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Thermomechanical characteristics of chalcogenide glasses from the $GeSe_2$-GeTe-PbTe system

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ABSTRACT

Chalcogenide glasses from the $GeSe_2$-GeTe-PbTe system are synthesized. The temperatures of glass-transition, crystallization and melting are determined using differential thermal analysis. On the basis of the obtained values the glass forming ability K_G of the glasses is determined by Hruby's criterion. The maximum value of K_G is obtained for composition $(GeSe_2)_{60}(GeTe)_{20}(PbTe)_{20}$. The minimal volume of the micro-voids V_h and the energy for their formation E_h are calculated. The values of V_h and E_h vary within 0.0219 – 0.0320 nm^3 and 15.89 – 17.31 kJ/mol, respectively. The influence of the composition on the investigated characteristics is analyzed.

KEYWORDS

Thermal characteristics;
Thermomechanical characteristics;
Glass forming ability.

INTRODUCTION

The chalcogenide glasses are important class of materials in the contemporary life. They are used as material for high-speed switchers[1,2], optical fibers and lenses[3-5], optical storage media[6,7], chemical and gas sensors[8-12], etc.

Before proving that a given chalcogenide material is appropriate for any of the above-listed applications the researchers have to perform a row of experiments: outlining of the glass-forming region and establishment of the optimal synthesis conditions of the chalcogenide glasses in it[13-15], determination of their main physico-chemical[13-16], electrical[17,18], and optical[19] characteristics.

Without knowing the three main temperatures, which characterize a glass (temperatures of glass-transition, crystallization and melting), the performance of any investigation at temperature different from the room one is unthinkable. This is due to the fact that at any of these temperatures structural changes occur in the investigated material.

Important indices about the possibility of modeling of these materials (in the shape of lenses and fibers for example) are their mechanical, respectively thermomechanical characteristics. It is well known that the glass often possesses looser structure compared to a crystal with the same composition. This fact supports the possibility of usage of the chalcogenide glass as matrix for many kinds of sensors, since, depending on the size of these micro-voids, this material can selectively absorb or leak particles with desired scale.

The glasses from the $GeSe_2$-GeTe-PbTe system are interesting because semiconductors with quite opposite properties are combined in them. Moreover, on the basis of the available data in the literature, one can suppose that the presence of PbTe in the glassy $GeSe_2$-GeTe matrix will give possibility for application of these materials in the sensorics.

The glass forming region in the $GeSe_2$-GeTe-PbTe system (Figure 1) is situated around the point corresponding to 100 % $GeSe_2$ and lies partially on the $GeSe_2$-GeTe (0-58 mol % GeTe) and $GeSe_2$-PbTe (20-57.5 mol % PbTe) sides. No glassy phases have been obtained in the binary GeTe-PbTe system[13].

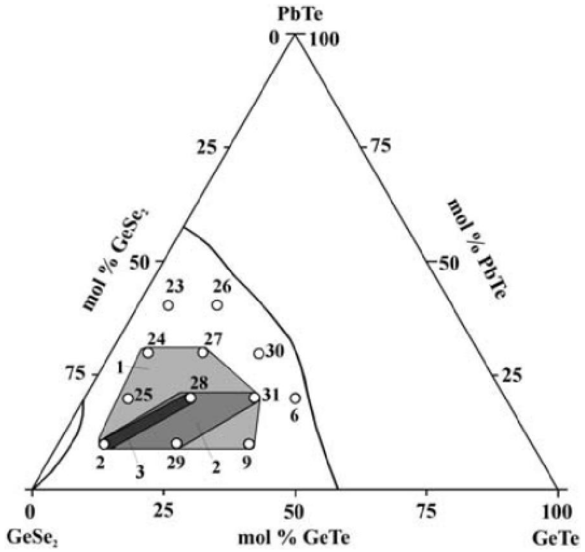

Figure 1 : Region of glass formation in the $GeSe_2$–GeTe–PbTe system.

The aims of the present work are: 1) determination of the characteristic temperatures (glass-transition T_g, crystallization T_{cr} and melting T_m) of chalcogenide glasses from the $GeSe_2$-GeTe-PbTe system, as well as their glass-forming ability K_G and 2) calculation of their thermomechanical characteristics (minimal volume V_h and energy for formation E_h of micro-voids).

EXPERIMENTAL

For determination of the thermal and thermomechanical characteristics of glasses from the $GeSe_2$–GeTe–PbTe system 12 samples were synthesized, which compositions are shown in TABLE 1. The initial components $GeSe_2$, GeTe and PbTe, as well as the samples from the investigated system were synthesized by direct monotemperature synthesis in evacuated to a residual pressure of 1.10^{-3} Pa quartz ampoules. The initial elements used for the synthesis of $GeSe_2$, GeTe and PbTe were Ge, Se and Te with purity of 5N and Pb with purity of 4N. The initial mixture was with weight of 4 g. The synthesis conditions (temperature, duration of the isothermal steps and heating rate) were conformed to the physicochemical features of the initial components. The maximum synthesis temperature of the samples from the investigated system was 975±10°C (duration 2 h, continuous vibration stirring of the melt). After a temperature decrease to 850±10°C the melt was tempered for 10 min and then quenched in ice cold water (cooling rate of 10-15 °C/s).

The thermal characteristics of the glasses were determined by differential thermal analysis (DTA apparatus from the F. Paulic - J. Paulic - L. Erdey system, produced by the MOM-Hungary company) at the following conditions: heating rate of 10 °C/min and reference substance α-Al_2O_3 (measurement accuracy of ± 5 °C). The glassforming ability of the glassy samples was calculated using the Hruby's criterion, K_G[20]:

$$\mathbf{K_G = \frac{T_{cr} - T_g}{T_m - T_{cr}}} \qquad (1)$$

For calculation of the thermomechanical properties (micro-voids volume V_h and energy for their formation E_h) the following equations were used[21]:

$$\mathbf{V_h = 5.04 \cdot 10^{-3} \frac{T_g}{HV} [nm3]} \qquad (2)$$

$$\mathbf{E_h = 29.75 T_g [J/mol]} \qquad (3)$$

RESULTS

The glass-transition T_g, crystallization T_{cr} and melting T_m temperatures of glasses from the $GeSe_2$-GeTe-PbTe system were determined from the DTA heating curves. The glassforming ability K_G, as well as the micro-voids volume and minimal energy needed for their formation were also calculated. The results are given in TABLE 1. The ratio between the components $GeSe_2$

and GeTe is expressed by m, where m=[GeTe]/([GeSe$_2$]+[GeTe]).

TABLE 1 : Thermomechanical properties of samples with composition (GeSe$_2$)$_x$(GeTe)$_y$(PbTe)$_z$, where x+y+z=100 mol % and m=y/(x+y)

№	Composition, mol %			m	K$_G$	HV, kgf/mm^2[13]	E$_h$, kJ/mol	V$_h$.10^{-3}, nm^3
	x	y	z					
2	81	9	10	0.1	2.53	97	17.17	0.0321
29	67.5	22.5	10	0.25	1.62	107	17.31	0.0274
9	54	36	10	0.4	1.42	113	16.84	0.0252
25	72	8	20	0.1	1.30	114	16.72	0.0248
28	60	20	20	0.25	3.31	120	16.87	0.0238
31	48	32	20	0.4	1.85	122	16.45	0.0228
6	40	40	20	0.5	0.36	123	15.89	0.0219
24	63	7	30	0.1	1.11	113	16.45	0.0247
27	52.5	17.5	30	0.25	1.17	119	16.63	0.0237
30	42	28	30	0.4	0.55	121	16.24	0.0227
23	54	6	40	0.1	0.83	111	15.92	0.0243
26	45	15	40	0.25	0.25	117	16.01	0.0232

DISCUSSION

With the increase of the PbTe content the glass-transition temperature T$_g$ decreases as the curves are almost equidistantly shifted one by another with weakly expressed maximum at m=0.25 – Figure 2. In the concentration interval 0.10≤m≤0.25 the T$_g$ slightly increases, which should be related to the modifying properties of GeTe. The T$_g$ decreases in the concentration interval 0.25≤m≤0.50, which can be indirectly connected to the strengthened influence of the near glass-forming border, as a result of which the system becomes more stable, since it gradually rearranges towards formation of crystalline phase (s). The almost equipotential shift of the T$_g$(m) dependencies with the increase of the PbTe concentration towards decrease of T$_g$ is logically related to the approximately even increase of the crystallization trend from curve to curve.

The crystallization temperature T$_{cr}$ (Figure 3) decreases with the increase of PbTe content at m=const, which makes sense since the PbTe is typical crystalline compound and at this method of synthesis it not likely to exist in practice in amorphous (glassy) form. This means that when its content is increased less energy is needed for its crystallization. Moreover, at a defined value of m, which should be examined as critical one (m$_{crit}$), two phases crystallize and the area under the crystallization effect is directly related to the content of the crystallizing phase. With the increase of the PbTe the m$_{crit}$ shifts towards the higher values, for example at z=40 m$_{crit}$=0.1; z=30 m$_{crit}$=0.25, etc. At z=10, the m$_{crit}$ does not appears due the approach to the glassforming border, i.e. the m$_{crit}$ should appear at a value higher than 0.4. Such regularity is logical, since at lower z values the probability for crystallization of PbTe is small, and the probability for GeTe crystallization is not high too, since in this three-component system the GeTe, regardless of its modifying role, is hard to be obtained in amorphous (glassy) state. The linear path of the T$_{cr}$(m) dependence at z=10 shows that the crystallizing phase is GeTe.

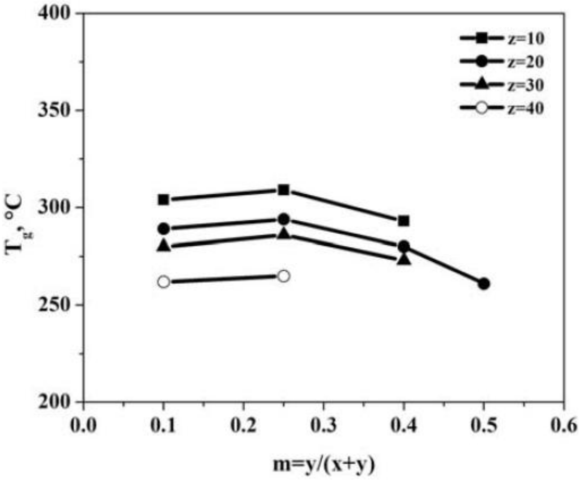

Figure 2 : T$_g$(m)$_{z=const}$ dependence.

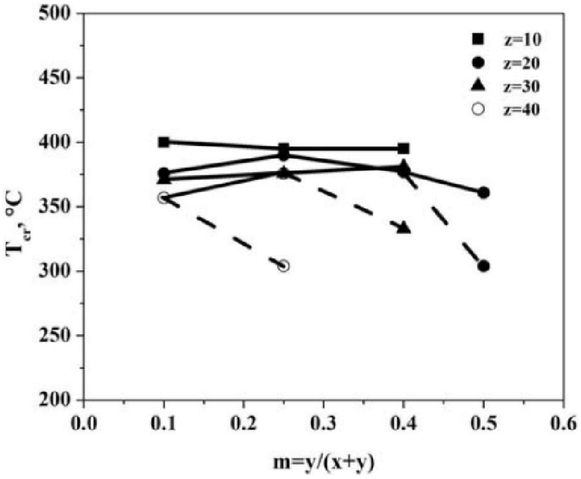

Figure 3 : T$_{cr}$(m)$_{z=const}$ dependence.

The T$_m$(m) curves family (Figure 4) at z=const (0.1≤m≤0.5 and 10≤z≤40) is characterized by the following peculiarities:

- at z=10 and m=0.10 and 0.25 two melting peaks are observed, as the high-temperature one strongly depends on the GeTe content and the low-temperature does not depend in practice. Such behavior synonymously shows that the high-temperature effect is related to the liquidus line of the pseudobinary system, defined by the $(GeSe_2)_{90}(PbTe)_{10}$-GeTe section. The low-temperature effect is related to the eutectic temperature of the phases, situated in the concentration borders 0.1≤m≤0.5. Since the melting temperatures of $GeSe_2$ and GeTe are almost equal, the melting temperatures of the glasses, which fall in the above interval of concentrations, will also weakly depend on m;
- For all other curves of the T_m(m) dependencies at z=const (20≤z≤40) the m influence is weakly expressed and the curves themselves are situated in a narrow temperature interval of 419-472 °C, which means that in these concentration borders the investigated alloys act as compositions from the sub-eutectic region. In addition, the eutectic horizontal weakly depends on the PbTe concentration, since it is situated in the same concentration interval.

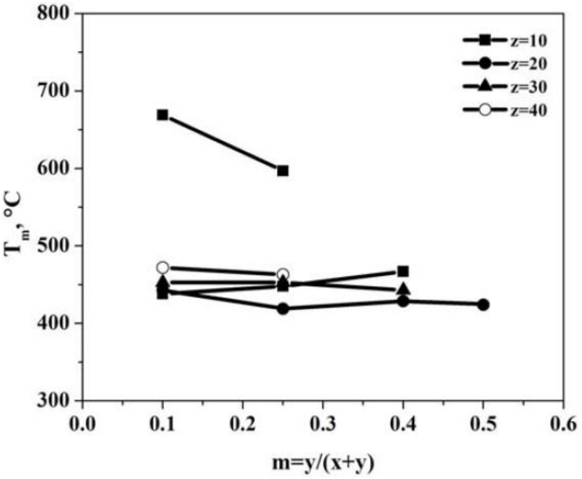

Figure 4 : $T_m(m)_{z=const}$ dependence.

The Hruby's criterion K_G characterizes the ability of a given composition to transform in glassy state. For calculation of the K_G the lower values of T_{cr} and T_m have been used. As it can be seen from Eq. (1) the numerical value depends in three independent characteristics of the glasses - T_g, T_{cr} and T_m, as each one of them depends on their composition. This explains to a large extent the complicated form of the concentration dependencies $K_G(m)_{z=const}$ and $K_G(z)_{m=const}$. Nevertheless, these composition-property diagrams show certain tendencies in the K_G deviation. The following specifics are obvious:

- The modifier GeTe advantages the glassformation to a defined concentration range. In the $GeSe_2$-GeTe system this range at first approach is from 0 to m~0.25. The influence of PbTe, which is in the same homologous series formed by the compounds with general formula MeTe (Me=Ge, Sn, Pb), is similar. This approach is confirmed by the analogical influence of PbTe on the K_G (K_G increases in the concentration interval from 0 to ~ 20 mol % PbTe at m=0.25). By this reason the maximum value of K_G is obtained for the composition, marked with p. 28 (Figure 1);
- The increase of the crystalline components GeTe and PbTe content over the defined critical value mentioned above, leads to decrease of the probability for glassformation, which finds it expression in the absolute value of K_G;
- It makes sense when approaching the glassforming border, which physical sense is increase of the probability for crystallization and decrease of the glassforming ability, a decrease of K_G to be observed. This is confirmed by the present experiments;
- The deduced regularities, based on the experimental results, allow us to outline, even very roughly, three sub-regions with different glassforming ability - Figure 1 (in region 1 $K_G \geq 1.0$; in region 2 – $K_G \geq 1.5$ and in region 3 – $K_G \geq 2.0$).

During the glass structure formation with the increase of the GeTe content (m increases, z is constant) and increase of the PbTe (m=const) disparate structural units participate (tetrahedrons $GeSe_{4/2}$ and linear structural units –Ge–Te– and –Pb–Te–), as well as atoms with different ionic radii (Ge, Pb, Te), as each of them has limiting influence in a certain concentration interval. Such behavior of the glass composition on the microhardness HV was discussed in our previous work[13]. It makes sense these factors also to influence any other property of the chalcogenide glasses from the $GeSe_2$-GeTe-PbTe system, in the particular case the concentration dependence of K_G.

Analogically, the above-counted structural changes influence the concentration dependencies of E_h, which is confirmed by the even weakly expressed maximum at m=0.25 in the concentration dependencies $E_h(m)_{z=const}$. A change of the angle coefficient at m=0.25 is also observed in the $V_h(m)_{z=const}$ dependencies. Since the densification of the glass structure is related to change of one kind of atoms (Se and Ge) with another (Te and Pb), having larger ionic radius, then the energy, needed for micro-voids formation, decreases with the increase of the PbTe content. If the densification is related to partial filling of the interknots either with Ge atoms or with Se atoms, displaced by Pb-, respectively Te-atoms (which is less probable), then the E_h should increase due the necessity of additional energy for this second, significantly more complicated type of rearrangements in the network of the chalcogenide glass.

CONCLUSIONS

On the basis of the synthesized chalcogenide glasses from the $GeSe_2$-GeTe-PbTe system and the preformed differential thermal analysis the glass-transition (T_g), crystallization (T_{cr}) and melting (T_m) temperatures have been determined. It is established that:

i) The glass-transition temperature T_g changes between 261 and 309 °C and decreases with the increase of the PbTe content;

ii) The crystallization and melting temperatures vary between (304÷400 °C) and (419÷669 °C), respectively, as for some compositions two crystallization and melting effects are observed;

iii) On the basis of the obtained results from the calculation of the glassforming ability by the Hruby's criterion, three sub-regions with different glassforming ability are outlined;

iv) The influence of the glasses composition on the volume of the micro-voids, formed in them, and the minimal energy, needed for their formation, is studied.

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REFERENCES

[1] K.Makino, J.Tominaga, M.Hase; Optics Express, **19(2)**, 1260 **(2011)**.

[2] A.Zakery, M.Hatami; J.Phys.D: Appl.Phys., **40(4)**, 1010 **(2007)**.

[3] M.Asobe; Opt.Fiber Technol., **3(2)**, 142 **(1997)**.

[4] A.Saitoh, T.Gotoh, K.Tanaka; Opt.Lett., **25(24)**, 1759 **(2000)**.

[5] A.Saitoh, T.Gotoh, K.Tanaka; J.Non-Cryst.Solids, **299-302(2)**, 983 **(2002)**.

[6] A.V.Kolobov, J.Tominaga; J.Mater.Sci.: Mater. Electron., **14(10-12)**, 677 **(2003)**.

[7] A.A.El-Sebaii, S.A.Khan, F.M.Al-Marzouki, A.S.Faidah, A.A.Al-Ghamdi; J.of Lumin., **132(8)**, 2082 **(2012)**.

[8] V.S.Vassilev, S.V.Boycheva; Talanta, **67(1)**, 20 **(2005)**.

[9] J.P.Kloock, Y.G.Mourzina, Y.Ermolenko, T.Doll, J.Schubert, M.J.Schöning; Sensors, **4**, 156 **(2004)**.

[10] A.V.Legin, E.A.Bychkov, Y.G.Vlasov; Sens. Actuators B, **24(1-3)**, 309 **(1995)**.

[11] S.Marian, D.Tsiulyanu, H.D.Liess; Sens.Actuators B, **78**, 191 **(2001)**.

[12] D.Tsiulyanu, S.Marian, V.Miron, H.D.Liess; Sens.Actuators B, **73(1)**, 35 **(2001)**.

[13] L.Aljihmani, K.Petkov, V.Vassilev; J.Non-Cryst.Solids, **358**, 364 **(2012)**.

[14] V.Vassilev, K.Tomova, V.Parvanova; Mat.Chem. Phys., **114**, 874 **(2009)**.

[15] V.Vassilev, M.Radonova, S.Boycheva, E.Fidancevska; Optoelectron.Adv.Mater. – Rapid Comm., **3(8)**, 751 **(2009)**.

[16] V.Vassilev, S.Parvanov, K.Tomova, E.Fidancevska, V.Vachkov, M.Milosevski, L.Aljihmani; J. Univ.Chem.Technol.Met., **42(1)**, 61 **(2007)**.

[17] B.Stefanova, D.Nesheva, K.Petkov, M.Radonova, G.Vassilev, V.Vassilev; J. Optoelectron.Adv.Mater., **13(11-12)**, 1454 **(2011)**.

[18] A.Feltz, G.Kley, I.Linke; J.Non-Cryst.Solids, **33(3)**, 299 **(1979)**.

[19] K.Petkov, J.Tasseva, V.Vassilev, L.Aljihmani; J.Optoelectron.Adv.Mater., **13(11-12)**, 1514 **(2011)**.

[20] A.Hruby; Czech.J.Phys.B, **22(11)**, 1187 **(1972)**.

[21] V.Vassilev, G. Vassilev, E.Fidancevska; Chalcogen. Lett., **5(12)**, 415 **(2008)**.