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Reproducibility of properties of As_xSe_{1-x} glasses on the synthesis temperature

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Abstract. As_xSe_{1-x} glasses with x from 0.05 to 0.55 were prepared at two melting temperatures, 700 and 850 °C. Batch materials from several suppliers were used for glass synthesis. Density and IR transmittance of glasses were measured. It was found that data for density of glasses prepared at 700 °C have sufficient scatter, so dependence of molar volume on composition is not smooth. Data for glasses synthesized at 850 °C are in good agreement with reference ones. According to data of IR spectroscopy, the main defects in glasses are oxide impurities in several molecular forms. Oxygen gets in glass together with arsenic. Its content can be noticeably decreased by the heat treatment of As before weighting and by the heat treatment of batch at 200 °C before the sealing of silica ampoule. Optical quality of glass samples is good enough for the use of them as IR transparent material for lens manufacturing.
Keywords: chalcogenide glasses, arsenic, selenium, oxygen impurity, density, IR transparency, optical homogeneity.

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Introduction

Chalcogenide glasses are the topic of great interest among scientists and researchers because of their versatile properties and widespread applications in the field of science and technology [1,2]. In the 1950s, chalcogenide glass received great attention mainly for infrared optical applications because of its low maximum phonon energy (~350 cm^{-1}), broad infrared transparency range, and high third-order optical nonlinearity (~10^{-11} esu) [3]. The glasses of As-Se system are transparent in IR from 0.7 up to 17 μm. They are low melting and are used for precise molding of lenses for thermal vision systems [4]. When precise optical elements are made of glasses, the reproducibility of physical chemical properties is a key requirement for their application.

For homogenization, usually chalcogenide melts are treated at temperature higher than melting temperature of any components and compounds that glass consists of. The highest possible temperature of synthesis is chosen taking into account vapor pressure and the strength

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of silica ampoule. For As-Se glasses, synthesis temperature is usually used from 700 to 850 °C [5].

If data of different authors are compared, one can see non reproducibility of data, especially for glasses enriched by selenium. For example, it is clearly seen from data presented in [6]. We suppose that this discrepancy between data of different authors may be caused as by difference in the batch materials quality, as by the different concentration of defect states caused by impurities.

The objective of present research is to choose optimal synthesis condition for As-Se glasses with the use of different batch materials. At that, we aimed at as simple synthesis process as possible.

Experimental

For synthesis, high pure arsenic and selenium were placed in silica ampoules with the following evacuation and sealing. All steps of batch preparation have been doing in air as quickly as possible. Samples were taken with a total weight of 10 g. Glasses were synthesized by melting for 4 hours at maximum temperatures of 700 and 850 °C. With subsequent cooling of the melt to 450 °C with constant rocking of the furnace and quenching it in air. For synthesis of all glasses, arsenic and selenium from two suppliers have been used. The first is imported (Japan) arsenic with a declared purity of 99.9999, the second is domestic with a purity of OSCh 17-4 supplied by ADV-Engineering. Selenium was supplied from two domestic manufacturers, NPK LENPROMKHIM and ADV-Engineering, with a purity of OSCh 17-4.

In order to improve transparency of glasses in thermal vision area, several additional stages for batch preparation have been used. The first of them is arsenic preheating. Preheating has been done in evacuated and sealed glass ampoule. The lower part of ampoule with the arsenic pieces was into the furnace room at from 300 to 350 °C, and upper part was at the room temperature. According to our measurements oxygen content in arsenic is changed. After heat treatment, the upper part of ampoule was coated by white precipitation of arsenic oxide. For some arsenic samples, precipitate was colored, most probably by sulfide impurities. Preheating duration was from 4 to 100 hours.

Another way to improve optical transmittance in IR was the preheating of selenium. For that, selenium was put in glass ampoule and was heated at 310 °C under dynamic vacuum up to stopping of bobbles formation. Usually bobble formation was stopped for from 0.5 to 1 hour in dependence on supplier.

A third way for batch pretreatment was a degassing of the batch before the sealing of silica ampoule. Degassing has been done at 200 °C for about 30 min in dynamic vacuum.

Density of glasses was measured by hydrostatic weighting method [7,8], IR transmittance spectra were recorded with the use of Fourier spectrometer FSM – 1201 for polished plates with thickness from 7 to 10 mm [9].

Results

The results of density measurements are presented on Fig. 1. One can see, that there is a difference between density of glasses synthesized at 700 and 850 °C. This difference is more sufficient than the difference between glasses prepared from As from two suppliers. For glasses enriched by selenium, for example $As_{20}Se_{80}$ composition, this difference exceeds measurement error. It is possible that temperature about 700 °C is non-sufficiently high for equilibrium between chain and cyclic structures of selenium. Behavior like this was also described by Borisova [4] where glasses were synthesized during 4 hours at 700 °C with vibration mixing.

Our data for glasses prepared at 850 °C are in good agreement with data [10,11]. Taken into account that difference in density for glasses prepared at different temperatures is obtained for glasses enriched by selenium, we suppose that this difference is caused by the strong dependence of structure of liquid selenium on temperature. Glass structure for them is labile, that is because authors of [11] obtained fast ageing effect in the first few minutes (5 mol.% As glass) to hours (10 and 20 mol.% As glasses) after synthesis. At the ageing both the density and microhardness of glasses are increased. This behavior can be explained by the annealing of glasses at room temperature because the glasses enriched by selenium have low glass transition temperature.

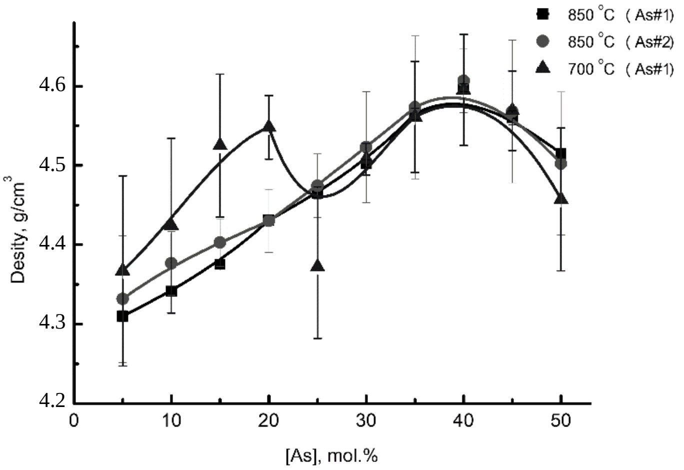

Fig. 1. Density of As_xSe_{1-x} glasses

In accordance with physical-chemical analysis, dependence of molar volume on the molar fraction of a component has to be linear for ideal system. Deviation from linearity is caused by chemical interaction between components. Calculation results for As-Se glasses are presented on Fig. 2 together with data of Yang et al. [10]. Minimal molar volume is obtained at congruent melting As_2Se_3. For systems Se-As_2Se_3 and As_2Se_3-As, linear dependences take place only for glasses synthesized at 850 ^oC. These data are in good agreement with data [10]. For glasses prepared at 700 ^oC data are characterized by strong spread and are similar to data of Borisova [5], where glasses were synthesized also at 700 ^oC.

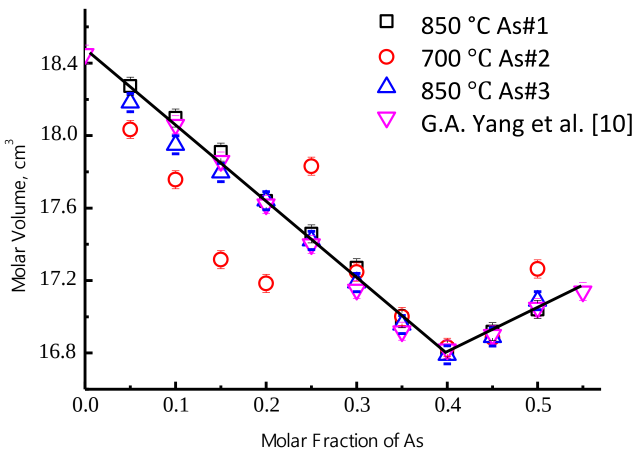

Fig. 2. Molar volume of As_xSe_{1-x} glasses

Absorption of glasses in thermal vision area (8-12 μm) is less sensitive to the synthesis temperature [12]. For example, Fig. 3 presents absorption spectra for As_xSe_{1-x} glasses synthesized at 850 °C. Base lines of spectra are shifted for convenience. Absorption bands at 9-16 μm caused by arsenic oxide impurity in form $AsO_{3/2}$, As_4O_6, $AsSe_{2/2}O_{1/2}$ [13,14]. The higher is As concentration in glasses, the higher absorption is. It means that oxygen impurity in glasses is got to glasses together with arsenic. Using data of [14] we can estimate oxygen content in glasses prepared by different way. The most intensive impurity absorption band in As_xSe_{1-x} glasses is 790 cm^{-1} (12.6 μm) [15]. For our glasses, maximal content of oxygen did not exceed 200 ppm.

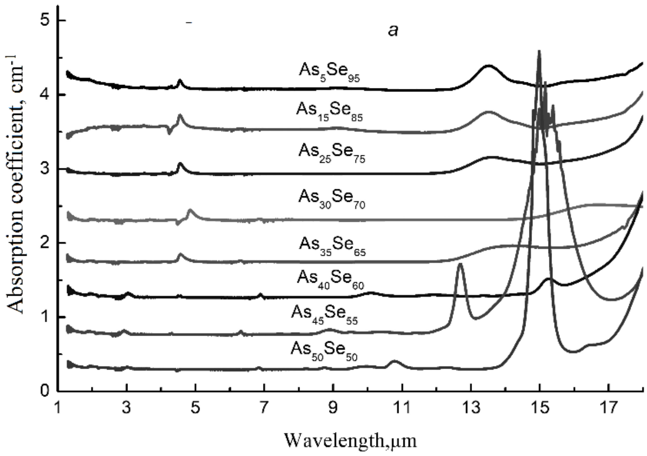

Fig. 3. Absorption spectra of As_xSe_{1-x} synthesized at 850 °C

The possible contamination of chalcogenide glasses due to the permeability of silica glass has not been experimentally investigated. This may be important for the analysis of the effect of hydrogen [16,17].

Effect of As preheating on $As_{36}Se_{64}$ glass transparency can be seen on Figure 4. As one can see, preheating of arsenic is a very effective method for oxygen removal.

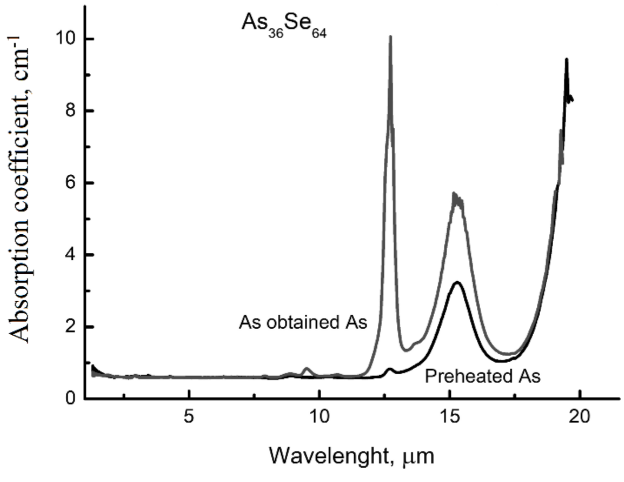

Fig. 4. Absorption spectra of $As_{36}Se_{64}$ glasses synthesized from as obtained and preheated As

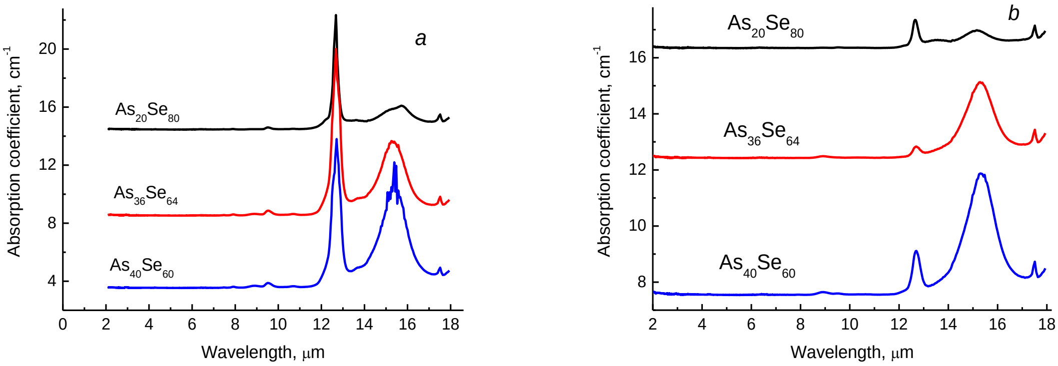

Fig. 5. Absorption spectra of glasses synthesized from non-preheated (a) and preheated batch (b)

One can compare the optical transparency of glasses synthesized with no batch preheating (Figure 5(*a*)) and glasses prepared from preheated batch (Fig. 5(b)).

Optical transparency is not the only one property important for application as the component of thermal vision systems. Another property is optical homogeneity. Usually it is measured as the data spread for the refractive index of the material. The impurity inclusions with the refraction indices differing strongly from that of a glass represent the main source of the non-selective losses [18]. Optical homogeneity has influence on the image quality. Standard method for its measurement is interferometric one [19]. Standard measurement of optical homogeneity is very complicated for IR area.

For checking of optical homogeneity, we used IR microscopy. Tests were carried at the wavelength from 0.9 to 1.1 μm [20]. The polished sample was placed between the microscope lens and the plate with the test image. The image quality and its sharpness can be considered as a performance criterion for optical quality of the sample. For example, two images seen through the $As_{20}Se_{80}$ glass are presented on Fig. 6. The left sample on Fig. 6 was obtained from a batch preheated before sealing, the right one was sealed as weighted. We assume that the glass obtained from non-preheated batch contain oxide inclusions, which are to make worse the image quality.

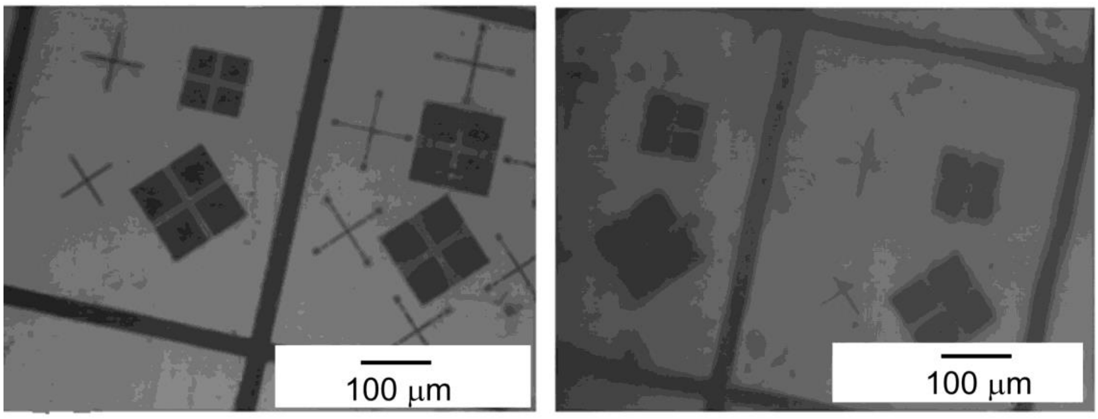

Fig. 6. The test images that are seen through $As_{20}Se_{80}$ glass. The batch was preheated before sealing (left) and non-preheated (right)

The image resolution was tested with the use of a ruler with the scale of 10 μm. An example of the image seen through the glass sample is presented on Fig. 7.

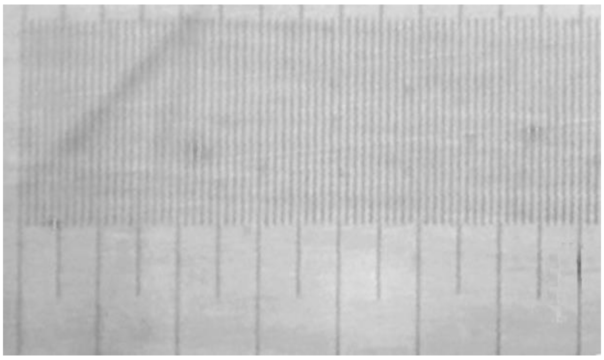

Fig. 7. The test image of ruler with 10 μm scale seen through the glass sample with the thickness 10 mm. Glass was synthesized at 850 °C

One can see, that image resolution through the glass sample is higher than 10 mm. Lines on the image are slightly curved, with deviation about 1 μm. Optical homogeneity of the all of the glasses synthesized at 850 °C was good enough to resolve 10 μm bars. It is enough to use glass lens thermal vision systems, with the typical size of photodetector about 15 μm.

Thus, the synthesis of glasses at 850 °C assures their optical quality and reproducibility of properties.

Conclusion

Glasses of As-Se system were prepared. It is demonstrated that maximal synthesis temperature is important to obtain glasses with reproducible properties. The temperature 850°C is sufficient to obtain glasses with the density agreed with reference data, regardless of batch material supplier. To decrease the defect content caused by oxygen impurity, heat treatment of the batch starting materials before their weighting and of batch in silica ampoule before sealing are very useful. Optical quality of glasses after these steps is also made better.

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