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Glass formation in the $GeSe_2$-Sb_2Se_3-AgI system

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Chalcohalide glasses from the $GeSe_2$-Sb_2Se_3-AgI system were synthesized for the first time. The glass forming region was determined by the help of visual, XRD and electron microscopic analyses. It lies partially on the $GeSe_2$-Sb_2Se_3 (0-70 mol % Sb_2Se_3) and $GeSe_2$-AgI (0-30 mol % AgI) sides. The maximum solubility of AgI in the glasses is ~ 70 mol %. The basic physicochemical parameters such as density (d), microhardness (HV) and temperatures of phase transformations (glass transition T_g, crystallization T_{cr} and melting T_m) were measured. Compactness and some thermo-mechanical characteristics such as volume (V_h) and formation energy (E_h) of micro-voids in the glassy network as well as the elasticity module (E) were calculated. The glass-forming ability was evaluated according to Hruby's criterion (K_G). A correlation between the composition and the properties of the $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ glasses was established and comprehensively discussed.

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1. Introduction

During the last few years an increased interest on the investigation of new oxychalcogenide, oxyhalide, chalcohalide and oxychalcohalide glasses is observed. These complicated by chemical composition and structure "mixed" glasses should unite in themselves the advantages of already known oxide, chalcogenide and halide glasses. The halide ones possess wide window in the IR part of the spectra and low optical losses, but their chemical stability is poor. For example, the oxide glasses are characterized by high thermal stability and high transmittance in the visible and IR part of the spectra. The chalcogenide glasses are chemically stable, with good transmittance in the IR region, but possess relatively high optical losses. The amorphous semiconductors, including the chalcogenide glasses, are suitable for development of highly effective solar energy transformers. Besides, they are eligible as media for information storage and transport, as well as materials for optical windows in the IR part of the spectra. Multiple functional elements in the integral micro-, nano- and optoelectronics are developed on their basis. Three main processes in the chalcogenide glasses determine the possibility for their usage as optical storage media: photoinduced change of the absorbance and the refractive index – Ge-Se-As [1], photocrystallization – Se, Ge-Se [2] and the difference between the conductivity in dark and light - Se, As_2S_3, As_2Se_3 [3], Se-Bi-I [4].

Furthermore, the chalcohalide glasses possess high ionic conductivity, which increases with the change from room temperature to temperatures above 1000-1200 K [5]. Since in most of the cases their high ionic conductivity is accompanied by slightingly low electron conductivity, their application as solid electrolytes for different kind of batteries and fuel cells is of particular interest [6-8].

As a rule, with the complication of the chemical composition and the structure of the glass, the probability for appearance of new properties increases, as a result of which the spectrum of possible application areas widens. Due to the above said advantages the count of scientific publications related to the obtaining and the investigation of these "mixed glasses" constantly increases [9-19].

The aim of the present work is to outline the glass forming region in the $GeSe_2$-Sb_2Se_3-AgI system and to investigate the main properties of some new glassy phases.

2. Experimental

The glass forming region in the $GeSe_2$-Sb_2Se_3-AgI system was outlined by the help of 64 compositions.

The initial compounds Me_nCh_m (Me = Ge and Sb; Ch = Se) and the samples with composition $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$ (4 g) 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 was used AgI produced by Merck. At the maximum temperature of the glasses' synthesis, which is defined by their composition and is in the range (700-900) ± 10 °C, a vibration agitation of the smelter was performed with duration of 2 h. The smelter was tempered at temperature (650-800)±10 °C and cooled in a water+ice mixture with a cooling rate of 10-15 °C s^{-1}.

The obtained bulk samples were investigated by visual, XRD (diffractometer TUR-M16 with CuK_α-radiation and Ni-filter) and electron microscope (electronic microscope TEM Philips-3003) analyses.

The temperatures of glass transition (T_g), crystallization (T_{cr}) and complete melting (T_m) were defined by differential thermal analysis using apparatus from the F. Paulik-J. Paulik-L. Erdey system at heating rate of 10 ºC/min and standard substance γ-Al_2O_3.

The samples' density (d) was measured by hydrostatic method using toluene as immersion fluid.

The microhardness (HV) was determined by the Vickers' method at load of 10 g. A metallographic microscope MIM-7 with built in microhardness-meter PMT-3 was used. The HV values were obtained after averaging of the values from 20 measurements.

The compactness (C), which expresses the density deviation between a glass and a crystal with a same composition ($C=\Delta/d_i$; $\Delta=d_i-d$), was calculated using the equation:

$$C = d\left\{\sum_i \frac{M_i x_i}{d_i} - \sum_i \frac{M_i x_i}{d}\right\}\left[\sum_i M_i x_i\right]^{-1}, \quad (1)$$

where M_i, x_i и d_i are the molecular mass, the molar part and the density of the i^{th} component and d is the experimentally obtained density of the sample.

The thermo-mechanical characteristics (volume (V_h) and formation energy (E_h) of micro-voids in the glassy network) and the elasticity modulus E of the chalcohalide glasses were calculated using Eqs. (2)-(4) [20]:

$$E = 0.147.HV \text{ [GPa]}; \quad (2)$$

$$V_h = 5.04.10^{-3}.\frac{T_g}{HV} \text{ [nm}^3\text{]}; \quad (3)$$

$$E_h = 29.75.T_g \text{ [J/mol]}. \quad (4)$$

3. Results and discussion

The visual analysis of the glassy samples shows presence of strong luster and shell-like surface.

The results from the XRD show that some of the compositions (group a) are amorphous, without peaks on the diffractograms and with the charac-teristic X-ray amorphous plateau – these compo-sitions form the glass forming region (Fig. 1 a). Other compositions (group b, Fig. 1b) show diffraction peaks with small intensity (composi-tions on the region's boundary). The diffracto-grams of the samples from group c show well expressed peaks. These samples are crystalline and get outside the region of glass formation (Fig. 1c).

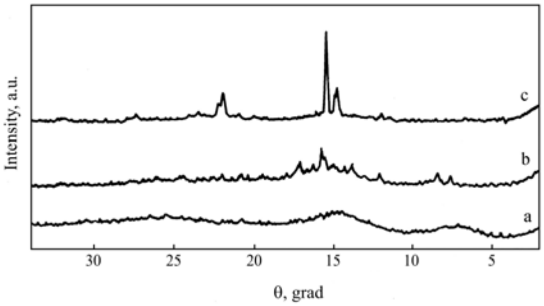

Fig. 1. Typical diffractograms of a) glassy $(GeSe_2)_{81}(Sb_2Se_3)_9(AgI)_{10}$, b) glassy+crystalline $(GeSe_2)_{20}(Sb_2Se_3)_{60}(AgI)_{20}$ and c) crystalline $(GeSe_2)_6(Sb_2Se_3)_{54}(AgI)_{40}$ samples.

The EMA investigations show smooth and homogenous surface for the samples from group a and for the compositions of group b small crystalline objects (micro-crystals) appear. The surface of the samples from group c is rough, without the characteristic for the glassy phase regions.

The glass forming region of the $GeSe_2$-Sb_2Se_3-AgI system (Fig. 2) lies partially on the $GeSe_2$-Sb_2Se_3 (0-70 mol % Sb_2Se_3) and $GeSe_2$-AgI (0-30 mol % AgI) sides. The maximum solubility of AgI in the glasses is ~ 70 mol %. On the Sb_2Se_3-AgI side glasses were not obtained.

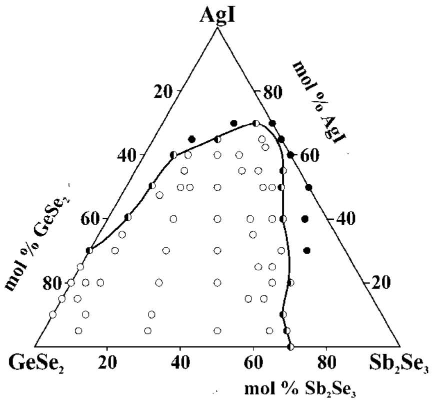

Fig. 2. Glass forming region in the $GeSe_2$-Sb_2Se_3-AgI system.

The results from the determination of the thermal properties (temperatures of glass transition T_g, crystallization T_{cr} and melting T_m) and the Hruby's criterion are presented in Table 1.

The results from the investigation of the microhardness, density and the thermo-mechanical properties of the glassy samples are presented in Table 2.

4. Discussion

The glass transition temperature (T_g) of the investigated glasses changes from 162 to 246 °C (Table 1). It depends both on the $GeSe_2$ and the AgI content. At z=const and m>0.3, T_g practically does not depend on the Sb_2Se_3 content and at m=const – it decreases with the increase of the AgI concentration. The first objective seems logical if one takes under account the specific features in the state diagram of the $GeSe_2$-Sb_2Se_3 system [21]. It is by eutectic type with composition and temperature of the eutectic point 40 mol % Sb_2Se_3 and 480 °C, respectively. According to the eutectic law, the melting temperature around this composition should be the lowest and T_g to be constant. The addition of AgI (an ion-built compound) leads to decrease of T_g of the glasses, since the ionic content of the chemical bond is increased.

With the increase of the Sb_2Se_3 concentration (at z=const), the crystallization temperature (T_{cr}) decreases almost proportionally with the decrease of the glass former $GeSe_2$ content (Table 1). In the concentration interval $0.3 \leq m \leq 0.5$ a relatively weak deviation of T_{cr} from the glasses composition is observed. The addition of AgI from 0 to 40 mol % at m=const leads to insignificant change of T_{cr}. This behavior of T_{cr} gives us the reason to suggest that in these glasses crystallizes one and the same phase. In the glasses with composition $(GeSe_2)_{80}(AgI)_{20}$ and $(GeSe_2)_{30}(Sb_2Se_3)_{30}(AgI)_{40}$ crystallizes a phase, which is different from that of the others compositions.

From the analysis of the melting temperature of these two compositions and of the $(GeSe_2)_{85.5}(Sb_2Se_3)_{9.5}(AgI)_5$ glass a conclusion can be made that in these three glasses crystallizes a rich of $GeSe_2$ phase. The melting temperatures of these glasses are higher than T_m of AgI, because of which one can not talk about crystallization of new phase based on AgI. At the same time, these temperatures are lower than T_m of $GeSe_2$, i.e. this is a crystallization of solid solutions based on $GeSe_2$.

Table 1. Thermal properties of glassy samples with general composition $(GeSe_2)_x(Sb_2Se_3)_y(AgI)_z$, m=y/(x+y).

№	Composition, mol %			m	T_g, °C	T_{cr}, °C	T_m, °C	K_G
	$GeSe_2$	Sb_2Se_3	AgI					
1	85.5	9.5	5	0.1	246	414	611	0.85
2	66.5	28.5	5	0.3	217	352	448	1.41
3	47.5	47.5	5	0.5	213	337	443	1.17
4	33.25	61.75	5	0.65	217	285	491	0.33
5	80	0	20	0	241	342	640	0.34
6	72	8	20	0.1	210	-	-	-
7	56	24	20	0.3	194	355	420	2.48
8	40	40	20	0.5	193	347	414	2.30
9	25	55	20	0.69	193	285	472	0.49
10	49	21	30	0.3	180	-	-	-
11	35	35	30	0.5	184	352	400	3.50
12	17.5	52.5	30	0.75	184	261	472	0.36
13	42	18	40	0.3	162	-	-	-
14	30	30	40	0.5	165	385	597	1.07

Table 2. Physicochemical properties of glasses from the $GeSe_2$-Sb_2Se_3-AgI system.

№	Composition, mol %			m	T_g, K	HV, kgf/mm^2	d, g/cm^3	C	E, GPa	$V_h, 10^{-3}$, nm^3	E_h, kJ/mol
	$GeSe_2$	Sb_2Se_3	AgI								
1	85.5	9.5	5	0.1	519	149	4.50	-0.060	21.9	17.6	15.4
2	66.5	28.5	5	0.3	490	106	4.84	-0.051	15.6	23.3	14.6
3	47.5	47.5	5	0.5	486	86	5.13	-0.041	12.6	28.5	14.5
4	33.25	61.75	5	0.65	490	117	5.14	-0.066	17.2	21.1	14.6
5	80	0	20	0	514	123	4.51	-0.051	18.1	21.1	15.3
6	72	8	20	0.1	483	92	4.65	-0.052	13.5	26.5	14.4
7	56	24	20	0.3	467	76	5.02	-0.028	11.2	31.0	13.9
8	40	40	20	0.5	466	71	5.38	$-3.64.10^{-4}$	10.4	33.1	13.9
9	25	55	20	0.69	466	91	5.40	-0.028	13.4	25.8	13.9
10	49	21	30	0.3	453	72	5.08	-0.025	10.6	31.7	13.5
11	35	35	30	0.5	457	67	5.44	0.005	9.8	34.4	13.6
12	17.5	52.5	30	0.75	457	75	5.51	-0.019	11.0	30.7	13.6
13	42	18	40	0.3	435	64	5.12	-0.027	9.4	34.3	12.9
14	30	30	40	0.5	438	64	5.49	0.010	9.4	34.5	13.0

In the first case, the $GeSe_2$ has dissolved up to 20 mol % AgI and in the second - up to 30 mol % Sb_2Se_3 and 40 mol % AgI.

Except the above-mentioned glasses, the others melt in the temperature interval 400-490 °C (Table 1). These values of T_m are most probably connected with the melting of solid solutions based on AgI. Here, as well as in the $T_g(m)$ and $T_{cr}(m)$ dependencies, T_m does not change in the concentration interval $0.3 \leq m \leq 0.5$.

For some of the glasses the temperature difference T_{cr}-$T_g > 100$ °C. This is a criterion about their stability. The more accurate criterion for determination of the glass-forming tendency is the Hruby's criterion ($K_G = (T_{cr}$-$T_g)/(T_m$-$T_{cr})$) - Table 1. The high values of K_G show that the nucleation process and formation of crystallites is highly embarrassed.

The microhardness (HV) changes in a wide range depending on the glass' composition (Table 2). A well expressed regularity is observed on both HV(m) at z=const and HV(z) at m=const dependencies. The HV(m) have a salient minimum at m=const which becomes more and more flowing (rounded) with the increase of the AgI content and at z=40 mol % AgI the minimum smoothens. The presence of this minimum is most probably related to structural changes with the composition alternation. On the one hand, in the building of the glass' structure three different structural units participate – tetrahedrons ($GeSe_{4/2}$), pyramids ($SbSe_{3/2}$) and mono-atomic fragments (–Ag and –I). At constant and low AgI content the two branches in the HV(m) dependence can be related to the limiting action of the $GeSe_{4/2}$ (at m<0.5) and $SbSe_{3/2}$ (at m>0.5) structural units. With the increase of the AgI the structural units are destroyed because of the tearing of the Ge-Se bonds and their closing with –Ag and/or –I fragments. On the other hand, the presence of a minimum at the HV(m) dependence at m=0.5 can be related to the existence of an eutecticum in the binary system $GeSe_2$-Sb_2Se_3 at m=0.4 [21]. At this proportion of $GeSe_2$ and Sb_2Se_3 the glass forming ability is most strongly expressed as the deviation on the left and on the right of the eutectic point decreases this ability and leads the system towards the steady crystalline state.

The density changes between 4.5-5.5 g/cm^3 (Table 2). The addition of Sb_2Se_3 and AgI, together or separately, leads to increase of the density, since $d_{AgI} \approx d_{Sb_2Se_3} > d_{GeSe_2}$. At m > 0.5 the d(m,z) dependencies tend to saturation.

The compactness of the investigated glasses is very close to this of the crystals with the same composition (Table 2). The high compactness is related to a re-arrangement of the structure with the addition of AgI. It builds in the structural units constructing the glass ($GeSe_{4/2}$ and $SbSe_{3/2}$), as well as between them. Due to the fact, that during the AgI forms fragments Ag-I, which tear the bonds in the planes, as well as between them and dense the glass' structure. This is confirmed by the C(z) dependence at m=const. The compactness through a maximum at m=0.5, i.e. at this proportion of $GeSe_2$ and Sb_2Se_3 a maximum densification of the structure is observed.

The elasticity modulus (E) logically follows the tread of HV and the energy for formation of micro-voids (E_h) – this of T_g.

The $V_h(m)$ dependence at z=const goes through a maximum at m=0.5, independently that depends directly on T_g and HV. This thread shows that on the V_h a priority influence renders the HV deviation. At m=0.5 a complicated dependence between V_h and the AgI concentration is observed, which evidently is connected to the specific influence of AgI on T_g and respectively on E_h.

5. Conclusions

New chalcohalide glasses from the $GeSe_2$-Sb_2Se_3-AgI system were synthesized for the first time and the glass forming region in it is outlined.

The thermal (temperatures of glass transition, crystallization and melting), physicochemical (density, microhardness, compactness) and thermo-mechanical (elasticity modulus, volume of micro-voids and energy for their formation) properties of the glassy phases were studied.

A correlation between the properties and the composition of the glasses from the investigated system is established and a method for its explaining is proposed.

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