at 4.01; 3.65; 3.11; 2.05  $\mu\text{m}$ ; water in the molecular form is responsible for absorption bands with maxima at 2.79; 2.86 and 6.16  $\mu\text{m}$ ; OH-groups—for the bands at 2.92  $\mu\text{m}$ . The impurities of  $\text{CO}_2$ ,  $\text{COS}$  and  $\text{CS}_2$  are due to absorption bands with maxima at 4.33; 4.95 and 4.65; 6.68  $\mu\text{m}$  [6]. The intrinsic losses in  $\text{As}_2\text{S}_3$  glass in the 2.1–5.6  $\mu\text{m}$  range are less than 1 dB/km [1]. The intensity of the impurity absorption bands in the glass with intrinsic losses should not exceed this value. The admissible content of hydrogen impurity corresponding to these optical losses is at the level of 0.01 ppb wt. At the present time SH-groups is the main absorbing impurity in arsenic-sulfide glasses. In typical optical fibers the intensity of the SH-group band is 1–5 dB/m which corresponds to hydrogen impurity content of 10–40 ppb wt. The lowest losses in the optical fiber of  $\text{As}_2\text{S}_3$  glass in the range of 4  $\mu\text{m}$  are  $\approx 0.2$  dB/m ( $\approx 2$  ppb wt of hydrogen) [4]. The content of OH-groups in the best samples of  $\text{As}_2\text{S}_3$  glasses is 1 ppb wt and the intensity of the corresponding absorption band in the total optical loss spectrum of the optical fiber does not exceed 0.01 dB/m [7]. It follows from a comparison of these quantities that the required reduction in the content of impurity hydrogen in the form of SH-groups by 2 orders

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of magnitude in comparison with that achieved is an actual scientific and applied problem.

Elemental sulfur and arsenic are the starting materials for the synthesis of arsenic-sulfide glasses.  $As_4S_4$  [8] and  $As_4S_3$  [9] sulfides can be used as an arsenic-containing component. They are more volatile than elementary arsenic which makes their purification from heterophase inclusions of micro- and nano-size more efficient.

Hydrogen as impurity in commercial highly pure sulfur and arsenic is not directly included in the list of normalized impurities. Approximately its content can be estimated from the concentration of water and bitumen (hydrocarbons) regulated at a level of ~10 ppm. Estimation of the possible contribution of the initial components to the hydrogen content in arsenic sulfide is hampered by the lack of highly sensitive methods for determining hydrogen in sulfur and arsenic, and the chemical form of its presence in them. There is a strong dependence of the content and chemical form of hydrogen-containing compounds on the origin of precursors of technical quality used to produce highly pure sulfur and arsenic. In recent decades, sulfur, extracted from natural gas and oil during processing, and arsenic from secondary sources (waste from the semiconductor industry, products of detoxification of chemical weapons-lewisite) have entered the production turnover. The content and molecular forms of the presence of gas-forming impurities (carbon, hydrogen, oxygen) in them have not been sufficiently studied. They differ markedly from those in precursors of traditional origin. Possible forms of the presence of hydrogen in elemental sulfur are hydrogen sulfide, water, hydrocarbons and their derivatives, in arsenic—water and elemental hydrogen. The quantitative relationship between them depends on the nature of the starting material, the set of chemical and physico-chemical processes used in the purification of substances.

During preparation of optical-grade arsenic-sulfide glasses, additional sources of hydrogen impurity are its entry into the glass-forming melt from the walls of the silica reactor and from the surrounding medium. In the first case, hydrogen, initially located in the glass of evacuated silica ampoule, diffuses into the reaction volume. In the second case, the supply of hydrogen from outside may be due to its penetration through the reactor wall. Contamination by the first mechanism was confirmed experimentally but was not investigated in detail [10]. The possible contamination of chalcogenide glasses due to the permeability of silica glass has not been experimentally investigated. The probability of its occurrence is evidenced by high values of the permeability coefficients of silica glass for hydrogen at high temperature [11].

The aim of this work was to determine the sources of hydrogen in the As-S glasses and in fiber optics fabricated on their basis at the level of 1–100 ppb wt, to search for and experimentally develop the ways to reduce its content.

## 2. Experimental

The general scheme for preparing arsenic-sulfide glasses of optical quality includes loading the dosed amounts of batch components into specially prepared ampoule-container made of silica glass; deep evacuation and sealing-off the ampoule; melting of the batch, synthesis and homogenization of the glass-forming melt at 700–750 °C; quenching the melt to a glassy state; removing the preform of glass from the container. From the prepared glasses the optical fibers are drawn by double-crucible method or from the “rod-in-tube” preform. The content and chemical form of the presence of hydrogen is determined by the purity of the initial substances and the apparatus material, by the kinetics and thermodynamics of the chemical and physicochemical processes taking place at all stages of glass preparation.

### 2.1. Investigation of impurity composition of starting materials

To determine the composition and concentration of hydrogen-containing substances, the samples of especially pure sulfur from various manufacturers were investigated. The study included the extraction of impurities from the investigated sulfur and the chromat-mass spectrometric analysis of the resulting concentrate. The extraction of impurities was carried out as a vacuum extraction during distillation of the studied sample in dynamic vacuum. Light-volatile impurity components were frozen in the trap cooled by liquid nitrogen after condensation of the vapors of the main substance. The condensate of the volatile substances was frozen in ampoule-receiver which was then filled with especially pure argon to a pressure of 1 atm and analyzed by a chromat-mass spectrometric method. Details of the processes of extraction of impurities and analysis are given in Ref. [12].

### 2.2. Investigation of hydrogen entry into chalcogenide melt from silica glass

For experimental study of the effect of reactor material on the hydrogen content in arsenic-sulfide glass, 6 samples of glasses in silica ampoules with different initial contents of OH-groups ( $C_o(OH)$ ) were prepared given in Table 1. Ampoules 1–3 were made from silica tube with the initial content of OH-groups of 103 ppm wt which was determined by IR Fourier spectroscopy by the absorption band at  $3675\text{ cm}^{-1}$  and the known extinction coefficient. Ampoules 2 and 3 were additionally annealed at 900 °C for 30 and 90 min, respectively, to control the concentration of OH-groups in them. Ampoule 4 was made from tube of TKG grade with the initial content of OH-groups of 171 ppm wt fabricated by melting silica grits in atmosphere of oxygen-hydrogen burner. Ampoules 5–6 are made of tubes of F-300 grade from Heraeus Company with the initial content of OH-groups <1 ppm wt. Ampoule 6 was placed in F-300 tube of larger diameter and baked for 4 h at 1000 °C under continuous evacuation conditions for further removal of hydrogen impurity. Vacuum loading of batch components (pre-purified arsenic and sulfur monosulfide) into reactors and glass synthesis was carried out according to the procedure described in Ref. [13]. The same sample of each precursor was used to load simultaneously into all 6 reactors in one all-welded system. This ensured the same content of impurities in the batch for each of prepared glass samples. The glass melt was homogenized in the rocking furnace mode at a temperature of 750 °C for 4 h. The melt was then cooled to 350 °C at a rate of 2 deg./min, quenched in air, and the prepared glasses were annealed at 170 °C. Macro-composition of glass was determined by atomic-emission spectrometry with inductively coupled plasma on iCAP 6300 Duo spectrometer. The content of OH-groups in the silica glass of the reactors before and after synthesis of chalcogenide glasses was determined by the absorption band in the  $3675\text{ cm}^{-1}$  range by IR Fourier spectroscopy. The content of SH- and OH-groups was determined by IR absorption spectra of arsenic-sulfide glasses.

### 2.3. Investigation of the entry of hydrogen impurity into the chalcogenide melt from atmosphere

To get the direct evidence to the entry of hydrogen from the outside into the closed reactor with the melt of the chalcogenide glass during its synthesis, the following experiment was carried out. 23.7 g sample of  $As_2S_3$  glass with the content of SH-groups of 75 ppb wt was placed in silica glass ampoule with wall thickness of 1.5 mm and the content of OH-groups <1 ppm wt. The ampoule with sample was evacuated to the residual pressure of  $10^{-5}$  mm Hg,

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