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Absorption Edge and Optical Band Gap of Ag-$As_{40}S_{30}Se_{30}$ Amorphous Samples

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The paper describes the results of a study of the influence of silver content on the absorption edge and optical band gap of the newly synthesized glasses of the $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$ type for $x = 0$, 0.5, 1, 2, 3, 5 at.% and of the corresponding films. The synthesis of bulk samples was performed in a rocking furnace from high-purity elemental components by a melt quenching method. Films were prepared from the synthesized bulk samples by pulsed laser deposition. Transmission spectra of the investigated samples were recorded at room temperature. The absorption edge and the optical band gap were determined by extrapolating the linear parts of the absorption spectra. It was found that the investigated range of Ag doping concentrations has a great influence on the absorption edge and optical band gap. Namely, with the increase of the silver content in the material the optical band gap showed a decrease. For films, it decreased from 2.02 eV, for the glass without silver, to 1.805 eV for the composition with 5 at.% Ag, whereas for the analogous bulk samples this decrease was from 1.84 eV to 1.609 eV.

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1. Introduction

Considering a wide range of their practical applications, the preparation, structure and other properties of chalcogenide glasses and thin films doped with silver are of great interest. The electrical, optical, and structural characteristics of the system Ag-As-S-Se were intensively studied [1, 2]. Owing to their ionic conductivity, silver-containing glasses have found their application in the industry as batteries [3] and programmable metallization cell memories [4]. Previous investigations of optical characteristics of silver-doped chalcogenide glasses showed that they are prone to photoinduced structural changes, which makes them suitable for high-resolution display devices and manufacture of diffractive optical elements [5].

Bearing in mind that the investigated samples are the newly synthesized bulk glasses and films from the $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$ system, this work presents the preliminary results of a study of the influence of the silver content on the absorption edge and optical band gap.

2. Experimental

The chalcogenide glasses from the system $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$ for $x = 0$, 0.5, 1, 2, 3 and 5 at.% Ag, were synthesized from the elemental components of high degree of purity 5N by the method of cascade heating. Two different regimes were applied. For the silver-containing glasses the synthesis lasted approximately 48 hours, as can be seen from the technological map shown in Fig. 1. As it is evident from the figure, there were six plateaus and two heating rates, and the maximum temperature of the synthesis was 950 °C. At that temperature, the ampoules with the melt were taken out from the oven and air-quenched. In order to improve homogeneity and reduce strain in obtained glasses, ampoules were placed in alumina powder after quenching. The synthesis of the three-component glass $As_{40}S_{30}Se_{30}$ was performed in a different regime, in which the maximum temperature of 720 °C was reached during 33 hours.

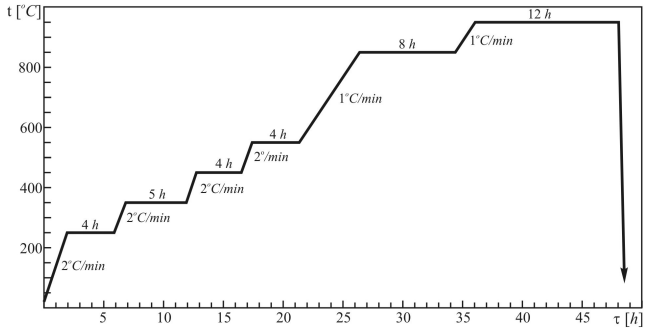

Fig. 1. Heat treatment profile during the synthesis of samples from the system $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$.

The Ag-As-S-Se films were prepared by pulsed laser deposition (wavelength = 248 nm, energy = 250 mJ/pulse, 30 ns pulse duration, spot size ~ 4 mm^2, frequency 20 Hz, angle of incidence of laser beam 45°). The analogous bulk samples were used as a target, at ~ 10^{-4} Pa. Cleaned glass microscope slides were used as substrates. The distance between the target and glass substrate was 5 cm.

Transmission measurements were carried out on a double-beam UV/VIS/NIR Perkin-Elmer spectrophotometer, model Lambda-950, in the range from 400 nm to 2500 nm, at a slit width of 1 nm. All experiments were

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performed at room temperature. The width of the light beam was ~ 3.5 mm. The bulk samples, prepared by mechanical treatment in the form of plane-parallel plates of different thickness, were polished to a mirror-like appearance using abrasives of different grain size. The optical absorption coefficient is calculated from the transmission measurements and sample thickness. The evaluation of the optical band gap, i.e. of the absorption edge, was made by extrapolation of the correlation between the absorption edge and the sample thickness.

3. Results and discussion

An illustration of the results of the transmission measurements in the VIS and IR regions for the composition $Ag_{0.5}(As_{40}S_{30}Se_{30})_{99.5}$ in the form of bulk and analogous films is shown in Fig. 2.

Although the newly synthesized glasses are of a markedly dark-grey colour, they are characterized by a relatively high transparency in a wide range of wavelengths in the IR range of the spectrum. As can be seen from Fig. 2, the value of the transmission of the film is by about 25% higher compared to that of the bulk sample. Such difference in the T values is expected, bearing in mind that the thickness of the thinnest plane-parallel plate was of the order of magnitude of less than 0.2 mm, whereas the thickness of the film was of the order of magnitude of μm. The absorption peak at 860.8 nm, present on the transmission curve for the bulk sample, is a consequence of the change of the detector during the recording.

Values of the optical band gap for the bulk and film samples. TABLE

Glass	E_g [eV], Bulk	E_g [eV], Film
$As_{40}S_{30}Se_{30}$	1.84 (5)	2.02 (9)
$Ag_{0.5}(As_{40}S_{30}Se_{30})_{99.5}$	1.78 (4)	1.94 (7)
$Ag_1(As_{40}S_{30}Se_{30})_{99}$	1.76 (5)	1.93 (9)
$Ag_2(As_{40}S_{30}Se_{30})_{98}$	1.68 (3)	1.90 (6)
$Ag_3(As_{40}S_{30}Se_{30})_{97}$	1.640 (19)	1.89 (5)
$Ag_5(As_{40}S_{30}Se_{30})_{95}$	1.609 (19)	1.805 (14)

The absorption edge for the bulk sample (679 nm) is shifted toward lower energies, compared to the value measured for the film of the same composition (639 nm) (Fig. 2). For the films, the E_g value is somewhat higher compared to that of the analogous bulk samples (Table). It can be noticed that this difference ranges from 0.16 eV for the composition with 0.5 at.% Ag, to 0.25 eV for the composition with 3 at.% Ag. However, it is a common phenomenon with chalcogenide glassy semiconductors that many properties of bulks are different from those of the films of the same composition. A similar value of the band gap for the film of the glass $As_{40}S_{30}Se_{30}$ was also reported by some other authors (2.01 eV) [6, 7] and (2.08 eV) [8]. The same trend of the change in the value of E_g with silver doping was also found in some other systems such as Ag–As–Se [9], Ag–As–S [10] and Ag–As–S–Se [1, 11].

The larger value of E_g can indicate on the increase in network connectedness in films, compared to analogous bulks. Increased interaction between the atomic species widens the separation between bonding and antibonding states and thus increases E_g. Furthermore, the energy of the conduction band edge is determined by the number of atoms per unit volume, where a decrease in that number leads to an increase in the energy of the conduction band edge and increases E_g. Previous leads to the assumption that some structural changes have occurred during the preparation of films; this will be in the focus of further investigations. The behaviour of the absorption edge as a function of the silver content in the composition of the material is also visible from the results presented in Fig. 3a. It shows a shift from the absorption edge of $As_{40}S_{30}Se_{30}$ at the value of transmission of 30%. The shift goes even up to 124 nm for the sample with 5 at.% Ag compared to the sample without silver.

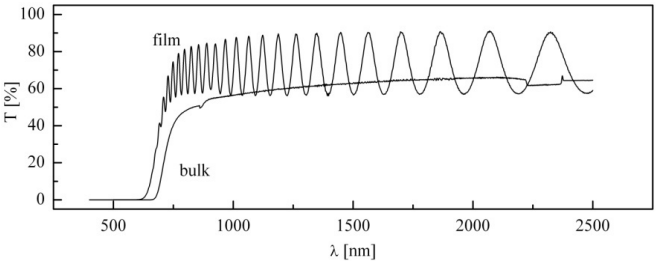

Fig. 2. Transmission spectra of the bulk and film glasses from the $Ag_{0.5}(As_{40}S_{30}Se_{30})_{99.5}$ system.

The dependence of the optical band gap on the silver content in the composition of the materials is presented in Fig. 3b.

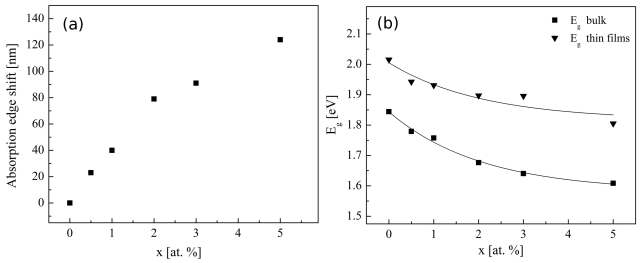

Fig. 3. (a) Absorption edge shift vs. silver content for the bulk samples at transmission value of 30%; (b) Dependence of E_g for the $Ag_x(As_{40}S_{30}Se_{30})_{100-x}$ bulk and film samples on silver content.

It can be seen that the increase in the silver content induces a decrease in the optical band gap for both bulk and film samples. This interdependence can be fitted by the following functions: $E_g = 1.583 + 0.261 \exp(-0.483x)$ for bulk samples and $E_g = 1.817 + 0.188 \exp(-0.483x)$ for film samples, where x is the silver content in the material. Although monotonicity of the previous functions is sometimes regarded as confirmation of the formation of solid solutions [12], based on previously published results on similar composition [13] phase separation can be

expected in the investigated system.

The obtained experimental results enabled the preliminary analysis of the structure of the amorphous matrix. Namely, it is known that the optical band gap in the chalcogenide glasses depends on the nature of the structural units participating in the structural network, i.e. on the nature and the strength of the bonds existing in a complex system [14]. According to Pauling, the energy of a heteropolar bond can be calculated using the energies of the homopolar bonds and electronegativities of the atoms involved, using the relation [15]: $D_{\mathrm{A\text{-}B}} = [D_{\mathrm{A\text{-}A}} D_{\mathrm{B\text{-}B}}]^{1/2} + 30\,(\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^2$, where $\mathrm{D_{A\text{-}A}}$ and $\mathrm{D_{B\text{-}B}}$ are the energies of the homopolar molecules expressed in the units of kcal/mol for the elements A and B, whereas the electronegativities of the corresponding atoms are given as χ_{A} and χ_{B}.

The bond energies in the investigated system were calculated using the following values: $D_{\mathrm{Ag\text{-}Ag}} = 163$ kJ/mol, $D_{\mathrm{S\text{-}S}} = 425.3$ kJ/mol, $D_{\mathrm{Se\text{-}Se}} = 330.5$ kJ/mol, and $D_{\mathrm{As\text{-}As}} = 386$ kJ/mol [16]. The calculated values of the bond energies for Ag-S, Ag-Se, As-S, and As-Se are 316.33 kJ/mol, 280.35 kJ/mol, 425.26 kJ/mol and 374.36 kJ/mol, respectively. These results made it possible to explain the changes of the optical band gap with the increase in the Ag content, based on the strength of the bonds formed in the heteropolar molecules. Namely, according to the Chemical Bond Approach [17], in order to decrease the bond energies it is more desirable to have formation of chemical bonds between the atoms of different elements. Thus, on the account of the stronger S-S (425.3 kJ/mol), Se-Se (330.5 kJ/mol) and As-As (386 kJ/mol) bonds, the addition of silver to the basic glass matrix yielded the formation of the weaker bonds Ag-S (316.33 kJ/mol), Ag-Se (280.35 kJ/mol), which, with the increase in the silver content, led to a decrease of the value of E_g.

4. Conclusions

The objective of the work was to analyze the transmission spectra of the newly synthesized glasses from the $\mathrm{Ag}_x(\mathrm{As_{40}S_{30}Se_{30}})_{100-x}$ system for $x = 0$, 0.5, 1, 2, 3 and 5 at.%. The recorded spectra showed a high degree of transparency in the IR spectral region. The behaviour of the absorption edge appeared to be influenced by the silver content, which was evident from its shift toward higher wavelengths with the increase in the silver content in the material. The introduction of silver into the matrix of the $\mathrm{As_{40}S_{30}Se_{30}}$ glass resulted in a decrease of the optical band gap, for both the bulk and film samples. The analytical form of this dependence can be fitted by exponential function.

Acknowledgments

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