



Contents lists available at ScienceDirect

## Journal of Non-Crystalline Solids

journal homepage: [www.elsevier.com/locate/jnoncrysol](http://www.elsevier.com/locate/jnoncrysol)

## Contamination of glassy arsenic sulfide by SiO<sub>2</sub> particles during melt solidification in silica glassware

M.F. Churbanov, S.V. Mishinov, V.S. Shiryaev\*, L.A. Ketkova

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

## ARTICLE INFO

## Keywords:

Arsenic sulfide  
Silica glass  
Adhesion  
Contamination  
Inclusions

## ABSTRACT

It is found that the content of SiO<sub>2</sub> inclusions in the As<sub>2</sub>S<sub>3</sub> volume is increased during chalcogenide glass melting in silica glassware with subsequent cooling to solid sample and separation from the container walls. The experiment consisted in repetition of cycles of “chalcogenide ingot melting and heating to 450–600 °C - cooling the melt to a glass transition temperature - separation of the sample from the silica-glass container walls - cooling to room temperature”. Content and size of the inclusions in the initial glass and the samples after the “melting–solidification” cycles was controlled by means of laser ultramicroscopy and optical microscopy. The concentration of micrometer-sized particles was found to increase with cycles of melting and solidification.

The increase of particles concentration is explained by the combined effect of a number of factors such as high adhesion of glassy arsenic sulfide to silica glass and strong radial and longitudinal shrinkage of the chalcogenide ingot during cooling compared with silica-glass container due to significant differences in their linear coefficients of thermal expansion. It leads to destruction of the adhesion contact along the boundary of solid phases and the surface layers of glasses with separation of microprotrusions and fragments of silica glass surface and their fixation in the surface layers of As<sub>2</sub>S<sub>3</sub> glass.

The excess optical losses in glassy arsenic sulfide, caused by this type of contaminating action of apparatus, have been estimated.

### 1. Introduction

Application of chalcogenide glasses for the middle infrared optics requires a high level of chemical purity and phase homogeneity. The theoretical value of the minimum optical losses in As<sub>2</sub>S<sub>3</sub> glass estimated only from Rayleigh scattering and multiphonon absorption is 0.08 dB/km in the spectral range of 4–6 μm. However, the optical losses of real fibers are higher by 3–4 orders, which limit their fields of application [1,2]. Additional optical losses are associated with light scattering by heterogeneous particles and selective absorption of impurities. Heterogeneous inclusions in the optical materials increase optical losses, reduce the laser strength, initiate crystallization processes [3].

The traditional method for preparation of bulk chalcogenide samples with a low content of optically active impurities (metals, gas-forming impurities) is the direct melting of high purity initial components in evacuated silica-glass ampoule with subsequent solidification, annealing and cooling to room temperature. Silica glass is the main container material for the processes of synthesis and purification of chalcogenide melt as well as for chalcogenide preform molding. The presence of silica inclusions, poor soluble in the chalcogenide glass

melt, in the resulting samples is associated with their transport from the container walls. The selection of time-temperature modes of synthesis, purification and preform fabrication, which minimizes the content of heterophase inclusions in chalcogenide glasses, is the actual task.

Contamination of chalcogenide glass melt by heterophase inclusions in the step of synthesis was mentioned in [4–6]. An increase in the content of submicron-size silica inclusions with increasing temperature of As<sub>2</sub>S<sub>3</sub> glass synthesis in the temperature range of 700–950 °C was observed [4]. Significant effect of temperature and time of melting of the initial components of the Ge-Sb-S glass system in silica glassware on the content and size of SiO<sub>2</sub> inclusions at the synthesis and purification temperature of 800–950 °C was noted [6]. Size of inclusions was ranged from few tens of micrometers at 800 °C to tens of nanometers at higher temperatures; concentration of particles was ranged from 10<sup>2</sup> to 10<sup>9</sup> cm<sup>-3</sup>.

Two mechanisms of heterophase inclusion's formation in the chalcogenide glasses during high temperature synthesis can exist. Macrocomponents of chalcogenide glass and some impurities (TeO<sub>2</sub>, CS<sub>2</sub>) can react chemically with silica glass, formed thin layers of new solid components on the inner surface of the glassware, which can be

\* Corresponding author.

E-mail address: [shiryaev@ihps.nnov.ru](mailto:shiryaev@ihps.nnov.ru) (V.S. Shiryaev).<http://dx.doi.org/10.1016/j.jnoncrysol.2017.04.006>Received 11 January 2017; Received in revised form 4 April 2017; Accepted 9 April 2017  
0022-3093/ © 2017 Elsevier B.V. All rights reserved.

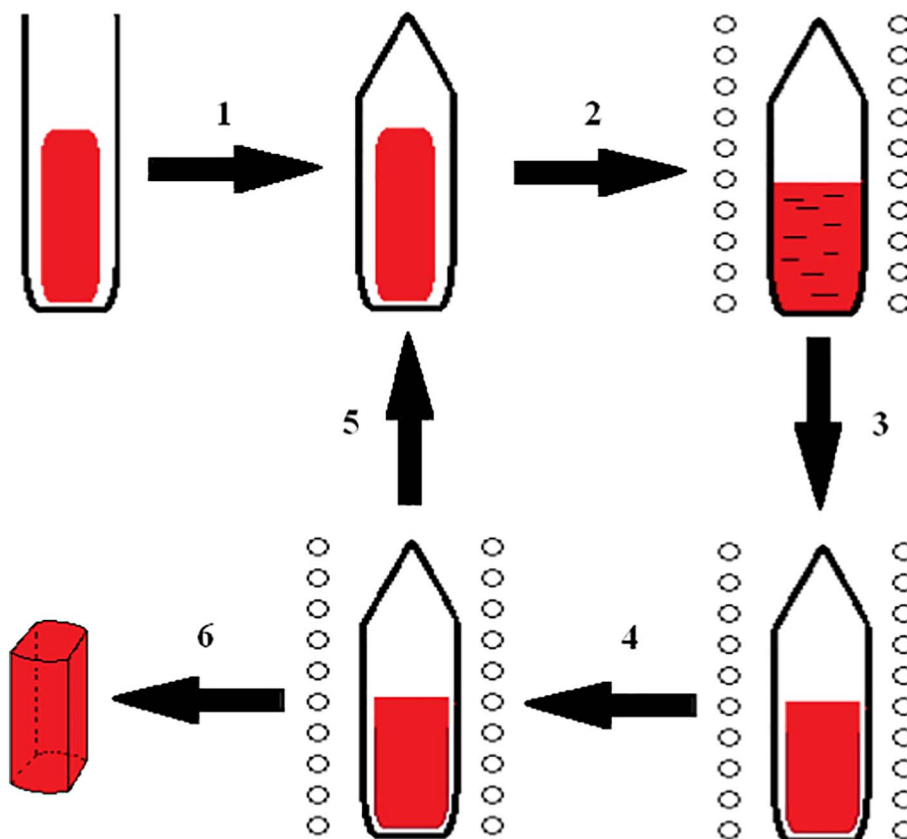


Fig. 1. Sequence of operations during the experimental investigation of  $\text{SiO}_2$  particles injecting to  $\text{As}_2\text{S}_3$  glass from the surface of silica-glass container: 1 - ampoule evacuation and sealing, 2 - melting at  $450^\circ\text{C}$ , 3 - furnace-cooling to  $250^\circ\text{C}$  and "separation" of the sample, 4 - annealing at  $180^\circ\text{C}$ , 5 - cooling to room temperature, 6 - cooling to room temperature, polishing treatment of sample, investigation by means of optical microscopy and laser ultramicroscopy.

mechanically separated from silica glass and contaminate the chalcogenide melt [7–11]. Inclusions of soluble reaction products can be formed by condensation mechanism during melt cooling when their concentration exceeds the solubility limit.

During the formation of tubular chalcogenide preforms for microstructured optical fibers by centrifugal melt casting technique in a silica-glass ampoule, the defects caused by mechanical separation of silica particles from glassware walls were observed on the outer surface of chalcogenide tubes. The reason for that is high adhesion of chalcogenide glasses to silica glass and significant difference in their coefficients of thermal expansion [11,12]. During the stages of chalcogenide glass solidification, cooling and separation of ingot from the walls of silica reactor, microprotrusions of silica apparatus surface, under the action of arising mechanical stresses, can break off and be retained on the surface of a chalcogenide ingot [11]. During the subsequent use of the glass for drawing optical fibers, the particles can contaminate the melt causing the additional optical losses and a decrease in mechanical strength. This problem is topical for As-S glasses used for fiber optics, since they have the highest adhesion to silica glass as compared to other chalcogenide glasses.

The aim of this work was to investigate the  $\text{As}_2\text{S}_3$  glass contamination by  $\text{SiO}_2$  inclusions during the formation of monolithic samples in silica glassware as well as to study the concentration and sizes of heterophase particles entering the chalcogenide glass sample volume.

## 2. Experimental

### 2.1. Preparation of silica glassware

The silica ampoules used for preparation of  $\text{As}_2\text{S}_3$  glass and molding of samples were made of quartz tubes produced by "TekhnoQuartz"

(Gus Crystal, Russia). The ampoules were subjected to chemical etching with hydrofluoric acid (45%) for 5 min, washed with distilled water, and annealed at  $500^\circ\text{C}$  for 5 h to remove impurities adsorbed on a surface.

The surface roughness of the silica glass was determined by means of atomic force microscopy. The average roughness  $R_a$  of inner surface of ampoules was 15–20 nm. Numerous protruding defects were found on the surface of ampoules, which can serve as potential sources of contamination by silica particles during contact with chalcogenide glass.

### 2.2. Synthesis and investigation of arsenic sulfide glass

Glassy  $\text{As}_2\text{S}_3$  was prepared by the direct melting of high pure initial elements in the evacuated silica-glass ampoules using the standard procedure for the preparation of chalcogenide samples of optical quality [4,5]. The melt was homogenized at  $750^\circ\text{C}$  for 10 h, with subsequent quenching in air. In the final stage, the glass samples were annealed at a glass transition temperature for 2 h and cooled slowly to room temperature.

The content of gas-forming impurities (hydrogen, oxygen and carbon) in the glass samples was determined by IR spectroscopy using the known values of extinction coefficients [5]. The content of metals and silicon impurities was determined by laser mass spectrometry. The measurements were carried out by means of the EMAL-2 (Ukraine) laser mass spectrometer with photographic registration. When laser mass spectrometry analysis, evaporation and ionization of the sample were performed by scanning the glass surface with focused laser pulsed radiation at a wavelength of  $1.06\ \mu\text{m}$  with a power density of  $\approx 2.109\ \text{W}/\text{cm}^2$ . The quantitative processing of the mass analyzer spectra of the elements recorded on the photographic plate was carried

Download English Version:

<https://daneshyari.com/en/article/7900226>

Download Persian Version:

<https://daneshyari.com/article/7900226>

[Daneshyari.com](https://daneshyari.com)