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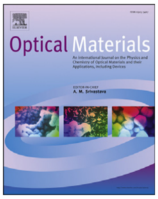

Preparation of special purity Ge − S − I and Ge − Se − I glasses

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ABSTRACT

The paper considers the new approaches for the production of special pure Ge − S − I and Ge − Se − I glasses via the germanium(IV) iodide, germanium(II) sulfide, as well as the Ge_2S_3, $Ge_2S_3I_2$ and $Ge_2Se_3I_2$ glassy alloys. The glass samples containing 0.03–0.17 ppm(wt) hydrogen impurity in the form of SH-group, 0.04–0.15 ppm(wt) hydrogen impurity in the form of SeH-group, and 0.5–7.8 ppm(wt) oxygen impurity in the form of Ge-O were produced. Using a crucible technique, the single-index $[GeSe_4]_{95}I_5$ glass fibers of 300–400 μm diameter were drawn. The minimum optical losses in the best fiber were 1.7 dB/m at a wavelength of 5.5 μm; the background optical losses were within 2–3 dB/m in the spectral range of 2.5–8 μm.

1. Introduction

The rising interest to Ge-based chalcogenide glasses is determined by a combination of their physical, chemical and optical properties. These glasses have a high transparency in the near and mid-IR ranges, a significant ability to dissolve the rare earth metals, high glass transition temperatures, considerably lower toxicity as compared with the glasses on the basis of arsenic chalcogenides [1]. The main disadvantage of binary germanium-chalcogen glasses is a tendency of most of the compositions to crystallize. An effective way to increase the stability of binary glasses against crystallization is to add a third component [2]. Such a third component, used for chalcogenide glasses, is possibly to be the element of V-VII groups (P, As, Sb, Se, Br, I). The objects of the investigation in this work were glasses in the Ge − S − I and Ge − Se − I systems. The choice of iodine as a component that enhances the stability against crystallization is due to the absence of impurity absorption bands of iodine bonds in the glass transparency range and the ability to use the volatile germanium(IV) iodide for glass-forming melt synthesis [3].

Traditionally, Ge − S − I and Ge − Se − I glasses are prepared by reacting simple substances in evacuated silica-glass ampoules at a temperature of 850–950 °C for 12–48 h [4]. High temperature and long duration of the synthesis are caused by a refractoriness of germanium ($T_m(Ge) = 937\ ^\circ C$) and its low reactivity ability towards chalcogens. Significant vapor pressures of sulfur and iodine at temperatures of glass synthesis require slow step heating of the charge to prevent a reactor rupture. Prolonged exposure of the glass-forming melt at elevated temperatures results in a marked entering of impurities (hydrogen, silicon, oxygen, etc.) from the equipment material to the glass melt [5]. This degrades the optical transparency of glasses and limits their practical application.

The aim of this study was to develop and compare the effectiveness of different approaches to the production of special pure glasses in the Ge − S − I and Ge − Se − I systems with a low content of optically active impurities.

2. Experimental

To prepare the Ge − S − I and Ge − Se − I glasses, the initial commercial granulated germanium of purity 6N, sulfur and selenium of purity 5N, and iodine of purity 3N were used. Additionally, the initial commercially sourced S and Se were further purified by means of triple vacuum distillation. Commercial iodine of 3N purity was melted in a conical heat-resistant glass flask under a layer of highly pure concentrated sulfuric acid at a temperature of 130–140 °C for 3 h in the intensive mixing mode. At this stage, the removal of impurities of organic compounds and certain metals

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forming highly soluble sulfates was occurred. The iodine, after its being multiple washed with deionized water and dried in a desiccators over phosphorus(V) oxide, was subjected to triple vacuum sublimation. The evaporator temperature was within 100–110 °C, the amount of the cube residue was not higher than 2 wt.% at each stage of sublimation. Iodine was obtained in an amount of 200–250 g depending on the weight of the initial batch. The total weight loss of the basic substance at all stages of purification was 6–7 wt.%. Germanium(IV) iodide was synthesized by passing the obtained iodine vapors over metallic germanium (6N purity) at a temperature of 380–400 °C; its yield with respect to germanium was 98–99% of the theoretical value. The prepared germanium(IV) iodide was subjected to the triple sublimation and distillation purification at the evaporator temperature of 140–160 °C and under vacuum of 10^{-3} Pa.

The glasses were prepared by several methods. The first method, traditionally used for the synthesis of chalcogenide glasses, consists in the reaction of simple special pure substances in evacuated silica-glass ampoules. The batches of iodine, sulfur or selenium were loaded into the reactor with the germanium batch via vacuum evaporation from of intermediate silica-glass ampoules (Fig. 1). The reactor was sealed-off under vacuum (~10^{-3} Pa), placed in a muffle rocking furnace, and raised at 10 °C/min up to a temperature of 300 °C. Then, the reactor was raised at 2 °C/min up to 750 °C in the mode of furnace rocking and experienced a 6 h dwell at this temperature to achieve homogenization. To achieve glass solidification, the ampoule was air-quenched and subsequently annealed at a temperature of T_g-10 °C for 2 h.

The second method consists in the use of germanium(IV) iodide as the source of iodine. The chalcogen and germanium(IV) iodide were successively loaded by evaporation into the reactor containing the batch of germanium (Fig. 1). The reactor was sealed-off from the vacuum pump and placed in a muffle rocking furnace. The furnace temperature was raised at 10°/min to 600 °C, then at 5°/min to 750 °C. Duration of homogenizing melting of glass-forming melt was 4 h. The quenching the melt and annealing the glass were under the above-mention conditions.

To prepare the glasses in the Ge-S-I system with a low content of germanium oxides, the third method was used. In this case, germanium monosulfide and Ge_2S_3 glassy alloy were synthesized previously. Synthesis of these sulfides was carried out by reacting the simple substances in evacuated silica-glass ampoules at 800 °C and 750 °C, respectively. The produced substances were purified by double vacuum distillation. Sublimation of GeS was performed at a temperature of evaporator of 600 °C (P (GeS) = 23 mmHg [6]). The Ge_2S_3 alloy was evaporated in the temperature range of 550–600 °C with decomposition. By X-ray diffraction (X-ray diffractometer XRD-6000 Shimadzu, CuKα-radiation), it was found that the degradation products are crystalline germanium monosulfide and germanium disulphide:

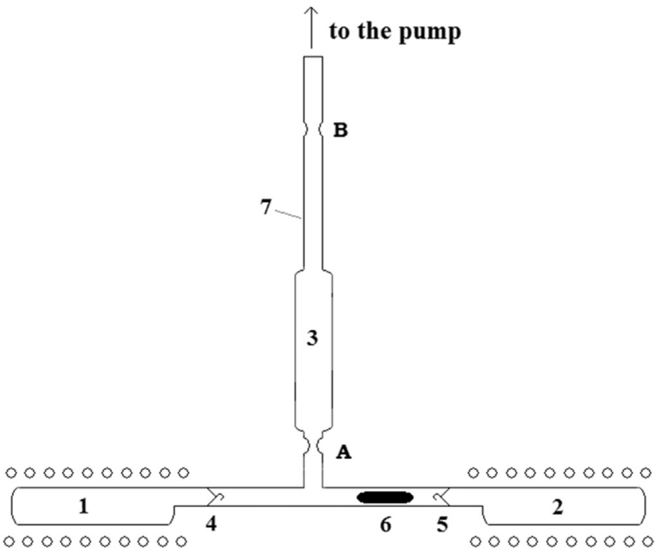

Fig. 1. Silica-glass set-up for vacuum loading of charge components into the reactor. 1 – Section containing iodine or germanium(IV) iodide; 2- Section containing sulfur or selenium; 3 – Reactor containing germanium, germanium(II) sulfide or Ge_2S_3 alloy; 4, 5 – Smashing baffle; 6 – Magnetic anvil; 7 – glass-forming tube; A,B – waists.

$$Ge_2S_3 = GeS + GeS_2. \tag{1}$$

Due to the formation of low volatile germanium(IV) sulfide, the temperature of evaporator was gradually raised to 680 °C. To obtain the glasses of required chemical composition, the batches of sulfur and germanium(IV) iodide were loaded in the reactor containing purified GeS and Ge_2S_3. Synthesis of the glass-forming melt was performed at 750 °C for 4 h.

The fourth method was a melting of the products of thermal decomposition of $Ge_2S_3I_2$ and $Ge_2Se_3I_2$ glassy alloys. It has previously been found [7] that the products of thermal decomposition of $Ge_2S_3I_2$ are germanium(IV) sulfide and germanium(IV) iodide. This allows preparing the charge in the Ge – S – I system of specified chemical composition by varying temperature and duration of thermal decomposition of $Ge_2S_3I_2$. Based on the results of macrokinetics study of decomposition of this alloy, the method for producing Ge – S – I glass has been developed [8]. In this paper, by means of the methods of X-ray diffraction and X-ray microanalysis (scanning electron microscope SEM-515 (Philips), equipped with an energy dispersive analyzer EDAX-9900 (EDAX)), it was found that the products of $Ge_2Se_3I_2$ decomposition are germanium(IV) selenide and germanium(IV) iodide. Synthesis of $Ge_2S_3I_2$ and $Ge_2Se_3I_2$ was carried out by the reactions

$$GeI_4 + 6S + 3Ge = 2Ge_2S_3I_2, \tag{2}$$

$$GeI_4 + 6Se + 3Ge = 2Ge_2Se_3I_2 \tag{3}$$

in the evacuated two-section silica-glass reactor at 500 °C for 5 h. The section of the reactor with the melt was then placed in a horizontal furnace, heated to 500–600 °C and kept at this temperature for 1–5 h depending on the desired composition of the charge (Fig. 2). Homogenization of glass-forming melt was performed at 750 °C for 2 h. The Ge-S-I glasses with a ratio of S/Ge = 2.1–2.6 and the iodine content within 4–15 at.%. were obtained. To prepare the Ge-Se-I glasses with high Se content (up to 80 at.%), after decomposition of the $Ge_2Se_3I_2$ alloy, an additional amount of high-purity selenium was loaded in the reactor.

Chemical macro-composition and glassy nature of the prepared samples was confirmed by X-ray microanalysis and differential scanning calorimetry (microcalorimeter Netzsch 409), respectively. The transparency of glasses in the range of 2–18 μm was investigated by means of FT-IR spectrometer Tensor 27 (Bruker). Using a crucible technique, the single-index $[GeSe_4]_{95}I_5$ glass fibers of 300–400 μm diameter and a length of 20 m were drawn. The optical losses in the fibers were measured by standard cut-back technique using the FTIR spectrometer IFS-113 (Bruker).

To estimate the chemical form of impurities in glasses, thermodynamic modeling of the system $0.025GeI_4 - 0.35Ge - 0.54S - 0.0001H_2O$ was carried out. Composition of system corresponds to the macro-composition of $[GeS_{1.5}]_{90}I_1$ glass having a high stability against crystallization, with initial content of water impurity of 100 ppm mol. That water impurity content is typical for