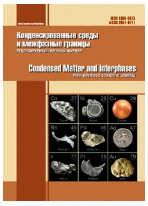

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Advanced methods for preparing especially pure glasses based on germanium and gallium chalcogenides. Part 1. Synthesis via volatile and low-melting compounds. Review

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Abstract

Glasses based on germanium and gallium chalcogenides are promising optical materials for the near and mid-infrared (IR) regions. They are used to develop fiber-optic sensors, sources of supercontinuum, luminescent and laser radiation, glass-ceramic materials with improved mechanical properties, memory cells, and other optical and optoelectronic devices. The most important characteristic of chalcogenide glasses is the content of limiting impurities that have the most negative effect on their optical properties. Conventional methods for producing these materials include melting simple substances with getters in evacuated silica-glass ampoules and then distilling the melt. These methods do not allow achieving extremely low concentrations of impurities that do not affect optical transparency of glasses. Therefore, new approaches need to be developed.

The purpose of the review is to systematize the scientific information related to the methods for preparing especially pure chalcogenide glasses which have been developed over the past 15 years at the Institute of Chemistry of High Purity Substances of the Russian Academy of Sciences. The methods discussed in the first part of the paper include: 1) synthesis of p-element chalcogenides via volatile iodides; 2) preparing a batch by thermal decomposition of germanium sulfide and selenide iodides; 3) synthesis and deep purification of germanium monochalcogenides. The developed methods made it possible to reduce the content of hydrogen, oxygen, and carbon impurities and heterogeneous inclusions in chalcogenide glasses by 1–2 orders of magnitude as compared to conventional methods. In conclusion, the article discusses the possibilities for further reduction of the content of impurities in glasses based on germanium and gallium chalcogenides to achieve extremely low optical losses.

Keywords: Chalcogenide glasses, Especially pure substances, Optical materials, Synthesis, IR spectrometry, Chemical transport reactions

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1. Introduction

Chalcogenide glasses are a promising material for mid-infrared (IR) optics. It is a broad class of glassy inorganic materials based on sulfides, selenides, and tellurides of elements belonging to groups 13–15 of the periodic system. These glasses have a wide transparency region in the IR range (Fig. 1), high optical nonlinearity, and pronounced semiconductor and acoustooptical properties [1–3]. Typical chalcogenide glass forming systems include: As – S, As – Se, As – S – Se, As – Se – Te, Ge – S, Ge – Se, Ge – As – S, Ge – As – Se, Ga – Ge – S, Ga – La – S, Ge – Sb – S, Ga – Ge – Se, Ga – Ge – Te, etc. [4, 5]. There is an increasing interest in glasses based on gallium and antimony chalcogenides, which do not contain arsenic or germanium [6, 7]. This is due to their better transparency in the long-wave IR range.

Chalcogenide glasses are widely used as materials for IR lenses in night vision equipment and thermal visors and for the manufacture of fiber-optic light carriers used in aircraft protection systems [8, 9]. Chalcogenide glasses are used to develop fiber-optic sensors, supercontinuum sources, memory cells, and other optical and optoelectronic devices [10–12]. These materials can also be used to manufacture optical glass-ceramics with improved mechanical and thermophysical properties as compared to glass [13]. The most important area of application of chalcogenide glasses doped with rare earth elements (REE) is the development of mid-infrared luminescent and laser sources [14, 15].

The key characteristic of chalcogenide glasses, which largely determines their practical application, is the content of limiting impurities that have the most negative effect on their optical properties. Among such impurities are: 1) hydrogen in the form of SH-, SeH-, TeH-, and OH-groups and water; 2) oxygen in the form of oxides of glass components and impurity elements; 3) carbon-containing compounds: CS_2, CO_2, COS, and organic substances; 4) transition metals; 5) heterogeneous impurity inclusions, which, first of all, include silicon(IV) oxide used as a material for glass synthesis equipment. These impurities have intense absorption bands within the region of optical transparency of chalcogenide glasses (Table 1) [16–19]. Heterogeneous inclusions reduce the overall transparency in a wide spectral range due to the scattering of IR radiation [20]. The influence of heterogeneous inclusions on the optical transparency of glasses is mainly determined by their size. For $Ge_{25}Sb_{10}S_{65}$ glass, it was shown that with a SiO_2 particle size of 0.1 μm and a concentration of 10^9 cm^{-3} optical losses in the fiber are at least 1 dB/m in the spectral range of 1.1–7.4 μm. Particles with a size of 1 μm cause the same losses but at concentrations of 10^5 cm^{-3} [21].

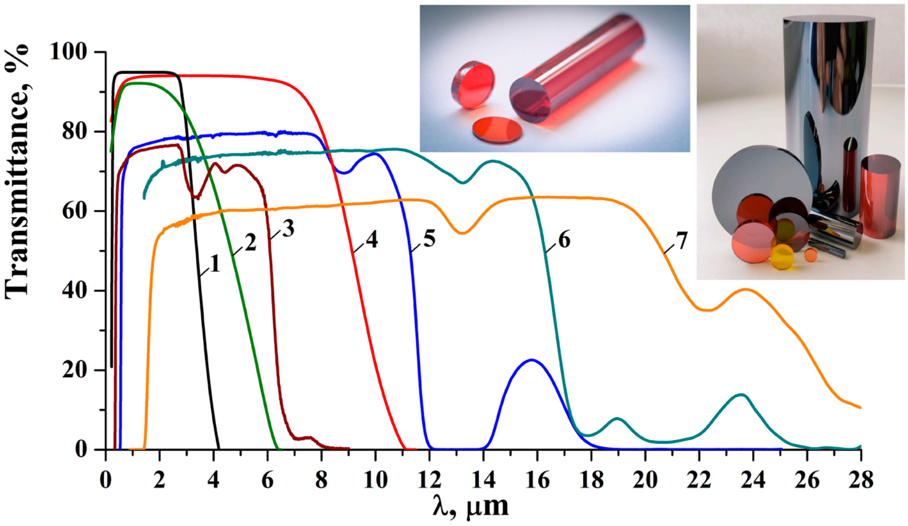

Fig. 1. Transparency windows of several optical materials in the near and middle IR ranges. *1* – silica glass; *2* – Al_2O_3; *3* – ZnO–TeO_2 tellurite glass; *4* – CaF_2; *5* – $Ga_5Ge_{35}S_{60}$ sulfide glass; *6* –$Ge_{28}Sb_{12}Se_{60}$ selenide glass; *7* – $(GeTe_4)_{50}(AgI)_{50}$ telluride glass. An optical path-length of samples can be different, therefore a comparison of transparency spectra is estimate. Inserts give photos of chalcogenide glasses prepared at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences

Table 1. The position of the absorption bands of impurities, $\lambda_{max.}$; their absorption coefficients, ε; and their limiting contents in As_2S_3 glass corresponding to the intrinsic optical losses, $C_{lim.}$ [16–19, 24]

Impurity	λ_{max}, µm	ε, dB/km/ppm(wt.)	C_{lim}, ppb(wt.)	Impurity	λ_{max}, µm	ε, dB/km/ppm(wt.)	C_{lim}, ppb(wt.)
SH	4.0	2,500 ppm(at.)	0.4	SO_2	8.63	43	2300
SeH in As_2Se_3 glass	4.5	1,000 ppm(at.)	0.1	Se–O in As_2Se_3 glass	10.6	380	2.6
GeH	4.85	–	–	Te–O	13.1	–	–
OH (in SiO_2)	2.92	10^4	0.3	Ga – O	15–20	–	–
Ge–O in $Ge_{25}Se_{15}Te_{60}$ glass	7.8	2610	0.4	Si–O	9.1	28000	–
	12.5	99000	0.01	CO_2	4.33	$1.5·10^4$	0.04
As_2O_3 in As_2Se_3 glass	12.65	$4.3·10^4$	100	COS	4.95	10^5	0.004
	9.5	1030	400	CS_2	6.68	$4.8·10^5$	0.2

The intrinsic (excluding the effect of impurities) optical losses in As_2S_3 glass, calculated from the absorption spectra of an ultra-pure bulk sample, are <20 dB/km in the spectral range of 2–6 µm with a minimum of about 0.3 dB/km at 5.2 µm [22]. According to the theoretical evaluation, the minimum optical losses for As_2Se_3 glass in the range of 2.5–6.6 µm do not exceed 1 dB/km [23]. From the known absorption coefficients of impurities [24], it was calculated that their content in As_2S_3 glass, corresponding to the intrinsic optical losses, should not exceed 0.4 ppb(wt.) for hydrogen in the form of SH-groups and 0.2, 0.004, and 0.04 ppb(wt.) for carbon in the form of CS_2, COS, and CO_2, respectively. To provide minimum optical losses in As_2Se_3 glass, the content of hydrogen impurity in the form of SeH-groups should not exceed 0.1 ppb(wt.), of oxygen in the form of oxides 0.1 ppm(wt.), and carbon 0.1–0.01 ppm(wt.) [25]. The content of impurities in samples of chalcogenide glasses prepared by the conventional method including the purification of the melt by distillation is 3–4 orders of magnitude higher than the permissible values [16]. This significantly limits the practical use of such materials for the manufacture of fiber-optic light carriers and makes it impossible to use them to manufacture laser radiation sources. The intrinsic optical losses in glasses based on germanium and gallium chalcogenides have so far been only evaluated for the $Ge_3PS_{7.5}$ composition [26], which makes it difficult to determine the maximum permissible concentration of impurities in these materials.

The purpose of this review is to systematize the scientific information related to the methods for preparing ultra-pure chalcogenide glasses which have been developed over the past 15 years at the Institute of Chemistry of High Purity Substances of the Russian Academy of Sciences. The key idea of the new methods was to use germanium and gallium compounds, which are more volatile, low-melting, and have better reactive properties as compared to the simple substances which had been used traditionally. Among such compounds were: germanium(IV) iodide, gallium(III) iodide, germanium sulfide and selenide iodides, and germanium(II) chalcogenides.

2. Traditional method for preparing chalcogenide glasses

Traditionally, chalcogenide glasses are prepared by the interaction of especially pure substances of grades 4–7 N in evacuated silica-glass ampoules [27]. The synthesis temperature is determined by the glass composition and is usually in the range of 750–950 °C. To ensure the uniformity of the glasses, the process is carried out in rocking furnaces. The melt is usually quenched in air or in water, depending on the crystallization stability of the glasses. To relieve mechanical stresses after quenching, the samples are annealed at the glass transition temperature.

The main method of reducing the content of impurities in chalcogenide glasses involves adding getters to the batch, which selectively bind impurities and convert them into a form which can be easily removed, and a subsequent purification of the melt by distillation [27]. Aluminum and magnesium is used to bind oxygen impurities, while tellurium(IV) chloride and aluminum(III) chloride contribute to a decrease in hydrogen content. This method allows reducing the concentration of impurities in glasses by 1–2 orders of magnitude. In the best samples of germanium-containing glasses prepared by the traditional method, the content of hydrogen impurity in the form of SH-groups was 7.5 ppm(at.) in $Ge_{25}Sb_{10}S_{65}$ [17]; the content of hydrogen impurity in the form of SeH-groups was 2.7 ppm(at.) and the content of oxygen in the form of germanium oxides was 0.2 ppm(wt.) in $Ge_{20}Se_{80}$ [28].

The disadvantage of using getters is their interaction with the walls of the silica-glass reactor, which leads to the introduction of impurities into the chalcogenide melt.

$$2Al + 3SiO_2 \rightleftarrows Al_2O_3 + 3SiO, \quad (1)$$

$$xAl_2O_3 + ySiO_2 \rightleftarrows xAl_2O_3 \cdot ySiO_2, \quad (2)$$

$$4Mg + SiO_2 \rightleftarrows 2MgO + Mg_2Si. \quad (3)$$

During subsequent purification of the glass-forming melt by distillation, reaction products (1)–(3), which have low solubility in the chalcogenide melt, can be only partly removed. This results in the appearance of heterogeneous impurity inclusions and absorption bands in the glasses in the regions of 9.1 μm (Si–O) and 13.2 μm (Al-O) [19]. The interaction of aluminum with the walls of the silica-glass reactor can lead to its rupture during cooling of the melt. This significantly complicates the production of chalcogenide glasses and makes synthesis more hazardous.

The main disadvantage of the purification of the batch by distillation is the high temperature and duration of the process. They are due to the relatively low volatility of germanium dichalcogenides and the need for slow evaporation of the melt for its effective purification from heterogeneous impurities. High temperatures contribute to the entry of hydrogen, metal, and silicon oxide impurities from the walls of the silica-glass reactor into the chalcogenide melt [22, 29]. During preparation of telluride-germanium glasses, there is another limitation of purification by distillation, i.e. the dissociative evaporation of GeTe, which makes it difficult to obtain charge of a specified chemical composition [30].

The main challenge for the production of especially-pure glasses containing gallium is related with the low volatility of this metal and its chalcogenides [31, 32]. This makes the purification of the glass-forming melt by distillation impossible. Therefore, gallium is added to the batch by loading the sample in air or into a glove box with an inert atmosphere. When using this method, gallium oxide and hydroxide impurities, which are present on its surface and which form during the reactor soldering, enter the glass-forming melt. These impurities significantly reduce the transparency of chalcogenide glasses in the mid IR range.

These problems associated with the production of optical materials based on especially pure chalcogenide glasses mean that novel approaches to their synthesis need to be developed. Reducing the content of absorbing and scattering impurities by 2–3 orders of magnitude will significantly improve the optical characteristics of chalcogenide glasses. This will expand the scope and the efficiency of their application. To improve the purity of chalcogenide glasses, it is highly important to establish the nature and limits of the influence of impurities on the properties of these materials.

3. Preparation of chalcogenide glasses via volatile iodides

The main idea of the developed method was to synthesize batch components by the interaction between iodides and chalcogen [33–35]. Using the Ge – Sb – S – I and Ge – Sb – Se – I systems, germanium and antimony chalcogenides were synthesized by reactions of the following type:

$$GeI_4 + 2S(Se) \rightleftarrows GeS(Se)_2 + 2I_2\uparrow, \quad (4)$$

$$2SbI_3 + 3S(Se) \rightleftarrows Sb_2S(Se)_3 + 3I_2\uparrow. \quad (5)$$

According to the thermodynamic modeling of reactions (4) and (5), the degree of iodides conversion to the corresponding chalcogenides under equilibrium conditions was expected to be low, up to 26% for sulfides and up to 11% for selenides at a temperature of 500 °C [36]. A significant increase in the yield of chalcogenides was possible due to the selective isolation of iodine from the reaction melt. In practice, this involved using a vertical unit made of silica-glass and consisting of three parts which were successively soldered together: 1) reactor; 2) mass transfer section; 3) iodine receiver. Batch components were synthesized at a temperature of 500–650 °C. Heating of the reaction mixture resulted in the release of iodine vapors by reactions (4) and (5) and their entering the receiver. One part of the iodine condensed as crystals, the other part in the form of liquid drained back into the reactor. The presence of the mass transfer section allowed selectively extracting iodine from the reaction melt without the significant removal of volatile iodides from it. As the synthesis proceeded, the batch was depleted of iodine and its viscosity increased, which required a gradual increase in the reactor temperature to ensure the batch was molten.

The content of metal impurities in the prepared glass samples did not exceed 0.5 ppm(wt.); the content of silicon, which was the main source of heterogeneous inclusions, was 0.02–0.1 ppm(wt.); the content of the impurities which were the most difficult to remove, impurities of hydrogen in the form of SH- and SeH-groups, was 0.1–0.3 ppm(at.) [33, 34]. This was 1–2 orders of magnitude lower than in glasses prepared by the interaction of simple substances with purification of the melt by distillation. The achieved purity was provided by the following main advantages of the method:

– Before the synthesis of the batch component, iodides of *p*-elements were subjected to deep purification from hydrogen, oxygen, and carbon impurities and heterogeneous inclusions by vacuum distillation at temperatures that did not exceed 200 °C. The content of these impurities in the corresponding simple substances of especially pure grades was not controlled and could be significant.

– Iodides were loaded into the reactor by vacuum evaporation, which excluded the contact of reagents with atmospheric impurities (oxygen, water, organic substances, dust, etc.).

– The synthesis temperature of the glass-forming components of the batch did not exceed 650 °C, which significantly reduced the contamination effect of the silica-glass reactor.

– Iodides of *p*-elements converted the hydrogen impurity in the form of SH- and SeH-groups into an easily removable form due to the following chemical reactions:

$$GeI_4 + 2H_2S(Se) \rightleftarrows GeS(Se)_2 + 4HI\uparrow, \tag{6}$$

$$2SbI_3 + 3H_2S(Se) \rightleftarrows Sb_2S(Se)_3 + 6HI\uparrow, \tag{7}$$

$$I_2 + H_2S(Se) \rightleftarrows S(Se) + 2HI\uparrow. \tag{8}$$

The formed hydrogen iodide was removed from the reaction melt and concentrated in the iodine receiver.

The main disadvantage of the method is the difficulty of providing a specified chemical composition of the glass by a controlled removal of iodine from the reaction mixture. Deviations in the content of components can reach 3–5 at. %.

The developed method was used for the synthesis of crystalline binary and complex sulfides and selenides of *p*-elements with the actual yield of 70–98% and a residual iodine content of <0.1 to 2 at. %. [37–40] (Table 2). Such amount of iodine did not have a noticeable negative effect on the optical properties of chalcogenides, but allowed growing their single crystals by chemical transport directly in the synthesis reactor [42]. This

Table 2. Chemical composition and actual yield of some chalcogenides prepared via volatile iodides

Sample	Element concentration, at. %				Yield, %
	p-element	Zn	S(Se)	I	
Ga_2S_3	40.2	–	59.7	0.04	95
In_2S_3	39.1	–	59.4	1.5	72
Sb_2S_3	38.2	–	61.2	0.6	88
GeS_2	33.9	–	65.9	0.2	92
ZnS	–	50.5	48.7	0.8	91
Ga_2Se_3	41.3	–	57.3	1.4	82
In_2Se_3	42.3	–	56.1	1.6	70
$GeSe_2$	36.4	–	63.4	0.2	90
ZnSe	–	50.9	48.3	0.8	90
$ZnGa_2S_4$	29.2	14.8	55.6	0.4	94
$ZnGa_2Se_4$	26.9	16.2	56.5	0.4	88

means there was no need in the extra step which involves adding a transport agent and leads to the contamination of the material. It was theoretically predicted and experimentally confirmed that the yield of chalcogenides of *p*-elements increases with a decrease in the atomic mass of the element in the group and with the transition from selenides to sulfides. Synthesis was most effective when aluminum(III) iodide and gallium(III) iodide interacted with sulfur. To prepare Ga_2S_3 and complex sulfides based on it, a reactor with two temperature zones without a mass transfer section was used. At synthesis temperatures of up to 550 °C, γ-Ga_2S_3 with the cubic structure of the unit cell was formed (Fig. 2a). Annealing the resulting sulfide at higher temperatures led to the formation of monoclinic β-Ga_2S_3. The synthesis of indium, germanium, antimony, and bismuth chalcogenides was complicated by the formation of relatively stable sulfide and selenide iodides as intermediate products (Fig. 2b, 2c). The decomposition of these compounds led to the formation of chalcogenides, for example, by reactions:

$$3SbSI \rightleftarrows Sb_2S_3 + SbI_3, \quad (9)$$

$$Bi(Bi_2S_3)_9I_3 \rightleftarrows 9Bi_2S_3 + BiI_3. \quad (10)$$

Preparing tellurides of *p*-elements of groups 13–15 by the proposed method is complicated due to thermodynamic limitations with regard to the high melting point of tellurium (T_m = 451 °C [43]) and the formation of relatively stable TeI_4.

4. Preparation of glasses of the Ge – S(Se) – I system by thermal decomposition of germanium sulfide and selenide iodides

It is known that the Ge – S – I system has low-melting compounds of the $GeSI_2$ (T_m = 150 °C) [44] and $Ge_2S_3I_2$ (T_m = 310 °C) composition [45], which form stable glasses. Thermal decomposition of these sulfide iodides in a temperature gradient was accompanied by the release of germanium(IV) iodide and the formation of germanium(IV) sulfide [46] (Fig. 3), which in a simplified way can be described by the following chemical reactions:

$$2GeSI_2 \rightleftarrows GeS_2 + GeI_4\uparrow, \quad (11)$$

$$2Ge_2S_3I_2 \rightleftarrows 3GeS_2 + GeI_4\uparrow. \quad (12)$$

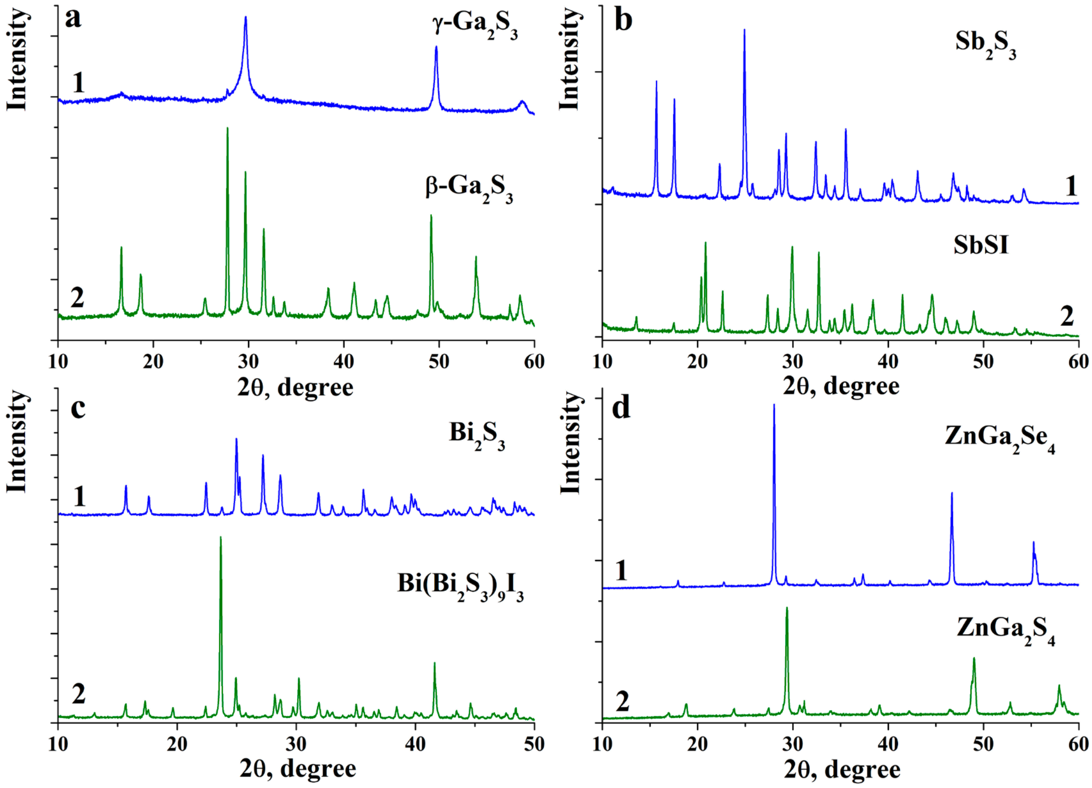

Fig. 2. X-ray diffraction patterns of the reaction products of some iodides with chalcogens; a1 – GaI_3 + S <550 °C (PDF 49-1361 [41]); a2 – GaI_3 + S >550 °C (PDF 76-0752); b1 – SbI_3 + S (PDF 75-1310); b2 – SbI_3 + S intermediate product (PDF 74-2244); c1 – BiI_3 + S (PDF 84-0279); c2 – BiI_3 + S intermediate product (PDF 73-1157); d1 – ZnI_2 + GaI_3 + Se (PDF 47-1590); d2 – ZnI_2 + GaI_3 + S (PDF 84-2007)

By controlling the degree of decomposition of sulfide iodides, it is possible to specify the composition of the non-volatile reaction product. The method for preparing glasses of the Ge – S – I system at low temperatures is based on this idea [47, 48].

The synthesis of the glassy $Ge_2S_3I_2$, its subsequent thermal decomposition, and melting of the resulting batch were carried out in one evacuated silica-glass reactor, which excluded contamination of the melt with impurities from the atmosphere [47]. $Ge_2S_3I_2$ was prepared by the reaction between germanium(IV) iodide, germanium, and sulfur at a temperature of 550 °C

$$GeI_4 + 3Ge + 6S \rightleftarrows 2Ge_2S_3I_2. \qquad (13)$$

When a temperature gradient from 550 °C to room temperature was created in the reactor, the resulting sulfide-iodide was thermally decomposed. The degree of decomposition was controlled by its duration (from 1 to 5 hours) according to a predetermined experimental dependence of the glass composition on the duration of the process. This allowed specifying the content of components with deviations of no more than ± 2 at. %. Further, the evaporator with the resulting batch was sealed-off from the unit and the glass-forming melt was homogenized at 750 °C under the stirring action of a rocking furnace. Similarly, glasses of the Ge – Se – I system were prepared by the thermal decomposition of $Ge_2Se_3I_2$ [49].

According to the results of the IR Fourier analysis, in the best samples of the prepared glasses, the content of hydrogen impurity in the form of SH- and SeH-groups was 0.1–0.5 ppm(at.); OH-groups <0.05 ppm(wt.); oxygen chemically bound to germanium up to 0.5 ppm(wt.), and carbon in the form of CO_2, CS_2, and COS <0.01 ppm(wt.). The achieved content of absorbing impurities was due to a significant decrease in the synthesis temperature and effective removal of highly volatile impurity compounds at the stage of thermal decomposition of $Ge_2S_3I_2$ and $Ge_2Se_3I_2$.

The main limitation of the developed method is that it can only be applied to two glass-forming systems: Ge – S – I and Ge – Se – I. To prepare glasses of the compositions beyond the $GeS(Se)_2$ – GeI_4 quasi-binary section, it is necessary to use source alloys with a corresponding excess (*y*) or deficiency (-*y*) of chalcogen:

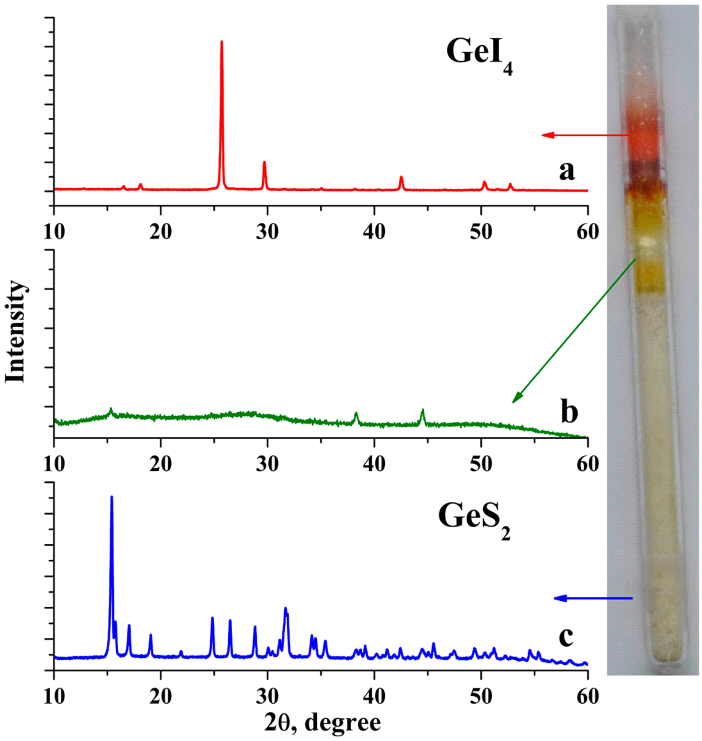

Fig. 3. X-ray diffraction patterns of the thermal decomposition products of $Ge_2S_3I_2$ glass. a – cold section of the reactor, corresponds to GeI_4 (PDF 75-0982); b – intermediate section, amorphous product with weak reflections from GeS_2; c – high-temperature section, corresponds to GeS_2 (PDF 71-0003). The insert on the right shows a photo of the reactor

$$2Ge_2S_{(3+y)}I_2 \rightleftarrows 3GeS_{(2+2/3y)} + GeI_4\uparrow. \quad (14)$$

Along with the use of sulfide and selenide iodides, the glasses of the Ge – S and Ge – Se systems can be prepared by thermal decomposition of $GeSBr_2$ and $Ge_2S_3Br_2$ [50]. The disadvantage of this method is the need to use liquid bromine to synthesize starting compounds.

5. Preparation of glasses via germanium monochalcogenides

5.1. Ge – S, Ge – Se systems

Another approach was aimed at alleviating the disadvantages of the conventional vacuum distillation of the chalcogenide melt described in paragraph 2. The novel method involved synthesis and purification of germanium monochalcogenides. The synthesis was carried out by passing chalcogen vapors over a mixture of germanium granules with a getter [51, 52]. The by-products of the proposed method for the germanium monochalcogenide synthesis were dichalcogenides. According to the results of thermodynamic modeling of the Ge – S and Ge – Se systems by the method of equilibrium constants, the formation of GeS and GeSe is facilitated by an increase in the reactor temperature and a decrease in the temperature of the chalcogen evaporator [51, 53]. The results of thermodynamic modeling are in good agreement with the experimental values of the optimal conditions for the synthesis of germanium monochalcogenides: reactor temperature of 550–600 °C and chalcogen evaporator temperature of 240–260 °C for sulfur and 330–350 °C for selenium.

The developed method was used to prepare especially pure glasses of the $Ge_{20}Se_{80}$ composition [54]. The content of impurities in the optical fibers fabricated from such glass was as following: hydrogen in the form of SeH-groups was 1.8±0.1 ppm(at.); oxygen chemically bound to germanium was 0.013±0.002 ppm(wt.). According to these values, the obtained fibers were the best among those made of glasses based on germanium selenides. The minimum optical losses in the fiber were 0.77 dB/m at a wavelength of 5.6 μm (Fig. 4). The relatively high losses may be due to partial crystallization of the glass due to unoptimized conditions for fiber drawing. The lowest losses in germanium selenide optical fibers - obtained to date [28] are 0.1 dB/m at a wavelength of 6.5 μm. The content of hydrogen impurities in the form of SeH-groups and oxygen chemically bound to germanium in this fiber was 2.7 ppm(at.) and 0.2 ppm(wt.), respectively.

For sulfide systems, the developed method in combination with the synthesis of gallium(III) sulfide by the interaction of gallium(III) iodide with sulfur was used to especially pure $Ga_5Ge_{35}S_{60}$ and $Ga_8Sb_{32}S_{60}$ glasses [53]. The absorption spectra of the samples and the photographs of diffraction spots caused by submicron inclusions recorded by 3D laser ultramicroscopy are shown in Fig. 5. The content of hydrogen impurities in the samples in the form of SH-groups was 0.2–0.6 ppm(at.), which was 2 orders of magnitude lower than during the synthesis from simple substances. In the glasses prepared by the conventional method, the content of heterogeneous micron-sized inclusions determined by optical microscopy was $n\cdot10^3$ pcs/cm³. The content of submicron inclusions (0.1–0.9 μm) recorded by 3D laser ultramicroscopy reached $n\cdot10^8$ pcs/cm³. The samples prepared by the developed method had single micron inclusions (<10² pcs./cm³). In the submicron region, there was only background scattering, i.e. intrinsic scattering on frozen fluctuations or on small (<100 nm) inclusions that did not contribute significantly to optical losses in the mid-infrared range.

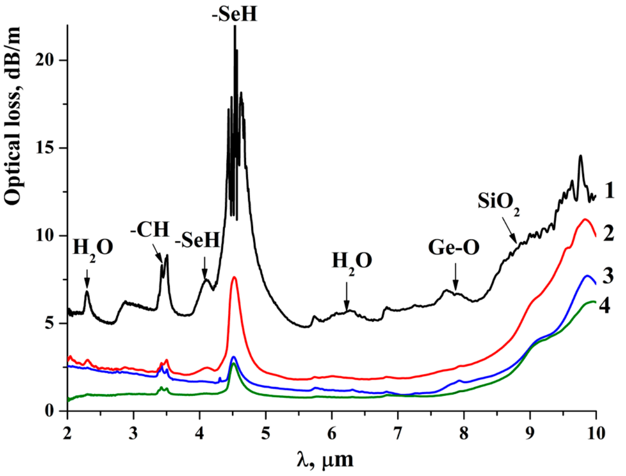

Fig. 4. Spectra of total optical losses of optical fibers without a reflective cladding, made of $Ge_{20}Se_{80}$ glasses prepared: from simple substances without additional purification (1); with the addition of aluminum to the batch and double distillation of the melt (2); by passing selenium vapor over germanium (3); by passing selenium vapor over a mixture of germanium and aluminum (4) [54]

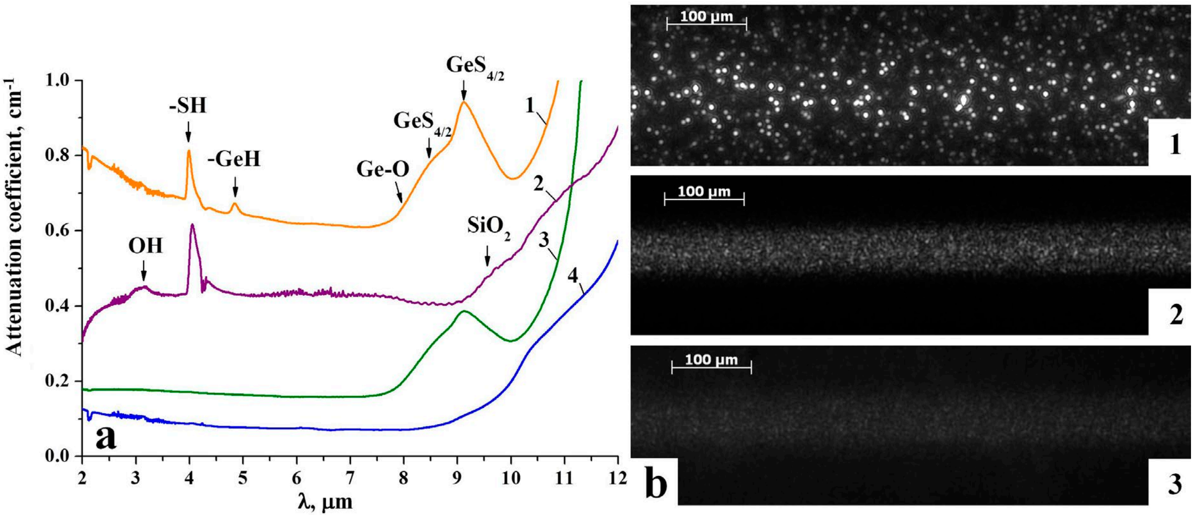

Fig. 5. Absorption spectra (a) and photographs of diffraction spots from submicron inclusions (b) of $Ga_5Ge_{35}S_{60}$ and $Ga_8Sb_{32}S_{60}$ glasses; $Ga_5Ge_{35}S_{60}$ samples prepared by the traditional method (a1, b1) and by the developed method (a3, b2); $Ga_8Sb_{32}S_{60}$ samples prepared by the traditional method (a2) and by the developed method (a4, b3) [53]

The developed method has the following key advantages as compared to the conventional distillation of the melt:

– Higher volatility of germanium monochalcogenides as compared to dichalcogenides allows reducing the temperature of the vacuum purification of the batch by 50–100 °C.

– The addition of the getter to the intermediate ampoule with germanium minimizes the products of its interaction with impurities and the silica-glass reactor entering the glass-forming melt.

– Passing chalcogen vapors over the mixture allows for preliminary chemical etching of germanium granules before the batch components are loaded into the reactor. This contributes to the removal of surface contamination from the granules (adsorbed gases, water, OH-groups, oxides, and heterogeneous inclusions) due to the capture of germanium monochalcogenide by the vapors or due to chemical reactions of type (15)–(17):

$$3S + GeO_2 \rightleftarrows GeS_2 + SO_2, \quad (15)$$

$$3S + 2H_2O \rightleftarrows 2H_2S + SO_2, \quad (16)$$

$$(y/2+2x)S + C_xH_y \rightleftarrows y/2H_2S + xCS_2. \quad (17)$$

For this, the first portions of germanium monochalcogenide (50–100 mg), in which surface impurities can be concentrated, are removed from the system.

5.2. The Ge – Te system

Another limitation of the conventional vacuum distillation of the batch during the preparation of glasses based on the Ge-Te system (for example, $Ge_{20}Te_{80}$, $Ga_{10}Ge_{15}Te_{75}$) is the dissociative evaporation of germanium monotelluride [30].

$$(x+y+z)GeTe_{(кр.)} \rightleftarrows$$
$$\rightleftarrows xGeTe_{(г.)} + y/2Te_2 + z/2GeTe_{2(г.)} + (y+z/2)Ge_{(кр.)}. \quad (18)$$

The released germanium remains in the evaporator, which leads to a noticeable deviation of the glass composition from the specified value. According to the experimental results, after single, double and triple distillation of the melt, the deviations in the content of germanium in $Ge_{20}Te_{80}$ glasses reached 0.5, 0.9, and 2.1 at. % [55]. This corresponds to the degree of GeTe decomposition of 2.5, 4.5, and 10.5 %, respectively. In the developed method, the problem of preserving the chemical composition of the batch is solved due to the constant presence of tellurium vapors over GeTe, which shifts the equilibrium of reaction (18) to the left. However, re-distillation of the $(GeTe)_xTe_{100-x}$ batch aimed at further reduction in the content of impurities was accompanied by a noticeable decomposition of GeTe. This could be explained by the fact that at the initial stage of low-temperature distillation tellurium evaporates completely. Suppression of the germanium(II) telluride dissociation caused by excess chalcogen in the vapor phase is impossible during the final stages of purification.

To solve this problem, a novel method for purification of the $(GeTe)_xTe_{100-x}$ batch by distillation was developed [55]. The main idea of the proposed method is to provide for the separate condensation of tellurium and germanium(II) telluride during the purification of the glass-forming melt by distillation. The separation of the batch components allowed for its subsequent purification without GeTe dissociation. This was achieved by the possibility of sequential distillation of GeTe and tellurium from separate ampoules. During the final stages of the germanium(II) telluride evaporation, tellurium vapors were passed over it, which suppressed reaction (18) in the forward direction. In the case of partial decomposition of GeTe during distillation, tellurium vapors interacted with the released germanium and transferred it to the vapor phase. This eliminated the incomplete transition of germanium from the evaporator to the receiver during the purification of the $(GeTe)_xTe_{100-x}$ batch.

The deviations of the compositions of Ge_xTe_{100-x} glasses prepared by the developed method of purification did not exceed 0.2 at. % even after triple distillation of the melt. The corresponding degree of the GeTe decomposition was 1.0%. Such deviations do not have any noticeable effects on the key properties of chalcogenide glassy materials. This method is an integral part of comprehensive approaches to the production of especially pure glasses based on the Ge-Te system.

6. Conclusions

The developed methods allow significantly (by 1–2 orders of magnitude) reducing the content of impurities in glasses based on germanium and gallium chalcogenides. This is largely due to the fact that the methods implement the chemical principles of the deep purification of substances. As a rule, the efficiency of a single stage of purification from impurities using chemical reactions is higher than that using physicochemical methods (distillation, crystallization, etc.) [56]. In chemical methods, the partition coefficient is determined by the difference in the thermodynamic potentials of reactions with the participation of the main substance and impurity. This difference can significantly exceed the differences in the thermodynamic functions of the phase transitions of the impurity and the purified substance (melting, evaporation), on which the physicochemical methods of separation are based. In turn, these differences are determined by the fact that in chemical methods the purification effect is due to the re-distribution of intramolecular bonds, the energy of which, in general, is higher than that of intermolecular bonds. The efficiency of separation in chemical methods depends on the type of reaction. By selecting the appropriate reagent, it is possible to provide high values of the partition coefficients. A definitive advantage of chemical methods is their applicability in cases when the main substance is a non-volatile, high-melting or thermally unstable compound. Nonetheless, to prepare chalcogenide glasses with a low content of all types of impurities, it is necessary to use a set of methods with regard to the purification and loading of the batch components into the reactor, including vacuum distillation.

An important technique implemented in the developed methods is the transformation of the chemical form of the batch components in order to increase their volatility and meltability and to change (increase or decrease) their reactivity properties. This allows: 1) significantly reducing the temperature and duration of the synthesis; 2) reducing the interaction with the silica-glass reactor; 3) increasing the efficiency of the removal of impurities.

The main disadvantage of chemical methods of purification is the contamination of the main substance with the elements present in the reagents. In the developed methods, the key reagents are iodides. At moderate concentrations iodine does not have any noticeable negative effects on the target properties of chalcogenide glasses. Moreover, it is known that the addition of iodine increases the crystallization stability of glasses, increases their overall transparency and expands its range, and contributes to the dissolution of REE [57–60]. This makes iodides of *p*-elements one of the most suitable transport agents for the production of especially pure chalcogenide glasses.

Despite a significant increase in purity, the achieved content of impurities is still 2 orders of magnitude higher than the upper values, which do not affect the optical properties of chalcogenide glasses. This means that it is necessary to further improve the developed methods, their temperature and time regimes, and equipment. To reduce the contamination effect of the silica-glass reactor during chemical transport with the participation of iodides, individual elements or coatings can be developed for the zones of the highest temperature. These elements or coatings can be made of materials such as corundum, pyrolytic boron nitride, etc. The original silica-glass tubes should meet high quality standards in terms of the content of impurities of OH-groups and metals. Surface defects should be under strict control since they are the most chemically active centers when the reactor walls come into contact with the chalcogenide melt. It is necessary to develop methods for reducing the content of these impurities and defects in reactors for thermal, chemical, plasma-chemical, and other types of treatment [61, 62]. An important area for further research is the assessment of the minimum achievable optical losses in glasses based on germanium and gallium chalcogenides to determine the limits of the influence of impurities on this key property.

Author contributions

A. P. Velmuzhov: research concept, methodology development, conducting research, text writing, final conclusions. M. V. Sukhanov: research concept, methodology development, conducting research, editing. E. A. Tyurina: methodology development, conducting research, editing. V. S. Shiryaev: research concept, conducting research, editing.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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