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THE NATURE OF DC CONDUCTIVITY AND STRUCTURAL FEATURES OF GLASSES OF THE Ag – As – Se SYSTEM AS MATERIALS FOR PHOTONICS AND INTEGRAL OPTICS

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Abstract. The physical and chemical properties (density, microhardness, thermal effects, elastic modulus, dc conductivity, and the transfer number of silver ions) of glasses of the As – Se – Ag system along the AsSe – Ag and $AsSe_{1.5}$ – Ag sections were investigated. The transfer numbers of Ag^+ ions were determined by a direct method; from their changes, it was found that the glasses of the investigated sections have mixed ion-electronic conductivity. The threshold concentration of silver at which the ionic component of the conductivity becomes dominant over the electron was determined. The volume fraction of the fluctuation free volume was calculated using elastic modulus, microhardness, and glass-transition temperatures values. It was shown that Ag^+ ions do not experience serious steric hindrances during the process of migration.

Keywords: chalcogenide glass, dc conductivity, ionic conductivity, femtosecond laser, glass microhardness, transfer number

1. Introduction

The advent of femtosecond lasers has led to an increasing number of studies on laser recording of gradient 3D structures in optically transparent materials. The use of femtosecond pulses markedly expands the possibilities of modifying glassy materials by implementing multi-photon absorption in the microvolume of material around the focal point. With the precision focus of the laser beam, it is possible to carry out a local change in the structure of the optical media, and consequently, modify their physical and chemical properties with high resolution. The femtosecond laser is able to obtain a significant local change in the refractive index in glass and to form a waveguide (including in the volume of glass) [1,2], to create crystallized tracks and metal threads in the volume of glass [3-5], micro- and nano-cavities [6], which is undoubtedly of interest for the development of photonics and integrated optics technologies. It should be noted that existing studies are carried out mainly with oxide glasses, transparent in the visible region. the number of such researches for glasses based on oxygen analogs – sulfur, selenium, and tellurium, is just a few.

The unique optical properties of chalcogenide glasses are well known for a long time. Nevertheless, interest in chalcogenide glasses does not fade away and there are works devoted to the study of them as optical elements in photonics, as well as a new generation of information storage devices, which is also implemented using laser radiation, including femtosecond. There is no doubt that when obtaining gradient structures, it is necessary to take

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into account various diffusion processes. In this regard, the study of the migration characteristics of glasses is of fundamental importance.

This work is devoted to the study of the physical and chemical properties of the As – Se – Ag glass system enriched with silver. The research aimed to determine the influence of the features of the glass structure on the migration characteristics of the Ag^+ ion. Ag^+ ions determine both the nature and the conductivity of glasses under the influence of various factors – applied voltage, temperature, concentration, thermal history, and temperature gradient.

The research is aimed at obtaining information on the migration processes of monovalent ions in chalcogenide glasses under the influence of femtosecond laser radiation. According to [7], laser radiation in the glass leads to the appearance of an induced potential difference between the high-temperature region at the focal point of the laser beam and the cold boundaries of the affected region. This is the reason for the noticeable migration of monovalent ions from the focal point to the edges of the laser action area, which causes a local change in some physical and chemical properties of the glass. Processes of this kind are not only of theoretical but also practical interest since laser processing can form a gradient optical structure in a single technological stage.

However, this migration of monovalent ions under the influence of the induced potential is hindered by a counter process – the migration of the same ions from the "cold" region to the "hot" one (closer to the focal point of the laser beam). This is a manifestation of the Soret effect, well known for gases and liquids.

A relatively small number of works [8] are devoted to the study of thermal diffusion processes in solid oxide glasses, which is mainly determined by methodological difficulties when working with such a fragile material as glass (exclusively oxide) when creating a high-temperature gradient over the sample. To understand the physical essence of the processes occurring under the action of laser radiation, the study of the migration characteristics of the Ag + ion in model and relatively simple in composition and structure chalcogenide glasses of the Ag – As – Se system is of great importance.

2. Experimental technique (Methods)

Chalcogenide glasses were synthesized in an electric furnace from elementary substances of semiconductor purity in evacuated quartz ampoules with stirring at a maximum temperature of 950°C for 4-6 hours. The sample weight was 5-8 grams. Elemental selenium was preliminarily distilled in a vacuum to remove impurities of hydrocarbons (carbon) and water. The glasses were tempered in the air or ice water, depending on the composition; the subsequent annealing to remove residual stresses was carried out at a temperature ~ 15°C below T_g for 4-5 hours. As a result, homogeneous monolithic samples were obtained without signs of crystallization.

Electrical conductivity was measured at direct current using a Wheatstone bridge (P4060) in heating and cooling mode. Silver amalgam (anode) and mercury (cathode) were used as electrodes. In all cases, the temperature dependence of the specific electrical conductivity (σ) was a straight line, no hysteresis was observed ($-\log\sigma = f(1/T)$). The measurement error did not exceed ± 5%.

The activation energy of electrical conductivity (E_σ) was calculated using the Arrhenius equation:

$$\sigma = \sigma_0 exp\ (- E\sigma /\ 2kT), \tag{1}$$

where σ_0 is the preexponential factor, k is the Boltzmann's constant, and T is the temperature.

Keysight N5769A stabilized power supplies, X603 electrolytic integrator, and an Instek GDM-8145 multimeter were used to conduct electrolysis and determine the transfer numbers of silver ions.

The density of the samples was determined by the method of hydrostatic weighing in CCl_4 with an accuracy of $\pm 5 \times 10^{-4}$ g using a Vibra HT-224RCE analytical balance, the microhardness by the method of indentation of a diamond pyramid (according to Vickers) was determined by PMT-3M (LOMO) device with an accuracy ± 5%.

The speed of propagation of longitudinal and transverse ultrasonic waves was measured using a UD 2-12 flaw detector. Thermal effects were determined on derivatographs Q-1500 (Hungary, "MOM") and "Termoscan-2M" (Analitpribor) in heating mode; fused quartz and Al_2O_3 powders were used as standards; the weighed portion of the studied glass was 0.5 g, the heating rate was 5-15 deg/min. Measurements accuracy was ± 5°C.

3. Results and discussion

Physical and chemical properties. The area of glass formation of arsenic-selenium-silver glasses has been studied systematically for a relatively long time (for more details see [9,10]). Different authors obtained two noticeably different regions of glass formation, separated by regions of compositions in the crystalline and glass-crystalline states. The region in which glassy samples can be obtained under not very severe conditions consists of two parts (Fig. 1). Thus, according to the sections $AsSe_{0.8}$, AsSe, $AsSe_{1.5}$ – Ag, it is possible to obtain homogeneous glasses, and from the sections, $AsSe_{2.5}$, $AsSe_4$ – Ag with a high selenium content, inhomogeneous glasses [9,10] are obtained.

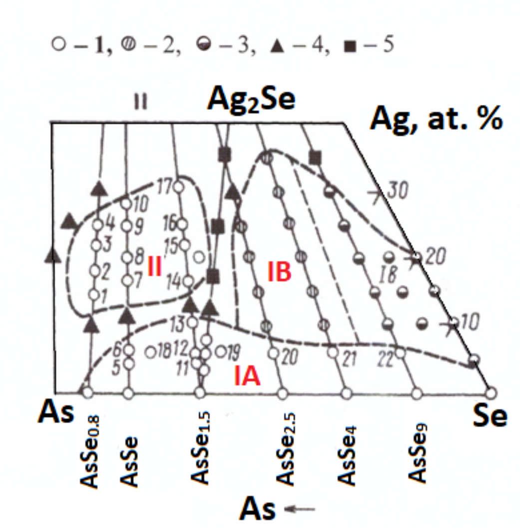

Fig. 1. The region of glass formation in the Ag – As – Se system according to [9 and 10]. 1 – homogeneous glasses, 2 – heterogeneous glasses, 3 – liquidating glasses, 4 – crystals, 5 – glass crystals

The regions of homogeneous and inhomogeneous glasses are separated by crystalline and glass-crystalline compositions along the As_2Se_3 – Ag_2Se section. This section contains several ternary compounds ($AgAsSe_2$, Ag_7AsSe_6, Ag_3AsSe_3), which have not been obtained in glassy form; along with the binary compound Ag_2Se, they are not glass-forming agents in the Ag – As – Se system. However, the ability of all three components to interact and form complex structural chemical units (s.c.u.) contributes to glass formation in this system.

Region **IA** mainly corresponds to the field of crystalline selenium and As_2Se_3 crystallization. Silver in these glasses plays the role of an impurity, as the content of which increases in the glass structure, the accumulation of s.c.u. $AgAsSe_2$ occurs, which leads to a significant increase in its crystallization ability. Compositions with a predominant content of $AgAsSe_2$ do not form glasses at all. Region **IB** corresponds to the area of liquation.

The region of homogeneous glasses (Fig. 1, II) is in the field of arsenic evolution. For glass formation in this region, the ability of arsenic to easily pass into an amorphous state is of great importance. Glass formation in this area is also facilitated by the complex structural and chemical composition of alloys, in which the formation and interaction of at least four types of spatially different structural chemical units (s.c.u.) complicate the separation of crystalline phases from the glass melt [9,10]. This region of compositions, which easily forms homogeneous glasses, was chosen in this study.

Glasses of the following sections were selected as objects of study: AsSe – Ag and $AsSe_{1.5}$ – Ag. Some properties of the synthesized glasses are presented in Table 1. It should be noted that the data of this work are in satisfactory agreement with the literature data (Table 1).

Table 1. Some physical and chemical properties of glasses from sections AsSe – Ag and $AsSe_{1.5}$ – Ag

Section	Ag, at. %	d, g/cm^3	H, kgf/mm^2	d,* g/cm^3	T_g, °C	H*, kgf/mm^2	T_g*, °C
AsSe	-	4.55	136	4.48	171	130	164
AsSe – Ag	5.0	4.68	110	4.71	155	95	148
	6.0	-	-	4.76	-	90	140
	10.0	4.93	107	-	158	-	-
	15.0	5.16	118	-	167	-	-
	16.7	-	-	5.30	-	99	150
	20.0	5.43	138	5.50	171	112	160
	25.0	5.69	155	5.86	178	147	172
	28.0	-	-	6.04	-	161	176
$AsSe_{1.5}$	-	4.550	150	4.59	172	150	169
$AsSe_{1.5}$ – Ag	1.0	4.550	150	-	170	-	-
	3.4	4.800	153	-	-	-	-
	5.0	4.862	142	4.85	155	150	152
	10	5.105	155	5.09	147	138	146
	15	5.309	127	5.62	150	146	150
	20.0	5.581	134	-	150	-	147
	25.0	5.776	115	5.76	155	150	149
	30.0	6.015	110	6.04	170	155	158

(d – density, H – Vickers microhardness, T_g – glass-transition temperature. * – data from [9,10])

The character of the H and T_g changes with an increase in the silver content depends both on the arsenic/selenium ratio and on the position in the region of glass formation. For example, for glasses from the $AsSe_{1.5}$ – Ag section, the first silver additions exhibit a sequential decrease in microhardness, while the T_g values, after a slight decrease, practically do not change at a silver content from 5 to 25 at.%.

Determination of the nature of conductivity. Until the mid-seventies of the last century, it was believed that all chalcogenide glasses are *p*-type semiconductors, and only by the eighties the first works appeared, indicating the presence of ionic conductivity in certain silver-containing compositions of some chalcogenide systems [9-10]. It should be noted that the presence of ionic conductivity and the determination of the transport numbers of current carrier ions for a number of silver-containing chalcogenide glasses was carried out using a highly simplified electromotive force (emf) method [10,11], and the values of the transport numbers of Ag^+ ions obtained using this method, in our opinion, cannot be considered indisputable.

The essence of the emf method is to create a concentration element of the following type:

C, Ag $|$ CG_{Ag} $|$ Ag_2S $|$ S, C,

where CG_{Ag} is the investigated silver-containing chalcogenide glass, C is graphite contact. Upon contact of the studied glass with metallic silver on the one hand and elemental sulfur on the other, according to [10,11], a redox reaction begins in the element, the emf of which is fixed and compared with the emf of the reaction:

$$2Ag_m + S_m = (Ag_2S)_m, \qquad (2)$$

which occurs in this system.

The cell emf values obtained experimentally (E_{exp}), as a rule, are lower than the theoretical value (E_{theor}): the mean transfer numbers of silver ions (t_{Ag+}) are determined from the ratio of the experimentally obtained emf of the indicated reaction and its theoretical value:

$$t_{Ag+} = E_{exp} / E_{theor}. \qquad (3)$$

Thus, for the $AsSe_{1.5} – Ag_x$ glass system with a silver content from 10.7 to 30.6 at.% (in the temperature range from 30 to 800°C), the values of the transfer numbers of Ag^+ ions lie in the range 0.70-0.75 [10,11].

It should be noted that the emf method itself does not have any theoretical justification, and, most importantly, the reaction that may occur in the element used is postulated and has no real experimental confirmation. Some time ago, we studied the nature of conductivity and determined the transport numbers of current carrier ions in a number of glassy systems, including chalcogenide ones, using the direct method - the weight modification of the Hittorff method - the modernized Tubandt method, which has shown its validity for the noted problem [12].

The classical Hittorff technique, developed for solutions, involves the determination of the transfer numbers of current carrier ions through the analytical determination of the concentration change in the near-electrode regions of the electrolyte after passing a known amount of electricity. Nevertheless, the real values of the transport numbers of current carrier ions cannot be determined by this method (or it is extremely difficult), since the change in the concentration of carriers in the near-electrode spaces involves ions surrounded by a hydration shell. In other words, during migration, ions carry with them attracted solvent molecules, which affects the change in the concentration of the electrolyte and affects the result obtained.

The Tubandt method was developed for solids and is devoid of this drawback, since migration in a solid of any associate is unlikely, and the result obtained by this technique allows one to obtain the true transfer numbers of charge carrier ions. So, in the case of the transfer of electricity by ions of the same sign (a cation or anion, or an ion and an electron, i.e., when migration processes are accompanied by a transfer of mass in one direction), the transfer numbers of these ions can be determined by the change in the mass of the electrodes between which the investigated sample after electrolysis. In the classical version, the same solid electrolyte was used as these electrodes (cathode and anode), which was the subject of research [13].

If a known amount of electricity is passed through the electrolyte, then the transport numbers of carrier ions can be determined from the ratio of the decrease in the weight of the anode (and the increase in the weight of the cathode) and the amount of carrier released as a result of electrolysis (according to Faraday's law). In this case, the condition for the correct conduct of the experiment is the constancy of the weight of the test sample before and after electrolysis should not change. In this work, a PTFE thermocell was used to determine the transfer numbers of silver ions (shown in Fig. 2). A silver wire dipped into a silver amalgam was used as an active anode, and pure mercury was used as a cathode. The cell is detachable, allows quantitative weighing of electrodes before and after electrolysis.

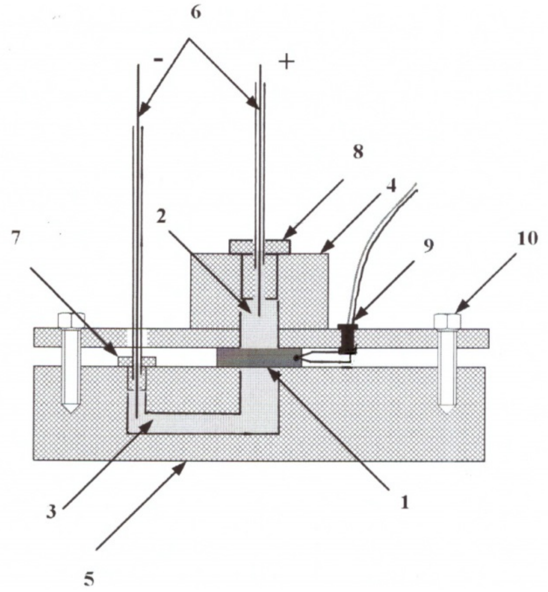

Fig. 2. Thermocell with active electrodes for determination of the transfer numbers of glassy solid electrolytes.
1 – glass sample, 2 – amalgam anode with a silver wire (+), 3 – mercury cathode (-),
4 – upper part of the cell, 5 – lower part of the cell, 6 – electrodes in metal tubes, 7, 8 – plugs,
9 – thermocouple, 10 – connecting screws

Electricity is supplied through silver wires passing through thin nickel tubes. The mercury electrodes and sample are weighed before and after the experiment. The transport numbers of Ag + ions are determined from the ratio of the amount of silver obtained as a result of a known amount of electricity passed through the sample and theoretically calculated according to Faraday's law. The experimental conditions and some of the results obtained within the framework of this study are presented in Table 2. It should be noted that the presented results are consistent with the literature data [9,10,12].

Table 2. Experimental conditions and the values of the transfer numbers of silver ions, obtained by the Hittorff method

Composition	x	Ag, at.%	t, °C	Q, C	$\Delta m_{average} \cdot 10^5$, g	t_{Ag+}
$AsSe_{1.5} – Ag_x$	0.064	2.5	100	1.01	40	0.3_5 *
	0.13	5.0	80	1.1	70	0.5_8 *
	0.28	10.0	80	0.8	70	0.7_9 *
	0.44	15.0	60	1.4	130	0.8_3 *
	0.63	20	60	3.1	304	0.8_8 *
	0.83	25	80	2.8	277	0.8_8 *
	0.28	10	110	2.5	215	0.7_7
	0.44	15	110	1.95	175	0.8_1
	0.63	20	100	2.13	205	0.8_5
	0.83	25	100	1.66	165	0.8_9

(Here: t is the temperature of the experiment, Q is the amount of passed electricity, $\Delta m_{average}$ is the average change in the mass of electrodes after electrolysis, t_{Ag+} is the transfer numbers of silver ions, (*) – data obtained earlier, see [12]).

The electrical conductivity of glasses in the arsenic-selenium-silver system varies widely depending on the ratio of all three components, but silver has a decisive influence. When the first 10 at. % silver is introduced into glassy $AsSe_{1.5}$, the conductivity increases by more than five orders of magnitude. Glasses of sections AsSe – Ag and As_2Se_3 – Ag_2Se behave similarly.

For the glasses with a constant Ag (for example, ~ 6 at.%), a conductivity decrease was observed with an increase in the As/Se ratio. The complex structural and chemical composition complicates the process of electrical transfer in glasses of this system (almost all glasses of the As – Se – Ag system have underestimated $log\sigma o$ values), with the exception of glasses of the As_2Se_3 – Ag_2Se and As_2Se_3 – Ag sections, which have the simplest structure, the conductivity of which approaches the through [9,10] (for more details see Table 3).

In addition, for glasses of the As-Se-Ag system, with an increase in the silver content, not only the magnitude but also the conduction mechanism changes: the values of the silver transfer numbers become more than 0.5. With an increase in the silver content to 5-10 at. %, The type of current carriers changes: the purely electronic conductivity, characteristic of the initial arsenic selenides, is replaced mainly by the ionic one [9,10,12].

Table 3. Electrical properties of glasses in sections AsSe – Ag and $AsSe_{1.5}$ – Ag

Section	Ag, at. %	$-lg_{\sigma}$, ohm$^{-1}\cdot$cm^{-1}	E_{σ}, eV	$-lg\sigma_0$	$*-lg_{\sigma}$, ohm$^{-1}\cdot$cm^{-1}	$*\ E_{\sigma}$,eV	$*-lg\sigma_0$
AsSe – Ag	5.0	5.8	1.15	1.7	12.2	1.45	-0.3
	6.0	-	-	-	8.8	1.07	-1.0
	10.0	4.0	0.93	2.2	-	-	-
	15.0 (17*)	4.1	0.67	2.4	4.8	0.72	1.6
	20.0	3.9	0.63	2.4	4.6	0.68	1.5
	25.0	3.9	0.63	3.0	4.4	0.65	1.4
	30.0 (28.6*)	-	-	-	3.9	0.56	1.4
$AsSe_{1.5}$ – Ag	1.0	12.9	1.81	2.4	12.8	1.80	2.2
	3.4	11.2	1.77	2.3	-	-	-
	5.0	9.7	1.30	2.7	9.8	1.36	2.0
	10 (11*)	6.9	0.83	3.3	7.6-7.8	1.10	1.0
	15 (17*)	6.4	0.85	3.3	6.3	0.90	2.2
	20.0 (22*)	5.3	0.80	2.3	5.6	0.81	1.2
	25.0 (24*)	4.9	0.65	1.7	5.5	0.78	1.3
	30.0	4.2	0.63	1.8	4.6	0.70	2.0

($-lg_{\sigma}$ is electrical conductivity at room temperature, E_{σ} is the activation energy of electrical conductivity, $log\sigma_0$ – preexponential factor. (*) – generalized literature data according to [9,10] and the closest compositions to those investigated in this work)

To determine the ratio between the ionic and electronic components of conductivity in glasses enriched with a silver (with content from 10 to 30 at.%) in [9,10] in the temperature range from 30 to 80°C, the transfer numbers of Ag^+ ions were determined using the emf method. The obtained values of the average transfer numbers of Ag^+ ions lie in the range from 0.75 to 0.70. Moreover, with an increase in the silver content, the values of the transfer numbers slightly decrease. Nevertheless, despite the relatively low reliability of the indicated emf method, it is noted that in glasses of the As – Se – Ag system with a silver content of more than 15 at%, the main type of charge carrier changes: predominantly electronic conductivity is replaced mainly by ionic conductivity [9,10]. This conclusion is partially confirmed by a joint study of the diffusion of silver ions and the electrical conductivity of glasses of this system, described in [11]. It should be noted that in chalcogenide glasses in general, and the As – Se – Ag system in particular, diffusion processes have practically not been studied and we have not found other works on this topic. In [11], a rather narrow concentration interval was studied along the AsSe – Ag and $(AsSe_{1-x})_{0.8}$ – $Ag_{0.2}$ sections (with a constant silver content). The calculated diffusion coefficients of Ag^+ ions (at 100°C) for the studied glasses are in the range $(2.5\text{-}7.9)\cdot10^{-9}$ and $(5.0\text{-}0.8)\cdot10^{-9}$ cm^2/s, respectively. In this case, the activation energy of diffusion for glasses from the AsSe – Ag section is constant. While in glasses $(AsSe_{1-x})_{0.8}$ – $Ag_{0.2}$ the activation energy of diffusion decreases from 0.74 to 0.57 eV and correlates with a decrease in the selenium content.

For all studied glasses, the activation energy of electrical conductivity (E_σ) and the activation energy of diffusion practically coincide in magnitude, which allowed the authors to conclude the identity of the nature of electrical and mass transfer [11].

In the study of diffusion, the question of the migration mechanism is of particular interest. To elucidate the mechanism of migration of Ag^+ ions in the studied chalcogenide glasses, we analyzed the value of the correlation factor (f) in the Nernst-Einstein equation: for all glasses, with an increase in the silver content, there is a slight decrease in f values (from 0.8 to 0.5), and for glasses with a constant silver content – with a decrease in selenium content. The obtained values do not allow an unambiguous answer to the question of the mechanism of silver migration in these glasses, since according to [14], these values can be attributed to both relay and vacancy mechanisms and direct interstitial mechanisms.

Structural features of ionic conductivity. The electrical properties of glasses of the As-Se-Ag system are satisfactorily described from the point of view of the model of the micro-inhomogeneous structure of glass, which, from a unified standpoint, describes the physical and chemical properties of both oxide and chalcogenide glasses. According to this model, at high temperatures in the melt, a selective interaction of the components of the initial charge occurs, during which structural and chemical groups are formed.

These groups in multicomponent glasses determine the physical and chemical properties of future solid glasses. In this case, all structural fragments (s.c.u.) can be divided into two groups: polar and non-polar. Non-polar s.c.u. (which do not dissociate and block both possible processes of dissociation of current carrier ions and their subsequent migration in their environment) include fragments linked by a non-polar or weakly polar covalent bond. These s.c.u. are mainly involved in the formation of a three-dimensional glass network: these include $BO_{3/2}$, $SiO_{4/2}$, $PO_{4/2}$, $AsS_{3/2}$, $AsAs_{3/3}$, selenium chains, etc. In a medium formed mainly by these fragments (with low dielectric constant), dissociation of ionogenic chemical units and subsequent migration of current carrier ions is hindered.

Polar (ionogenic) fragments have in their composition a bond with a significant ionic component: these are fragments of the type $Na^+[BO_{4/2}]^-$, $Li^+O^-SiO_{3/2}$, $Ag^+Se^-AsSe_{2/2}$, etc. Consequently, the environment formed by them has a relatively high dielectric constant and to some extent, they behave like electrolyte solutions. That is, in glass, these fragments, on the one hand, dissociate with the formation of current carrier ions, on the other hand, the medium formed by similar chemical units contributes not only to dissociation processes (in contrast to nonpolar chemical units) but also facilitates the subsequent migration of these ions with lower energy costs. It is clear that the concentration of polar agricultural units is proportional to the number of components with increased bond ionicity introduced into the glass composition, i.e. those that contain potential current carrier ions (both cations and anions).

At low concentrations of components with increased bond ionicity, the regions formed by polar s.c.u. are isolated from each other by the medium of nonpolar chemical units. Glasses with such a structure have no ionic conductivity. The reduced electrical conductivity of these glasses is limited both by the small number of free current carriers and by the need for their migration in the main nonpolar medium, which requires overcoming high activation barriers. The ionic conductivity in glasses appears when isolated regions of polar s.c.u coalesce with each other and form continuous areas that permeate the entire volume of the glass. At the same time, not only the number of current carriers increases (due to the dissociation of polar chemical units) but also the activation energy of electrical conductivity decreases due to their migration in a polar medium.

To determine the critical concentration of polar chemical units, at which they merge into continuous channels, penetrating the glass throughout the entire volume, thereby violating the blockade of through migration of ions and the appearance of ionic conductivity, the parameter "degree of blocking" (γ) was adopted. γ is determined by the ratio of the concentration of non-polar and polar s.c.u. by the following equation:

$$\gamma = \frac{polar\_s.c.u.}{non-polar\_s.c.u.}. \tag{4}$$

For a number of oxides and halogen-containing glasses, the blockade of ion migration by a medium from nonpolar chemical elements is observed at values of γ~6: in this case, a nonpolar fragment ceases to fit between two polar fragments. In other words, when $\gamma > 6$, polar s.c.u. are isolated by non-polar s.c.u. and ionic conductivity is practically absent. At values $\gamma \leq 6$, polar s.c.u. are combined into a continuous sublattice, their degree of dissociation increases, and the dissociated ions acquire the ability to migrate throughout the glass volume with lower energy consumption in the medium formed by them. With an increase in the concentration of the ionogenic component and the degree of its dissociation, ionic conductivity appears. Therefore, knowing the probable structural-chemical composition of multicomponent glasses, one can calculate the degree of blocking and judge both the presence of ionic conductivity in them and the boundary compositions in which this conductivity appears. (A more detailed model of the microheterogeneous structure of glass and its application for a wide range of glasses is described in [15]). However, in contrast to the description of the unit cell of a crystal, for which there are direct experimental methods, there are no such direct methods for the structural-chemical unit of multicomponent glass. Complex s.c.u. in glasses are the model that reflects some approximation to real structural units in the glass.

As mentioned above, in the As – Se – Ag system, the compositions along the sections AsSe – Ag and $AsSe_{1.5}$ – Ag with a silver content of up to 30 at. % lie in the crystallization field of the ternary compound $AgAsSe_2$, with a congruent melting point of 410°C, and As_2Se_3 [9,10]. We chose these sections because, despite a certain deficiency of selenium, it is possible to introduce up to ~ 30 at. % of silver into these glass compositions. In addition, at Ag concentration less than 30 at. % the only polar fragments are s.c.u. type $Ag^+Se^-AsSe_{2/2}$, corresponding to the compound $AgAsSe_2$, in which the Se – Ag bond has an approximately (6-8)% higher degree of ionicity than, for example, the As – Se bond. Assuming that all silver introduced into the glass composition of the investigated sections binds to polar s.c.u. type $Ag^+Se^-AsSe_{2/2}$, and all other fragments – As_2Se_3, AsSe, and $AsAs_{3/3}$ – are non-polar and blocking, we calculated the degree of blocking γ. For glasses of the $AsSe_{1.5}$ – Ag section, the results of such calculations are presented in Table 4 and Fig. 3.

Figure 3 shows that with an increase in the silver content, all electrical parameters change rather smoothly, while near the compositions with 4.5-5.0 at. % of silver, a sharp change in the slope of the concentration dependence of γ is observed. The last one can be explained by the actual violation of the blockade of ion migration Ag^+. This is confirmed by the values of the transfer numbers of these ions: in glasses containing more than 4-5 at. % of Ag ($\gamma \approx$ 4.5-5), the values of the transfer numbers of silver ions exceed 0.5; the nature of the conductivity changes from predominantly electronic to predominantly ionic.

Table 4. Probable structural-chemical composition and magnitude of the degree of blocking (γ) for glasses from the $AsSe_{1.5}$ – Ag section

Glass composition	Ag, at. %	Probable structural and chemical composition	γ
$AsSe_{1.5}$ $Ag_{0.026}$	1.04	$0.05\ AgAsSe_2 \cdot 0.9As_2Se_3 \cdot 0.05AsSe$	19.0
$AsSe_{1.5}$ $Ag_{0.21}$	7.9	$0.3\ AgAsSe_2 \cdot 0.4As_2Se_3 \cdot 0.3AsSe$	2.33
$AsSe_{1.5}$ $Ag_{0.33}$	11.8	$0.4\ AgAsSe_2 \cdot 0.2As_2Se_3 \cdot 0.4AsSe$	1.5
$AsSe_{1.5}$ $Ag_{0.5}$	16.7	$0.5\ AgAsSe_2 \cdot 0.5AsSe$	1.0
$AsSe_{1.5}Ag_{0.61}$	19.6	$0.55\ AgAsSe_2 \cdot 0.25AsSe \cdot 0.05AsAs_{3/3}$	0.55
$AsSe_{1.5}$ $Ag_{0.75}$	23.1	$0.86\ AgAsSe_2 \cdot 0.14AsAs_{3/3}$	0.16

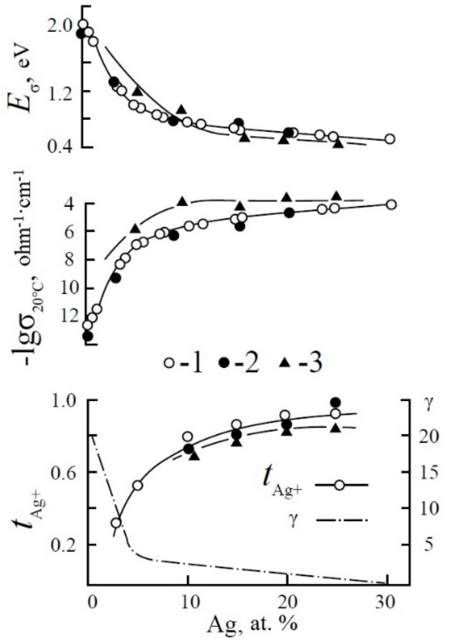

Fig. 3. Concentration dependences on the electrical conductivity parameters (lg_σ), the transfer numbers of Ag^+ ions (t_{Ag^+}), and the degree of blocking (γ) for glasses $AsSe_{1.5}$ – Ag (2) and AsSe – Ag (3). (1) – literature data [9,10]

In this concentration range, isolated nonpolar s.c.u. areas of polar s.c.u. type $Ag^+Se^-AsSe_{2/2}$ for the first time merge into fragments penetrating the entire glass fragments. This is probably due to the dipole-dipole interaction with the formation of quadrupoles of the following type:

$$\left[\begin{array}{l} Se_{2/2}As-Se^{-}Ag^{+} \\ \qquad\qquad \mathrm{Ag}^{+}Se^{-}-AsSe_{2/2} \end{array}\right]$$

Their formation causes a change in the main type of current carrier. At a higher silver concentration, there are more and more such quadrupoles, the conductivity of glasses increases, and the transfer numbers reach their maximum values of 0.86-0.88 for compositions at the boundary of the glass formation region, which, as expected, is limited by the release of crystalline arsenic. For glasses of the section AsSe – Ag, depleted in silver, the study of the electrical properties and determination of the transfer numbers of silver ions were not carried out. The electrical properties and transfer numbers for silver-enriched glasses from this section are also shown in Fig. 3.

Estimation of the conductivity value from the concentration of current carriers. Since the electrical conductivity of metal-containing chalcogenide glasses noticeably exceeds the electrical conductivity of other classes of glasses – silicate, borate, and phosphate, it is of interest to evaluate the conduction mechanism depending on the concentration of current carriers and their structural and chemical features and compare the results with similar data for other types of glasses [22]. For this, it is advisable to determine the activation volume of migration of the silver cation in chalcogenide glasses with conductivity with their participation. The activation volume of migration is a certain effective parameter that includes not only the thermodynamic characteristics of the migration process, the geometric dimensions of the ion migrating in a solid but also the geometric dimensions of structural defects along which this migration is carried out. This approach was theoretically developed for crystals [16] but has been successfully applied to a number of oxide glasses. However, such studies are extremely few, since they require unique installations that allow one to measure the electrical conductivity of samples when high pressure is applied (tens of thousands of atmospheres). Under the action of high pressure, the electrical conductivity of ion-conducting materials decreases, while in the case of conductors with electronic conductivity, its growth is observed [17,18]. It should be noted that, as applied to glasses, it is possible to use other parameters instead of the activation volumes of migration - the volumes of fluctuation microcavities, which are much easier to determine, but for several classes of oxide glasses these parameters practically coincide (for more details, see, for example, [12,19]). In accordance with Eyring's theory [20], the electrical conductivity of solutions is given by:

$$\sigma = \sigma_o exp\left(-\Delta G^{\#} / RT\right), \tag{5}$$

where σ is the specific electrical conductivity, $\Delta G^{\#} = \Delta H^{\#} + P\Delta V^{\#}$ – ($\Delta G^{\#}$ is the original notation, according to [20]) is the activation free energy of the process – a value identical to the activation energy of electrical conductivity (E_σ).

The multiplier in the exponent determines the probability of the activated complex existence. The activated complex in this case is some effective value characterizing the migration process, i.e. the number of particles with the energy required for the process of dissociation of an ionogenic structural fragment and subsequent migration of the dissociated ion.

Parameters $\Delta H^{\#}$ and $\Delta V^{\#}$ are the minimum values of molar enthalpy and molar activation volume required for the formation of this activated complex [20], which can be determined from the following thermodynamic equalities:

$$\Delta H^{\#} = \left[\frac{\partial(\Delta G^{\#}/T)}{\partial(1/T)}\right]_P = -R\left[\frac{\partial \ln\sigma}{\partial(1/T)}\right]_P, \tag{6}$$

$$\Delta V^{\#} = \left[\frac{\partial(\Delta G^{\#})}{\partial P}\right]_T = -RT\left[\frac{\partial \ln\sigma}{\partial P}\right]_T, \tag{7}$$

where R and T are gas constant and temperature. The numerical values of $\Delta H^{\#}$ can be determined from the temperature dependences of electrical conductivity at constant pressure, and the values of $\Delta V^{\#}$, respectively, from the data on the effect of high pressure (uniform compression) on electrical conductivity under isothermal conditions.

The free activation energy of electrical conductivity $\Delta G^{\#}$ (in this work, E_σ) can be divided into two components and presented in the following form:

$$\Delta G^{\#} = \frac{1}{2}\Delta G_d + \Delta G_a, \tag{8}$$

where ΔG_d is the free energy of dissociation, and ΔG_a is the free activation energy of ion displacement.

Then the expression for the temperature dependence of the electrical conductivity can be written in the following form:

$$\sigma = \sigma_o exp\left[-\frac{1}{RT}\left(\frac{\Delta G_d}{2}+\Delta G_a\right)\right]. \tag{9}$$

Taking into account the ratio

$$\Delta V^{\#} = \left(\frac{\partial \Delta G^{\#}}{\partial P}\right)_T, \tag{10}$$

total activation volume will be equal to

$$\Delta V^{\#} = \frac{1}{2}\Delta V_d + \Delta V_a, \tag{11}$$

where ΔV_d is the partial activation volume of the formation of a dissociated ion (vacancy), and ΔV_a is the partial activation volume of the movement of this ion.

There is a correlation between $\Delta H^{\#}$ and $\Delta V^{\#}$ of the form $\Delta V^{\#}$ = const·$\Delta H^{\#}$ [16] and this constant has the dimension of compressibility, therefore, the expression for $\Delta V^{\#}$ can be written in the following form:

$$\Delta V^{\#} = \xi \cdot \vartheta \cdot \Delta H^{\#}, \tag{12}$$

where ϑ is the compressibility (in the first approximation, χ_S is the adiabatic compressibility), ξ is a dimensionless constant, the value of which can be determined from the following relation:

$$\xi = \frac{2}{3}\left(\frac{1+\mu}{1-2\mu}\right). \tag{13}$$

Then the theoretical value of the volume of the activated complex ($\Delta V^{\#}_{th}$) can be calculated through the elastic modulus from a ratio:

$$\Delta V^{\#}_{th} = \frac{2(1+\mu)}{E}\cdot \Delta H^{\#}, \tag{14}$$

where E is Young's modulus, μ is Poisson's ratio.

Earlier, we investigated the electrical conductivity of several chalcogenide glassy compositions under the influence of high (up to 6000 atm) pressure [12,19]: it was shown that glass of the $AgAsS_2$ composition, with purely cationic conductivity for silver (t_{Ag+} = 0.999), the electrical conductivity under high pressure decreases, while the conductivity of the compositions $Ag_{0.8}Tl_{0.2}AsS_2$ (t_{Ag+} = 0.86) and $Ag_{0.63}AsSe_{1.5}$ (t_{Ag+} = 0.88) increases. It is impossible to calculate the activation volume for mixed ion-electronic conductors, but for the $AgAsS_2$ composition, the calculated activation volume is $\Delta V^{\#}$ = 4.0 ± 1.0 cm^3/mole.

It was of interest to compare the values of activation volumes obtained from data on the effect of high hydrostatic pressure on electrical conductivity with values calculated through elastic modulus. It is known from the literature that these values are close for different classes of glasses, for example, silicate or phosphate glasses [17]. Previously, we measured the propagation velocity of longitudinal and transverse ultrasonic waves and calculated elastic modulus, including for $AgAsS_2$ glass [12]. It is known that the process of compaction of the structure of a solid (including glass) under the influence of all-round (hydrostatic) compression is by its nature identical to compaction in a small volume under the influence of an indenter when determining the Vickers microhardness by the indentation method [21]. This process of structure compaction can be considered as the process of liquidation of fluctuating microcavities in glass, which can ultimately be described within the framework of the free volume theory. Within the framework of this theory, it is possible to satisfactorily describe and explain the various properties of glasses and their melts.

It is known that the volume of solid glass is always greater than the volume of a crystal of the same composition. The reason for the increase in the volume fraction of the fluctuation free volume (f_g) in the glass is the freezing of the structure of the glass-forming melt during the glass transition, and the presence of bridging atoms with distorted bond angles in the glass is precisely the main reason for this phenomenon. The fluctuation volume of amorphous (glassy) substances is caused by freezing in the process of glass transition, the displacement of structural fragments from equilibrium positions [22]. Therefore, f_g is a floating parameter and directly depends on the thermal history of a particular sample.

In general, the free volume can be used to judge the degree of loosening of the glass structure, which partially determines steric hindrances in the process of ion migration in solid glass and to some extent explains the fact that the conductivity of glass is usually higher than the conductivity of a crystal of the same composition.

The volume of fluctuation microcavity in glass (V_h) can be calculated in terms of elastic modulus, Vickers microhardness, and softening temperature by the following expressions:

$$V_h = \frac{3(1-2\mu)}{f_g} \cdot \frac{kT_g}{E}, \tag{15}$$

$$V_h = ln\left(\frac{1}{f_g}\right) \cdot \frac{kT_g}{H}, \tag{16}$$

where H is the microhardness and f_g is the volume fraction of the fluctuation free volume "frozen" below the glass-transition temperature.

The value of f_g can be determined through the elastic modulus (E, μ) from the following relationship:

$$f_g \cdot ln\left(\frac{1}{f_g}\right) = \frac{(1-2\mu)^2}{2(1+\mu)}. \tag{17}$$

Based on the presented expressions, we determined the values of these parameters. The f_g values obtained for chalcogenide glasses are approximately 2-3 times lower than for oxide glasses (f_g values, for example, for silicate glasses, are in the range 0.027-0.030) [23,24]. It is known that with an increase in the degree of connectivity of the glass network, an increase in Young's modulus and Poisson's ratio is observed, i.e. low values of μ correspond to increased elasticity of the material. In this case, it can be concluded that the degree of cohesion of chalcogenide glasses decreases in comparison, for example, with silicate glasses. From the values of elastic constants (Table 5), the volume fraction of the fluctuation free volume and microcavity volumes were calculated.

Table 5. Elastic constants, Young's modulus (E), Poisson's ratio (μ), *the* volume fraction of the fluctuation free volume (f_g), microcavity volume (V_h), the molar volume of glasses (V_{mol}), and equilibrium distance between the particles (r_n) of glasses from the $AsSe_{1.5}$ – Ag section

Ag, at. %	$\upsilon_l \cdot 10^{-3}$, m/s	$\upsilon_t \cdot 10^{-3}$, m/s	μ	$E \cdot 10^{-8}$, H/m^2	f_g	V_h, Å^3	V_h, cm^3/mole	V_{mol}, cm^3/mole	r_n, Å
5	2.80	1.40	0.330	280	0.008	6.7	4.0	42.6	1.17
10	2.65	1.30	0.334	240	0.006	8.0	4.8	44.2	1.24
15	2.45	1.20	0.338	200	0.007	9.0	5.4	45.5	1.29
20	2.25	1.10	0.347	190	0.008	8.3	5.0	46.7	1.25
25	2.15	1.05	0.350	180	0.008	8.5	5.1	49.0	1.25

(Note: the molar volume of glass is V_{mol} = M/d (M is the molecular weight of glass, d is the density), $r_n \approx (V_h)^{1/3}$).

According to [25], the formation of an activated complex for inorganic network structures occurs without breaking valence bonds but is realized by switching them. It is with the switching of bridging bonds that the jump of an ion into microcavities in the case of silicate glasses is associated. Probably, in the case of ion-conducting chalcogenide glasses, including the aforementioned $AgAsS_2$ and the compositions of the sections AsSe – Ag and $AsSe_{1.5}$ – Ag with a high ionic component, a similar phenomenon is observed. Comparison of the activation volumes $\Delta V^{\#}$, calculated from the dependence of electrical conductivity on pressure, for $AgAsS_2$ glass ($\Delta V^{\#}$ = 4.0 ± 1.0 cm^3/mole) with the volumes of fluctuation microcavities (V_h = 5.0 ± 1.0 cm^3/mole) indicates their proximity, not only for the series oxide glasses but also for chalcogenide glasses [17,19].

Taking into account the volume of the migrating silver cation (V_{Ag+} = 3.7 cm^3/mole), it can be concluded that the migration of these ions in the structure of chalcogenide glasses does not experience serious steric hindrances and rather resembles the mechanism of ion migration in liquids [17,19], than in crystals for which $\Delta V\# \approx V_{Me+}$.

The values of the activation volumes for silver-containing chalcogenide glass and, for example, silicate glass with a volume of migrating silver cation, allows one to clearly explain the higher electrical conductivity of chalcogenide glasses with ionic conductivity compared to other classes.

4. Conclusions

Based on a comprehensive study of the electrical and structural properties of chalcogenide glasses with different silver content, it was found that glasses of the As – Se – Ag system along the AsSe – Ag and $AsSe_{1.5}$ – Ag sections have mixed ion-electronic conductivity, the magnitude, and the main carrier of which change in depending on the silver content. The study showed that at a silver concentration of more than 5 at.%, The main current carrier changes: predominantly electronic conductivity is replaced by predominantly ionic. In chalcogenide glasses, the activation volumes of the migration of silver ions are close in magnitude to the volumes of fluctuation microcavities and noticeably exceed the volume of the migrating Ag^+ ion, which allows us to conclude that there are no serious steric hindrances during their migration and the high electrical conductivity of glasses in the AsSe – Ag and $AsSe_{1.5}$ – Ag sections.

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