

COMPOSITIONAL TRENDS OF THE PHYSICO-CHEMICAL PROPERTIES IN PSEUDOTERNARY CHALCOGENIDE GLASSES

L. Aljihmani, V. Vassilev, P. Petkov^{a*}

Department of Semiconductors, University of Chemical Technology & Metallurgy,
8 Kl.Ohridsky blvd, 1756 Sofia, Bulgaria

^aDepartment of Physics, University of Chemical Technology & Metallurgy,
8 Kl.Ohridsky blvd, 1756 Sofia, Bulgaria

Bulk glasses of $(Ag_4SSe)_x(As_2Se_3)_y(SnTe)_z$ system were prepared by melt-quenched technique, using the respective binary compounds. Some physico-chemical characteristics were investigated: density, microhardness. Glass transition temperature, crystallization temperature and melting temperature were obtained by calorimetric investigations. The free-volume theory gives the correlation between the microhardness and the glass transition temperature, which considers the formation and migration of the micro-volumes in glasses, without breaking the valence bonds. Values of micro-void formation energy in a corresponded volume, module of elasticity and compactness were calculated. The strength of the chemical bond is connected to the "free volume" in material or density of the defects in the sample. The biggest changes in the structure (higher sensitivity) are expected in the samples with small compactness of the structure. The correlations between the composition and properties of the glasses are discussed bearing in mind the structural transformation in glassy matrix due to the compositional changes in the glasses.

(Received July 9, 2003; accepted August 28, 2003)

Keywords: Chalcogenide glasses, Glassforming region, Physico-chemical properties

1. Introduction

Ion-selective electrodes (ISE) with functional membranes based on chalcogenide glasses (CG) have been widely used in the last decade. The glassy chalcogenides are more stable in electrolyte solutions than polycrystalline chalcogenides due to their resistance and chemical durability in aggressive media [1,2]. Chalcogenide glasses are suitable materials for membranes preparation in ion selective for Ag(I)-, Pb(II)-, Fe(III)- and Cu(II)-[2-5] ions detection.

The investigation of new glassy materials on the basis of As-chalcogenides with Me_mCh_n (Me=Ag, Cu, Zn, Cd, Ni, Sn, Pb, Tl, Cr; Ch=S, Se, Te) is attractive from scientific point of view and from the point of view of exploration of amorphous materials.

The aim of the present work is to synthesize multi-component chalcogenide glasses in the system As_2Se_3 - Ag_4SSe - $SnTe$ and to investigate their physico-chemical properties. It is expected the new synthesized glasses to be a suitable material for Sn (II) ion-selective electrodes. The idea of our investigation is to observe the role of SnTe addition and the increase of ionic conductivity due to this additive [6].

* Corresponding author: p.petkov@uctm.edu

2. Experimental

The glassforming region was determined by the help of 26 synthesized compositions of As_2Se_3 - Ag_4SSe - $SnTe$ system. Starting components were 5N purity elements As, Sn, Ag, S, Se and Te. Bulk binary glasses As_2Se_3 , Ag_4SSe and $SnTe$ were prepared by direct monotemperature synthesis at highest temperature 900 °C. The same method were used for synthesizes of the samples of of As_2Se_3 - Ag_4SSe - $SnTe$ system from the binary compounds as described in [7]. A vibrational rotating oven were used for the synthesizes, the highest temperature was kept for about 6 hours with a following quenching in a water-ice mixture.

The bulk glasses were analyzed by a visual, X-ray phase analysis (diffractometer TUR – M16 with $Cu_{K\alpha}$ radiation and a Ni filter) and electron-microscope (Philips) analyses. The density (d) of the samples was measured by a hydrostatic method using toluene as immersion fluid and the microhardness (HV) was measured by Vickers' method. A thermograph (DTA) was used to record the thermal characteristics of the samples. The module of elasticity was (E_j), the minimum volume of microvoids (V_h), the energy of their creation (E_h), Hruby criteria (K_G), the compactness (δ) and the number of constrains per atom (N_{co}) were calculated by the equations 1-6, [8,9]:

$$E_j = \frac{3}{2} 10^7 HV \quad (1)$$

$$V_h = 5.04 \frac{T_g}{HV} \quad (2)$$

$$E_h = 30.729 T_g \quad (3)$$

$$K_G = \frac{T_{cr} - T_g}{T_m - T_{cr}} \quad (4)$$

$$\delta = d \left\{ \sum_i \frac{M_i x_i}{d_i} - \sum_i \frac{M_i x_i}{d} \right\} \left[\sum_i M_i x_i \right]^{-1} \quad (5)$$

where M_i and x_i are the molar weight and fraction of the i^{th} component, respectively.

$$N_{co}(Z) = \frac{Z}{2} + Z \frac{Z-1}{2} \quad (6)$$

where Z is the average co-ordination number

3. Results

The synthesized bulk samples of As_2Se_3 - Ag_4SSe - $SnTe$ system are dark coloured with a strong lustre. The results from the X-ray diffraction show that several compositions (group A) are typical glasses without peaks on the roentgenograms – these compositions define the glassforming region. Some other compositions (group B) show diffraction peaks with small intensity (compositions on the region's boundary). The peaks in the diffractograms of the samples from group C are strong typical for crystalline samples outside the glassforming region. Diffractograms of the samples from group C after thermal treatment of the samples show peaks corresponded to As_2Se_3 phase. The line of As_2Se_3 is shifted to the direction of lower atom layer distance in some samples with higher amount of As_2Se_3 due probably to the crystallization of solid solution based on As_2Se_3 .

The electron microscopy study evidences a smooth and homogeneous surface of the samples from the glassforming region. Small crystalline regions are shown on the surface of the samples from the boundary region.

The investigated thermal characteristics of the samples - glass transition temperature (T_g), crystallization temperature (T_{cr}), melting temperature (T_m) and Hruby criteria determined by DTA-analysis are summarized in Table 1. The physico-chemical parameters, measured and calculated, (E_J , V_h , E_h , δ and N_{co}) are presented in Table 2.

4. Discussion

The glassforming region is determined on the basis of the result from the visual, XRD and electron microscopic analyses of the samples from three-component $(As_2Se_3)_x(Ag_4SSe)_y(SnTe)_z$ system, where $x+y+z = 100$ and $m = y / (x+y)$. The results are presented in Fig. 1. The region is situated in the As_2Se_3 - rich region and partially on the As_2Se_3 - Ag_4SSe side (0 - 25 mol % Ag_4SSe) and As_2Se_3 - $SnTe$ side (0 - 45 mol % $SnTe$).

Table 1. Thermal characteristics of glassy samples from the $(As_2Se_3)_x(Ag_4SSe)_y(SnTe)_z$ system.

Composition			m	T_g , °C	T_{cr} , °C	T_m , °C	K_G
x	y	z					
100	0	0	0.0	173	355	360	36.4
90	10	0	0.1	118	275	355	1.96
80	20	0	0.2	113	230	350	0.97
90	0	10	0.0	140	320	350	6
81	9	10	0.1	115	255	345	1.5
67.5	22.5	10	0.25	111	198	350	0.57
58.5	31.5	10	0.35	120	173	340	0.32
80	0	20	0.0	134	280	345	2.24
64	16	20	0.2	107	203	345	0.67
52	28	20	0.35	102	158	345	0.30
70	0	30	0.0	111	240	345	1.23
59.5	10.5	30	0.15	108	210	340	0.78
52	18	30	0.26	102	178	330	0.50
60	0	40	0.0	106	225	345	0.99
48	12	40	0.2	104	172	340	0.40

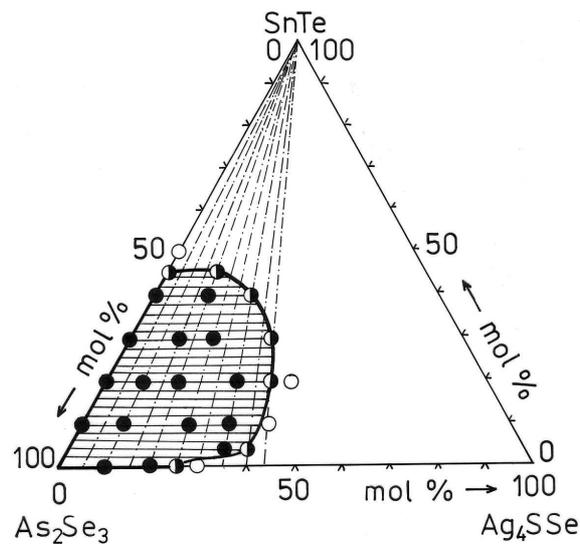
We observed two different effects in the thermograms of glassy samples: first exothermal corresponded to the crystallization of the glass, second - endo-effect is connected to the melting temperature of the investigated glassy sample. The melting effects are determined from the variation of the slope in temperature-time relation. The melting temperatures $-T_m$ vary in the range 100÷175 °C. Glass transition temperature (T_g) values decrease with increasing of m ($z = \text{const}$) and z ($m = \text{const}$).

The crystallization temperatures T_{cr} are in the temperature range 155 - 355 °C; the values are lower when m ($z = \text{const}$) and ($m = \text{const}$) increase.

The larger difference in T_{cr} - T_g values and the smaller temperature interval T_{cr} - T_g determine the larger glassforming ability according to the Hruby criteria - K_G . The values calculated in Table 1 show a decrease in the ability with the increase in $SnTe$ (at $m = \text{const}$) and Ag_4SSe (at $z = \text{const}$) contents. The relation is best expressed when $0.0 \leq m \leq 0.1$ and $0 \leq z \leq 10$.

Table 2. Thermomechanical properties of glassy $(As_2Se_3)_x(Ag_4SSe)_y(SnTe)_z$ samples.

Composition			m	Nco	V_h	δ	E_h	E_J
x	y	z			\AA^3		kJ/mol	kgf/mm ²
100	0	0	0.0	2.88	9.582	-0.042	5.32	1365
90	10	0	0.1	2.60	6.997	-0.088	3.63	1275
80	20	0	0.2	2.33	7.119	-0.111	3.47	1200
90	0	10	0.0	2.78	8.018	-0.681	4.30	1320
81	9	10	0.1	2.50	6.983	-0.072	3.53	1245
67.5	22.5	10	0.25	2.20	7.172	-0.094	3.41	1170
58.5	31.5	10	0.35	1.94	7.855	-0.105	3.68	1155
80	0	20	0.0	2.69	7.853	-0.061	4.12	1290
64	16	20	0.2	2.24	6.826	-0.074	3.29	1185
52	28	20	0.35	2.04	6.591	-0.091	3.13	1170

Fig. 1. Glassforming region of As_2Se_3 - Ag_4SSe - $SnTe$ system.

The measured density values (d) of the investigated glasses are in the range $4.45 \div 5.40 \text{ g cm}^{-3}$ - Table 2. The values increase with increasing of Ag_4SSe amount (at $z = \text{const}$) as the values of binary compound increase in the range $d_{Ag_4SSe} > d_{As_2Se_3}$ - ($d_{Ag_4SSe} = 7.4 \text{ g cm}^{-3}$ [10], $d_{As_2Se_3} = 4.45 \text{ g cm}^{-3}$ [11] and $d_{SnTe} = 6.3 \text{ g cm}^{-3}$ [12]). In the compositional interval $0.00 \leq x < 0.62$ ($m = \text{const}$), the density values increase with $SnTe$ content (when $d_{SnTe} > d_{As_2Se_3}$).

The microhardness values of the investigated glasses are compositional dependent and vary in the range $77 \div 91 \text{ kgf mm}^{-2}$ as it is presented in the Table 2. HV values decrease when Ag_4SSe (at $z = \text{const}$) and $SnTe$ (at $m = \text{const}$) increase. The relation is expected as it is known that

$HV_{As_2Se_3} > HV_{SnTe} > HV_{Ag_4SSe}$ ($HV_{As_2Se_3} = 150 \text{ kgf mm}^{-2}$ [11]; $HV_{SnTe} = 70 \text{ kgf mm}^{-2}$ and $HV_{Ag_4SSe} = 24 \text{ kgf mm}^{-2}$ [10]).

Compositional variations of $V_h(m)$ and $E_h(m)$ at $m = 0.1-0.2$ show a characteristic variation – the decrease in their values is much slower in the interval $0.1 \leq m \leq 0.2$, than in the compositional interval $0.0 \leq m \leq 0.1$ (at $z = \text{const}$). A minimum in the relation is observed at $z = 10$ (Table 2). Probably the addition of Ag_4SSe up to 10–20 mol % ($m = 0.1-0.2$) is connected to a densification of the structure due to placement of silver atoms in the microvoids of As_2Se_3 - glass.

Further addition of $Ag_4SSe > 20 \text{ mol\%}$, respectively increase of silver content leads to a replacement of arsenic by silver atoms. As result the glassy net becomes more loose and the volume of microvoids increase. The processes explained above require more energy that explains the increase in E_h values. The amount of 10 mol% $SnTe$ do not affect the process. The bigger amount of $SnTe$ is associated to an introduction of Sn and Te atoms in the glassy matrix and a respective increase of the glassy compactness due to the bigger atomic radii of Sn and Te. As a result the compactness increases and the V_h values decrease irrespective of m values.

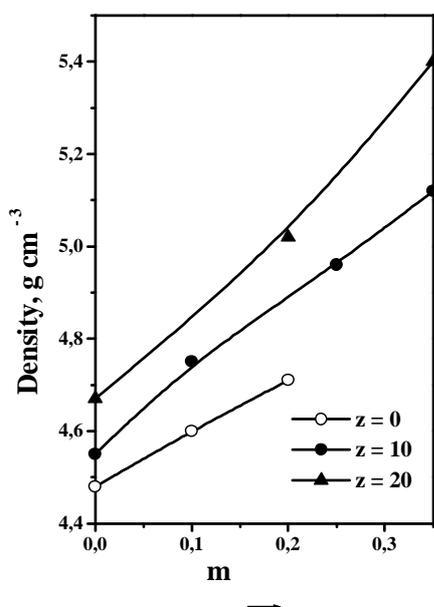


Fig. 2. Relationship density versus composition of the glasses.

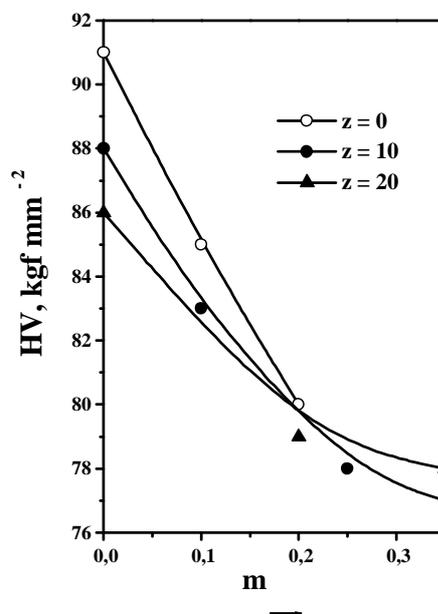


Fig. 3. Relationship microhardness versus composition of the glasses.

The increase in the glassy compactness is connected to an increase in density values as it is depicted in Fig. 2.

The elasticity module $E_f(m)$, repeats the compositional relation of microhardness $HV(m)$ (Fig. 3) as it is predicted by equation (1). The relation values show saturation at $m \approx 0.2$ due to the same structural variations discussed above.

5. Conclusions

New chalcogenide glasses were synthesized and the glasforming region of As_2Se_3 - Ag_4SSe - $SnTe$ system has been determined.

Compositional correlation among physico-chemical characteristics and thermal characteristics were discussed. The observed variations in all mentioned characteristics were explained on the basis of

the structure of the glasses and structural transformations due to the replacement of atoms with smaller radius by atoms with bigger one.

Acknowledgement

This research was supported by the Bulgarian Science Foundation (under contracts NT – 1102/2001 and H - 1204/ 2002) to whom we are deeply indebted.

References

- [1] H. Hirata, K. Higashiyama, *Talanta* **19**, 391 (1972).
- [2] Y. Vlasov, E. Bychkov, *Ion-Sel. Electrode Rev.* **9**, 5 (1987).
- [3] Y. Vlasov, *Fresenius' Z. Anal. Chem.* **335**, 92 (1989).
- [4] C. Koenig, E. Grabner, *Electroanalysis* **7**, 1090 (1995).
- [5] E. Pungor, *Anal. Sci.* **14**, 249 (1998).
- [6] Y. Vlasov, E. Bychkov, A. Medvedev, *Anal. Chem. Acta* **185**, 137 (1986).
- [7] V. Vassilev, Z. Boncheva-Mladenova[†], *Physical Chemistry of Semiconducting Materials*, Ed. of Ministry of Education, Sofia, (1991).
- [8] S. Boycheva, V. Vassilev, P. Petkov, *J. Optoelectron. Adv. Mater.* **3**, 503 (2001).
- [9] Z. Ivanova, E. Cernoskova, V. Vassilev, S. Boycheva, *Materials Letters* **57** 1025 (2003).
- [10] V. Vassilev, V. Vachkov, Z. Ivanova, *J. Mater. Sci.* **12**, 161 (2001).
- [11] Z. Borissova, *Chalcogenide Semiconducting Glasses*, Ed. University Press, Petersburg, (1983).
- [12] V. Vassilev, V. Vachkov, I. Markova, P. Petkov, *Materials Letters* **12**, 104 (2001).