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Preparation and investigation of $Ga_xGe_{25}As_{15}Se_{60-x}$ ($x = 1 \div 5$) glasses

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ABSTRACT

Chalcogenide glasses of $Ga_xGe_{25}As_{15}Se_{60-x}$ ($x = 0; 1; 2; 3; 4; 5$) compositions are prepared; their transmission range, optical band gap energy, thermal properties and stability against crystallization are studied. It is shown that these glasses have a high transparency in the mid-IR region (from 0.8 to 15 μm), a high glass transition temperature (≥320 °C) and a low tendency to crystallize. The optical band gap energy of $Ga_xGe_{25}As_{15}Se_{60-x}$ ($x = 0; 1; 2; 3; 4; 5$) glasses decreases from 1.68 to 1.43 eV as the gallium content increases and the selenium decreases. Their glass network, according to IR spectroscopy data, consists of $Ge(Se_{1/2})_4$ tetrahedrons and $AsSe_{3/2}$ pyramids. The $Ga_2Ge_{25}As_{15}Se_{58}$ and $Ga_3Ge_{25}As_{15}Se_{57}$ glasses have highest stability against crystallization. The content of hydrogen and oxygen impurities in the purest glass samples, fabricated using a combination of chemical distillation purification method and vapor transport reaction technique, does not exceed 0.06 ppm (wt) and 0.5 ppm (wt), respectively.

1. Introduction

The glasses in the Ga-Ge-As-Se system is of particular interest as the host matrix for development of rare-earth ions doped active laser mediums [1,2]. Gallium in the glass acts as a co-dopant that increases the solubility of the rare-earth ions in chalcogenide glasses, as well as improves their glass-forming ability [1–3]. To our knowledge, there are only the published data on rare-earth-doped Ga-Ge-As-Se glasses having a low enough value of glass transition temperature (180–220 °C). For practical laser applications, to provide the necessary threshold pump power, most likely, that the high-temperature glasses having the glass transition temperature ≥300 °C will be needed. Other important properties of glasses for active middle infrared (mid-IR) fiber optics are high transparency in the spectral range 0.8–10 μm, low content of limiting impurities (oxygen, hydrogen, carbon, heterophase inclusions), low phonon energy, an ability to dissolve the rare earth elements, a low tendency to crystallize. Despite the fact that glasses in the Ge-As-Se system of different compositions have been studied in detail, including the high-temperature glasses containing 25–40 at.% Ge [3–5], but the main optical, thermal and crystallization properties of these glasses, opening the possibility of their use for modern perspective directions of middle IR fiber optics, such as the creation of fiber lasers, amplifiers and supercontinuum generators, previously were not investigated well. As an example, the authors of paper [5] reported that the $Ge_{20}As_{30}Se_{50}$ and $Ge_{25}As_{25}Se_{50}$ glasses have the glass transition temperature of 290 °C and 326 °C, respectively, have no crystallization peaks, as well as they gave some physical and chemical properties of these glasses. Currently, there are commercially available glasses, such as AMTIR-1 ($Ge_{33}As_{12}Se_{55}$, T_g = 362 °C, Amorphous Materials Inc.) and GASIR1 ($Ge_{22}As_{20}Se_{58}$, T_g = 310 °C, UMICORE) to create, mainly, bulk optical IR products. The lack of data in the literature on fabrication of optical fibers from these high temperature glasses may be explained by the presence of impurities that do not allow to achieve the acceptably low optical losses for real applications.

Published data on influence of gallium, incorporated into the germanium-rich Ge-As-Se glass, on their optical, thermal and crystallization properties are limited. According to [6], glasses in the Ga-Ge-Se system have a tendency to crystallization and phase separation; their T_g values vary from 400 °C for $Ga_5Ge_{33}Se_{62}$ to 140 °C for $Ga_{20}Ge_{20}Se_{60}$ glass. The T_g value decreases with increasing Ga and Se content. According to [3,6], up to 2–4 at.% Ga can be incorporated into As_2Se_3 glass. During crystallization of these glasses, the Ga_2Se_3 crystalline phase is formed.

The aim of this paper was to prepare the $Ga_xGe_{25}As_{15}Se_{60-x}$

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(x = 0; 1; 2; 3; 4; 5) glasses and to study their optical, thermal and crystallization properties.

2. Experimental

To prepare the glass samples of $Ga_xGe_{25}As_{15}Se_{60-x}$ (x = 1÷5) compositions, the traditional method of melting of initial special pure elements in an evacuated silica-glass ampoule was used. For this, the gallium of purity 6N, the granular germanium of purity 6N, the selenium of purity 5N additionally purified by double vacuum distillation, and the arsenic of purity 5N additionally purified by vacuum sublimation were used. The batches of purified selenium and arsenic were loaded into a silica-glass reactor with batches of germanium and gallium by vacuum evaporation from intermediate ampoules [7]. Preparation and homogenization of the glass-forming melt were carried out in a rocking muffle furnace at a temperature of 850 °C for 7 h. The glass samples were prepared by quenching the melt in air with subsequent annealing at 280 °C and slow cooling to room temperature. The glass samples were prepared in the form of rods of diameter 10 mm and length 40–50 mm. These produced $Ga_xGe_{25}As_{15}Se_{60-x}$ (x = 1÷5) glasses were used to study their optical transmission, thermal and crystallizing properties. To measure the optical transmission, the glass samples were cut in the form of discs (rods) of diameter 10 mm and length: 2, 5 and 20 mm with parallel-plate polished surface plates.

To prepare high-purity glasses, several samples were produced using the multi-stage purification method, developed by us and described in detail in Refs. [8–10]. The method includes the following stages:

- The chemical distillation purification of Ge-As-Se glass using the Al and $TeCl_4$ getters [11,12];
- A transport reaction route of metallic Ga transfer in a GaI_3 vapor flow to purify and add the batch of metallic gallium into the silica-glass reactor [8,9];
- Loading of purified Ge-As-Se glass into a silica-glass reactor with batches of purified gallium by vacuum evaporation;
- Melting of mixture of these compounds (Ge-As-Se and Ga) and homogenization in the muffle rocking furnace at 850 °C for 8 h;
- Quenching of the glass in air with subsequent annealing at 280 °C and slow cooling to room temperature.

The prepared glasses were analyzed by means of IR-spectroscopy using Fourier transform IR spectrometer IRP Prestige–21 (Shimadzu, Japan) in the spectral range 7000–350 cm^{-1} and Perkin Elmer Lambda 900 in the wavelength range from 600 to 3200 nm.

The concentration of hydrogen and oxygen impurities was determined from the IR absorption spectra of the bulk glass samples using the known values of extinction coefficients (ε): ε(Se-H) = 1780 cm^{-1}/wt.% at 4.57 μm wavelength [13] and ε(As_2O_3) = 27 cm^{-1}/wt.% at 9.4 μm wavelength [14].

Thermal analysis (DSC) of glass samples was carried out using a synchronous Netzsch STA 409 PC Luxx analyzer with sensitivity of 1 μV/mW and accuracy with respect to temperature ±1 K, at the heating rate 10 K/min in the temperature range of 50–560 °C. The characteristic temperatures, such as the glass transition temperature (T_g), the temperature for the onset of crystallization (T_c), were determined from the intersection points of tangents in the initial region of thermal events [7]. The temperature of exothermal maximum (T_p) was determined as the temperature at the crystallization peak.

Stability against crystallization and the phase composition of glasses were investigated by means of X-ray diffraction (XRD) using X-ray diffractometer XRD-6000 Shimadzu (CuKα-radiation). For this, the glass samples in evacuated silica-glass ampoules were heat-treated for 1 h and 8 h at 460 °C (the fiber drawing temperature) and at 500 °C (the temperature of crystallization maximum). The samples cooled to a room temperature were then triturated into powder and investigated by XRD in the range of 2θ = 10–60° with an exposure time of 0.6 s θ 10 s. Identification of crystalline phases was carried out by ICDD PDF-2 database. The typical detection limit for $GeSe_2$ and Ga_2Se_3 crystalline phases, calculated from the triple value of standard deviation of the background divided by the intensity of the analytical peak in the XRD comparison pattern for polycrystalline samples, was within 0.15–1.1 vol.%.

3. Results and discussion

Fig. 1 gives the transmission spectra of $Ga_xGe_{25}As_{15}Se_{60-x}$ samples (x = 0, 2 and 3; optical path-length is 2 mm) prepared by direct melting of special pure elements and $Ga_3Ge_{25}As_{15}Se_{57}$, glass produced by multi-stage technique. It is seen, that the spectra of glasses prepared by direct melting of elements show selective absorption bands of Se-H groups (2180 cm^{-1}), Ge-H groups (2040 cm^{-1}), CO_2 (2320 cm^{-1}), As_2O_3 (790 and 1050 cm^{-1}). The absorption spectrum of $Ga_3Ge_{25}As_{15}Se_5$ glass (curve 4 in Fig. 1), produced using a multi-step purification technique, does not show intensive impurity absorption bands.

The transmission spectra were transferred in absorption spectra. As an example, Fig. 2 compares the absorption spectra of $Ga_3Ge_{25}As_{15}Se_{57}$ glasses produced by direct synthesis of elements (curve 1) and using a multi-stage purification method (curve 2). It can be seen that the absorption coefficient of the most intense absorption band of Se-H group (at 2190 cm^{-1}) in the glass obtained by the multi-stage method is by 45 times lower than that for the glass fabricated by direct melting of elements. Estimated values of hydrogen content in the form of Se-H and oxygen content in the form of As-O in sample 1 (Fig. 2), calculated by using the above mentioned extinction coefficients, were 2 and 12 ppm (wt), respectively. Estimated values of hydrogen content and oxygen content in sample 2 (Fig. 2) were 0.06 ppm (wt) and ≤0.5 ppm (wt), respectively. Comparison of the spectra of samples 1 and 2 and their concentrations shows the advantage of glass prepared using a combination of chemical distillation purification of Ge-As-Se glass

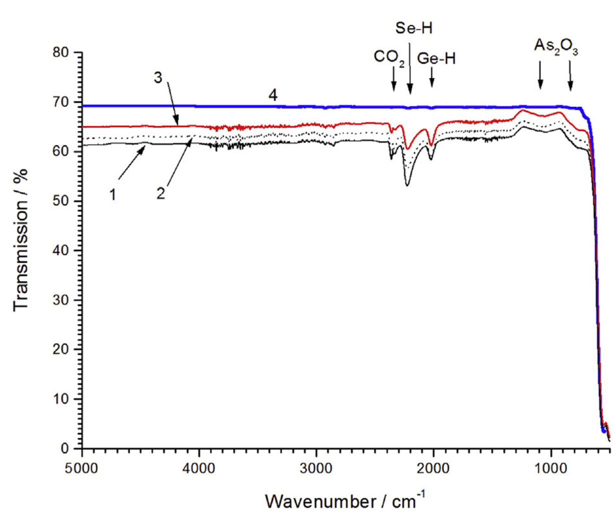

Fig. 1. Transmission spectra of chalcogenide glass samples (optical path length is 2 mm): 1 - $Ge_{25}As_{15}Se_{60}$ (direct synthesis of elements); 2 – $Ga_2Ge_{25}As_{15}Se_{58}$ (direct synthesis of elements); 3 - $Ga_3Ge_{25}As_{15}Se_{57}$ (direct synthesis of elements); 4 - $Ga_3Ge_{25}As_{15}Se_{57}$ (multi-stage purification).