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# Novel chalcohalide glasses from the Ge–S–AgI system and some physicochemical features

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**Abstract** Novel bulk glassy samples of the pseudoternary chalcohalide Ge–S–AgI system have been prepared. Glasses have been obtained by monotemperature synthesis in evacuated ampoules and standard melt-quenching technique. The glass-forming region in the system determined by X-ray diffraction is situated in the S-rich region on the Ge–S side (S/Ge = 1.2, 1.5, 2 and 3) with AgI content up to 20 mol.%. Some physicochemical properties of the amorphous materials and their compositional dependence have been investigated. In addition, the theoretical average coordination number (Z), the total constraints per atom ($N_{co}$), the radial ($N_a$) and axial ($N_b$) strength of the bonds have been calculated and related to the experimental results.

## Introduction

In the last decades silver-containing chalcogenide glasses have become attractive materials for the scientists due to their various applications in optics, optoelectronics, chemistry and electrochemistry as optical elements, gratings, microlenses, sensors, electrochemical capacitors, batteries, etc.

Glasses of different silver containing chalcogenide and chalcohalide systems such as $GeS_2$–AgS and $GeS_2$–AgS–AgI [1, 2]; Ge–Se–AgI [3]; Ge–S–I [4, 5], Ge–S–Ag [6, 7]; $Ga_2S_3$–$GeS_2$–AgI [8]; $GeS_2$–CdS–$Ag_2Se$ [9] have been investigated. Data about glasses from the Ge–S–AgI system synthesized from elemental germanium and sulphur and silver iodide, however, has not been found in the literature and this lack of information motivated the present study. We defined the boundaries of the glass-forming region, measured some physicochemical properties of the glasses and traced the influence of Ge–S backbone and of the incorporated halide salt (AgI) on the structure and physicochemical properties of the synthesized materials. The main purpose of AgI introduction in the Ge–S network is to increase the ionic conductivity at room temperature, which would make these glasses potential materials, for various applications, for example as solid electrolytes in batteries. It is known that the properties of chalcohalide based materials are significantly influenced by the introduction of the doping salt, especially in the case of silver halides [3]. Moreover, high halide concentrations favour the ionic conductivity, since they provide a good medium for the migrating $Ag^+$ ions [1].

## Experimental

Bulk glasses from the system $(GeS_y)_{100-x}(AgI)_x$ where x = 5, 10, 15, 20 mol.% and ratio (y) between host elements Ge and S, y = 1.2, 1.5, 2, 3 were synthesized. The samples were prepared in evacuated (~$10^{-3}$ Pa) and sealed

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quartz ampoules from elemental Ge and S with 4N purity and AgI (5N, Merck) by conventional direct monotemperature synthesis in a rotary furnace. Stepwise heating regimes were employed for the preparation of the glassy materials, as follows: (i) heating to 473 K with a rate of 4 K/min and temperature maintenance for 1800 s, (ii) heating to 673 K with a rate of 3 K/min, (iii) increasing the temperature up to 973–1123 K with a rate of 2 K/min (applying vibrational stirring), (iv) heating up to 1273 K with a rate of 1 K/min, (v) quenching in a mixture of ice and water. The annealing conditions (temperature regimes and heating rates) have been chosen in accordance with the melting points of the initial components.

The glassy state of the samples was studied by X-ray diffraction (diffractometer APD-15 Philips 2139 with $\mathrm{CuK}_\alpha$ radiation and Ni filter) in the angle range $2\theta$ from 10° to 60° with a step 0.05° per second.

The density ($\rho$) of the materials was estimated by pycnometer technique using toluene as immersion fluid. The average accuracy of the method was about 0.5%.

The molar volume ($V_m$) of the materials was calculated by means of the following relation:

$$V_m = \left(\sum C_i A_i\right)/\rho \tag{1}$$

where $C_i$ is the molar content of the corresponding i-component (Ge, S, AgI) in the sample, $A_i$ the atomic (molecular) weight of the respective component, $\rho$ the density of the material.

The microhardness experiments on the studied amorphous materials were performed by Knoop approach using MHP 160 microindentor combined with a Vertival microscope (Carl Zeiss) [10]. A standard load of 3.75 g was used to induce imprint in the film. The formula used for calculation of the microhardness ($H_\mu$):

$$H_\mu = P/Ad^2 \tag{2}$$

where P is applied load in kgf, d (mm)—the length of the longer diagonal imprint and A-technological parameter equal to 0.07028. The error of the microhardness values is below 2%.

The average coordination number of the investigated amorphous chacohalides is estimated using the expression:

$$Z = Z_{Ge} \cdot C_{Ge} + Z_S \cdot C_S + Z_{Ag} \cdot C_{Ag} + Z_I \cdot C_I \tag{3}$$

where C is the molar concentration of the corresponding component in the sample and Z, the coordination number of the respective chemical element. Applying the classical rule *8—N*, where *N* is the group of the corresponding element in the Periodic table, the coordination numbers of Ge, S, I were estimated to be 4, 2 and 1, respectively. The coordination number of silver was accepted to be 3 as it has been already reported for such glassy systems [11].

The total number of constraints per atom ($N_{co}$) is expressed as a sum of the radial (bond-stretching, $N_a$) and axial (bond-bending, $N_b$) bond strength [12]:

$$N_{co} = N_a + N_b = Z/2 + (2Z - 3) \tag{4}$$

where Z is the average coordination number of the synthesized glasses discussed above.

## Results and discussion

### Glass-forming region and XRD analysis

The synthesized glasses from the Ge–S–AgI system differ in colour depending on the composition: the Ge-rich glasses (the ratios S/Ge = 1.2 and 1.5) are dark with a strong lustre and the S-rich ones (S/Ge = 2 and 3) converts from dark red–brown (at S/Ge = 2) to red–yellow coloured at S/Ge = 3, which are occasionally inhomogeneous.

The glass-forming region in the system was determined on the basis of the results from the X-ray diffraction patterns. The region lies on the Ge–S side in the sulphur-rich area for cross-sections S/Ge = 1.2, 1.5, 2 and 3, with AgI content up to 20 mol.% (Fig. 1).

The results from the X-ray analysis show that most of the compositions are typical glasses without peaks in the diffractogramms (Fig. 2); these compounds constitute the glass-forming region. Some compositions (with S/Ge ratio of 4) outside the glassforming region but close to the boundary, reveal diffraction peaks with a relatively low intensity (amorphous matrix with crystalline inclusions) as

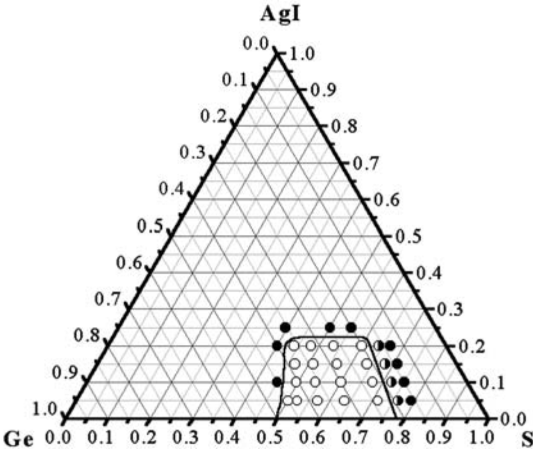

**Fig. 1** Glass-forming region in the chalcohalide Ge–S–AgI system. *open symbol*, amorphous phase; *semi full symbol*, intermediate phase; *full symbol*, crystalline phase

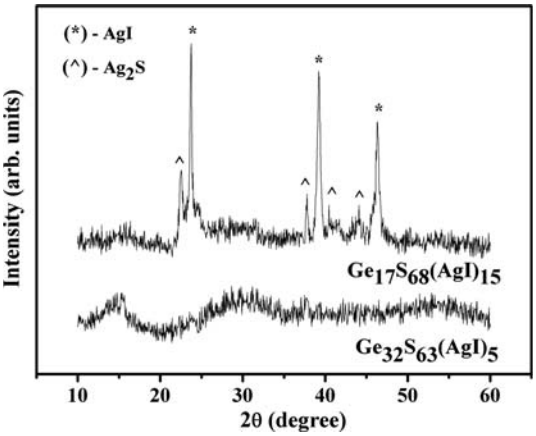

**Fig. 2** X-ray diffraction patterns of intermediate and amorphous bulk samples

for example $Ge_{17}S_{68}(AgI)_{15}$ (Fig. 2). The peaks in the XRD patterns of the samples $Ge_{17}S_{68}(AgI)_{15}$ could be assigned to crystalline AgI and $Ag_2S$ phases [13] as shown on the figure. The presence of AgI bands is supposed to be due to silver iodide which is not incorporated in the Ge–S glassy network. Part of the weak diffractions peaks can be related to $Ag_2S$, most probably a product of the reaction between the silver halide (AgX) and germanium chalcogenide:

$$GeS_2 + 4AgX = GeX_4 + 2Ag_2S, \qquad (5)$$

which could occur in studied Ge–S–AgI glasses. In such a way Kuznetsov et al. explain the appearance of Ag–S bonds in the system $Ga_2S_3$–$GeS_2$–AgX [8].

The rest samples show very strong peaks, indicating their pure crystalline nature, i.e. they are outside the glassy area.

## Physicochemical properties

The densities values of the amorphous samples are in the range 2.80–4.43 × $10^3$ kg/m$^3$, which are between the values of crystalline Ge, S and AgI ($\rho_{Ge} = 5.32 \times 10^3$ kg/m$^3$, $\rho_S = 1.96 \times 10^3$ kg/m$^3$, $\rho_{AgI} = 5.68 \times 10^3$ kg/m$^3$) [14]. The higher density of silver iodide (as compared to the other components) together with the fact that the silver (106.87) and iodine (126.90) atoms are much larger and heavier than the germanium (72.61) and sulphur (32.066) define a substantial rise of the average molar mass and hence increase in the density values [4, 5]. The molar volume stable increases with silver iodide addition (with exception of S/Ge = 2) but more slowly than $\rho$ as can be seen from the Table 1. The compositional dependence of $V_m$ is probably due to the above mentioned statement (increased molar mass) and atomic radius of the constituting elements: Ag (160 pm), I (140 pm), Ge (125 pm), S (100 pm) [10].

**Table 1** Molar volume, Z, $N_{co}$, $N_a$ and $N_b$ of amorphous materials from the Ge–S–AgI system

| Composition | Z | $V_m \times 10^{-5}$ (m$^3$) | $N_{co}$ | $N_a$ | $N_b$ |
|---|---|---|---|---|---|
| S/Ge = 1.2 | | | | | |
| $Ge_{43}S_{52}(AgI)_5$ | 2.86 | 1.60 | 4.15 | 1.43 | 2.72 |
| $Ge_{40}S_{50}(AgI)_{10}$ | 2.81 | 1.78 | 4.03 | 1.41 | 2.62 |
| $Ge_{38}S_{47}(AgI)_{15}$ | 2.77 | 1.80 | 3.93 | 1.39 | 2.54 |
| $Ge_{36}S_{44}(AgI)_{20}$ | 2.72 | 1.97 | 3.80 | 1.36 | 2.44 |
| S/Ge = 1.5 | | | | | |
| $Ge_{38}S_{57}(AgI)_5$ | 2.76 | 1.70 | 3.90 | 1.38 | 2.52 |
| $Ge_{36}S_{54}(AgI)_{10}$ | 2.72 | 1.80 | 3.80 | 1.36 | 2.44 |
| $Ge_{34}S_{51}(AgI)_{15}$ | 2.68 | 1.96 | 3.70 | 1.34 | 2.36 |
| $Ge_{32}S_{48}(AgI)_{20}$ | 2.64 | 2.19 | 3.60 | 1.32 | 2.28 |
| S/Ge = 2 | | | | | |
| $Ge_{32}S_{63}(AgI)_5$ | 2.64 | 1.97 | 3.60 | 1.32 | 2.28 |
| $Ge_{30}S_{60}(AgI)_{10}$ | 2.60 | 2.02 | 3.50 | 1.30 | 2.20 |
| $Ge_{28}S_{57}(AgI)_{15}$ | 2.57 | 1.92 | 3.43 | 1.29 | 2.14 |
| $Ge_{27}S_{53}(AgI)_{20}$ | 2.54 | 2.09 | 3.35 | 1.27 | 2.08 |

On other hand, the density values are similar and they rise slightly with the addition of AgI when S/Ge is lower (1.2 and 1.5) while the increase is more considerable for samples with S/Ge = 2 as can be viewed on Fig. 3. One can be suggested that similarity of this property's dependences is probably due to germanium enriched local range order based on corner-sharing (CS) and edge-sharing (ES)

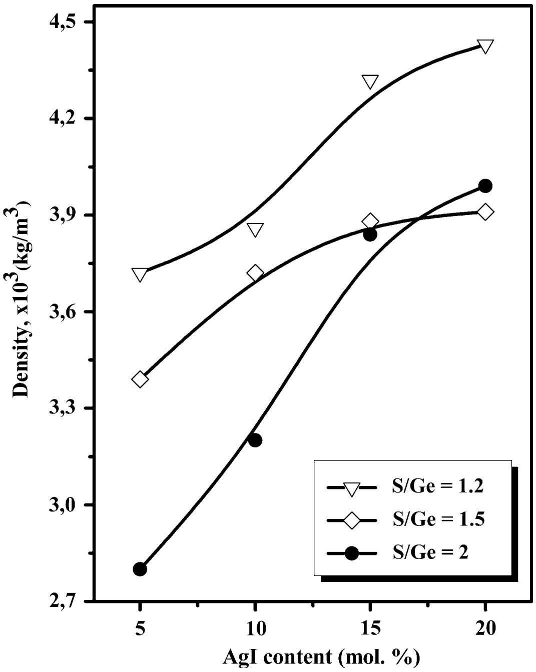

**Fig. 3** Compositional dependence of the density in the Ge–S–AgI glassy system at S/Ge ratios = 1.2, 1.5, 2

$GeS_{4/2}$ tetrahedra. In these glassy samples we have predominantly Ge–Ge and Ge–S bonds [15], and silver and iodine atoms are randomly distributed in the glassy structure. The role of silver iodide as we suppose is most likely as network former [16]. According to the conventional ideas of the constraint theory we may suggest classification of such materials using average coordination number (Z), the total number of constraints per atom ($N_{co}$) and corresponding bond-stretching ($N_a$) and bond-bending ($N_b$) strengths. The glassy materials from the ratios 1.2 and 1.5 we suppose are possessing rigid ($Z > 2.64$) and overconstrained (high values of $N_{co}$) structural network.

The glasses at S/Ge proportion = 2 exhibit bigger jump in the density values and the materials may be described as underconstrained (lower $N_{co}$ values) and possessing floppy structural network ($Z < 2.64$). The unusual behaviour in the dependence of molar volume on silver iodide content at S/Ge = 2 is evidence of this statement. The structure of these amorphous samples is based on, as we suggest, CS and ES tetrahedral units constituting the Ge–S backbone. In addition, our recent rough structural data (from IR analysis) reveal presence of ethane-like clusters ($Ge_2S_6$) into the glassy structure which is also confirmed by investigation upon Raman study on $GeS_2$ bulk glass, reported from Mateleshko et al. [17]. In that the case we suggest the role AgI is changed to network modifier thus modifying the structure of the glassy samples and leading to structural rearrangements and increasing of structural disorder [2].

In general, the materials from ratio S/Ge = 3 are not subject of our investigation at this time because of their inhomogeneous nature due to assumed phase separation as was mentioned by Mitkova et al. [16].

The results of microhardness experiments on the investigated Ge–S–AgI glasses for S/Ge ratios = 1.5 and 2 are shown on the Fig. 4. It becomes obvious that the microhardness values are clearly decreasing with increase of the silver iodide content. At macroscopic point of view most reasonable explanation is connected with the very low microhardness of the silver iodide, which is about $167 \times 10^6$ Pa [18]—two orders of magnitude lower as compared to the experimental microhardness values of the studied samples. This network “plasticizing effect” of the silver iodide was already reported by Ibanez observed in similar bulk glasses [2].

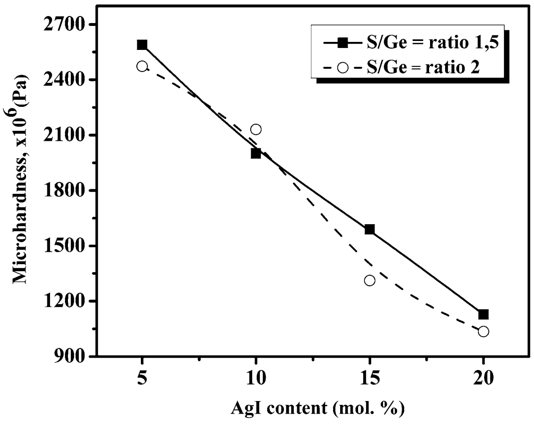

**Fig. 4** Dependence of the microhardness on the composition of the investigated glasses, at S/Ge ratio = 1.5 and 2

From the other hand the reduced concentration of Ge–S structural units (possessing higher hardness) when AgI is added unambiguously leads to decrease in the microhardness of the glasses. In such manner, is explained the compositional dependence of microhardness when third component is introduced in the Ge–S host, for example to $GeS_2$–Cd–I [9] and Ge–S–Sb [19] glassy materials.

Moreover, an opposite dependence of density and microhardness on the adding of the third component in these materials is observed similar to that obtained by the introduction of AgI in the investigated chalcohalide glasses.

The compositional dependence of microhardness viewed at atomic scale is related to the energies of the bonds that should be broken down when the microindentor penetrates into the glassy sample. That approach supposes that the more high energetic bonds define (corresponds to) the bigger microhardness of the material. As we assume (in accordance with chemically ordered covalent network) the most probable bonds presented in the studied glasses are Ge–S (551 kJ/mol) и Ag–I (234 kJ/mol). In addition, it could be expected some other bonds like Ag–S (217 kJ/mol), Ge–I (212 kJ/mol) and S–S (213 kJ/mol) [14]. By increase of the AgI concentration at given S/Ge ratio the number of Ag–I bond and other low energy bonds rises, and consequently the microhardness of the glasses decreases. This phenomenon is also observed by the microhardness’ values of the glassy Ge–S–AgI thin films [10].

## Conclusions

The glass-forming region in the novel chalcohalide Ge–S–AgI system was determined. The region is situated in the S-rich region on Ge–S side with AgI content up to 20 mol. %. The amorphous nature of the synthesized materials is proved by means of X-ray diffraction analysis. The average coordination number and the number of constraints per atom of the as-prepared homogenous samples with S/Ge ratio = 1.2, 1.5 and 2 were determined and the glasses were classified. The sulphur enriched glasses at S/Ge = 3 are inhomogeneous therefore not included in the classification. The density and molar volume increases when silver iodide is added at constant S/Ge proportion while the microhardness becomes smaller. These dependences are probably related with the materials’ structure transformations.

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