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Electrical characterization of $GeSe_2$-Sb_2Se_3-AgI glasses

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Electrical properties of new $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ chalcohalide glasses with six different compositions and z varying between 5 and 40 mol.% are explored. Current-voltage (I-V) characteristics are measured by applying aluminium or gold contacts in sandwich and planar configuration. The applied dc electric fields are in the range 0.025-1000 V/cm. No significant long term changes of the dark current are observed for most samples with the exception of the glass with the highest molar percent of AgI. The I-V characteristics of the sample with the lowest molar percent of AgI are Ohmic-like ($I \sim U$) while those of all other samples consist of two parts. At applied fields < 1 V/cm the characteristics are Ohmic-like, while the part at higher fields is described by a power low $I \sim U^{\gamma}$, $1< \gamma <2$. Temperature dependences of the dark current are also measured and thermal activation energies determined for all compositions are in the range 0.33 - 0.46 eV. A power law dependence of the room temperature conductivity on the at. % of the Ag content is obtained. The value of the power low extent depends on the applied voltage. The results obtained are discussed in terms of 3D percolation of Ag ions which is affected by the applied electric field.

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1. Introduction

Chalcogenide glasses have been widely investigated for many years since they are transparent in the infrared wavelength region (up to the far IR ~ 20μm for the telluride glasses) and have been used as glasses for night vision [1], as optical fibers [2] and when prepared in a thin film form as components for integrated optics [3,4].

Chalcogenide glasses possess electrical and optical band gaps of 1 to 3 eV and accordingly they can be regarded as amorphous semiconductors. However, electrically, glasses exhibit smaller conductivities than the corresponding crystals [5]. This is because the electronic mobility is suppressed by band tail and gap states, which are manifestations of disordered structures. On the other hand, chalcogenide glasses containing group I elements such as silver show a high ionic conductivity, which is even higher than that of the oxide glasses with the same mobile ion content [6]. For example the conductivity of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses changes by 7 orders of magnitude for $x \sim 10$ at.% [7,8]. Therefore, Ag-doped chalcogenide glasses and thin films, are promising systems acting as sensitive membranes for the development of chemical sensors for the detection of heavy ions in aqueous media [6,9-11].

The complication of the chemical composition of glasses increases the probability for observation of new properties and therefore the number of publications in this direction constantly increases.

In this work electrical properties of new $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ chalcohalide glasses with z varying between 5 and 40 mol.% are investigated. I-V characteristics and temperature dependences of the dark current are measured by means of aluminium or gold contacts in sandwich and planar configuration. The results obtained are discussed in terms of percolation of Ag^+ ions.

2. Experimental details

The initial compounds Me_nCh_m (Me = Ge and Sb; Ch = Se) and samples with composition $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ were synthesized by direct monotemperature synthesis in sealed under residual pressure of 1.10^{-3} Pa quartz ampoules. The starting materials used for the synthesis of the Me_nCh_m compounds were with purity: Ge, Se - 5N (Fluka) and Sb – 4N (Merck). The synthesis characteristics (temperatures and duration of isothermal steps, as well as heating rate) were conformed to the physicochemical characteristics of the initial components, the intermediate and the final phases. For the synthesis of the samples from the $GeSe_2$-Sb_2Se_3 - AgI system AgI was used produced by Merck. More details on the glass preparation may be found elsewhere [12] The compositions of the investigated $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ glassy samples are listed in Table 1.

Table 1. Compositions of the investigated $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ glasses.

Sample No	$GeSe_2$, x mol. %	Sb_2Se_3, y mol. %	AgI, z mol. %	Ag, I at.%
1	66.5	28.5	5	1.42
2	56	24	20	6.1
3	40	40	20	5.6
15	49	21	30	9.6
17	25	55	20	5.1
20	42	18	40	13.5

The $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ samples investigated were plates having thickness of 2 – 4 mm whose top and bottom faces were well polished. For the electrical measurements both aluminium and gold sandwich contacts (having area of 1x1 mm^2) and planar contacts (having length of ~ 2 mm and separated by ~ 1 mm) have been used. The applied dc voltages were in the range $U = 0.1 – 100$ V. Current-voltage characteristics and temperature dependences of the dark current were measured by a Keithley Picoammeter 6487 in the temperature range 293-393 K. For the temperature measurements a heating rate of 0.03 K/s ware used. All measurements were carried out in air.

3. Results and discussion

Current-voltage characteristics of a glass sample with composition denoted in the figure, taken with planar Al and Au contacts are depicted in Fig. 1.

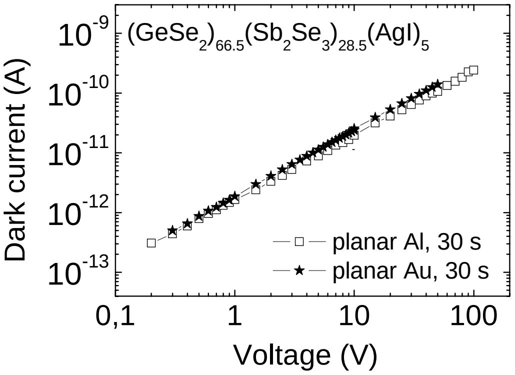

Fig. 1. Current-voltage characteristics of a sample with composition denoted in the figure, taken with planar Al and Au contacts. Each point in the curves was obtained 30 s after the voltage application (further referred to as waiting time).

Similar pairs of curves have been obtained for all compositions. It is seen that there is no appreciable difference between the currents measured with Al and Au contacts. A high defect concentration can be expected in multicomponent materials. Therefore the observed similarity of the I-V characteristics has been related to existence of high concentration of defect states in the forbidden gap of the glasses, which mask the effect of the different work function of Al and Au. Based on this result all further experiments were carried out by applying Al contacts.

The so called high voltage polarization is well known phenomenon in low-conductive chalcogenide glasses that do not contain group I elements [13]. The polarization causes current decrease with the time and it was assigned to charge capturing in defect states in the sample volume or close to the contacts. This motivated experiments aiming to check for existence of polarization in the glasses studied. Fig. 2 shows five I-V characteristics measured at sandwich and planar contact configurations. Four different waiting times were used in those measurements. One can see that the obtained characteristics are very similar which indicates that no significant polarization takes place. All samples, except for sample No20 with the highest $z = 40$, have not shown significant polarization effect.

Fig. 3 compares the I-V characteristics of samples with all compositions investigated. It is seen that only the glass with the lowest $z = 5$ displays a linear characteristic ($I \sim U$). In all other characteristics two parts with different slopes are resolved: i) a linear part at low applied voltages ($U < 1.0$ V) and ii) a super linear part at higher applied voltages in which $I \sim U^{\gamma}$ ($1 < \gamma < 2$). The exponent γ increases with increasing the mol.% of AgI. The minimum Ag content in our glasses (1.42 at.%) is at the percolation threshold reported for similar $Ge_{28}Sb_{12}Se_{60}Ag_m$ glasses ($0.1 \leq m(at.\%) \leq 22.5$). Therefore it has been assumed that the linear part is due to transport of Ag^+ ions whose concentration is not affected by the applied electric field. Since the fields applied are relative low ($\leq 10^3$ V/cm), one cannot assume that the superlinearity is due to charge carrier injection

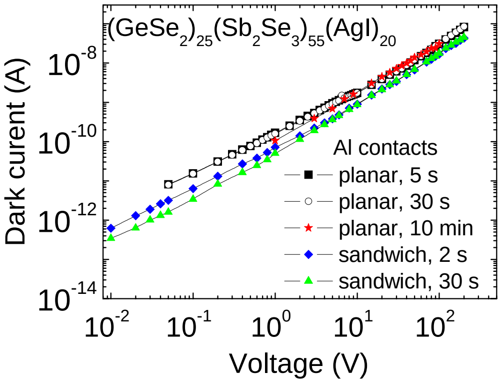

Fig. 2. Current-voltage characteristics of a glass sample with composition denoted in the figure. Both planar and sandwich Al contacts were applied. The different waiting times used in the measurements are shown in the figure.

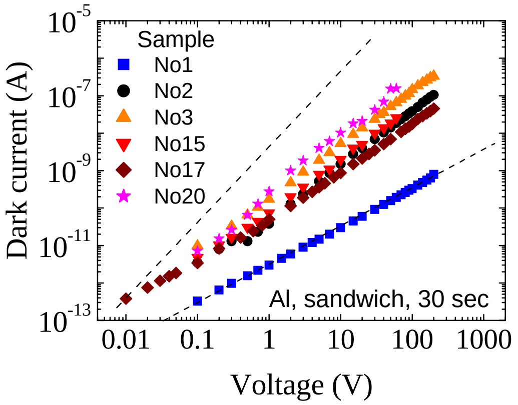

Fig. 3. Current-voltage characteristics of all glass samples studied measured with Al contacts at sandwich configuration and waiting time of 30 s. The dashed lines represent I ~ U and I ~ U^2 dependences.

from the contacts. Transport of Ag^+ ions has been considered as dominating transport mechanism in the high voltage range but it has been suggested that the observed superlinearity is due to a field-induced increase of the Ag^+ ion concentration. Thus, we assume that only a fraction of the mobile ions in the glasses takes part in the current through samples and this fraction depends on the applied voltage; it increases with increasing voltage. The observed γ increase with increasing z indicates that the field-stimulated creation of Ag ions is more effective at higher mol.% of AgI.

Fig. 4 shows the dark current decay measured on the sample No20, z = 40. It is seen that the current decreases with the time with more than one order of magnitude. This observation can be ascribed to accumulation of Ag ions at the interface between the glass and negatively charged contact. The current decay in the first 300 s has been fitted by a third order exponential decay which implies that more than one defects take place in the Ag^+ ion capturing. It has been ascertained that the initial current through the sample can be restored by applying a high reverse electric field, by a 60 min annealing at 373 K or by a long time (> 24 h) stay at room temperature.

Specific electrical conductivity of the glasses studied at room temperature has been calculated from both the linear and super linear parts of the I-V characteristics. (For the super linear part it has been assumed that the contacts do not affect the current.) The obtained compositional dependences of the glass conductivity are shown in Fig. 5 along with data taken from [14] which concern glasses from the $Ge_{28}Sb_{12}Se_{60}Ag_m$ system, for comparison. One can see that the conductivity, σ, of the $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ glasses increases with increasing the Ag and I content. It shows a power dependence $\sigma \sim m^t$ with an exponent $t = 1.64$ at $U = 0.5$ V and $t = 2.74$ at $U = 50$ V (the t values have been calculated from a least-square fit of the experimental data). The power-low exponent obtained for the low applied voltages concedes with that reported for the $Ge_{28}Sb_{12}Se_{60}Ag_m$ system [14] at low Ag content ($m \leq 2$ at%).

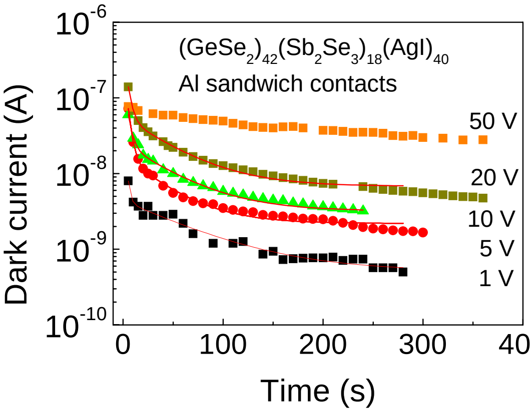

Fig. 4. Dark current decay upon applying five different voltages measured on the sample with the highest mol.% of AgI. The lines are obtained by fitting with third order exponential decay.

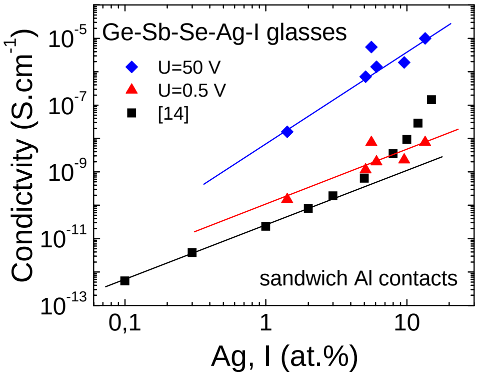

Fig. 5. Compositional dependences of the specific electrical conductivity calculated from the linear (U = 0.5 V) and super linear (U = 50 V) parts of the I-V characteristics. The lines are linear fits of the experimental points. The black squares represent data for glasses from $Ag_mGe_{28}Sb_{12}Se_{60}$, taken from [14] for comparison.

It has been shown [14,15] that the power law form is a general behaviour of the glass conductance in the critical region just above the percolation threshold. The values of t expected for the 3D models are $t = 1.5 - 1.7$. The power law exponent appears to lie between 1.0 and 1.3 for a 2D bond percolation model. Hence, the $t = 1.64$ value obtained indicates that in the low voltage range the silver ion conduction in the studied $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ system occurs within the framework of a 3D percolation. This conclusion is not unexpected, if one takes into account that silver doping does not change dimensionality of the germanium chalcogenide glass network that consists of distorted GeSe(S) tetrahedra. However, we note that, differently from the $Ge_{28}Sb_{12}Se_{60}Ag_m$ system, the power-low exponent $t = 1.64$ of the $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ system is observed in a rather wide range ot Ag doping levels ($1.42 \leq m \leq 13.5$ at.%). This result implies that the presence of iodine and/or five components significantly affects the percolation of Ag^+ ions in the $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ glasses.

The obtained t-value at high applied voltages $t = 2.74$ is much higher that the expected power-low exponents. It resembles the steep conductivity increase observed at Ag contents that are far above the percolation threshold [16], though the increase is not so steep (see Fig. 5). Such conductivity behaviour has been explained by dynamic structure models [16 and references therein]. It has been shown [17] that at silver content much higher than the percolation one the Ag^+ ion transport depends on the Ag content but not on the host matrix. This means that while at low mobile ion content the structure (or dimensionality) of the vitreous matrix affects ionic transport properties of glasses (as it has been concluded above), at high ion content the conduction properties are governed only by the amount of mobile species. Based on the observed t-changes with changing applied voltage, one can suggest that in the multicomponent glasses here studied no sharp percolation threshold occurs. Moreover, it can be concluded that the applied electric field affects the Ag^+ ion transport; at low voltages classical Ag^+ ion percolation takes place while at high voltages some fluctuating pathways within a dynamically determined structure [18] appear.

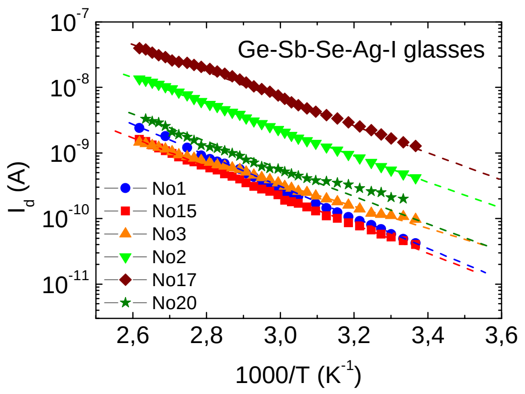

Fig. 6. Temperature dependences of the dark current of $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ samples with six compositions measured under an applied dc voltage $U = 10$ V.

Temperature dependences of the dark current are shown in Fig.6. As seen, the current, and hence the electrical conductivity, obeys the Arrhenius law

$$\sigma_d = \sigma_{do} \exp(-E_a/kT), \qquad (1)$$

where σ_{do} is the pre-exponential term, E_a is the activation energy, k and T have their usual meaning. Values of E_a were calculated from a least-square fit of the data to Eq. (1). The activation energies obtained for all samples are quite similar. They are in the range 0.33-0.46 eV and does not display a systematic change with the increase of the Ag content. The E_a values obtained are lower than those reported for $Ag_mGe_{28}Sb_{12}Se_{60}$ glasses [14], which in addition showed a systematic decrease from 0.734 to 0.525 eV when the Ag content increases from 1 to 15 at.%. The unsystematic and quite small E_a change with the silver content we observed is probably related to the the composition complexity. The complexity, which normally creates a higher defect density, along with the presence of iodine, are most likely the reasons for the low values of the conductivity activation energy.

4. Conclusions

The electrical conductivity and the transport mechanism in new $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ chalcohalide glasses with six different compositions have been explored. The measurements of current-voltage characteristics have shown that both aluminium and gold contacts can be used for electrical characterization of these glasses. No significant high voltage polarization has been detected for the most compositions. Only for the glass with the highest molar percent of AgI such polarization has been observed. It has been related to accumulation of Ag^+ ions at the contact. Based on the observed Ohmic-like I-V characteristics at low applied fields (< 0.3 V/cm) and the superlinearity seen at higher fields, it has been assumed that only a part of the Ag^+ ions has contribution in the current through the samples. The linear part of the I-V characteristics has been related to classical 3D percolation of Ag^+ ions, whose concentration does not change with the field. The observed superlinearity of the I-V characteristics and the rather high t-value obtained at higher electric fields have been explained by suggesting: (i) 3D percolation of Ag^+ ion, whose concentration increases with the increase of the field, and (ii) appearance of some fluctuating pathways within a dynamically determined structure. The quite low activation energies obtained for all glass compositions (0.33-0.46 eV) have been connected with a combined effect of the complex composition and the presence of iodine.

Acknowledgements

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