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CRYSTALLIZATION, KINETICS AND MEAN BOND ENERGY OF GLASSES FROM THE $GeSe_2$-GeTe-SnTe SYSTEM

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ABSTRACT

Chalcogenide glasses from the $GeSe_2$-GeTe-SnTe system were synthesized by direct synthesis with following quenching in ice cold water. The crystallization temperatures of the as-prepared samples were determined using differential thermal analysis at heating rates of 10, 15, 25 and 36 K/min. Al_2O_3 and Se were used as reference substances. The standard substances and the investigated sample in quantity of ≈ 0.3 g were placed in crucibles, which are sealed at residual pressure of ~ 1.10^{-3} Pa. The activation energy of crystallization, as main kinetic parameter characterizing this process, was calculated by the Kissinger and the Augis&Bennett models. The values, obtained by the two independent models, coincide.

The basic thermodynamic parameters of the crystallization process (enthalpy and entropy alternation) were defined. The enthalpy alternation of the selenium crystallization was calculated, as its crystallization heat is known.

The overall mean bond energy ‹E›, the mean coordination number ‹Z›, the mean bond energy of the average cross-linking/atom and the average bond energy per atom of the "remaining matrix" - $\bar{E}_c$ and $\bar{E}_{rm}$, as well as the average heteropolar bond energy E_{hb} and the degree of „cross-linking/atom" P_p are calculated.

A correlation between the investigated parameters and the glasses' composition was established.

Keywords: chalcogenides, glass transition, crystallization, kinetics, thermodynamics, mean bond energy.

INTRODUCTION

The chalcogenide glasses (ChG) have been subject of investigation by many authors due to their interesting physicochemical properties and to the wide possibilities for application in the electronic and the optoelectronics [1], which they offer. The ChG can be obtained relatively easy in bulk and thin film form, the impurities have weak influence on their properties and their price is acceptable. At the development of new glasses, one of the first investigations is the one connected with the determination of the thermal stability of the glasses and their thermodynamic characteristics which give abundant information for definition of their applicability. Many ChG undergo multiple thermal changes from the glass↔crystal type. These two conditions are characterized by completely different electroconductivity, which makes them suitable for media storage in binary code on thin chalcogenide films. Namely this reversible thermo-structural effect lies on the basis of the re-writable optical disks [2] and the energy dependent memories (non-volatile memory devices) [3].

The compounds from the $GeSe_2$–GeTe–SnTe system are very interesting for the science and technology because they are formed by typical semiconductors with quite opposite properties. By the interaction of $GeSe_2$ and GeTe with SnTe, new glasses with interesting properties could be obtained with possible application as optoelectronic devices, ionselective and gas sensors.

The chalcogenide glasses (ChG) from the $GeSe_2$-GeTe-

SnTe system are investigated [4]. The glassforming region lies partially on the $GeSe_2$-GeTe (0 - 58 mol % GeTe) side and on the $GeSe_2$-SnTe side (25 - 45 mol % SnTe). Glasses in the $GeSe_2$-SnTe system were not obtained [4].

The aim of the present work is investigation of the crystallization kinetics, the thermodynamic characteristics of the crystallization process and the mean bond energy of ChG from the $GeSe_2$-GeTe-SnTe system.

EXPERIMENTAL

For the accomplishment of the investigations, 8 ChG with composition $(GeSe_2)_a(GeTe)_b(SnTe)_c$ were synthesized. They were obtained by direct monotemperature synthesis in evacuated quartz ampoules and quenching in water+ice mixture. The obtained materials are characterized by X-ray diffraction analysis performed on apparatus TUR-M61 with CuK_α irradiation (Ni-filter, $\theta = 5 - 40°$).

The thermal investigations were performed on derivatograph from the F. Paulic-J. Paulic-L. Erdey system (MOM-Hungary) at different heating rates (10, 15, 20 and 36 K/min) and standard substances - Al_2O_3 and Se.

RESULTS AND DISCUSSION

Typical diffractograms of the samples from the investigated system are presented on Fig. 1. The compositions, lying into the region of glass formation show diffractograms, which are typical for amorphous materials – lack of well expressed peaks and presence of the characteristic X-ray amorphous plateau.

Using the differential thermal analysis curves of heating the characteristic temperatures (temperatures of glass-transition T_g and crystallization T_{cr}) of the glasses from the $(GeSe_2)_a (GeTe)_b(SnTe)_c$ system were determined. The results are given in Table 1 and Table 4. Typical thermograms of the investigated samples are presented on Fig. 2.

Kinetics of crystallization

The results from the investigation of T_{cr} at heating rates (b) of 10, 15, 20 and 36 K/min are presented in Table 1 (the glass composition is presented in Table 2). For some glasses there are two determined crystallization temperatures, i.e. more than one phase is crystallizing. This confirms the results from the previous investigations of the crystallizing phases, where the reflexes of GeSeTe, SnSe and SnTe were clearly registered [4].

The activation energy of the crystallization E_a was defined by the following models:

The Kissinger model [5]:

$$\ln\frac{v}{T_{\max}^2} = -\frac{E_a}{RT_{\max}} + const \qquad (1)$$

The Augis&Bennett model [6]:

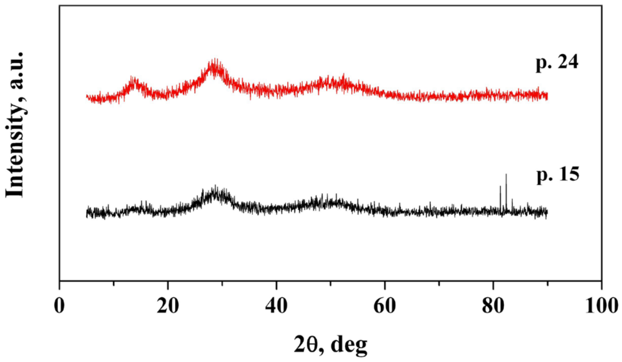

Fig. 1. Typical XRD patterns for samples from the $GeSe_2$-GeTe-SnTe system - p. 24 and p. 15.

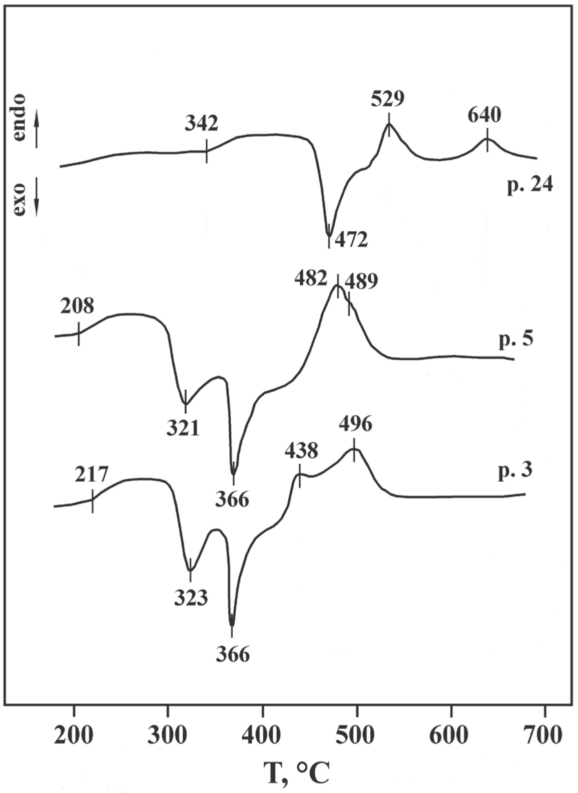

Fig. 2. Typical thermograms of chalcogenide glasses from the $GeSe_2$-GeTe-SnTe system.

Table 1. Crystallization temperatures at different heating rates and activation energy of the crystallization process of glasses from the investigated system.

p.	b, K/min	T_{cr}, K	E_a, kJ/mol		p.	b, K/min	T_{cr}, K	E_a, kJ/mol	
			Aguis& Bennett	Kissinger				Aguis& Bennett	Kissinger
24 m=0.2	10	753	174.5	179.8	13 m=0.2	10	639	120.8	120.0
	15	745				15	649		
	25	759				25	665		
	36	764				36	673		
4 m=0.2	10	668	139.6	138.3	5 m=0.4	10	590	188.1	188.1
	15	677				15	594		
	25	691				25	604		
	36	701				36	608		
15 m=0.4	10	631	140.2	139.5		10	631	107.9	107.1
	15	649				15	639		
	25	653				25	658		
	36	659				36	667		
	10	676	174.1	172.8	9 m=0.0	10	619	115.3	114.7
	15	683				15	634		
	25	695				25	648		
	36	703				36	651		
6 m=0.5	10	596	146.4	151.9	3 m=0.2	10	591	170.1	170.2
	15	601				15	596		
	25	613				25	607		
	36	619				36	611		
	10	631	128.8	128.0		10	632	102.9	102.1
	15	639				15	639		
	25	654				25	658		
	36	662				36	670		

$$\ln\frac{v}{T_{\max}-T_o}=-\frac{E_a}{RT_{\max}}+const \qquad (2)$$

where T_o is the temperature in the furnace at the beginning of the Differential Thermal Analysis (DTA)-measurements ($T_o = 298$ K).

The results from the calculation of the activation energy of the crystallization process are presented in Table 1.

The complicated structure of the investigated glasses is due to the simultaneous participation of the components $GeSe_2$, GeTe and SnTe, which are built in the glass structure with their structural units: tetrahedrons ($GeSe_{4/2}$) and linear chains (-Ge-Te- and -Sn-Te-). As T_{cr} of every one of the investigated samples is determined at four different heating rates, finding the correlation between the activation energy of the crystallization process in a limited numbers of samples is a complicated task.

The activation energy of the crystallization process of the chalcogenide glasses from the $GeSe_2$-GeTe-SnTe system depends on the glass composition and as far as crystallization of one or two crystalline phases it can be concluded that no composition is responsible for E_a alternation, but the structural units concentration are, which are determined by the initial component concentration. Furthermore, it should be taken into account the functions, which each component performs in the system ($GeSe_2$ - glassformer; GeTe - modifier; SnTe - component, which gives desired property). On the other hand, the increase of the ratio [GeTe]/[$GeSe_2$] expressed by the „m“ parameter (at [SnTe] = const, expressed by the “c” parameter), as well as the increase of the SnTe content at m = const the composition of the chalcogenide glass is close to the glassforming border. This means that the system is ready for the glass→crystalline phase transition. This tendency is quantified in energy Ea, needed for the crystallization process. These conclusions are confirmed by the dependencies $E_a(m)_{c = const}$ and $E_a(c)_{m = const}$. In both

Table 2. Alternation of the enthalpy (ΔH) and the entropy (ΔS) of the crystallization process of glasses from the $(GeSe_2)_a(GeTe)_b(SnTe)_c$ system, where a+b+c = 100.

№	Composition			m=b/(a+b)	T_{cr}, K	s, cm^2	M	ΔH, kJ/mol	ΔS, J/mol.K
	a	b	c						
24	80	20	0	0.2	745	2.121	224.4960	31.53	42.32
4	72	18	10	0.2	677	3.828	226.6774	55.54	82.04
15	54	36	10	0.4	649	0.525	221.2198	7.33	11.29
				0.4	683	1.775	221.2198	25.20	36.90
6	45	45	10	0.5	601	0.290	218.4910	3.90	6.49
				0.5	639	0.301	218.4910	4.13	6.46
13	64	16	20	0.2	649	4.464	228.8588	57.00	87.83
5	48	32	20	0.4	594	1.484	224.0076	20.39	34.33
				0.4	639	2.121	224.0076	29.83	46.68
9	70	0	30	0.0	634	3.103	235.2850	40.71	64.21
3	56	14	30	0.2	596	1.685	231.0402	21.71	36.43
				0.2	639	1.685	231.0402	21.72	33.99
Se					422	4,104	78.96	18.07	42.73

cases E_a decreases, as the reduction is less expressed at the first dependence, since the modifying action of the GeTe.

The obtained results for the E_a by the two methods are in good conformity. The deviation is insignificant (Table 1).

Enthalpy and entropy alternation in the glass-crystal phase transition

The glass-crystal phase transition is related to appearance of exothermal effect. The enthalpy renders an account to the heat, obtained by the system or given to the environment at constant pressure. The entropy is a criterion about the disorder (the chaos) of one thermodynamic system. For determination of the enthalpy alternation in the glass-crystal phase transition the following dependencies were used [7]:

$$\frac{\Delta H_A}{\Delta H_B} = X\frac{m_B}{m_A}\cdot\frac{M_A}{M_B}\cdot\frac{S_A}{S_B} \tag{3}$$

$$\Delta H = Q/\left(\frac{m}{M}\right) \quad \frac{Q_A}{Q_B} = \frac{s_A}{s_B} \tag{4}$$

where ΔH_A, ΔH_B, S_A, S_B are the enthalpy alternations and the areas under the $\Delta T(\tau)$ curves from DTA of the investigated (A) and the standard (B) substances; m_A, m_B - the masses of the two substances (m = 0.3 g); M_A, M_B - the molar weights; X - a coefficient rendering the difference of the phase transition temperatures of the probe and the standard, $X = 1+0.00058\ (T_A-T_B)$.

The enthalpy alternation (ΔH_B) of the selenium crystallization was calculated using Eq. (4), as its crystallization heat is known Q = 68.66 J/mol [8].

The entropy alternation (ΔS_B) of the crystallization process was defined by Eq. (5):

$$\Delta S_B = \frac{\Delta H_B}{T_{\max}} \tag{5}$$

The results from the calculation of the thermodynamic parameters (ΔH and ΔS) of the crystallization process for the investigated ChG are summarized in Table 2. The crystallization temperatures were obtained at heating rate of 15°C/min.

From the analysis of the values for ΔH and ΔS the following conclusions can be made:

a) The values of ΔH(m) and ΔS(m) decrease with increasing the GeTe content in the glasses, at a constant content of the third component (SnTe). Above one critical value of the GeTe concentration (above 58 mol % GeTe) [4] linear GeTe chains are included between the two Se-atoms by the sheme:

$$\ldots\text{–Se–}\ldots\text{–Se–}\ldots + (\text{–Ge–Te–})_n \rightarrow \ldots\text{–Se–}\ldots(\text{–Ge–Te–})_n\ldots\text{–Se–}\ldots,$$

as a result of which conditions for formation and growth of GeTe nuclei are formed. The introduction of GeTe in the vitreous matrix leads to significant reduction of the enthalpy of the process, i.e. the crystallisation aptitude of the glasses increases.

b) The dependencies ΔH(c) and ΔS(c) are characterized with maximum at constant $GeSe_2$ and GeTe ratio (at m = 0.2, c = 20 mol % SnTe). This alternation of ΔH is logical since the compositions lying near the glassforming border crystallize easier than the compositions lying in the centre of the glassforming area. The components GeTe and SnTe take the same position in the glasses structure (breaking the selenium bridges –Se–Se– and building in between the Se-atoms), which does not impose complicated structural transformations into the glassy network. This leads to the increase of the „chaos“ in the system as a result of which ΔH and ΔS increase.

Mean bond energy

For the calculation of the mean bond energy and its components the following notation of the system is convenient: $Ge_xSn_\ell^{2+}Se_pTe_n$, where x, ℓ, p and n are the mole parts of the components (x+ℓ+p+n = 1).

The mean coordination number ‹Z› of the glasses from the investigated system was estimated by eq. (6) [9], using the coordination numbers $Z_{Ge} = 4$ [10], $Z_{Sn} = 2$, $Z_{Se} = 2$ [10] and $Z_{Te} = 2$ [11]:

$$\langle Z\rangle = x.Z_{Ge} + \ell.Z_{\mathrm{Sn}} + \mathrm{p}.Z_{\mathrm{Se}} + \mathrm{n}.Z_{\mathrm{Te}} \tag{6}$$

The overall mean bond energy ‹E› was defined by the Tichy‘s formula for complex chalcogenide systems [10]:

$$\langle E\rangle = \overline{E}_c + \overline{E}_{rm} \tag{7}$$

where: $\overline{E}_c$ – mean bond energy of the average cross-linking/atom calculated by Eq. (8):

$$\overline{E}_c = P_p.E_{hb} \tag{8}$$

where: E_{hb} - average heteropolar bond energy for glasses with composition $Ge_xSn_\ell Se_pTe_n$. It was calculated using Eq. (9) and Table 3. The bonds, which bond energies are not referred are calculated using the Pauling formula: $E_{A\text{-}B} = (E_{A\text{-}A}.E_{B\text{-}B})^{1/2} + 30(\chi_A - \chi_B)^2$ [13], where $E_{A\text{-}A}$ and $E_{B\text{-}B}$ are bond energies and χ_A, χ_B - the electro-negativities of the A and B elements.

$$E_{hb} = \frac{x.Z_{Ge}.E_{Ge-Se} + x.Z_{Ge}.E_{Ge-Te} + \ell.Z_{Sn}.E_{Sn-Se} + \ell.Z_{Sn}.E_{Sn-Te}O}{x.Z_{Ge} + \ell.Z_{Sn}} \tag{9}$$

The coefficient R, which defines the chalcogen content in the glasses was calculated by Eq. (10):

$$R = (mZ_{Se} + nZ_{Te})/(xZ_{As} + yZ_{Ge} + zZ_{Sn}) \tag{10}$$

The investigated system is chalcogen poor since for all glasses R < 1. At R < 1, for calculation of the degree of „cross-linking/atom“ (P_p) the equation $P_p = (\mathrm{p}Z_{\mathrm{Se}} + \mathrm{n}Z_{\mathrm{Te}})/1$ was used; and for the average bond energy per atom of the “remaining matrix“ $E_{rm} = 2(0.5\langle Z\rangle - P_p)E_{\langle\rangle}/\langle Z\rangle$.

The average energy of the metal-metal bonds in the chalcogen poor part of the glassforming region $E_{\langle\rangle}$ was calculated by Eq. (11):

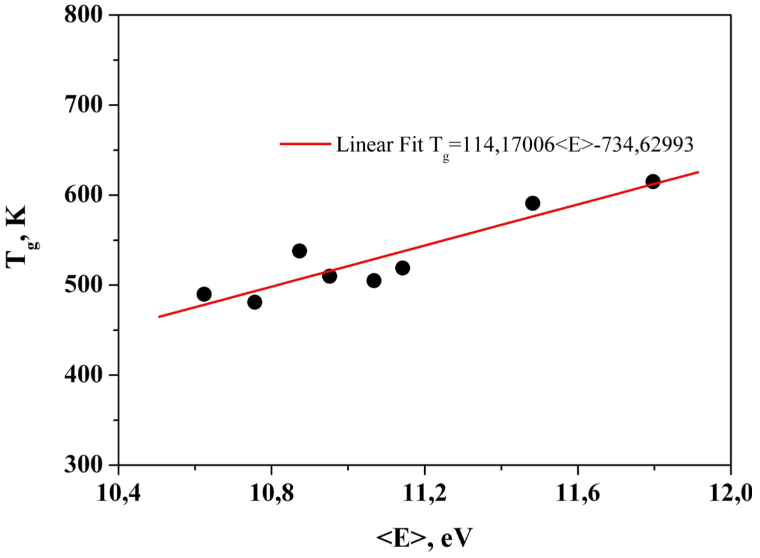

Fig. 3. Dependence of glass transition temperature (Tg) vs. overall mean bond energy $\langle \AA \rangle$.

Table 3. Bond energy between the elements constituting the $Ge_xSn_\ell Se_pTe_n$ glasses.

Bond	Bond energy, kJ/mol	Bond energy, eV	Bond	Bond energy, kJ/mol	Bond energy, eV
Ge-Ge	263.6 [12]	2.73202	Ge-Te	397 [12]	4.115
Se-Se	332.6 [12]	3.44716	Ge-Sn	222.32 [13]	2.304185
Te-Te	259.8 [12]	2.69264	Se-Te	291.6 [12]	3.02222
Sn-Sn	187.1 [12]	1.93916	Se-Sn	401.2 [12]	4.15815
Ge-Se	484.7 [12]	5.02356	Te-Sn	205 [12]	2.125

Table 4. Parameters of the chemical bond of the samples from the system $(GeSe_2)_a(GeTe)_b(SnTe)_c$, where a+b+c = 100.

№	T_g, K	⟨Z⟩	E_c, eV	E_{rm}, eV	⟨E⟩, eV	E_μ, eV
24	615	2.7144	11.7486	0.0480	11.7966	1.9496
4	591	2.6618	11.3664	0.1158	11.4822	1.8353
15	519	2.7084	10.8991	0.2431	11.1422	1.7117
6	510	2.7347	10.6395	0.3119	10.9514	1.6423
13	505	2.6060	10.9594	0.1081	11.0675	1.6845
5	481	2.6452	10.5293	0.2268	10.7561	1.5713
9	538	2.5186	10.8729	0.0002	10.8731	1.6139
3	490	2.5468	10.5238	0.0997	10.6235	1.5231

$$E_{\langle\,\rangle} = (E_{Ge-Ge} + E_{Sn-Sn} + E_{Ge-Sn})/3 \qquad (11)$$

The values of ⟨Z⟩, $\bar{E}_c$, $\bar{E}_{rm}$ and ⟨E⟩ are summarized in Table 4. Between T_g (heating rate 15 k/min) and ⟨E⟩ exists a linear dependence $T_g = 114.17\langle E\rangle - 734.63$.

The slope of the line $T_g = f(E_\mu)$ is 314.05 K/eV is very close to the theoretical value 314 K/eV, received by the Tanaka model: $T_g = 314.E_\mu$. It should be expected that the correlation between $T_g = f(\langle E\rangle)$ for all chalcogenide glasses from the investigated system is linear. It is confirmed in the accuracy (± 10°C) and from the Fig. 3.

CONCLUSIONS

Using differential thermal analysis at various heating rates the glass transition and crystallization temperatures of the glasses from the $GeSe_2$-GeTe-SnTe system were established. On the base of the Kissinger and Augis&Bennett models the activation energy of the crystallization process was defined. The activation energy varies in a wide range from 102 to 188 kJ/mol.

The thermodynamic characteristics (enthalpy and entropy alternation) of the crystallization process were calculated and are between 3.90 - 57.00 kJ/mol and 6.46 - 87.83 J/mol.K, respectively. A good correlation between these characteristics and the glass' composition was established.

The overall mean bond energy ⟨E⟩, the mean coordination number ⟨Z⟩, the mean bond energy of the average cross-linking/atom and the average bond energy per atom of the "remaining matrix" - $\bar{E}_c$ and $\bar{E}_{rm}$, as well as the average heteropolar bond energy E_{hb} and the degree of „cross-linking/atom" were determined. Between T_g and ⟨E⟩ exists a linear dependence $T_g = 114.17\langle E\rangle - 734.63$.

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