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RECENT PROGRESS IN PREPARATION OF CHALCOGENIDE As-Se-Te GLASSES WITH LOW IMPURITY CONTENT

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The methods of preparation of high-purity As-Se-Te glasses are developed. The glass compositions having a low tendency to crystallization are determined by differential scanning calorimetry (DSC) technique. To prepare high-purity As-Se-Te glass the method of melting essentially pure elements in evacuated silica ampoule is used. The chemical and distillation methods of purification are used to remove water, oxides, hydrogen and carbon impurities from glasses. The impurity content in glasses determined by the IR spectroscopy and laser mass spectrometry is as follows: oxygen 0.1-0.5 ppm, carbon ≤0.5 ppm, hydrogen ≤0.02 ppm, Si ≤0.5 ppm, metals ≤0.05 ppm. The prepared glass samples were used to manufacture low-loss optical fibers. Multimode core-clad (Ge)-As-Se-Te glass fibers with optical losses of 150-200 dB/km in the 6-7 μm wavelength range and losses less than 1000 dB/km in the 3.5-9.5 μm range are fabricated.

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1. Introduction

As-Se-Te glass is a very promising material for transmitting middle IR radiation and developing IR fiber-optics devices. Advantages of Te-As-Se glasses for manufacturing optical fibers are: low phonon energy, good transparency between 3 and 11 μm, the possibility of modifying the composition to obtain the required optical characteristics and good chemical stability.

The intrinsic multi-phonon absorption of As-Se-Te glasses is shifted to longer wavelengths in comparison with As_2Se_3 glass. Some glass compositions are stable against devitrification. When 30 % of Se is replaced by Te in $As_{40}Se_{60}$ glass, the shift of multi-phonon absorption edge is equal to 1.0 μm at the 0.01 cm^{-1} absorption level [1], and the critical cooling rate decreases by approximately 2 orders of magnitude [2].

The progress in producing low-loss optical fibers based on As-Se-Te glasses is connected with a decrease in content of such impurities as oxygen, carbon, sulfur, hydrogen, silica etc. These impurities induce an additional absorption in the middle and far IR ranges, as well as scattering losses due to micro inclusions. The impurity content depends on the purity of initial elements and method of glass preparation.

Additionally, some As-Se-Te glasses have a tendency to crystallization. The presence of crystals induces additional scattering loss and decreases the mechanical strength of the fibers. The use of crystallization kinetics data and glass stability criterion permits to choose stable As-Se-Te compositions against crystallization.

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In the literature there are some data on preparing As-Se-Te glass system by direct synthesis method from elements [3-5] and on glass-forming melt purification by chemical method using Al [1,6-8], Mg [9] and $TeCl_4$ [10] as reagents (getters) changing the impurity chemical form. The glasses prepared by direct synthesis possess a sufficiently high oxygen and hydrogen impurity content. The optical loss spectra of the fibers based on these glasses have intensive absorption bands caused by water, OH groups and arsenic oxides. Authors of [6] preparing $Ge_{30}As_{10}Se_{30}Te_{30}$ glass added in the charge a small amount of Al (10 ppm) melted at 900^0C and carried out vacuum distillation of the glass melt. A decrease in intensity of oxide absorption bands and an increase in Se-H (4.57 μm) band in prepared samples was observed. A single-index fiber based on this $Ge_{30}As_{10}Se_{30}Te_{30}$ glass was reported with optical losses of 0.11 dB/m and 1.88 dB/m at 6.6 and 10.6 μm, respectively. Core-clad fiber based on this glass having a 140/230 (μm) core/clad diameter ratio was manufactured by rod-in-tube drawing technique. It had optical losses of 0.7 dB/m at 5.56 μm and 2.5 dB/m at 10.6 μm.

The minimum optical losses in single-mode $As_{30}Se_{50}Te_{20}$ glass fiber purified with 700 ppm of Al getter were equal to 40 dB/km at 6.7 μm [1]. But spectrum of this fiber has a strong Se-H absorption band at 4.57 μm with intensity of 6 dB/m. Paper [7] informs about manufacturing core-clad As-Se-Te glass fiber with a plastic coating having minimal optical loss of 0.8 dB/m at 8.5 μm and 5 dB/m at 10.6 μm. In [8] the glass fiber production with the core-clad GeSeTe/GeAsSeTe structure was reported. These fibers had minimal optical loss of 0.25 dB/m at 7.2 μm and strong Se-H absorption bands.

The aim of this work was to develop the methods of production of As-Se-Te glass system with low oxygen, hydrogen, and carbon impurity content, as well as the fibers based on these glasses with low optical losses.

2. Experimental

The first and key stage at the problem solution as a whole is finding the glass macro-composition having more stability to crystallization.

To investigate the influence of $As_{40}Se_{60-x}Te_x$ (x=0-40) glass composition on glass-forming ability, a series of samples was prepared with different selenium and tellurium ratios. The initial commercial elements were purified to remove the impurities of oxygen, molecular water, carbon, silica and transition metals by vacuum distillation (sublimation) with low evaporation rate. Synthesis of $As_{40}Se_{60-x}Te_x$ glasses was carried out by melting the purified elements (As, Se and Te) in evacuated and sealed silica ampoules in a rocking muffle furnace at 850^0 C for 7 hours with subsequent quenching in water, annealing at glass transition temperature T_g and slow cooling to room temperature. The calorimetric measurements of characteristic temperatures were carried out using DSC2010CE (TA Instruments) with the calorimetric sensitivity of 1 μW and a temperature accuracy of ±2K. The characteristic temperatures included glass transition temperature (T_g), temperatures of crystallization (T_c) and exothermal maximum (T_p), and the liquidus temperature(T_l). The values of T_g, T_c and T_l were determined from intersection of the curve slope ratios for different heating rates. DSC thermograms of the bulk glass samples (20 mg) were investigated at the heating rates of 2.5, 5, 10, 15, 20 and 35 K/min.

The typical DSC thermograms of As-Se-Te glasses at a heating rate of 2.5 K/min are given in Fig. 1. The DSC study has shown that all As-Se-Te glasses have only one glass transition temperature indicating that there is no phase separation. We have observed a strong single-stage crystallization at the heating rate of 2.5 K/min in $As_{40}Se_{60-x}Te_x$ glasses with tellurium content x=0, 25, 30, 35 and 40, a weak crystallization in case of x=5, 10 and 15, and no crystallization in case of x=20.

The present investigation and calculation of glass-forming criteria have shown that the $As_{40}Se_{40}Te_{20}$ glass composition is more stable to crystallization. Increase or decrease of Te content reduces the glass-forming ability of the melts. All that is in good agreement with the literature data on critical cooling rate of the melt [3]. $As_{40}Se_{40}Te_{20}$ glass is chosen as the base for fiber manufacture. Doping of As-Se-Te glass with Ge increases the glass-forming temperature and microhardness of glass that significantly improves its performance.

At preparation of core and clad glasses for optical fibers the glass-forming melt is additionally purified by chemical distillation method. The purification method included changing the chemical form of impurity due to interaction with a reagent added to the initial charge, the subsequent vacuum distillation of the melt for a removal of impurity in the new form and traces of reagents, as well as homogenizing the fusion of distillate. Three reagents were tested: 1) Al, 2) $AlCl_3$ (2400 ppm), 3) Al (500 ppm) + $TeCl_4$ (1000 ppm).

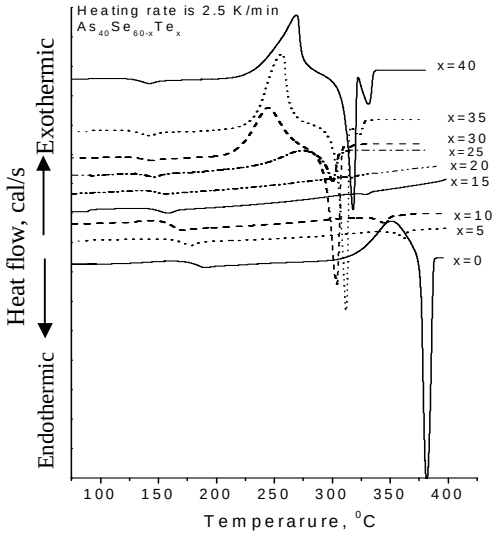

Fig.1. Typical DSC thermograms of As-Se-Te glasses at a heating rate of 2.5 K/min.

The appropriate amount of initial high-purity substances and a getter were loaded into the synthesis reactor and evacuated in an oil-free high vacuum (10^{-6} torr). Then the sealed ampoule was placed into a muffle rocking furnace and heated at 850 ^{0}C for 7 hours. After cooling to 400°C this ampoule was sealed to a silica system for double distillation of a chalcogenide glass. After double distillation with low rate, the melt was homogenized at 700^0 C for 7 hours. The glass was quenched in water. At the final stage the samples were annealed at a temperature near T_g for 30 min and cooled slowly to room temperature. The glass samples were obtained as rods with a diameter of 10-30 mm and length of 200-300 mm for the optical measurement and fiber drawing. To measure the optical transmission of a prepared glass, samples were cut and polished with a thickness of 50, 5 and 1 mm.

The macro composition of As-Se-Te glass samples after distillation was determined by the energy dispersive X-ray analysis with the 0.2 at.% accuracy.

The transmission spectra of the samples were recorded in the wavelength range from 2.0 μm to 28.5 μm on a Vector 22 and IFS-113V Fourier transform infrared spectrometers (Bruker), and in the wavelength range from 0.5 μm to 2 μm on CARY 5 UV-VIS-NIR spectrophotometer.

The content of metals and silicon impurities in glass samples was determined by laser mass spectrometry. The content of gas-forming impurities (hydrogen, oxygen and carbon) was determined by laser mass spectrometry on tandem laser mass reflectron [11] and IR spectroscopy using the known values of extinction coefficients [12,13].

The prepared high-purity As-Se-Te glasses were used to manufacture core-clad multimode fibers by using the double crucible technique [14]. The optical loss in the fibers was measured using the conventional cut-back technique. The FTIR IFS-113V spectrometer (Bruker) was used to detect the infrared light transmitted by the fiber. The initial length of measured fibers was more than 10 m, and after cutting the fiber length was reduced to 1 m. While measuring the optical loss spectra the cladding modes were removed at the input and output ends of the optical fiber. For this purpose, we removed the coating from the input and output ends of the fiber (several centimeters in length) and immersed these parts in liquid gallium. The error in determination of optical losses was about ±4% at the 1000 dB/km level and about ±8% at the 100 dB/km level.

The mechanical strength of the optical fibers was determined by the method of two-point bending between parallel plates [15]. The following measurement conditions were used: temperature was equal to 20 ^{o}C; air was used as environment; the closing rate of the plates was 1 mm/s; the number of samples in each measurement series was not less than 40.

The As-Se-Te fibers were used for delivering the continuous CO-laser radiation.

3. Results and discussion

Fig. 2 shows the influence of different Al getter charges on the content of impurities in the samples. When high-purity elements are melted without the oxygen getter, there are some oxide, hydroxide and water impurity bands in the absorption spectra. Addition of a small amount of Al (100 - 300 ppm wt.) is also not enough to remove all the oxide bands. And only the glass melting with 700 ppm wt. of Al with a subsequent triple distillation has allowed us to obtain the spectra without these absorption bands. The disadvantage of this method is an increase in SeH band intensity. According to our estimation, the hydrogen content is ranging from 0.5 to 4 ppm at.

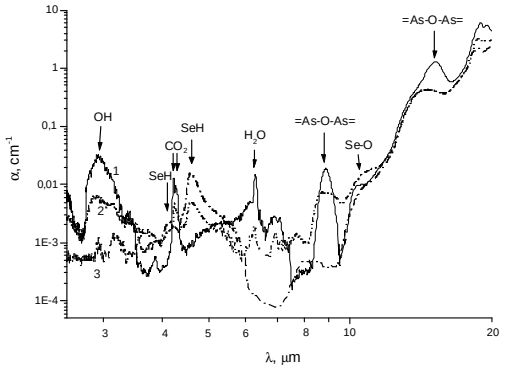

Fig. 2. Absorption spectra of $As_{30}Se_{50}Te_{20}$ glasses prepared under different conditions: 1 – direct synthesis from the elements; 2 – melting with adding 100-300 ppm wt. of Al and double distillation; 3 – melting with additional 700 ppm wt. of Al and triple distillation.

Fig. 3 presents the transmission spectrum of high-purity $Ge_2As_{38}Se_{40}Te_{20}$ glass prepared by melting with additional Al (500 ppm wt.) + $TeCl_4$ (1000 ppm wt.) and double distillation. There are no any oxide, hydroxide, water and Se-H impurity bands in the spectrum.

Table 1 gives the impurity content in the samples prepared by different methods. Three glass purification techniques are investigated: 1) melting of high-purity elements without the oxygen getter (loading by evaporation from intermediate ampoules), 2) melting with addition of Al (700 ppm wt.) and a subsequent triple distillation, 3) melting with addition of $AlCl_3$ (2400 ppm wt.) and a subsequent triple distillation.

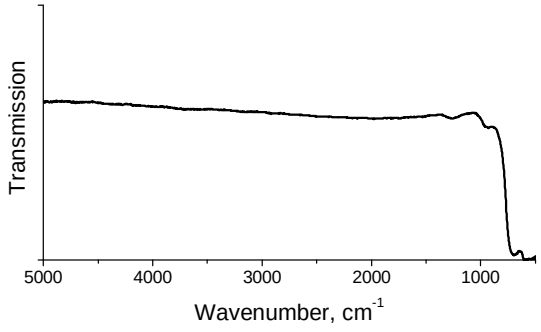

Fig. 3. Transmission spectrum of $Ge_2As_{38}Se_{40}Te_{20}$ glass prepared by melting with additional Al (500 ppm wt.) + $TeCl_4$ (1000 ppm wt.) and double distillation (sample thickness is 9 cm).

Table 1. Impurity content (ppm wt.) in (Ge)-As-Se-Te glasses prepared by different methods.

Impurity	Synthesis from elements	Melting with Al	Melting with $AlCl_3$
C	1	0.6	1
O	20	0.2	0.6
H	0.2	1	0.02
Si	6	4	0.5
Al	<0.4	<0.5	0.1
Cu	<0.1	<0.1	<0.02
Fe	1	0.8	<0.05
Cr, Ni	<2	<2	<0.03
Mg	0.5	0.3	<0.01
Sn, Cd	<0.4	<0.5	<0.3
Mn	0.1	<0.1	<0.03
Zn	<0.3	<0.3	<0.2
Pb	<0.5	<0.7	<0.03

The carbon impurity content in all glass samples is almost the same (~1 ppm). The oxygen impurity content in samples after chemical distillation purification is by 100 times lower (0.2-0.6 ppm) in comparison with the glass prepared by direct melting. The hydrogen impurity content in glass melted with Al is higher. The lowest hydrogen content (≤0.02 ppm) is observed in the glass melted with addition of $AlCl_3$ (or mixture of $TeCl_4$ and Al). The content of silicon and metals in the prepared samples is at a level of < 0.01-1 ppm depending on the degree of purity of initial elements and the glass purification technique.

High transparency of the prepared glasses in the 3-10 μm range is due to a low content of water, hydrogen and oxide impurities, as well as carbon and silica impurities in the form of inclusions. Hence, the optical losses in the fibers based on these glasses are very low.

Fig. 4 (curve 1) shows the spectrum of total optical losses of the fiber based on $Ge_2As_{38}Se_{40}Te_{20}$ (core) and $Ge_2As_{36}Se_{44}Te_{18}$ (clad). The main feature in manufacture of this optical fiber was that the double silica crucible served as a reactor for the glass synthesis. Core and clad melts were loaded into this double crucible by evaporation from intermediate volumes after purification. After homogenization of the core and clad glass melts a hot double crucible was placed in a thermostat of a drawing set-up heated up to 350^0C. The glass die of the double crucible was cut by a diamond cutter. The required fiber diameter was provided by changing the rotation rate of the take-up reel and the inert gas pressure over the melt. All fibers were coated with tetrafluoroethylene/1,1-difluoroethylene copolymer (F-42).

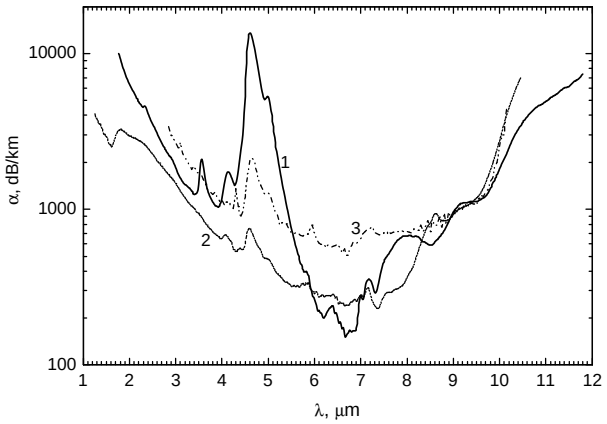

Fig. 4. Spectra of total optical losses in core-clad fibers based on glasses: (1) $Ge_2As_{38}Se_{40}Te_{20}$ (core) and $Ge_2As_{36}Se_{44}Te_{18}$ (clad) prepared with Al getter; (2) $Ge_{1,3}As_{37,1}Se_{41,3}Te_{20,3}$ (core) and $Ge_{1,2}As_{40,4}Se_{41,2}Te_{17,2}$ (clad) prepared with $(Al+TeCl_4)$ getter; (3) $Ge_{2,4}As_{32,4}Se_{38,2}Te_{27}$ (core) and $Ge_{0,8}As_{35}Se_{41,4}Te_{22,8}$ (clad) prepared with $AlCl_3$ getter.

The optical fiber with the core and clad diameter ratio of 210/330 (in μm) is manufactured. A high concentricity (80±5 %) and good merge of core and clad is observed. The thickness of polymeric coating is about 15 μm. Two transparency windows with optical losses less than 2 dB/m (2.9-4.4 μm and 5.2-10.1 μm) are present in the fiber spectrum. Minimal optical losses in this fiber are 150 dB/km at the wavelength of 6.6 μm. There are only few intensive impurity absorption bands due to the Se-H bond (3.5, 4.1, and 4.57 μm). Intensity of the absorption band at 4.57 μm is 12 dB/m. Besides, some weak bands due to OH groups and traces of molecular water at 6.33 μm are observed. The increase of optical losses in the short wavelength range (below 3 μm) is due to electronic transition. The average bending strength (at a failure probability of 63.2%) in this as-drawn fiber is 0.5 GPa. The effective numerical aperture of the fiber makes up 0.34.

The fibers were tested with continuous CO-laser radiation. Seven watts of such a radiation were delivered through the 1.5-m long fiber with the core diameter of 330 μm. The output energy was limited not so much by the fiber optical losses, but mainly by the input laser energy.

The pair of Ge-As-Se-Te glasses purified with the mixture of Al and $TeCl_4$ was used to manufacture core-clad multimode fiber by the double crucible technique. More than 150 m of such a fiber with the core diameter of 540 μm, the cladding diameter of 600 μm and the fluoro-polymer F-42 coating were fabricated. The average bending strength was 600 MPa. The fluctuations of the fiber diameter along its length did not exceed 5 μm. The minimal optical losses were 0.2 dB/m at a wavelength of 7.4 μm. Optical losses less than 1 dB/m were achieved in the wavelength range from 3.3 to 9.2 μm. The spectrum of this fiber (Fig.4) is characterized by low intensity of Se-H band (less than 0.2 dB/m) at 4.57 μm.

The low content of oxygen, hydrogen, carbon and water impurities was achieved by using the combination of chemical and distillation methods. The addition of Al (700 ppm wt.) is effective only for a removal of oxide impurities. The hydrogen content is ranging from 0.5 to 4 ppm at. The calculated contribution of hydrogen impurity to the total losses is between 20 and 90 % in the spectral interval of 3.0-8.5 μm.

Thermodynamic calculation of equilibrium conditions for the ($As_{40}Se_{40}Te_{20}$+O+H_2O+Al) system has shown that the effective decomposition of oxides and water takes place only when aluminum content in the mixture is more than 100 ppm. Aluminum and oxides interact with a formation of heavy-volatile aluminum oxides. Distillation is effective at purification from aluminum oxides formed. As a result, the oxygen content in the target product was less than 0.2 ppm. However, even double or triple glass distillation in a dynamic vacuum does not permit to remove the hydrogen impurity. An increase in Se-H band intensity is even observed in the spectrum of this glass in comparison with the glass prepared without melting with aluminum. This is related to the transfer of hydrogen impurity from OH groups and H_2O (bond energies are 460 kJ/mol and 494 kJ/mol [16], respectively), resulting at interaction with Al in glass decomposition to selenium and arsenic with the formation of Se-H and As-H bonds.

A significant decrease in Se-H absorption bands in the transmission spectra of glass purified using $TeCl_4$ or $AlCl_3$ was observed. It means that at glass melting with $AlCl_3$ (or with mixture of Al+$TeCl_4$) the hydrogen forms light-volatile HCl, which is removed from the system at a dynamic vacuum distillation. Fig. 5 shows the results of thermodynamic calculation of the components in the ($Ge_5As_{35}Se_{40}Te_{20}$+10 ppm H_2O) system as a function of $AlCl_3$ content at 850^0C. A sharp decrease in AsO, GeO and H_2O concentration is observed, when $AlCl_3$ in the mixture is more than 500 ppm. There is a continuous increase in HCl and Al_2O_3 concentration. As a result, a very low hydrogen (<0.02 ppm) and oxygen (0.5 ppm) content in glasses is observed after chemical purification.

The behavior of oxygen and hydrogen impurities at chemical purification can be explained in general as follows. The oxygen, being originally present in the form of As, Se, Te oxides and OH groups, after chemical treatment is bound in the thermodynamically stable compound - aluminum oxide. Hydrogen from the OH groups forms the Se-H groups. These groups are connected with the glass network and do not transform into the volatile H_2Se. Introduction of chlorine compounds leads to a formation of thermodynamically stable and volatile HCl that could be easily removed from glass at distillation.

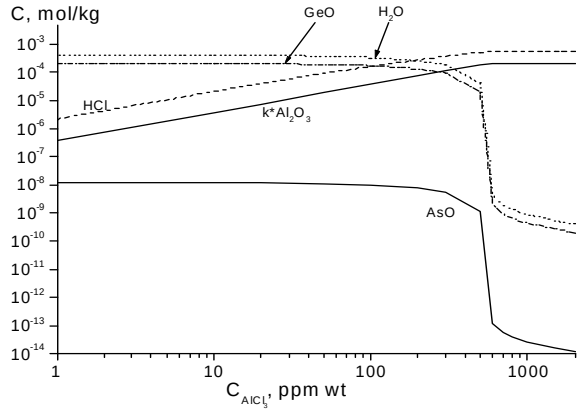

Fig. 5. Calculated thermodynamic equilibrium concentrations of the reaction of ($Ge_5As_{35}Se_{40}Te_{20}$+10 ppm H_2O) with $AlCl_3$ at 850 °C.

5. Conclusions

Crystallization ability of $As_{40}Se_{60-x}Te_x$ glass systems is investigated. It is shown that $As_{40}Se_{40}Te_{20}$ glass is the most stable composition to crystallization.

Glass samples with low impurity content (oxygen 0.1-0.5 ppm wt., carbon 0.6 ppm wt., hydrogen 0.02 ppm wt., Si < 0.5 ppm wt., metals <0.05 ppm wt.) are prepared.

The possibility of manufacture of optical fibers based on As-Se-Te glass system by double crucible technique is shown. Multimode fibers with the optical losses of 150-200 dB/km in the wavelength range of 6-7 μm and losses less than 1000 dB/km in the 3.5-9.5 μm range are fabricated.

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