



Review

Review article

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Advanced methods for preparing especially pure glasses based on germanium and gallium chalcogenides. Part 2. Synthesis using chemical transport reactions. Review

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Abstract

Purpose: The second part of the review presents the results of preparing especially pure glasses based on germanium and gallium chalcogenides with chemical transport reactions.

Experimental part: Deep purification and vacuum loading of metallic gallium, gallium(III) telluride and rare-earth elements (REE) using gallium(III) iodide as a transport agent made it possible to reduce the content of hydrogen, oxygen impurities and heterogeneous inclusions in glasses by 1–2 orders of magnitude compared to tradition direct glass synthesis. We have theoretically justified and experimentally confirmed the high efficiency of REEs as getters for binding and subsequent removal of oxygen impurities from the chalcogenide melt.

Conclusions: The key result achieved by reducing the impurity content is mid-infrared (IR) laser generation in bulk samples of REE-doped chalcogenide glasses and in optical fibers based on them, which was previously not possible in these materials.

Keywords: Chalcogenide glasses; Especially pure substances; Optical materials; Synthesis; Chemical transport reactions; Laser generation

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1. Introduction

The development of luminescent and laser sources of radiation in the mid-infrared (IR) range is a promising practical application of glasses based on germanium and gallium chalcogenides [1, 2]. Until recently, research in this area was limited to the evaluation of potential capabilities of chalcogenide glasses doped with rare-earth elements (REEs) as laser materials [3, 4]. In cooperation with Devyatikh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (ICHPS RAS), Dianov Fiber Optics Research Centre (FORC) and Prokhorov General Physics Institute of the Russian Academy of Sciences (GPI RAS), for the first time, laser generation at a wavelength $\geq 5 \mu\text{m}$ was achieved first in bulk samples of REE-doped chalcogenide glasses [5] and then in optical fibers based on them [6–8].

In recent years, there has been increasing interest in germanium and gallium telluride glasses due to their optical transparency in a wide spectral range up to $35 \mu\text{m}$ for bulk samples [9] and $16 \mu\text{m}$ for optical fibers [10]. This makes such glasses promising for the transmission of CO_2 laser radiation with operating wavelengths at 9.3 and $10.6 \mu\text{m}$ [11]. Optical devices based on telluride glasses can be used to solve problems related to space exploration [12–14].

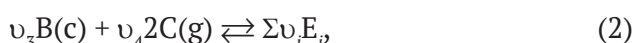
The main difficulty in preparing especially pure glasses, containing gallium and REE, is the extremely low volatility of these metals in the form of simple substances and chalcogenides [15, 16]. This virtually excludes the possibility of purification of the glass-forming melt by distillation, which is the most important step in preparing low impurity chalcogenide glasses [17].

The purpose of this review is to systematize the scientific fundamentals of the methods for preparing especially pure chalcogenide glasses developed at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences for the last 15 years. The first part of the review presents the results of batch synthesis via volatile iodides of p -elements, germanium monochalcogenides, and thermal decomposition of germanium sulfide and selenide iodides [18]. The second part focuses on the application of chemical transport reactions for preparing low impurity chalcogenide

glasses. The article presents data on REEs as effective getters for binding oxygen impurities in telluride glasses.

2. Preparation of chalcogenide glasses with chemical transport reactions

Chemical transport is one of the most effective methods for the deep purification of substances [19, 20]. The method is based on the interaction of the vapors of the transport agent with the target low volatile substance, resulting in the formation of one or more highly volatile compounds. For the “main substance – impurity” system, chemical transport reactions can be written in the following form:



where A – main substance; B – impurity; C – transport agent; D_i – product of interaction with the main substance; E_i – product of interaction with the impurity; ν_i – stoichiometric coefficient. If at T_2 the reactions (1) and (2) proceed mainly in the forward direction and at T_1 in the reverse direction, then by creating a temperature gradient $T_2 \rightarrow T_1$ it is possible to ensure the transport of components A and B from the zone with T_2 to the zone with T_1 . If the thermodynamic or kinetic reaction (1) is more favorable, component A will be transported preferentially. This leads to a spatial separation of the main substance and impurity, which provides the purification effect.

The partition coefficient α for chemical purification methods is determined by the ratio:

$$\alpha = \frac{x^*}{x^* + x} / \frac{y^*}{y^* + y}, \quad (3)$$

where x, x^* – concentrations of the main substance and impurity in the starting reagents; y, y^* – concentrations of the main substance and impurity in the reaction products. If the impurity is transported less efficiently than the main substance, the reaction products are impoverished by the impurity compared to the initial reagents, and $\alpha > 1$. For the simplified case, when all stoichiometric coefficients of the reactions (1) and (2) are equal to 1, α can be estimated by standard thermodynamic functions of chemical transport participants [20]:

$$\ln \alpha = \ln \frac{K_1^0}{K_2^0} = \frac{\Delta_r H_2^0 - \Delta_r H_1^0}{RT} - \frac{\Delta_r S_2^0 - \Delta_r S_1^0}{R}, \quad (4)$$

where K_1^0 and K_2^0 – standard equilibrium constants of reactions; $\Delta_r H_1^0$ and $\Delta_r H_2^0$ – changes in the standard enthalpies of reactions; $\Delta_r S_1^0$ and $\Delta_r S_2^0$ – changes in the standard entropies of reactions; R – universal gas constant; index 1 refers to the reaction involving the main substance, index 2 to the reaction involving the impurity. When modeling chemical transport by the method of minimizing thermodynamic potentials, the partition coefficient is estimated directly from the calculated equilibrium concentrations of the system components. It should be noted that the above calculation method is an estimation, since in reality chemical transport of substances occurs under conditions far from thermodynamic equilibrium. The separation effect in chemical transport can be based not only on differences in equilibrium constants, but also on differences in the rate constants of reactions involving the main substance and impurity.

2.1 Chemical transport of gallium

Gallium(III) iodide is a convenient reagent for vacuum loading of gallium into a reactor with a chalcogenide batch with chemical transport. The transport agent can be prepared by passing iodine vapor over metallic gallium in a vacuum reactor and further purified by multiple distillation. Chemical transport is based on the reaction:



At higher temperatures, the reaction proceeds in the forward direction, transferring non-volatile gallium to the vapor phase in the form of monoiodide. In the lower temperature region of the reactor, gallium monoiodide disproportionates, releasing metallic gallium and GaI_3 . The main impurities limiting the optical properties of chalcogenide glasses contained in especially pure gallium are Ga_2O_3 and $\text{Ga}(\text{OH})_3$. They have absorption bands in the range 10, 15–20 μm [21, 22] and may be in the form of heterogeneous inclusions at concentrations above the solubility limit. These impurities are formed when manipulating (weighing, loading, storage) metallic gallium and are not controlled in commercial high purity samples. To evaluate the optimal conditions of chemical transport

ensuring high efficiency of gallium loading and its purification from oxide impurities, the GaI_3 – $\text{Ga} - \text{Ga}_2\text{O}_3$ system was modeled using the method of minimization of thermodynamic potentials in the IVTANTERMO software package [23]. The quantitative evaluation of the efficiency of the purification of gallium from oxygen impurities was carried out on the basis of the calculation of the separation coefficient $\alpha_{[\text{O}]}(T)$, which was determined from the ratio of the initial concentration of this impurity in the condensed phase $n_{[\text{O}]}^0$ to the equilibrium pressure in the vapor phase $p_{[\text{O}]}(T)$ at a given temperature:

$$a_{[\text{O}]}(T) = \frac{n_{[\text{O}]}^0}{\sum n_i^0} / \frac{p_{[\text{O}]}(T)}{\sum p_i(T)} \quad (6)$$

where n_i^0 – initial content of the i -th component in the condensed phase; $p_i(T)$ – equilibrium pressure of the i -th component at temperature T .

Fig. 1a shows the results of modeling in terms of temperature dependence of the relative concentrations of the vapor phase components and oxygen impurity partition coefficient. The high content of gallium monoiodide in the system is reached at temperatures > 600 $^\circ\text{C}$. From the dependence of the concentration differences of the vapor phase components at 600 $^\circ\text{C}$ and a given temperature T (flow method [19]), it follows that efficient transport is observed at $\Delta T > 250$ $^\circ\text{C}$ (Fig. 1b). The oxygen-containing component of the vapor phase is gallium(I) oxide. At 600 $^\circ\text{C}$, the partition coefficient is about 10^3 , indicating the high efficiency of chemical transport to purify gallium from oxygen impurities. The data obtained was used as reference values for the development of the gallium loading method.

The method was used to prepare glasses of the $\text{Ga} - \text{Ge} - \text{As} - \text{Se}$ system [24]. The optimum conditions for chemical transport are as following: the temperature in the ampoule with gallium 600–650 $^\circ\text{C}$; temperature of the GaI_3 evaporator 220–240 $^\circ\text{C}$; the temperature of the gallium receiver 250–280 $^\circ\text{C}$. The $\text{Ge} - \text{As} - \text{Se}$ batch, previously alloyed with aluminum and TeCl_4 to bind oxygen and hydrogen impurities, was fed into the gallium reactor by vacuum distillation. The glass synthesis was carried out at 800 $^\circ\text{C}$ for 4 hours in a rocking furnace.

Figure 2 shows the absorption spectra of four glass samples prepared by different methods.

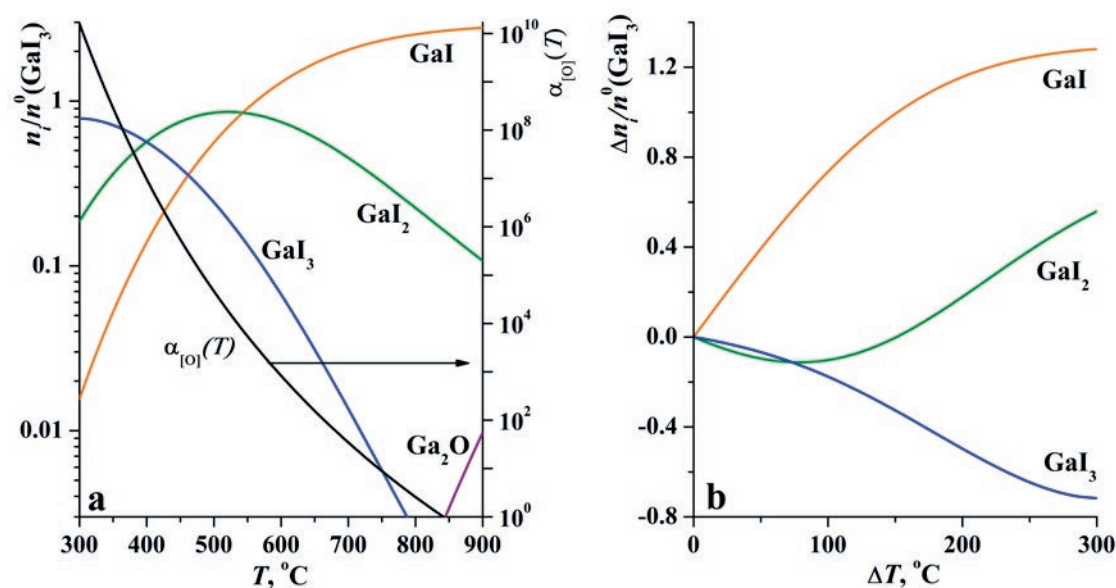


Fig. 1. Thermodynamically determined composition of the $\text{GaI}_3 - \text{Ga} - \text{Ga}_2\text{O}_3$ system (a) and the dependence of the amount of the transferred vapor phase component on the temperature difference $\Delta T = 600^\circ\text{C} - T$ (b)

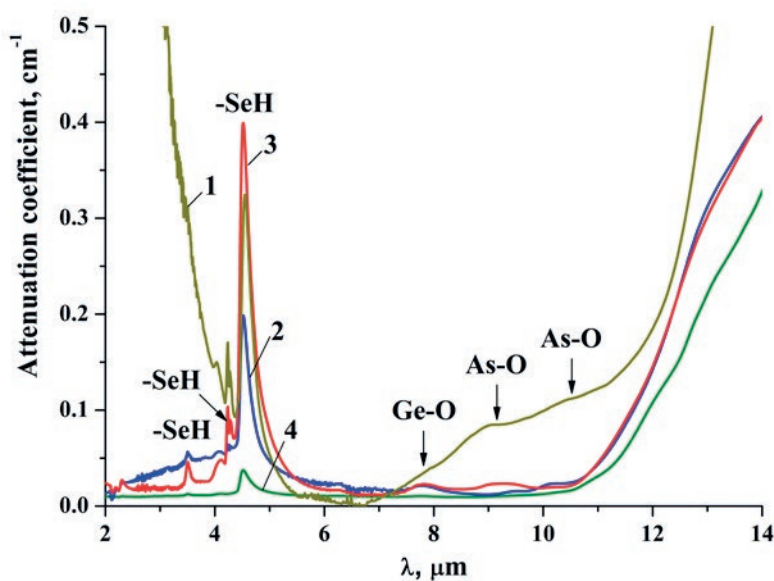


Fig. 2. Absorption spectra of glasses prepared by different methods: 1 – the $\text{Ga}_3\text{Ge}_{16}\text{As}_{17}\text{Se}_{64}$ sample, prepared by melting simple high purity substances; 2 – the $\text{Ge}_{16}\text{As}_{17}\text{Se}_{67}$ sample, prepared with the addition of getters and distillation purification of the melt; 3 – the $\text{Ga}_3\text{Ge}_{16}\text{As}_{17}\text{Se}_{64}$ sample, prepared from sample 1 with the addition of gallium by the usual loading; 4 – the $\text{Ga}_3\text{Ge}_{16}\text{As}_{17}\text{Se}_{64}$ sample, prepared by the method of sample 1 with the addition of gallium by the chemical transport method [69]

Sample 1, with the $\text{Ga}_3\text{Ge}_{16}\text{As}_{17}\text{Se}_{64}$ composition, was prepared by melting simple, especially pure substances without additional purification. Sample 2, with the $\text{Ge}_{16}\text{As}_{17}\text{Se}_{67}$ composition, was prepared by adding getters and purification of the melt by distillation. The other two samples,

with the $\text{Ga}_3\text{Ge}_{16}\text{As}_{17}\text{Se}_{64}$ composition were synthesized using the same technique with the addition of metallic gallium by conventional loading (sample 3) and chemical transport (sample 4). In sample 1, along with the high intensity of the absorption bands, we observe a significant

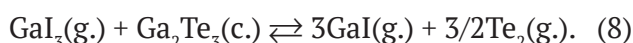
scattering in the short wavelength region of the spectrum. This is due to the presence of gallium(III) oxide impurities in the form of heterogeneous inclusions. The addition of gallium to the $\text{Ge}_{16}\text{As}_{17}\text{Se}_{67}$ glass by the conventional method leads to a 2-fold increase in the intensity of the absorption bands of the SeH- groups, germanium and arsenic oxides – by a factor of 3. This is due to the incorporation of Ga_2O_3 and $\text{Ga}(\text{OH})_3$ impurities (or a more complex composition) present in the initial metallic 7N gallium. In the glass prepared with Ga loading with chemical transport, the intensity of the impurity absorption bands is lower by an order of magnitude. Consequently, the developed method has high efficiency for preparing gallium-containing chalcogenide glasses with the low impurity content.

1.2. Chemical transport of gallium telluride(III)

The high chemical activity of gallium towards the silica glass reactor is a disadvantage of chemical transport in the form of a simple substance. This facilitates the formation of relatively volatile lower iodides of gallium and silicon, which enter the glass-forming melt:

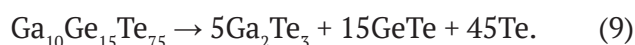


To avoid contact of metallic gallium with the reactor walls when preparing glasses of the Ga – Ge – Te system, a method of transport loading of gallium(III) telluride has been developed [25, 26]. The method is based on the reaction:



According to the results of thermodynamic modeling [25], a significant transition of gallium to the vapor phase in the form of GaI happens at temperatures above 600 °C. The minimum value of ΔT for effective chemical transport of gallium telluride(III) at 750 °C is 250 °C. The oxygen impurity content can theoretically be reduced by a factor of 10^3 – 10^4 at transport temperatures of 680–700 °C. It has been experimentally determined that the optimum conditions for chemical transport of gallium telluride are: the temperature in the ampoule with Ga_2Te_3 is 680–720 °C; the temperature of the GaI_3 vaporizer is 220–240 °C; the temperature of the Ga_2Te_3 receiver is 250–280 °C. The average loading rate of Ga_2Te_3 under these conditions was $0.3 \text{ g}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$.

A specific task in the transport loading of gallium(III) telluride for preparing especially pure chalcogenide glasses is the synthesis of this compound. The interaction of simple substances in the intermediate reactor requires the subsequent extraction of the synthesized telluride and its introduction into the chemical transport unit. These operations have a high probability of contaminating the reactant with atmospheric impurities. The tellurium vapor passing over metallic gallium, analogous to the synthesis of GeTe [27], is inefficient because the resulting layer of non-volatile Ga_2Te_3 prevents further reaction. In view of these difficulties, a method of Ga_2Te_3 synthesis has been developed which consists in preparing a glass with the composition $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ by the interaction of simple substances and its subsequent thermal decomposition. According to the results of X-ray diffraction phase analysis and atomic emission spectrometry with inductively coupled plasma [28], the decomposition of $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ glass at a temperature of 750 °C can be described by a chemical reaction:



The method was used to synthesize the especially pure $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ and $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}\text{I}_2$ glasses. In the first step, the $(\text{GeTe})_x\text{Te}_{100-x}$ batch was prepared by passing tellurium vapor over a mixture of germanium granules with aluminum and loaded into an ampoule with metallic gallium. The ampoule was sealed, and the batch was melted at 800 °C for five hours without being disconnected from the vacuum post. Tellurium and germanium(II) telluride were then extracted from the resulting $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ melt at 750 °C. Gallium(III) telluride was left in the evaporator. In the next step, the transport loading of gallium(III) telluride into the batch reactor was carried out by passing of gallium(III) iodide. To obtain $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}\text{I}_2$ glasses with improved stability against crystallization, the calculated amount of gallium(III) iodide was returned to the batch. The ampoule containing the batch was sealed-off and melted at 850 °C for five hours. The melt was quenched in water and annealed at 170 °C to relieve mechanical stress.

Fig. 3 shows the absorption spectra of glasses of the Ga – Ge – Te – I system, prepared

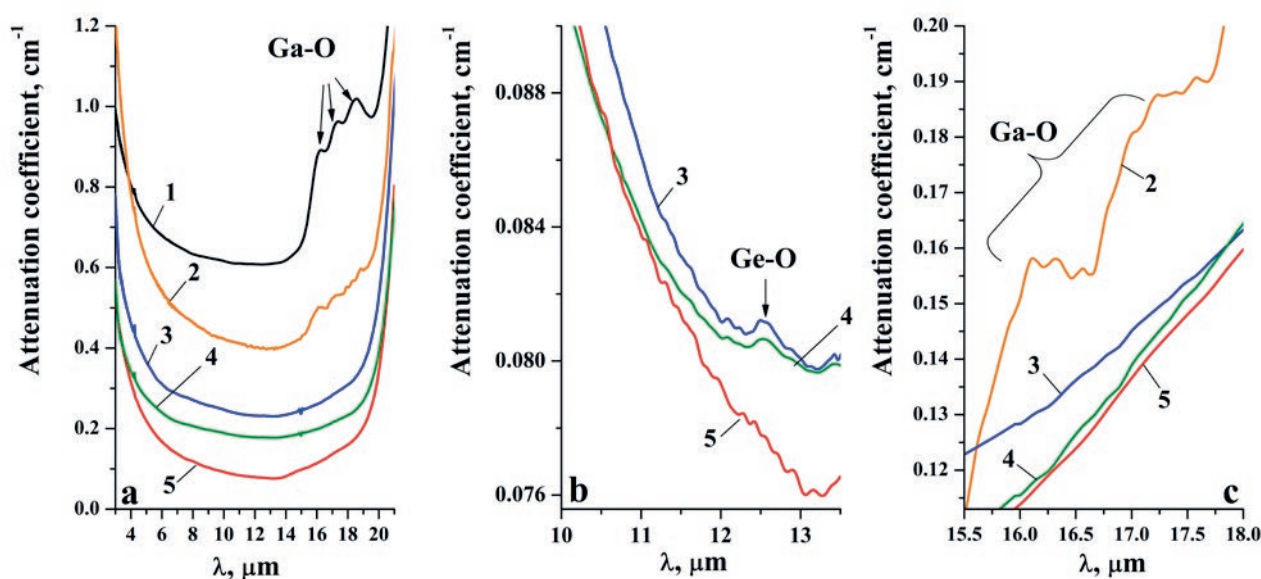


Fig. 3. Absorption spectra of Ga – Ge – Te – I glasses prepared by different methods: in a wide spectral range (a), in the absorption range of germanium oxide impurity (b), in the absorption range of gallium oxides (c). 1 – the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}\text{I}_2$ sample, prepared by melting simple substances and germanium(IV) iodide; 2 – the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ sample, prepared with preliminary synthesis of Ga_2Te_3 in an individual reactor and subsequent chemical transport; 3 – the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}\text{I}_2$ sample, prepared with preliminary synthesis of Ga_2Te_3 by passing tellurium vapor over gallium and subsequent chemical transport; 4 – the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}\text{I}_2$ sample, prepared with loading of metallic gallium by chemical transport [28]; 5 – the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ sample, prepared with preliminary synthesis of Ga_2Te_3 by decomposition of $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ and subsequent chemical transport [25]

by different techniques, in a broad spectral range (a), in the impurity absorption region of germanium oxides (b), in the absorption region of gallium oxides (c). The lowest intensity of the impurity absorption bands is observed for the sample prepared with Ga_2Te_3 chemical transport, synthesized by thermal decomposition of the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ glass. The intensities of the impurity bands in this sample are below the detection limit obtained for samples up to 30 mm in length. The estimated Ge–O impurity content calculated from the absorption in the 12.5 μm region is <1 ppb(wt). This is by far the best result for germanium and gallium telluride-based glasses. The absence of a known absorption coefficient for oxygen impurity in the form of gallium oxides makes it difficult to estimate its content.

2.3 Chemical transport of REE

The interest in REE-doped chalcogenide glasses is due to the possibility of achieving mid-IR laser generation in them. REEs have been shown to be a significant source of hydrogen

impurities and heterogeneous inclusions in chalcogenide glasses [29]. Hydrogen in REEs is present in dissolved form and as stable hydrides [30]. The difficulty in purifying REEs from hydrogen by conventional heating in vacuum is due to the thermal stability and refractoriness of the hydrides: most of them decompose significantly only above the melting point (> 1000 °C). Hydrogen impurity can have a significant negative effect on the luminescence and generation properties of doped chalcogenide glasses due to radiation-free impurity relaxation [31]. This is due to the spectral proximity of the absorption bands of SH- and SeH groups and the emission bands of REEs.

To prepare especially pure glasses, we proposed to use a method of vacuum alloying of metals with gallium for purifying REEs from hydrogen impurities [32]. The addition of gallium significantly reduces the decomposition temperature of REE hydrides due to the formation of fusible intermetallics, e.g. Ga_3Tm , Ga_2Pr , Ga_2Tb . This ensures efficient purification at

temperatures of 700–750 °C. In combination with germanium loading via monochalcogenides, the method made it possible to significantly reduce the content of hydrogen impurities in the form of SH- and SeH- groups in REE-doped $\text{Ga}_5\text{Ge}_{36}\text{S}_{59}$ and $\text{Ga}_5\text{Ge}_{36}\text{Se}_{59}$ glasses from $(10-26) \pm 2$ ppm(at.) to $(0.16-0.22) \pm 0.02$ ppm(at.) (Fig. 4) [32]. In the Tb-doped $\text{Ga}_5\text{Ge}_{36}\text{Se}_{59}$ sample prepared by the developed method, laser generation in the 5 μm range was achieved for the first time for chalcogenide glasses [5].

To prepare REE-doped optical fibers, the requirements for the content of heterogeneous impurities, which have a negative effect on the optical losses, increase significantly. The doping of chalcogenide glasses leads to contamination with REE oxide inclusions and products of their interaction with the silica glass reactor [33]. For deep purification of this type of impurity, a method consisting of chemical transport of REE in a gallium(III) iodide flow has been developed [34]:



where R – REE. According to the results of thermodynamic modeling of $\text{GaI}_3 - \text{R} - \text{R}_2\text{O}_3$ sys-

tems, the effective chemical transport of REE takes place at reactor temperatures above 650 °C and $\Delta T > 250$ °C. The equilibrium partition coefficient for oxygen impurity under these conditions is in the order of $n \times 10^3$. The formation of complex iodides may also facilitate chemical transport:



The volatility of such complexes is significantly higher than that of the simple iodides of the corresponding REE [35]. It has been found experimentally that the average rate of chemical transport increases by two orders of magnitude at preliminary alloying of REE with gallium. This may be due to the additional amount of GaI by reaction (12), which promotes the formation of complex iodides. This approach enables the simultaneous loading of REE and gallium into the batch reactor.

The $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ composition was chosen as a base glass for REE doping. This glass has high crystallization stability, which is a critical property for preparing low-loss optical fibers. The glasses

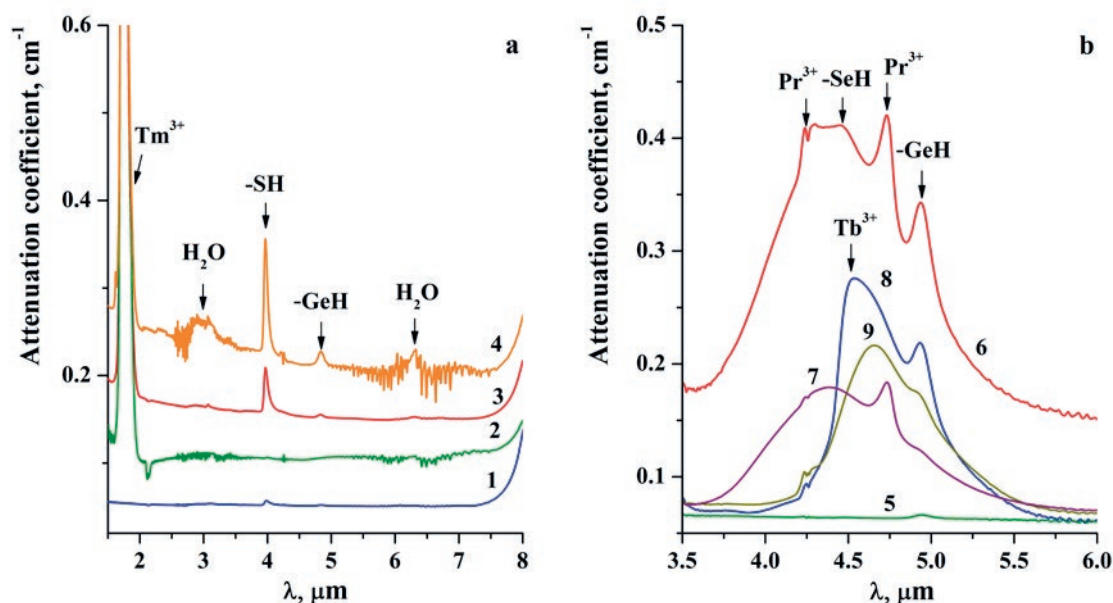


Fig. 4. Absorption spectra of $\text{Ga}_5\text{Ge}_{36}\text{S}_{59}$ glasses doped with 1400 ppm(wt) Tm (a) and $\text{Ga}_5\text{Ge}_{36}\text{Se}_{59}$ glasses doped with 760 ppm(wt) Pr or Tb, prepared using different methods of REE purification (b). 1 – undoped sample; 2 – vacuum alloying of Tm and Ga; 3 – treatment of Tm in sulfur vapor (the technique is proposed in [33]); 4 – without Tm purification; 5 – undoped sample; 6 – without Pr purification; 7 – vacuum alloying of Pr and Ga; 8 – treatment of Tb in selenium vapor; 9 – vacuum alloying of Tb and Ga [32]

were doped with Ce, Pr, Nd, Tb, Dy in the range of 0.05–1 wt. %. The developed process included the following main steps: 1) preparation of Ge – Sb – Se batch by passing selenium vapor over a mixture of germanium and antimony; 2) double distillation of the batch; 3) alloying of gallium with REE; 4) chemical transport of REE and gallium in the flow of gallium(III) iodide into the reactor; 5) loading of Ge – Sb – Se batch by distillation into the reactor with gallium and REE; 6) melting of $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ + REE batch, quenching of the melt, glass annealing and slow cooling.

It has been shown that at chemical transport loading of rare earth metals, some impurities (REE oxides, SiO_2 , Al_2O_3 , Ga_2O_3 , TiO_2 , Ta_2O_5 , REE oxofluorides), chemically inert to gallium iodide vapors, remain in the initial ampoule. Metal impurities (iron, manganese, titanium, aluminum, tin, etc.), capable of forming stable and volatile at temperatures of 300–700 °C simple and complex iodides, are transported together with the REE iodides; tungsten and molybdenum impurities do not completely transform into iodides and are partially transported. In the process of REE loading they are purified from impurities of fluorine, hydrogen, oxygen, some metals, and heterogeneous inclusions.

The glass samples doped up to 1 wt % REEs were prepared with reproducibly low content of hydrogen impurity in the form of SeH-groups not more than 1.5 ppm(at.); metals in total < 1 ppm(wt.); micron-sized inclusions

< 10^2 pcs/cm³ and submicron particles – at the level not exceeding the background scattering of the glass. Optical losses in the optical fiber with the 20 μm diameter $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ + 1130 ppm(wt) Tb core glass and $\text{Ge}_{12}\text{As}_{20}\text{Sb}_5\text{S}_{63}$ clad glass were 1.8 dB/m at a wavelength of 1.56 μm [6]. This is significantly lower than the values measured in 230 μm diameter unclad optical fibers doped with 500 ppm(wt) PrCl_3 or PrI_3 prepared by the conventional method in [36] (25–75 dB/m).

Fig. 5 shows the spectrum of laser generation in the optical fiber drawn from $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ + 1130 ppm(wt) Tb glass [7]. The 53 cm long fiber was pumped with a thulium laser ($\lambda = 1.98 \mu\text{m}$). The maximum output power was 150 mW. The possibility of achieving laser generation in the 5 μm region in doped chalcogenide glasses with practically significant properties correlates with the presence of micron heterogeneous inclusions and optical losses due to these inclusions. Significant characteristics of laser generation have so far been achieved only in samples prepared using the developed method of REE loading, in which the content of micron inclusions does not exceed < 10^2 pcs/cm³.

The limitation of the developed method of REE loading is due to the high reactivity of their iodides towards silica glass [37]:



In this reaction, REE iodides act as transporters for silica(IV), which enters the chalcogenide

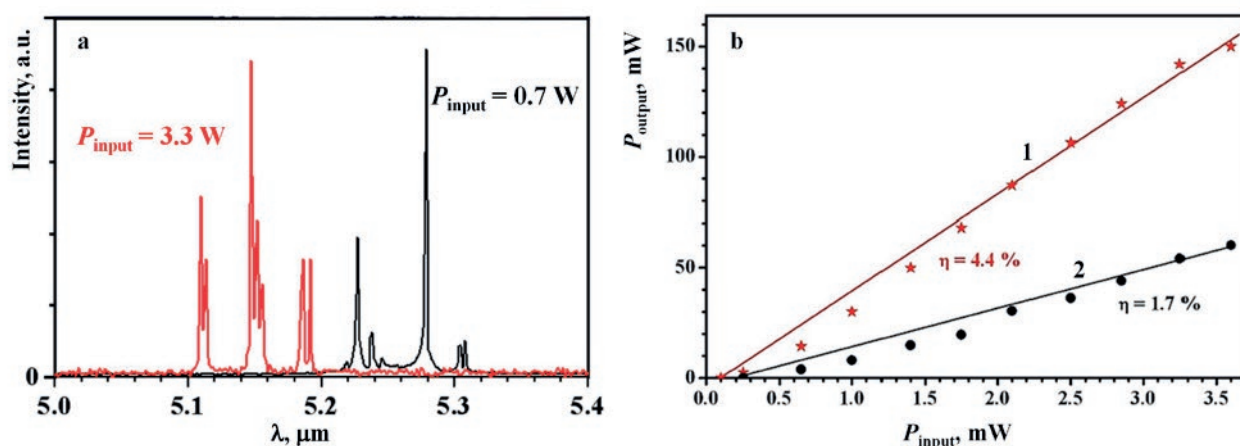


Fig. 5. Laser generation spectra of the optic fiber fabricated from the 1130 ppm(wt) Tb-doped $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ core glass and the $\text{Ge}_{12}\text{As}_{20}\text{Sb}_5\text{S}_{63}$ cladding glass (a); the dependence of the output power of generation P_{output} on the pump power P_{input} (b). Curves b1 and b2 refer to optical schemes with the use of an attached mirror and without it respectively. Parameter η is the slope efficiency [7]

batch. Heterogeneous SiO_2 inclusions appear to be the main source of excessive optical losses in fibers based on doped chalcogenide glasses. To improve the laser properties of chalcogenide optical fibers, it is necessary to further reduce the content of this impurity.

3. Application of REE for binding oxygen impurities

Due to the disadvantages of aluminum and magnesium mentioned in [18], a search was initiated for alternative getters to prepare especially pure chalcogenide glasses with a low content of oxygen impurities. It was found that along with an increase in the intensity of the absorption bands of hydrogen-containing impurities, the addition of REE leads to a significant increase in the transparency of the glasses in the absorption regions of germanium, tellurium and gallium oxides. The results of thermodynamic modeling predict a high ability of REE to reduce oxides of chalcogenide glass components, which increases in the series $(\text{Al}) \rightarrow \text{Eu} \rightarrow \text{Ce} \rightarrow \text{La} \rightarrow \text{Pm} \rightarrow \text{Pr} \rightarrow \text{Nd} \rightarrow \text{Sm} \rightarrow \text{Yb} \rightarrow \text{Gd} \rightarrow \text{Dy} \rightarrow \text{Tb} \rightarrow \text{Tm} \rightarrow \text{Lu} \rightarrow \text{Ho} \rightarrow \text{Er} \rightarrow \text{Y}$ [38].

To experimentally confirm the efficiency of REEs as oxygen impurity getters, a series of glasses with the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ + 1000 ppm (wt) REE composition were prepared [38]. The absorption spectra of the prepared samples are shown in Figure 6. The $\text{Ge}_{20}\text{Te}_{80}$ glass spectrum shows

intense absorption bands of Te-O (13.6 μm) and Ge-O (12.6 and 8.0 μm). In the spectrum of the $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ sample without the addition of the getter, the intensity of these bands decreases by a factor of 30–50. Intense Ga-O bands appear in the 15–20 μm region and a low intensity band in the 10 μm region, which may correspond to Ga-OH impurity [22]. Consequently, gallium is quite effective in reducing germanium and tellurium oxides and improving the transparency of telluride glasses in the 8–15 μm region. The addition of 1000 ppm(wt) of aluminum and REE to $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ glasses results in a significant decrease in the intensity ($< 5 \cdot 10^{-4} \text{ cm}^{-1}$) of the Ga-O , Ga-OH and Ge-O absorption bands due to the greater reducing power of these elements compared to gallium. This corresponds to a reduction in the impurity content of the gallium(III) oxide by 3 orders of magnitude. Absorption bands of the corresponding oxides appear in the spectra of glasses doped with Al, Pr, Sm, La and Eu [39]. When distilling the glass-forming melt, a significant decrease in the intensity of these bands can be expected due to the non-volatility of the oxides. However, the absence of absorption bands in the initial samples is preferable, as incomplete removal of oxides during distillation may occur. In the spectrum of the Eu-doped sample, the intensity of the oxide band is the highest among the REEs studied and the Ga-O absorption bands are present. This

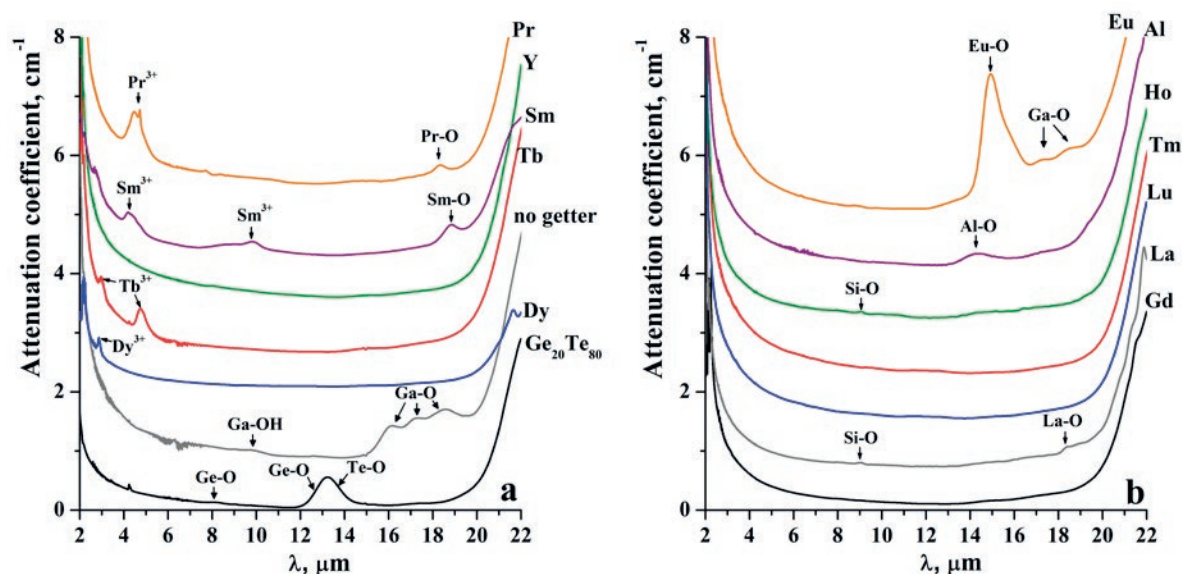


Fig. 6. Absorption spectra of $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ glasses with the addition of 1000 ppm(wt) of getter [38]

is due to the tendency of europium to oxidize rapidly in the air and to have the lowest reducing power among the REEs according to the results of thermodynamic modeling.

The spectra of glasses doped with Dy, Tb, Sm and Pr show absorption bands due to electronic transitions [40]. In the studied samples of $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ glasses in the spectral range of 2–20 μm , there are no intense absorption bands when doped with Y, Gd and Lu. These getters seem to be the most suitable for preparing especially pure telluride glasses with low oxygen impurity content. Ho and Tm can also be included in this series as their absorption bands as electronic transitions are in the short wavelength region ($< 2 \mu\text{m}$) and practically do not appear in the spectrum of the telluride glass. However, these bands will be present in the spectra of sulfide and selenide glasses.

Among 11 REEs investigated for their ability to bind oxygen impurities in chalcogenide glasses, the following groups can be distinguished:

- 1) give no absorption bands due to electron transitions and oxide impurities – Y, Gd, Lu;
- 2) give absorption bands due to electronic transitions but no oxide bands – Tm, Dy, Tb and Ho;
- 3) give oxide absorption bands – Eu, Sm, Pr, La.

The advantages of REE groups 1) and 2) in comparison with aluminum, which is conventionally used as a getter, are:

- high efficiency in the reduction of gallium, germanium and tellurium oxides;
- more complete removal at distillation of chalcogenide glass melt;
- absence of intense absorption bands from oxides in the glass transparency region;
- lower etching capacity of the silica-glass surface compared to aluminum.

These REEs are recommended as getters for preparing especially pure glasses with extremely low oxygen impurity content. For example, the efficiency of Dy as a getter for preparing especially pure glasses of the Ge – As – Sb – S system has been shown in [41].

The disadvantage of REEs as oxygen getters compared to aluminum is rapid oxidation when stored in the air. Aluminum in contact with oxygen and moisture is covered with a thin but dense protective film which prevents further

oxidation. REEs, mainly La, Pr, Ce, Nd, Eu and Sm, oxidize quite rapidly to form oxides, hydroxides, carbonates and hydrocarbonates. Oxidation penetrates deep into the metal volume, so the application of these REEs requires special sample preparation. To a lesser extent, oxidation in air is characteristic of Y, Gd and Lu.

4. Conclusions

The chemical transport method is highly efficient in preparing especially pure chalcogenide glasses with extremely low content of limiting impurities. This is due to the fundamental reasons that the separation factor in this deep purification method is determined by the ratios of equilibrium constants or rates of chemical reactions involving the main substance and impurities. By selecting a suitable transport agent and optimizing the process conditions, it is possible to achieve high values of the separation factor and ensure a reduction of the impurity content by several orders of magnitude in a single stage.

A major advantage of chemical transport is that it is not only a method of deep purification, but also of vacuum loading of the batch components into the reactor. This eliminates subsequent interaction of the purified materials with the air atmosphere until the finished glass is removed from the reactor.

P-element iodides are the optimal, but not the only transport agents for deep purification of chalcogenide batch components. There are several fundamental and technological reasons for this. Firstly, iodides exhibit less chemical activity against silica-glass at elevated temperatures than other halides. Secondly, residual iodines (typically less than 0.1 at.%) do not adversely affect the target properties of the glasses. As noted in the first part of the review [18], small additions of iodide increase the crystallization stability of the glasses, the overall level and range of transparency, and promote the dissolution of REE. Thirdly, iodides are easily synthesized under laboratory conditions without the use of highly toxic reagents. Along with gallium(III) iodide, germanium(IV) iodide can be used for the chemical transport of batch components, particularly in the preparation of gallium-free glasses.

A further improvement of the developed methods for preparing especially pure

chalcogenide glasses may be the multiple purification of the batch components with chemical transport. In this case, the efficiency of impurity removal compared to a single process increases in α^{n-1} time, where n – the number of stages. Another direction is to extend the range of batch components that can be purified and loaded with chemical transport. Silver iodide is one of such components. The addition of AgI significantly increases the crystallization stability of telluride glasses and makes it possible to fabricate optical fibers from them [10, 42].

The most significant result presented in the review is the achievement of mid- IR laser generation on REEs in chalcogenide glasses, which was previously not possible. This result is an example of a solution to a classic problem in the chemistry of high-purity substances – increasing the purity of materials led to the discovery of a new functional property in them, which was not manifest due to the high impurity content for this property. This brings chalcogenide glasses into the class of laser materials [43] and greatly expands their practical applications.

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. Shiryayev – 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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