SYNTHESIS OF CHALCOGENIDE GLASSES OF THE Se–Ge AND Se–As SYSTEMS WITHOUT TRACES OF OXYGEN

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A new method is described of the synthesis of chalcogenide glasses in the Se–Ge and Se–As systems without traces of oxide impurities, particularly of GeO, GeO_2, SeO_2, and As_2O_3, whose presence limits the use of these glasses in terms of an optical material having transmittance for infrared radiation up to 18 μm. Infrared spectra of the produced glasses are presented and absorption spectra of the appropriate glasses as well as those of the oxides are identified.

At present time, in the technology of chalcogenide glasses a great stress is laid on the preparation of oxygen-free chalcogenide glasses. Oxygen in these glasses, namely, forms oxides with individual components, which produce parasitic absorption in the region of $480-1200$ cm^{-1}, limiting thus the possibility of utilization of these glasses as infrared optical material in the region above 10 μm.

Usual preparation of these systems has been reported in a series of papers[1-10]. Most of the authors prepared the glasses by melting the starting materials in appropriate quantities in an evacuated fused quartz ampoule containing last traces of atmospheric air. They strived then to remove additionally the oxide impurities thus produced, by distillation in a stream of hydrogen[6] or inert gas, or by deoxidation with carbon[7]. These operations, however, were not always successful, removal of oxide impurities was not perfect, a change in the glass composition often occurred, and total glass losses took place. Likewise, difficulties with perfect homogenization of the synthetized glass arose. In this paper a new procedure is described which offers a possibility of avoiding these troubles. The removal of oxygen takes place prior to synthesis.

The presence of oxygen impurities in the chalcogenide glass of the system Se + x at.% Ge causes formation of GeO, and in some cases, if more oxygen is involved, even GeO_2, whose presence lowers transmittance of infrared radiation near 800 cm^{-1}.

Oxygen can be introduced into this chalcogenide glass either by means of both elements (in the form of respective oxides, *e.g.* SeO_2, GeO_2, or GeO) or as molecular oxygen dissolved in the material or adsorbed on its surface. Nevertheless, final oxide impurity is here present mainly as GeO, because GeO_2 reacts at higher temperature with the germanium excess to produce GeO and to evolve heat of 8·2 kcal.

In addition to the above-mentioned sources of oxygen, contamination of chalcogenide glass with oxygen may occur even during the glass synthesis itself, for at the temperature above 800°C

a reaction is partially induced between elementary germanium and quartz glass SiO_2 to form GeO_2 which further reacts with the surplus of Ge.

This analysis shows that in the synthesis of chalcogenide glass of the Se–Ge systems, the following principles must be kept in mind: *1*. The starting elements must be deoxidized and removal of their oxides before the synthesis must be made. *2*. The synthesis itself must be carried out under such temperature conditions to avoid undesirable side reactions leading to oxides and thus to contamination of the chalcogenide glass produced.

EXPERIMENTAL AND RESULTS

Germanium

The most suitable method to remove oxygen from germanium seems to be remelting germanium in a reducing atmosphere, followed by vacuum fusion.

As has been mentioned, a reaction of Ge with SiO_2 to produce GeO occurs at the temperatures above 800°C, and for that reason, the use of quartz glass material does not seem to be suitable. Another, more resistant material, such as for example higly pure graphite, must be employed. Graphite must be purified before use for example by chlorination at 1000°C with the subsequent vacuum heating (10^{-4} Torr) at the temperature of 1100°C. In this way, graphite can be freed from residual impurities produced mainly during mechanical treatment.

Germanium placed in a graphite boat is melted in hydrogen stream (1 l/min) at the temperature of 1000°C for a period of 5 hours. Traces of oxygen and water are removed from hydrogen in advance by passing it over catalysts Deoxo and molecular sieves.

The following vacuum melting of germanium is accomplished mainly to remove last portions of volatile contaminants. Germanium is heated in a graphite boat under a vacuum of 10^{-4} Torr at the temperature of 1000°C within 3—4 hours. The purified germanium is kept in a vacuum desiccator.

Selenium

Oxygen is contained in selenium mainly in the form of SeO_2 which is present both on the selenium surface and dissolved in it. Besides, molecular oxygen is adsorbed on the selenium surface and is likewise converted into SeO_2 by heating.

Selenium dioxide can be separated from elementary selenium by heating selenium up to a temperature of 350°C under vacuum of 10^{-4} Torr. Deoxidation of selenium is suitably carried out directly in the reaction ampoule. The procedure will be described below.

Chalcogenide Glasses of the Se–Ge *System*

Apparatus. The chalcogenide glass of the system Se + x atm. % Ge (where $x_{max} = 20$) is synthetized in a special quartz glass ampoule (Fig. 1) consisting of two parts *1* and *2* which are interconnected by means of a small tube. The two parts are separated from one another by a brittle easy-to-break quartz partition *3*. Im-

mediately before use, the whole ampoule is heated under a vacuum of 10^{-4} Torr for 3 hours at the temperature of 1000°C and afterwards cooled down in an inert argon or nitrogen atmosphere.

Procedures before the synthesis. The weighed amount of germanium, previously purified in the mentioned manner, is placed in part *2* of the ampoule. This part is thoroughly flushed with inert gas, nitrogen or argon (pp), evacuated down to a vacuum better than 10^{-4} Torr and heated at 700°C for 2 hours. Impurities due to weighing and handling the weighed material in the laboratory atmosphere are thus removed from the surface. At this temperature, there is still no danger of the reaction of Ge with quartz and hence of the contamination of germanium with oxygen. In the total part of the ampoule from 3 to 6, any lower temperature must not occur, as volatile impurities could be deposited in these places. Afterwards, vacuum seal *6* is being made. The amount of selenium, which corresponds to the desired composition of the chalcogenide glass is placed in part *1* of the ampoule. Here, a quartz rod is also inserted, which later serves for the breakdown of partition *3*. This part of the ampoule is again flushed with inert gas, evacuated to a pressure lower than 10^{-4} Torr, and heated at the temperature of 330°C for 3 hours. At the latter temperature, SeO_2 provides a vapour pressure of 1 atm. and sublimes from the ampoule. It is necessary that the temperature at places *3* and *4* should not decrease below 330°C. After cooling the ampoule down to room temperature, the vacuum seal *4* is being made. Since at the temperature of 330°C also selenium escapes in part from the system (selenium partial pressure amounts to 1 Torr at this temperature), a certain positive correction must be made to compensate weighing losses. This correction is found experimentally. The thin brittle partition is then broken down by means of the quartz rod and at the temperature of 600°C selenium is distilled over into the part *2* and vacuum seal *5* made. In this way, part *1* is separated from part *2* in which the synthesis itself is then accomplished.

Synthesis. The quartz ampoule with selenium and germanium, filled in the above-mentioned manner, is placed in a tube resistance furnace. The synthesis is carried out in two stages: *a*) The ampoule is heated to the temperature of 700°C for 3 hours. At this temperature, germanium is dissolved in selenium and reacts to form $GeSe_2$, but no reaction with SiO_2 occurs as yet. *b*) The furnace temperature is raised to $900-950°C$ and at this temperature, the ampoule is being kept for $6-7$ hours.
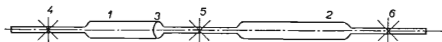

Fig. 1

Double-Part Quartz Glass Ampoule

At this temperature, the whole system is liquid and is being homogenized. After the reaction between selenium and germanium has been finished, reduction of SiO_2 with germanium and hence introduction of oxygen into the chalcogenide glass system does not take place at the second stage.

Cooling of molten glass. It is necessary that the melt be converted into the vitreous state within the whole volume during cooling, thus the crystals of $GeSe_2$ being not formed from the melt and stress of the material being removed. For that reason, the melt was left to follow spontaneous cooling of the furnace from the synthesis temperature of 950°C down to 600°C. The ampoule was then placed into the furnace heated to 400°C (close below the transformation point T_g, 410°C for $GeSe_2$ ref.[11]), and here, the material was gradually cooled down to the temperature of 20°C. In this way, a perfect vitreous material even with a higher germanium content, *i.e.* up to 20 at.% of Ge, could be obtained.

Evaluation of results by means of infrared spectroscopy. From the samples obtained, platelets of thickness $1-20$ mm were cut and mechanically treated to achieve optical quality of the surfaces. An example of the infrared spectrum of measured samples, obtained with use of spectrometer Zeiss UR-10, is given in Fig. 2, curve 1. Only absorption bands at 740 and 485 cm^{-1} or at 560 cm^{-1}, corresponding to the bonds Se—Se or Ge—Se, respectively, were found. Absorption bands at 800
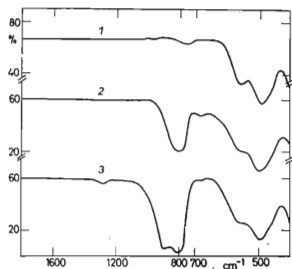

FIG. 2

Infrared Spectra of Glasses of Composition $GeSe_9$

1 Thickness of 1·49 mm, deoxidized; *2* thickness of 0·91 mm, doped with 500 p.p.m. O_2 as GeO or SeO_2; *3* thickness of 0·99 mm, doped with 500 p.p.m. O_2 in the form of GeO_2.
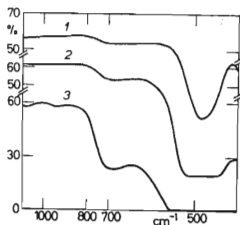
FIG. 3

Infrared Spectra of Deoxidized Vitreous As_2Se_3

Thickness of *1* 0·60; *2* 3·26; *3* 17·50 mm.

to 900 cm^{-1}, which are characteristic for oxide impurities, such as GeO_2, GeO, and SeO_2 in this chalcogenide glass system do not appear. These impurity bands appeared neither during the measurements of samples of higher thicknesses. In order to determine exactly the position of the absorption bands of the given oxides and to define the form of the oxide impurity, the glasses of the oxygen-free Se–Ge system were doped with GeO_2, GeO, and SeO_2. The weighings were chosen so as to obtain the oxygen content of 500 p.p.m. in each case. Infrared spectra of these experimental melting runs are of two types and are graphically presented in Fig. 2, curves 2, 3. Curve 2 corresponds to dopings with GeO and SeO_2, curve 3 corresponds to the sample doped with GeO_2. As can be seen from the spectra, a characteristic band at 800 cm^{-1} appears in both cases, which can be unambiguously assigned to absorption of GeO (ref.[12]). For curve 3, yet another absorption band at 880 cm^{-1} occurs beside the band at 800 cm^{-1}. It may be assumed that the reaction between germanium and germanium dioxide did not proceed quantitatively with this sample. As nonreacted residue GeO_2 remained in the measured sample, which is the very thing that exhibits a strong absorption at 880 cm^{-1}. Optically polished samples were also examined by means of an IR microscope which enabled observation in the wave-region up to 1·2 μm, and presence of crystalline phase was not detected. Equal results were achieved from the X-ray patterns.

Chalcogenide Glasses of the Se–As System

Presence of oxygen impurities in chalcogenide glasses in the system Se + x at.% As causes formation of oxide As_2O_3, whose presence diminishes transmittance of infrared radiation in the region of 630 and 800 cm^{-1}.

Preparation of vitreous As_2Se_3. The removal of oxygen from starting elements prior to the synthesis of As_2Se_3 was made on the basis of the assumption that oxygen may be present here in the form of As_2O_3 and SeO_2 oxides which both readily sublime at low temperatures and can be easily separated from the appropriate element.

Apparatus and treatment before the synthesis. The separation of undesired oxides was carried out directly in the synthesis ampoule in the following way. The weighed amount of selenium is placed into part 2 of the ampoule (Fig. 1), the latter is flushed several times with pure argon or nitrogen pp, and evacuated to 10^{-4} Torr. Afterwards, the whole ampoule is kept at the temperature of 330°C for about 3 hours. Further working procedure together with making the seal 6 of the ampoule is identical with the procedure presented for the system Se + Ge. Weighed amount of arsenic as well as the quartz rod are placed in part 1. The ampoule is again flushed with pure argon pp, evacuated to the pressure of 10^{-4} Torr and the whole ampoule is heated to 280−300°C, when As_2O_3 sublimes off. This temperature must not be lower at places 3 to 4. In view of the fact that even in this process a partial sublimation of arsenic takes place, an experimentally established weighed amount of arsenic

must be added. After one hour, a vacuum seal at place *4* is made and the ampoule left to cool down. The brittle quartz diaphragm *3* is broken down with use of the quartz rod and arsenic sublimes from part *1* at the temperature of 600°C into part *2* being kept at 20°C. After the resublimation, part *1* is separated from part *2* at *5*. Thus, the ampoule containing weighed amounts of both elements is ready for the appropriate synthesis.

The synthesis itself is carried out at 800°C in a vertical tube furnace with intermittent stirring for a period of 6—7 hours. The rate of cooling As_2Se_3 corresponded to the spontaneous cooling of the furnace after its switching off (the cooling rate is 20°C/min). Arsenic, of purity 99·9999%, supplied by the firm Hobboken, as well as selenium ($5 . 10^{-5}\% O_2$) manufactured by Boliden or by Elektropřístroj, Běchovice (purity of 99·999% and the O_2 content of $10^{-5}\%$) were used for the experiments. 25 g of vitreous As_2Se_3 was prepared per one melt. If arsenic having a considerably oxidized surface (dark-grey surface) is used for the investigations, a preliminary removal of As_2O_3 in a special quartz apparatus in nitrogen or hydrogen flow at 280—300°C is recommended. A similar method was used to carry out the synthesis of other glasses of the Se + *x* at.% As system up to a composition with *x* = 50. The samples thus produced were chemically analyzed and the achieved results confirmed that stoichiometry was essentially maintained. The error between the weighing and composition of produced glass amounts to max. 5%.

Evaluation of results by infrared spectroscopy. From the produced vitreous materials of As_2Se_3 and of the system Se + *x* at.% As, planparallel specimens
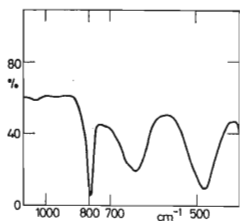

FIG. 4

Infrared Spectrum of Vitreous As_2Se_3 with Oxide Impurities, Thickness of 0·51 mm
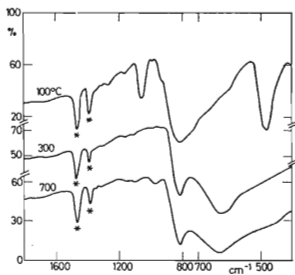

FIG. 5

Infrared Spectra of As_2O_3 after 4 h Heating at 100° (cubic form), 300°, and 700°C (vitreous form).

Measured in Nujol.

2—20 mm thick were cut and polished on both sides to provide optical quality of the surface. The samples were measured on spectrometer Zeiss UR 10 within 2—25 μm. Fig. 3 shows infrared absorption spectrum of As_2Se_3 prepared according to the method just described. An absorption band at 485 cm^{-1}, which corresponds to the As–Se bond and for greater thicknesses, a wide flat band within 620—760 cm^{-1} can be merely observed. In our opinion, this is likewise a weak absorption band of vitreous As_2Se_3, which is not caused by traces of oxide impurities. For the sake of comparison, infrared spectrum of vitreous As_2Se_3 sample is presented in Fig. 4, which was produced by melting together both elements, without any deoxidation being accomplished. The parasitic absorption bands at 630 and 800 cm^{-1}, whose position is consistent with the bands found in the infrared spectrum of the vitreous, but not cubic form of As_2O_3 (Fig. 5) are here strongly apparent. It follows from this that the impurity absorption in glasses of the As–Se system is due to the presence of traces of vitreous As_2O_3[12,13]. Similarly as in the case of chalcogenide glasses of the Se–Ge system, the basic oxygen-free material of As_2Se_3 was doped with SeO_2 and As_2O_3 in quantities corresponding to the O_2 content of 500 p.p.m. The infrared spectra showed that the result was always As_2Se_3 with parasitic absorption bands which correspond to the vitreous form of As_2O_3. By the method just described, many samples of vitreous As_2Se_3 were successfully prepared and synthesis of a series of glasses in the system Se $+$ x at.% As in a wide region of the vitreous state of this system was accomplished. From the measured infrared absorption spectra an unambiguous statement can be made that in no case, any absorption band belonging to the As_2O_3 traces was revealed. The described method is quite reproducible.

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