



Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrsol

Recent advances in preparation of high-purity glasses based on arsenic chalcogenides for fiber optics

M.F. Churbanov^a, G.E. Snopatin^a, V.S. Shiryaev^{a,*}, V.G. Plotnichenko^b, E.M. Dianov^b

^a Institute of Chemistry of High-Purity Substances of the Russian Academy of Science, Nizhny Novgorod, 603950, Russia

^b Fiber Optics Research Center of the Russian Academy of Sciences, Moscow, 119333, Russia

ARTICLE INFO

Article history:

Received 9 June 2010

Received in revised form 23 September 2010

Available online xxx

Keywords:

Chalcogenide glasses <C145>;

Impurities <I130>;

Infrared absorption <I160>

ABSTRACT

The processes of production of high-purity glasses based on arsenic chalcogenides and optical fibers with low optical losses in the middle IR have been analyzed. Physical-chemical, technological and methodological factors determining the degree of purity of glasses and the level of optical losses in optical fibers are considered. Dominant factors, rational actions and approaches optimizing the manifestation of these factors in glasses formed by arsenic chalcogenides are discussed. Vitreous As_2S_3 is produced with the content of hydroxyl groups not more than 1 ppb wt, of hydrogen in the form of SH-groups – 75 ppb mol, of silicon – 0.2 ppm wt. From this glass a multi-mode optical fiber was manufactured with optical losses of 12 and 14 dB/km at 3.0 and 4.8 μm , respectively, which is the best result published in literature for chalcogenide glass optical fibers.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Chalcogenide glasses are promising for fabrication of optical fibers with low optical losses for technical and medical diagnostics, fiber remote sensing systems, Raman and optical fiber lasers and amplifiers in the middle IR, high-speed switches and other devices for systems of non-linear optics and telecommunication [1]. Transparency of chalcogenide glasses and optical losses in chalcogenide optical fibers are the impurity-sensitive properties. Due to this reason the progress in development and application of chalcogenide optical fibers was always connected with lowering of impurities content in glasses [2]. The notions of chemical and phase purities are used with respect to optical materials. Chemical and phase purities characterize the material if the atoms (molecules) of other elements (compounds) and heterophase inclusions are considered as impurity, respectively [3].

At present a substantial increase in chemical and phase purity of chalcogenide glasses is of urgent importance due to the following reasons. Firstly, the content of chemical and phase impurities is rather high even in the purest samples: transition metals $\sim 0.1 \div 0.01$ ppm wt; oxygen, carbon, hydrogen, silicon 1–0.5 ppm wt; nano-size heterophase inclusions $10^4 \div 10^6 \text{ cm}^{-3}$. The presence of impurities at this level precludes the determination of actual values for a number of glass properties. Secondly, numerous practical implementations require chalcogenide optical fibers with lower optical losses as

compared with the attained losses and often at the level of intrinsic losses throughout the whole range of optical transparency or of its most part. According to the values of extinction coefficients of the limiting impurities [2] the content of the major part of these impurities in glasses should not exceed the units of ppb at. Optical losses in optical fibers are directly related to the content of impurities in glasses and rather exactly characterize the purity degree of glasses. In some cases they are the only source of quantitative data on the content of impurities in glass. The lowest losses of 23 dB/km at 2.2 μm wavelength were measured in As_2S_3 optical fiber as early as 1993 [4]. A prolonged lack of the progress in lowering of the optical losses makes it necessary to consider the factors determining the purity and micro-homogeneity of glasses as well as the optical losses in the produced optical fibers once again. These factors are represented by impurities in glasses, conditions for synthesis and cooling of glass-forming melt, micro-inhomogeneities in the form of heterophase inclusions and striaes, the chemical activity of chalcogenide melt, the tendency of glasses to micro-segregation and crystallization, the presence of metal-metal and chalcogen-chalcogen homo-bonds in glass network, the difference in volatility of macro-components. The results of this consideration, as well as new experimental results on production of high-purity glasses formed by arsenic chalcogenides, are briefly given below.

2. Impurities as the main source of excessive optical losses

The source, elemental composition, content, molecular form, nature and boundary effect on the optical properties of glasses and optical fibers are the main constituents of impurity problem in

* Corresponding author. Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinina street, Nizhny Novgorod, 603950, Russia. Tel.: +7 831 4627192; fax: +7 831 4624634.

E-mail address: shiryaev@ihps.nnov.ru (V.S. Shiryaev).

chalcogenide glasses for fiber optics. Extensive but not comprehensive data are given on these issues, including several reviews [2,5,6].

The impurities, absorbing and scattering the radiation in chalcogenide glasses and optical fibers, are the compounds of light elements (C, H, N, O) with macro-components and with one another, transition metals and silicon, chalcogens and pnictogens as analogs of the main components. Atoms of impurity elements can be embedded into the glass network both as bridging and non-bridging atoms. Stable impurity compounds (CO₂, CS₂, COS, SO₂, N₂ and others) are present in the form of a true solution. Substances, not readily soluble in chalcogenide melts (carbon, silicon dioxide), form heterophase inclusions.

The molecular form of impurity presence in glass manifests itself via functional groups responsible for the appearance of selective absorption bands in the transmission spectra. Their set and intensity are determined by the relative content of impurities in the initial components and melt, by temperature of homogenizing melt of the charge and by cooling rate of the melt into glass. Melts of arsenic chalcogenides refer to the so-called “living” polymer systems. The atoms of impurities, primarily O, C, H, participating in the reactions of elements-macro-components can redistribute between different molecular forms and functional groups. Change in the content of one of impurity elements can change the absolute and relative intensity of absorption bands corresponding to other impurities. For example, introduction of oxygen in the form of SO₂ into As₂S₃ melt leads to the presence of additional bands in the glass transmission spectrum due to As–O (9.5 μm) and S–S (10.15 μm) bonds [7]. Introduction of a small amount of sulfur into As₂Se₃ glass substantially decreases the intensity of absorption band of Se–H-groups (4.57 μm) with a simultaneous appearance of S–H (4.01 μm) band [8]. Hydrogen is predominantly bound with the atoms of sulfur due to a higher strength of S–H bond as compared with Se–H bond (339.6 and 309.6 kJ, respectively).

The maximum positions of a lot of impurity absorption bands in the transmission spectra of chalcogenide glasses are in the interval of 2–16 μm [2]. It is determined by impurity nature and weakly depends on the macro-composition of glass. The effect of impurity on optical losses in glasses is characterized quantitatively by the extinction coefficient ε in the well-known Lambert–Behr expression via ratio $\beta = \varepsilon \cdot x$, where x is the impurity concentration, β is the absorption coefficient. The extinction coefficient values for individual impurities are given in Table 1. It follows from these values that to attain the optical losses at the level of intrinsic ones the content of impurities of oxygen, carbon, hydrogen and silicon should not exceed 0.1–10 ppb.

The initial components and apparatus material used for the synthesis of glass-forming melts are the sources of impurities in chalcogenide glasses. Impurities from the initial substances are directly embedded into the target glass. Commercial samples of

special purity As, S, Se, and Te contain 0.1–0.01 ppm wt of metal impurities and 1–100 ppm wt of hydrogen, oxygen, carbon, and silicon. Silica glass is the main container material used for the synthesis of chalcogenide melts. It contaminates the melt with easily diffusing impurities (hydrogen, sodium, copper).

Chemical interaction of chalcogenides and impurities with silica glass at a high temperature leads to formation of thin layers of reaction products on its surface. Due to difference in thermal and mechanical properties of the base and layers the latter can separate from silica glass and enter the melt in the form of heterophase inclusions. Size and concentration of inclusions are experimentally determined by the method of laser ultramicroscopy based on registration of radiation scattered by a particle at a right angle. The method makes it possible to determine particles with a size of 50–200 nm in amount of 10²–10⁸ cm³ in glasses, including those non-transparent in the visible range [10]. Contamination with heterophase particles due to interaction of the melt with the walls of a silica container increases with the increase in temperature, especially in the case of glasses, containing component with increased “metallicity” (Ge, Sb, Te). Fig. 1 gives the microphotos of a laser beam passing through the samples of As₂S₃ glass made at different temperature as well as the corresponding histograms for size distribution of particles. Heterophase inclusions lead to optical losses in chalcogenide glass due to absorption and scattering. Their level is determined by concentration and size of particles and can be calculated with scattering models of Mie and Rayleigh–Gans [11].

3. Influence of phase inhomogeneities on optical transparency of glasses

Nano- and micro-crystals of macro-components, nano- and micro-drops of the second glass phase as well as extensive corrugated inhomogeneities (striae) manifest themselves as inhomogeneities in chalcogenide glasses. Their formation is due to inclination of chalcogenide glasses and their melts to crystallization and micro-segregation. Cooling of the melt into glass, annealing and fabrication of glass into optical fiber and other optical products in non-optimum time-temperature modes are accompanied by a formation of nano- and micro-crystals, which scatter the radiation transmitted through the optical fiber. Presence of the striae is due to non-optimum thermal fields and time-temperature modes during the melt solidification, especially in case of macro-components with a higher volatility. As an example, Fig. 2 gives the photo of the striae decorated with the particles from silicon dioxide in Ge₂₅Sb₁₀S₆₅ glass [12].

Glasses, comprising several individual or conditional glass-formers, are inclined to micro-segregation. Increase in optical losses in the final parts of the fiber as compared with the initial parts caused by micro-

Table 1
Values for extinction coefficients ε for impurities in chalcogenide glasses.

Impurity compound or functional group	Glass	Maximum of absorption band, μm	Extinction coefficient, dB/km/ppm wt*	Calculated content of impurity leading to optical losses equal to intrinsic losses, ppb*
OH**	SiO ₂	2.92	1 * 10 ⁴	~0.02
SH	As ₂ S ₃	4.0	2500 (ppm at)	0.3
SeH	As ₂ S ₃	4.5	1000 (ppm at)	0.1
CO ₂	As ₂ S ₃	4.33	1.5 * 10 ⁴	0.05
COS	As ₂ S ₃	4.95	10 ⁵	0.008
CS ₂	As ₂ S ₃	6.68	4.8 * 10 ⁵	0.2
SO ₂	As ₂ S ₃	8.63	43	2300
As ₂ O ₃	As ₂ Se ₃	12.65	4.3 * 10 ⁴	100
		9.5	1030	400
Se–O	As ₂ Se ₃	10.6	380	2000
S	As ₂ Se ₃	10.6	0.52 (ppm at)	10 ⁶
	As ₂ Se _{1.5} Te _{1.5}	14.5	32 (ppm at)	10 ⁴

*Intrinsic losses of glass calculated accounted for the “tail of weak absorption”.

**Data for silica glass [9].

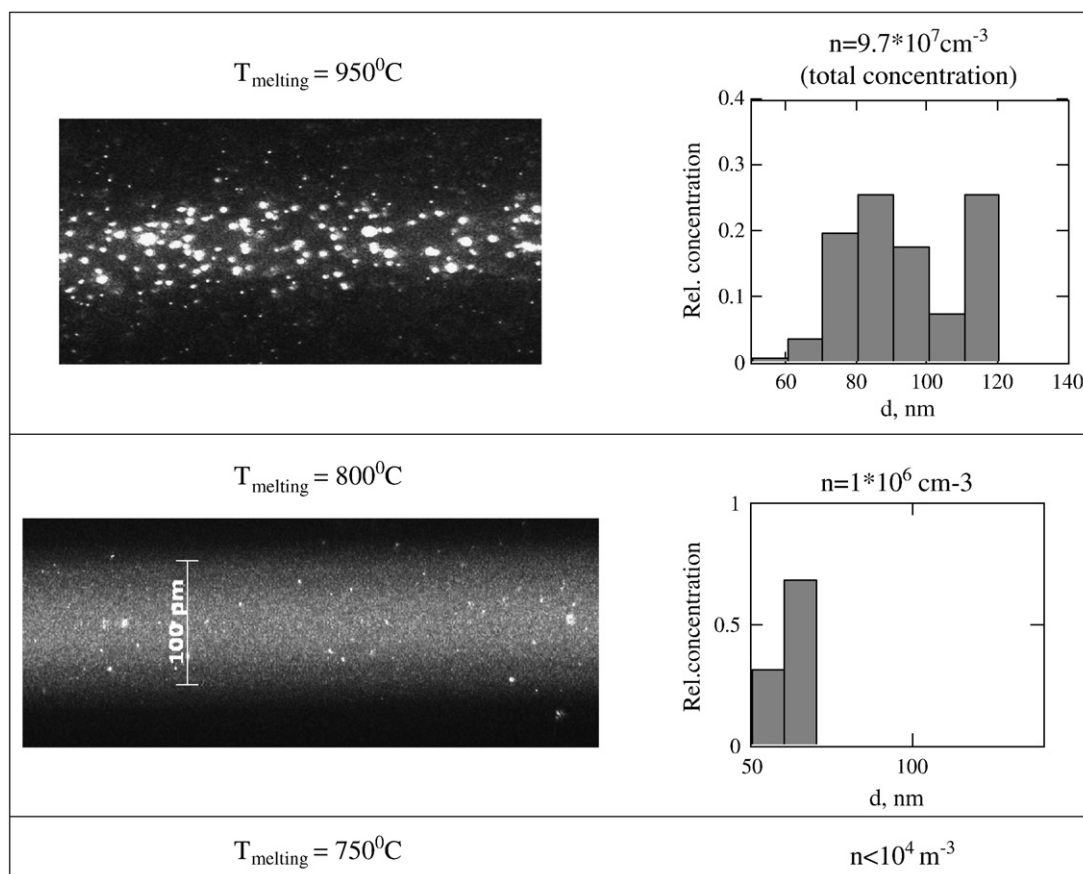


Fig. 1. Microphotographs and histograms of inclusions distribution on sizes in As_2S_3 glass samples prepared at different temperatures.

segregation of $\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}$ melt was observed at fiber drawing from a double crucible [13]. Differential thermal analysis of glass in the final parts of optical fiber indicated the appearance of the second glass phase. In the process of drawing the amount of new phase and size of its particles increased which led to the increase in optical losses mainly due to scattering in the produced optical fiber.

4. Absorption due to defects of glass network

The presence of metal–metal and chalcogen–chalcogen homo-bonds is a specific feature of atomic molecular structure of chalcogenide glasses [14]. It is due to relatively close energies of homo- and hetero-bonds. Homo-bonds are responsible for selective

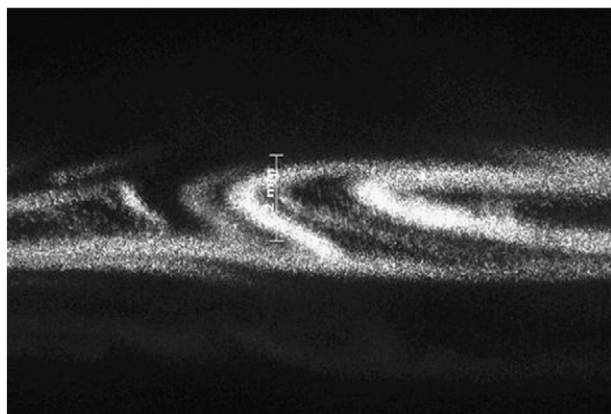


Fig. 2. Microphotograph of waviness in $\text{Ge}_{25}\text{Sb}_{10}\text{S}_{65}$ glass visualized by heterogeneous microinclusions.

absorption bands in transparency range of glasses and manifest themselves in the transmission spectra of glasses and optical fibers as the chemical purity of samples increases. For example, in As_2S_3 glass the absorption bands with the maxima at 5.1 and 5.5 μm , which we refer to combined vibrations with the participation of S–S bonds, become as intensive as impurity absorption bands with the total loss level of 10–100 dB/km in optical fiber [15] (Fig. 3). We have manufactured a set of glasses of As–S system with the content of arsenic 36–42 at.% with increment of 1 at.%. 5.1 and 5.5 μm bands are observed in the transmission spectra of the produced glasses with optical path exceeding 10 cm. In optical fibers their intensity depends on glass core composition changing from 0.2 to 1.2 dB/m. An obvious correlation between the intensity of these bands and the content of super stoichiometric sulfur proves the intrinsic but not impurity nature of the absorption bands at 5.1 and 5.5 μm . The intrinsic nature of these bands and bands with maximum at 6.85 and 7.6 μm determines the position of multi-phonon absorption edge of arsenic-sulfide glass and the level of optical losses in As–S fibers between 5 and 8 μm . Estimations, made in view of this fact and of the concentration constituent of Rayleigh scattering related to the presence of homo-bonds in glass, lead to the minimum optical losses which are by 3–5 times higher than the level of 8.10^{-2} dB/km at 4.8 μm given in literature [16,17].

5. Production of glasses with increased transparency

A general scheme for production of chalcogenide glasses for fiber optics comprises the preparation of initial high-purity substances and charge on their basis, melting of the charge with conservation of the attained purity of substance, cooling the melt into glass.

At the first stage the maximum possible degree of purity of the initial substances and of the charge is provided with respect to the

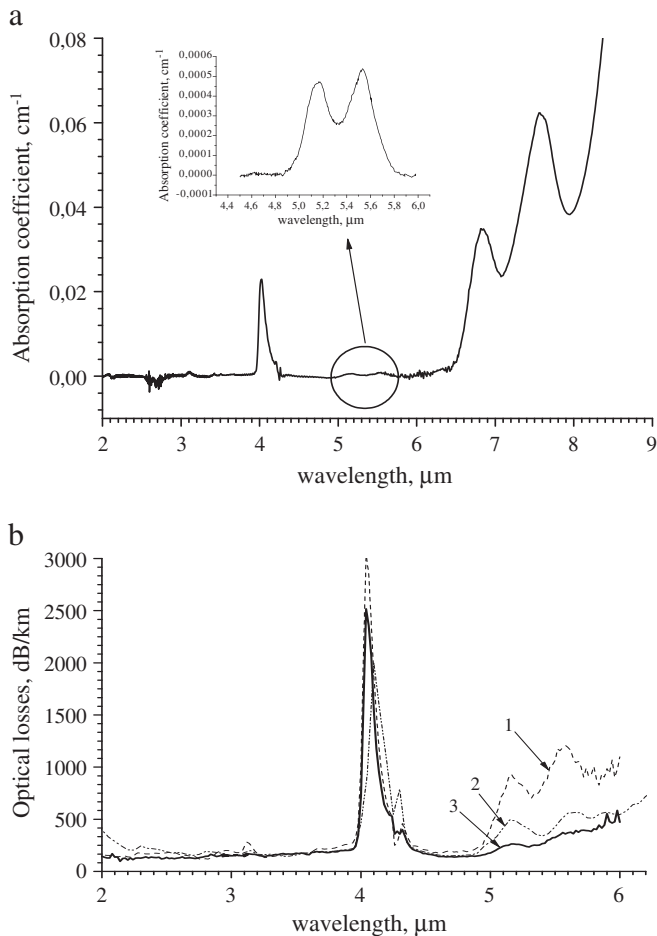


Fig. 3. (a) Absorption spectrum of As_2S_3 bulk samples. (b) Attenuation spectra of As–S optical fibers. Core glass composition (at.% As): 1 – 38.4; 2 – 39; 3 – 40.0.

impurities mostly affecting the glass transparency. In view of intensity of selective absorption the impurities (as chemical elements) can be arranged in the following sequence: oxygen>carbon>hydrogen. During their interaction with elements-macro-components the compounds (CS_2 , GeO_2 , TeO_2 , As_2O_3) are formed with a high chemical activity with respect to silica glass leading to contamination of the melt with heterophase inclusions consisting mainly of SiO_2 . Due to this fact the optical losses can be higher as compared with the contribution from the impurities in the initial form.

During the charge melting the optimum temperature and time of melting are being selected, as well as the melt mixing conditions (providing homogeneity of macro-composition) and minimization of the contamination effect of the reactor walls (in view of the mass of the produced sample). It is desirable to apply the lower synthesis temperature providing the uniform distribution of macro-components.

Table 2
Content of impurities (ppm wt.) in the best chalcogenide glass samples.

Impurity	Method of detection	Content of impurity (ppm wt.) in				
		As_2S_3	$\text{As}_2\text{S}_{1.5}\text{Se}_{1.5}$	As_2Se_3	$\text{As}_{40}\text{Se}_{40}\text{Te}_{20}$	$\text{Ge}_{25}\text{Sb}_{10}\text{S}_{65}$
Hydrogen	Fiber spectroscopy and tandem laser spectrometry	0.05	0.2	0.1	0.02	0.13
Oxygen		0.001	–	0.5	0.6	–
Carbon	Activation method, gas chromatography and laser mass spectrometry	≤ 0.2	< 0.02	0.5	0.6	≤ 5
Silicon	Laser mass spectrometry	0.1	< 0.4	0.1	0.05	0.6
Al, Fe, Ni, Cr, Mg, Mn, Ni	Atomic-emission spectroscopy	10^{-3} –0.1	< 0.2 –2	10^{-2} –0.1	10^{-2} –0.1	< 0.1 –1
Inclusions of 0.05–0.1 μm size	Laser ultramicroscopy	$\leq 2 \cdot 10^4 \text{ cm}^{-3}$	$5 \cdot 10^6 \text{ cm}^{-3}$	$2 \cdot 10^6 \text{ cm}^{-3}$	$2 \cdot 10^6 \text{ cm}^{-3}$	$2 \cdot 10^4 \text{ cm}^{-3}$

The main problem during the melt solidification into glass is maintaining its homogeneity, i.e., the phase purity. The reasons for inhomogeneities are as follows:

- segregation of the melt containing more than one glass-forming compound;
- boiling and formation of micro-bubbles in case of the component with a higher volatility (arsenic monosulfide in glasses containing sulfur and arsenic);
- transfer of the surface layers into the melt volume by convective flows.

Efforts, directed to decrease the negative consequences of specific physical–chemical or technological factors on glass quality, can produce the reverse effect due to the effect of other factors. For example, cooling of the melt at a low rate decreases the possibility of striae formation, i.e., improves glass micro-homogeneity. However, at the same time the entrance duration of impurities from the container walls into the melt increases, as well as the number of micro-crystals in case of glasses inclined to crystallization.

Realization of the above-stated general approach while producing As_2S_3 glass within this work comprised the following stages:

- use of arsenic monosulfide as an arsenic-containing compound;
- purposeful ultrapurification of the initial substances from oxygen;
- high-vacuum loading of the charge components;
- charge melting without overheating;
- solidification of the melt into glass at a low cooling rate.

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 [18]. The initial substances were purified by chemical and distillation methods. The charge weighting 0.5–0.6 kg was fused at 750 °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.

The produced glass was characterized by IR-spectroscopy of the bulk samples and optical fibers, laser ultramicroscopy, and laser mass spectrometry. The content of impurities in glass is given in Table 2.

The content of oxygen impurity in the form of OH-groups is 0.5–1 ppb wt, in the form of CO_2 – 0.5–1 ppb wt, in the form of SH-groups – 50–100 ppb, silicon – 0.2 ppm wt. Fig. 4 gives the spectrum of the total optical losses in the optical fiber made from this glass. The minimum optical losses in the optical fiber are 12 dB/km at 3 μm and 14 dB/km at 4.8 μm . It is obvious that a new lower level of losses contains a substantial contribution of impurity absorption.

6. Discussion

At present the lowest losses are achieved in the optical fibers produced from As–S glass [2]. The minimum optical losses in multimode optical fiber from arsenic sulfide are 12 and 14 dB/km at

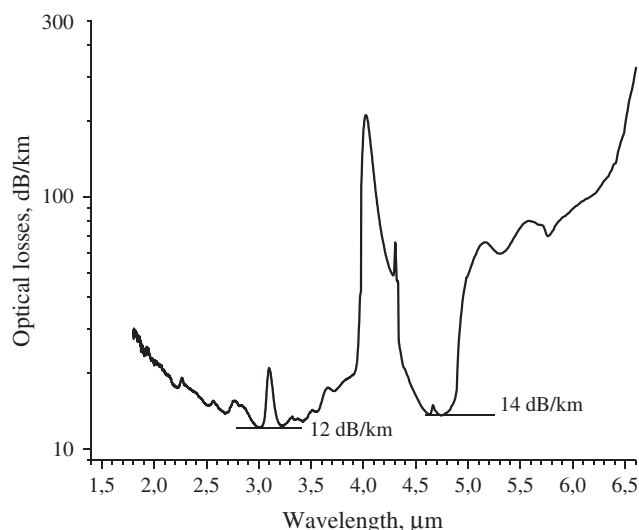


Fig. 4. Spectrum of the total optical losses in multi-mode As-S glass fiber.

3.0 and 4.8 μm , respectively. The minimum optical losses in multimode As–Se–Te and As–S–Se glass fibers are equal to 150 dB/km at the wavelength of 6.6 μm and 60 dB/km at 4.8 μm , respectively. The minimum optical losses in single-layer fibers are: 40 dB/km at 6.7 μm for As–Se–Te glass system and 78 dB/km at 4.2 μm for As–Se glass system. The level of optical losses in fibers correlates with attained low content of gas-forming dissolved impurities and heterogeneous nanosize inclusions in glasses (Table 2).

The attained transparency of As–S glass fibers is limited by the impurity absorption: at 4.8 μm the absorption contribution from SiO_2 (0.2 ppm wt) is ~ 8 dB/km, from hydrogen in the form of SH-groups (~ 0.07 ppm wt) is $\cong 1$ dB/km. It should be noted that lowering the oxygen impurity in As_2S_3 glass down to ppb level leads to binding of hydrogen impurity with sulfur atoms despite the fact that the binding energy of O–H is substantially higher than the binding energy of S–H (423.9 and 339.6 kJ/mol, respectively). The position of minimum of optical losses has shifted to 4.8 μm , i.e. to the theoretically predicted position [16]. To attain the optical losses of 1–5 dB/km in the maximum transparency range it is necessary to lower the content of silicon impurity down to ~ 10 ppb wt and of hydrogen impurity down to 1–5 ppb at. It is a rather difficult task, since silicon and hydrogen refer to abundant elements and enter the glass melt from the walls of silica glass reactor.

In the 1–6 μm transparency range the main limiting impurities are oxygen, carbon, and hydrogen connected with each other and with components of glass matrix. Glass transparency in the range of 6–16 μm is mainly affected by impurity absorption due to the oxides of macro-components and silicon. Presence of these impurities, both embedded in the glass network and in the form of heterophase inclusions, is promoted by high synthesis temperature of the glass-forming melt (850–950 $^\circ\text{C}$), chemical activity of macro-components and their oxides with respect to silica glass. Due to this fact a higher content of heterophase inclusions (up to 10^9 – 10^{10} cm^{-3}) can be the reason for a higher tendency of these glasses to crystallization. Physical-chemical and technological approaches, which make it possible to settle this problem, consist in the use of volatile compounds for the synthesis of glass-forming melts. Temperature of homogenizing melting of the batch prepared via volatile compounds can be substantially lower than it is in case of the batch made from elements. Fig. 5 gives the transmission spectrum of Ge–Sb–S glass system produced with the use of volatile compounds. Temperature of the synthesis of glass-forming melt did not exceed 700 $^\circ\text{C}$. For this reason the intensity of impurity SH band is noticeably lower than it is in the glass spectrum produced by a traditional technique at a higher temperature.

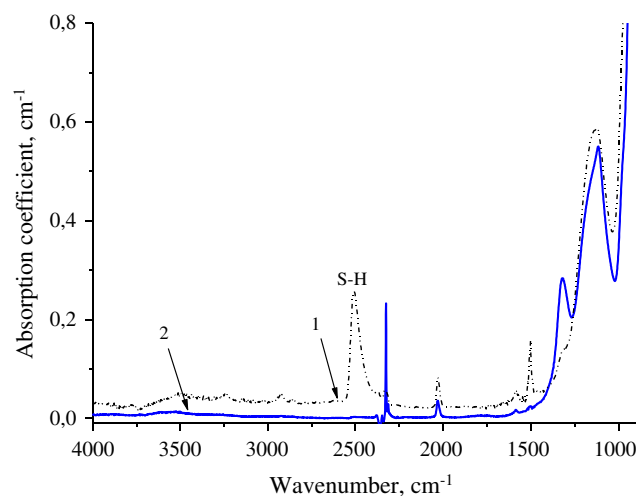


Fig. 5. Absorption spectra of $\text{Ge}_{25}\text{Sb}_{10}\text{S}_{65}$ bulk samples: 1 – glass prepared by elements direct melting; 2 – glass prepared from volatile compounds.

Micro-segregation in the process of production of chalcogenide glasses, containing several individual or conditional glass-formers, is the additional problem. A more thorough selection of time–temperature modes during the melt cooling and the optical fibers production is required.

7. Conclusion

The typical content of impurities in the currently produced glasses formed by arsenic chalcogenides for fiber optics is rather high: transition metals – 0.1–0.01 ppm wt; oxygen, hydrogen – 1–0.5 ppm mol; carbon, silicon – 10^4 – 10^6 cm^{-3} . From these glasses the optical fibers are manufactured with optical losses of 30–150 dB/km determined by impurities content.

The process of production of high-purity chalcogenide glasses of different glass-forming systems and optical fibers on their base is analyzed. As_2S_3 glass was produced with the content of OH-groups not more than 1 ppb wt, of hydrogen in the form of SH-groups – 75 ppb mol, of silicon – 0.2 ppm wt. The optical fiber manufactured from this glass has the optical losses of 12 and 14 dB/km at 3.0 and 4.8 μm . Production of glasses with the limiting impurities content of 1–10 ppb makes it possible to determine their intrinsic properties (transparency in optical range, laser damage resistance, and kinetic parameters of homogeneous crystallization) and to produce the optical fibers with optical losses close to the intrinsic losses.

References

- [1] Sanghera J.S., Aggarwal D., Summary, in: Sanghera J.S., Aggarwal D. (Eds.), *Infrared Fiber Optics*, CRC Press, Boca Raton, Boston, London, New York, Washington D.C, 1998, pp. 325–335.
- [2] G.E. Snopatin, V.S. Shiryayev, M.F. Churbanov, E.M. Dianov, V.G. Plotnichenko, *Inorg. Materials* 45 (2009) 1439.
- [3] M.F. Churbanov, *Inorg. Materials* 45 (2009) 995.
- [4] A.V. Vasiliev, G.G. Dyvyatykh, E.M. Dianov, V.G. Plotnichenko, I.V. Scripachev, G.E. Snopatin, M.F. Churbanov, V.A. Shipunov, *Sov. J. Quantum Electron.* 20 (1993) 109.
- [5] Churbanov M.F., Plotnichenko V.G., *Semiconducting Chalcogenide Glass. III. Application of Chalcogenide fibers and Glasses Semiconductor and semimetals*, Elsevier Academic Press, 2004, p. 209., 80.
- [6] V.S. Shiryayev, S.V. Smetanin, D.K. Ovchinnikov, M.F. Churbanov, E.B. Krukova, V.G. Plotnichenko, *Inorg. Materials* 41 (2005) 308.
- [7] M.F. Churbanov, G.E. Snopatin, M.Yu. Matveeva, *Inorg. Materials* 42 (2006) 1516.
- [8] M.F. Churbanov, V.S. Shiryayev, I.V. Scripachev, G.E. Snopatin, V.V. Gerasimenko, I.E. Fadin, S.V. Smetanin, V.G. Plotnichenko, *J. Non-Cryst. Solids* 284 (2001) 146.
- [9] O. Humbach, H. Fabian, U. Grzesik, U. Haken, W. Heitmann, *J. Non-Cryst. Solids* 203 (1996) 19.
- [10] L.A. Ketkova, A.V. Kurilin, M.F. Churbanov, *Inorg. Materials* 44 (2008) 773.
- [11] C.F. Boren, D.R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 1983.

- [12] V.S. Shiryaev, L.A. Ketkova, M.F. Churbanov, A.M. Potapov, J. Troles, P. Houizot, J.-L. Adam, A.A. Sibirkin, *J. Non-Cryst. Solids* 355 (2009) 2640.
- [13] M.F. Churbanov, A.A. Pushkin, V.V. Gerasimenko, A.I. Suchkov, V.S. Polyakov, V.V. Koltashev, V.G. Plotnichenko, *Inorg. Materials* 43 (2007) 436.
- [14] F. Kozek, J. Chlebny, Z. Cimpl, J. Masek, *Phil. Mag. B* 47 (1983) 627.
- [15] Snopatin G.E., M.F. Churbanov, Pushkin A.A., Gerasimenko V.V., E.M. Dianov, Plotnichenko V.G., *J. Optoelectron. Adv. Mater. - Rapid Commun.* 3 (2009) 669.
- [16] E.M. Dianov, M.Yu. Petrov, V.G. Plotnichenko, V.K. Sysoev, *Sov. J. Quantum Electron.* 12 (1982) 498.
- [17] M.E. Lines, *J. Appl. Physics* 55 (1984) 4058.
- [18] G.G. Devyatykh, M.F. Churbanov, I.V. Scripachev, G.E. Snopatin, V.P. Kolpashnikov, V.A. Shipunov, RF Patent No. 1721997, June 16, (1995).