Glassforming region and physicochemical properties of new oxychalcogenide glasses from the As_2Se_3-SnSe-SnO_2 system

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ABSTRACT

New oxychalcogenide glasses from the As_2Se_3-SnSe-SnO_2 system were synthesized from the initial compounds by melt quenching technique. The state of the samples (glassy, crystalline, glass-crystalline) was proven by visual, X-ray diffraction and electron microscopic analyses. The glassforming region within this system was outlined. It lies partially on the As_2Se_3-SnSe (0-50 mol % SnSe) and As_2Se_3-SnO_2 (75-87 and 93-100 mol % SnO_2) sides of the Gibbs concentration triangle. No glassy phases were obtained on the SnSe-SnO_2 side.

The phase-transition temperatures (glass-transition, crystallization and melting) of some glassy samples were determined by DTA. The density of the samples was measured by hydrostatic method. Their Vickers microhardness was also determined. A correlation between the investigated properties and the composition of the glasses is established.

INTRODUCTION

The multicomponent glasses are subjected to intensive study during the last 15-20 years due to the possibilities they offer for application in the optoelectronics, sensorics, analytics, energetics, etc. The "mixed" glassy materials are of particular interest, since they integrate the specific properties of the "simple" glasses (oxide, halide and chalcogenide) and acquire better properties or gain new ones.

When chalcogenide glasses are combined with oxide or halide ones, doped with rare-earth metals, high-effective materials for optical amplifiers, lasers and other elements for the IR optics[1-5] are formed, as well as materials with new properties: high ionic conductivity, specific resistivity, which varies in wide range, porosity, absorption and catalytic ability, thermal and chemical stability, etc[6-11], which broaden the possibilities for their application.

The aim of the present investigation is development of new oxychalcogenide glasses, which are perspective materials for elaboration of gas sensors, ionselective electrodes, sensitive elements for multifunctional sensors, optical amplifiers, nano-sensitive sensors type

QCM, galvanic elements, optical windows, catalyst panels, protective layers, capacitive and optoelectronic elements, etc. The subject of the present study is the three-component system As_2Se_3-SnSe-SnO_2, data for which was not found in the scientific literature. The goal is sintering of new oxychalcogenide materials, outlining of the glassforming region within this system and investigation of the basic physical properties of some of the obtained oxychalcogenide glasses.

As it is known, the glass' structure and properties depend on many factors, the main from which are: a) chemical composition; b) type of the structural units, which built the glassy network; c) the synthesis conditions; d) additional stress treatment of the initially obtained glass (mechanical, thermal, optical, electrical, magnetic, etc.).

During the development of new materials with preliminary given properties, the researchers need to know, as far as it is possible, each one of the above-counted factors to determine their particular area of application. For example, the possibility for application of a given material (glassy or crystalline) as sensitive element for a gas sensor or as carrying carcass for catalyst panel, the degree of porosity (looseness), which is defined by the compactness coefficient (C), has to be determined. If the system, subjected to present investigation, is analyzed on this basis, the following analysis-motivation can be made:

In this three-component system each of the components is charged with specific functions: As_2Se_3 is glassformer; SnSe – modifier, and SnO_2 – the component, which determines the property (in the current case, it influences the compactness (C), by itself or in combination with the modifier). Mainly two factors influence C: physical (by the density and the atomic radius of the participating elements) and structural (stereometric) – by the characteristic of the structural units. The As_2Se_3 builds the carcass of the glass with its structural units of trigonal units type ($AsSe_{3/2}$); the SnSe is included into the glass' network with its linear structural units (-Sn-Se-); the SnO_2 participates in the building of the glass with tetrahedral structural units ($SnO_{4/2}$). Depending on the inclusion way of the SnSe structural units into the glass' skeleton, formed by the glass former As_2Se_3, the SnSe can lead to decrease of C (SnSe breaks the Se-bridges and builds in between them: –Se–Sn–Se–Se–)

or to densification of the glass' structure (increase of C) – the Se from SnSe breaks a Se-chain and enters in it (–Se–Se–Se–), while the Sn atoms are settled into the micro-voids of the glassy matrix.

The structural units of SnO_2, as a rule, lead to decrease of C (the glass becomes with looser structure).

This analysis gives grounds to assume that oxychalcogenide glasses with variable compactness can be obtained by changing the concentration of SnO_2 and SnSe in the As_2Se_3-SnSe-SnO_2 system, which will be checked during our future investigations.

MATERIALS AND METHODS

For the synthesis of samples from the As_2Se_3-SnSe-SnO_2 system (in quantity of 4 g) we used preliminary synthesized by direct synthesis As_2Se_3 and SnSe (purity of the initial elements of 5N), as well as Merck SnO_2 with purity $\geq$ 99.99 %. For the obtaining of samples from the system, subjected to investigation, a multiple step direct monotemperature synthesis was performed in evacuated to a residual pressure of 10^{-2} Pa quartz ampoules. The synthesis was conformed to the physicochemical properties of the initial compounds ($T_m(As_2Se_3)$ = 360 °C[12]; T_m(SnSe) = 861 °C[13], $T_m(SnO_2)$ = 1630 °C[14]). The heating rate between the steps was 3-6 °C/min, as the duration of each step, at 300, 650 and 1100 °C (in crucible furnace), was 1.5 h. At the final stage of the synthesis a continuous stirring of the melt was performed. Before the sharp quenching of the melt in water+ice mixture (cooling rate of ~15 °C/s, the ampoule was taken from the furnace and cooled at air up to ~1000 °C.

The obtained materials were characterized by visual, XRD and SEM analyses.

The visual analysis includes observation with non-armed eye and with binocular magnifier (4ˣ) of freshly revealed surface, obtained by mechanical "fracture" of the sample. The condition of the obtained samples was determined by the characteristic crack of the freshly revealed surface.

The XRD investigations were performed on diffractometer D2 Phaser Bruker AXS using CuK_α-irradiation and Ni-filter, and the morphology of the samples was observed on scanning electron microscope Philips 515.

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The characteristic temperatures of the glasses were determined by differential thermal analysis (DTA) using apparatus from the F.Paulic-J.Paulic-L.Erdey system of the company MOM-Hungary at heating rate of 10 °C min⁻¹, standard substance – α-Al_2O_3, and accuracy of ± 5 °C.

The density (d) of the samples was measured with accuracy ± 5 % at air temperature of 25-30 °C by hydrostatic method using toluene as immersion fluid. The density of toluene was determined from the equation: $d = 0.879 - 0.001T$, where T is the temperature [°C], at which the measurement was made.

The microhardness (HV) was measured by the Vickers' method (a metallographic microscope MIM-7 with built in microhardnessmeter PMT-3 has been used at load of 10 g). The values of HV are an average of 20 measurements per sample; accuracy – ± 5 %.

RESULTS AND DISCUSSION

The region of glass formation within the As_2Se_3-SnSe-SnO_2 system was outlined using 44 samples, the compositions of which are shown in TABLE 1.

The results from the visual analysis showed that the glassy samples from the As_2Se_3-SnSe-SnO_2 system are dark colored, with strong luster and shell-like surface. The crystalline samples have matt and rough surface, while the mixed glass-crystalline phases, which are situated on the border of the glassforming region, are characterized by presence of both phases.

The electron microscopic observations show smooth and homogeneous surface of the samples, lying into the region of glass formation. Areas with crystalline objects (microcrystals) appear on the samples from the glassforming border. The surface of the samples, which are situated outside the region of glass formation, is rough, without areas, characteristic for the presence of glassy phase.

The results from the XRD analysis are shown on Figure 1.

The following conclusions can be made from the XRD patterns (Figure 1):

- the points, which compositions fall into the region of glass formation, are characterized by weakly expressed X-ray amorphous plateau at 2θ=33 °, even weaker one at 2θ ~18 °, and lack of reflexes or

presence of some with very small intensity, which are indexed to belong to SnO_2 (p. 16 and 28, Figure 1);

- the compositions, situated on the glassforming border or near it, have well expressed reflexes, but with relatively small intensity. They are also related to the SnO_2 phase (p. 3 and 14, Figure 1). The composition, corresponding to p. 4, which is outside the region of glass formation, but near its border shows "clear" XRD pattern with inherent for SnO_2 diffraction reflexes. The same is valid for p. 13, which besides all pointed above, falls into one small by area crystalline region;

- the others investigated compositions (p. 43 and 44, Figure 1) are with typical XRD patterns for a crystalline material. These compositions are situated away from the glassforming region and possess maximum SnSe content, due to which on their XRD patterns the lines of SnSe are indexed;

- no As_2Se_3 were registered, which makes sense since it is one of the best glassformers, can be obtained easily in amorphous (glassy) and only at special conditions in crystalline state.

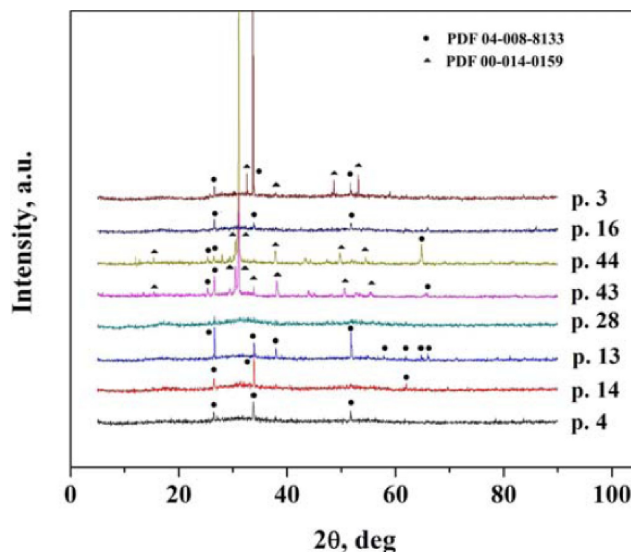**Figure 1 : XRD patterns of samples from the As_2Se_3-SnSe-SnO_2 system**

On the basis of the performed syntheses and the results, obtained from the visual, electron microscopic and XRD analyses the region of glass formation within the three-component As_2Se_3-SnSe-SnO_2 system was outlined (Figure 2).

It is drawn towards the Gibbs concentration tri-

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angle vertex, corresponding to As_2Se_3 and lies partially on its As_2Se_3-SnSe (0-50 mol % SnSe) and As_2Se_3-SnO_2 (75-87 and 93-100 mol % As_2Se_3) sides. No glassy phases were obtained in the binary SnSe-SnO_2 system.
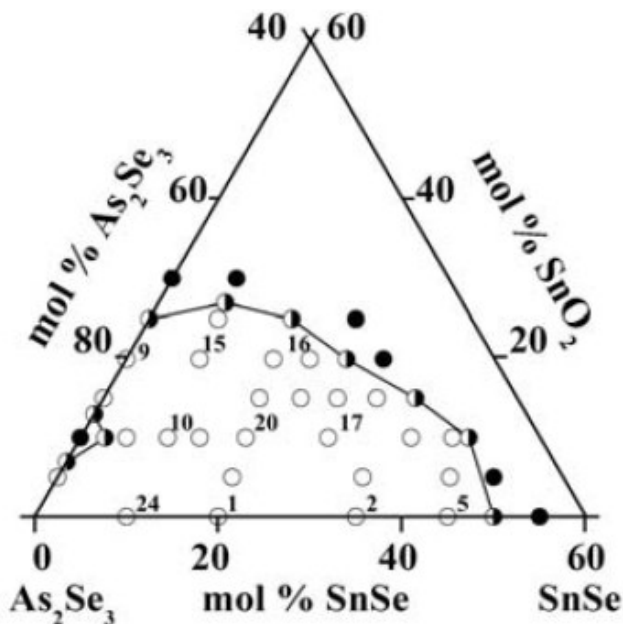

Figure 2 : Region of glass formation within the As_2Se_3-SnSe-SnO_2 system

The main physicochemical properties (temperatures of glass-transition, crystallization and melting, density and microhardness) of some of the obtained glassy phases were investigated.

The characteristic temperatures of the glasses from the As_2Se_3-SnSe-SnO_2 system were determined by the heating curves. The results are generalized in TABLE 2, where x+y+z=100 mol % and m=y/(x+y).

The complexity of the investigated system harshly increases the probability for crystallization of different phases, obtained during high-temperature processes (decomposition, substitution, oxidation, reduction and/or formation of intermediate phases with different chemical composition, as well as various solid solutions between them). This leads to difficulties during the interpretation of the concentration dependencies of the characteristic temperatures (T_g, T_{cr}, T_m) – TABLE 2. Yet, several general regularities appear.

The influence of the composition on the glass-transition temperature T_g is weakly expressed for both increase of SnSe (at z=const) and SnO_2 (at m=0.2) content. Such an influence of the composition can be interpreted on the basis of the chemical composition of the

two components SnSe and SnO_2, which participate with the same atoms (Sn) and the atoms of Se and O_2, which are elements from the same group of the Periodic table (VIA).

At first approach one can talk about crystallization of 3 phases, provisionally differentiated into 3 groups on the basis of the relatively near T_{cr} values.

The first group is formed by the compositions, corresponding to points 24, 1, 2, 5 and 10 with crystallization temperature of about 290 °C. The compositions, marked with points 20, 17, 9, 15 and 16 fall into the second group with T_{cr}~320 °C, and the third group is formed by p. 1 with T_{cr}=477 °C (the compositions are shown in TABLE 2).

Similarly to the concentration dependencies of the crystallization temperature, the melting temperatures of the two crystallizing phases can be united around 2 values of T_m ~ 440 and 460 °C. The second crystallizing phase of the composition, corresponding to p. 1 (T_{cr}=477 °C) melts at 588 °C, which represents an alloy between As_2Se_3 and SnSe.

The density and microhardness values (TABLE 2) are mainly influenced by 2 factors: the partial values of the density (microhardness) of the initial components (physical factor) and the structure of the investigated material – structural (stoichiometric) factor.

If the physical factor is limiting, the density of the oxychalcogenide glasses will increase with the increase of both SnSe and SnO_2 content, since the densities of the initial components increase in the row $d_{As_2Se_3} < d_{SnSe} < d_{SnO_2}$ and are 4.75; 5.00 and 6.86 g/cm^3[15], respectively.

If the structural factor is limiting, the density could increase (with the densification of the structure) or decrease (looseness of the structure). The influence of those two factors reflects on the path of the $d(z)_{m=0.2}$ dependence – in the $0 \leq z \leq 10$ interval the density increases because of the physical factor, while at z>10 it decreases due to the structural factor. In this case into the glassy network formed by the $AsSe_{3/2}$ structural units, new ones are built in - $SnSe_{1/2}$ and $SnO_{4/2}$, as the ratio between them has significant influence on the density concentration dependencies.

The path of the $HV(m)_{z=const}$ dependencies (TABLE 2) illustrates the influence of the physical factor – HV

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TABLE 1 : Composition and condition of the samples, used for outlining of the region of glass formation within the As_2Se_3-SnSe-SnO$_2$ system

№	Composition, mol%			Condition	№	Composition, mol%			Condition
	As_2Se_3	SnSe	SnO_2			As_2Se_3	SnSe	SnO_2	
1	80	20	0	glass	23	55.25	29.75	15	glass
2	65	35	0	glass	24	90	10	0	glass
3	56	24	20	glass+crystal	25	60	20	20	glass
4	70	0	30	crystal	26	76	19	5	glass
5	55	45	0	glass	27	95	0	5	glass
6	68	17	15	glass	28	85	5	10	glass
7	59.5	15.5	25	glass+crystal	29	85	0	15	glass
8	67.5	7.5	25	glass	30	77	13	10	glass
9	80	0	20	glass	31	63	7	30	crystal
10	80.5	9.5	10	glass	32	87	0	13	glass+crystal
11	45	55	0	crystal	33	93	0	7	glass+crystal
12	61.75	33.25	5	glass	34	87.3	2.7	10	glass+crystal
13	90	0	10	crystal	35	54	36	10	glass
14	75	0	25	glass+crystal	36	52.25	42.75	5	glass
15	72	8	20	glass	37	49.5	40.5	10	glass
16	64	16	20	glass	38	52.5	22.5	25	crystal
17	63	27	10	glass	39	51	34	15	glass+crystal
18	50	50	0	glass+crystal	40	47.5	47.5	5	crystal
19	63.5	21.5	15	glass	41	47.7	42.3	10	glass+crystal
20	72	18	10	glass	42	65.7	7.3	27	glass+crystal
21	59.5	25.5	15	glass	43	25.5	59.5	15	crystal
22	52	28	20	crystal	44	28.5	66.5	5	crystal

TABLE 2 : Thermal characteristics of samples with composition $(As_2Se_3)_x(SnSe)_y(SnO_2)_z$

№	Composition, mol %			m	T_g, °C	T_{cr}, °C	T_m, °C	d, g/cm^3	HV, kgf/mm^2
	x	y	z						
24	90	10	0	0.10	179	285	442	4.30	54
1	80	20	0	0.20	182	275, 477	361, 582	4.43	48
2	65	35	0	0.35	173	299	438	4.43	45
5	55	45	0	0.45	174	289	440	4.59	45
10	80.5	9.5	10	0.105	189	289	445	4.75	62
20	72	18	10	0.20	189	318	462	4.67	53
17	63	27	10	0.30	193	320	462	4.55	52
9	80	0	20	0.00	179	315	462	3.75	40
15	72	8	20	0.10	182	325	460	3.86	42
16	64	16	20	0.20	179	328	455	3.95	38

lightly decreases with the increase of the SnSe content, since $HV_{As_2Se_3} > HV_{SnSe}$, 54 kgf/mm$^{2[12]}$ > 33 kgf/mm$^{2[16]}$, respectively. We do not have literature data about the HV value of SnO_2, but the path of the $HV(z)_{m=0.2}$ is analogical the this of the $d(z)_{m=0.2}$ dependence due to the limiting influence of the structural factor.

CONCLUSIONS

- Oxychalcogenide glasses from the three-compo-

nent As_2Se_3-SnSe-SnO_2 system were synthesized for the first time.

- By the help of visual, electron microscopic and X-ray diffraction analyses, the region of glass formation within this system was outlined. It is drawn towards the vertex, corresponding to As_2Se_3 and lies partially on the As_2Se_3-SnSe (0-50 mol % SnSe) and As_2Se_3-SnO_2 (75-87 and 93-100 mol % SnO_2) sides. No glassy phases were obtained in the binary SnSe-SnO_2 system.

- The thermal characteristics of the oxychalcogenide glasses from the investigated system were determined. The glass-transition temperature changes between 173 and 193 °C and depends weakly on the composition. The crystallization temperature T_{cr} varies around 275 – 477 °C, as at first approach one can talk about crystallization of three phases. The melting temperature changes from 361 to 582 °C.

- The density of the glasses was measured. It varies from 3.75 to 4.75 g/cm^3, as it increases in the interval $0 \le z \le 10$ (m=0.2) and decreases at z>10 (m=0.2).

- The Vickers' microhardness of the glasses was determined. It decreases lightly with the increase of the SnSe content and changes in the interval 38 – 62 kgf/mm^2.

ACKNOWLEDGEMENTS

REFERENCES

[1] K.Abe, H.Takebe, K.Morinaga; J.Non-Cryst.Solids, **212**, 143 **(1997)**.

[2] J.Fick, E.J.Knystautas, A.Villeneuve, F.Schiettekatte, S.Roorda, K.A.Richardson; J.Non-Cryst.Solids, **272**, 200 **(2000)**.

[3] S.G.Bishop, D.A.Turnbull, B.G.Aitken; J.Non-Cryst.Solids, **266-269**, 876 **(2000)**.

[4] J.S.Sanghera, J.Heo, J.D.Mackenzie, J.Non-Cryst.Solids, **103**, 155 **(1988)**.

[5] X.H.Zhang, G.Fonteneau, J.Lucas; J.Non-Cryst.Solids, **104**, 38 **(1988)**.

[6] X.Zhao, H.Yin, W.Chen; J.Non-Cryst.Solids, **184**, 128 **(1995)**.

[7] V.Vassilev, G.Vassilev, K.Petkov, J.Optoel.Adv.Mat., **11**, 12, 2014 **(2009)**.

[8] L.Cervinka, J.Bergerova, A.Dalmaso, F.Rocca; J.Non-Cryst. Solids, **232&234**, 627 **(1997)**.

[9] L.Cervinka, J.Bergerova, A.Dalmaso, F.Rocca; J.Non-Cryst.Solids, **232&234**, 274 **(1998)**.

[10] Gan Fuxi; J.Non-Cryst.Solids, **140**, 184 **(1992)**.

[11] Z.G.Ivanova, V.S.Vassilev, K.G.Vassileva; J.Non-Cryst.Solids, **162**, 123 **(1993)**.

[12] Z.U.Borisova; Halkogenidnie poluprovodnikovie stekla, LGU, Leningrad, (in Russian), **(1983)**.

[13] D.M.Chijikov, V.P.Schastlivii; Selen i selenidii, Nauka, Moskva, (in Russian), **(1964)**.

[14] Tin dioxide (SnO_2) Debye temperature, heat capacity, density, melting point, In: 'Non-Tetrahedrally Bonded Elements and Binary Compounds', O.Madelung, U.Rössler, M.Schulz, (Eds); Landolt-Börnstein - Group III Condensed Matter, Springer, **41C**, 1-2 **(1998)**.

[15] Properties of the elements and inorganic compounds, in 'CRC Handbook of Chemistry and Physics', Internet version, D.R.Lide, (Ed); CRC Press, Boca Raton, FL, **(2005)**.

[16] V.Vassilev, K.Tomova, V.Parvanova; J.Therm.Anal. Cal., **86**, 199 **(2006)**.