

**CRYSTALLIZATION KINETICS AND SOME THERMODYNAMIC  
CHARACTERISTICS OF CHALCOGENIDE GLASSES  
FROM THE  $As_2Se_3$ - $As_2Te_3$ - $Sb_2Te_3$  SYSTEM**

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**ABSTRACT**

*The crystallization kinetics of samples from the  $As_2Se_3$ - $As_2Te_3$ - $Sb_2Te_3$  system is investigated with differential thermal analysis. Dialuminium trioxide ( $Al_2O_3$ ) and selenium (Se) are used as standard substances. The basic temperatures characterizing this process are identified. The values of the activation crystallization energy are calculated on the basis of four models. Some thermodynamic characteristics (alternation of the enthalpy and entropy) of the process are also defined. A correlation between these properties and the composition of the glasses is observed.*

*Keywords:* chalcogenide glasses, crystallization, kinetics, DTA, properties.

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**INTRODUCTION**

An increasing interest towards the investigations of the chalcogenide glasses (ChG) has been observed in the past years. This interest is due to their specific properties, as well as to the possibilities for their application in different fields of science. The optical devices, working on the basis of photoinduced phase transition amorphous  $\leftrightarrow$  crystalline state in the ChG, are a perspective for the micro- and the nanoelectronics. Besides, they find application in the devices for optical recording of information. As a result of the phase transition, a series of physical properties on the surface of the disk are changed. The recording is realized by melting of defined areas in the crystalline material with short laser impulses and the erasing - by heating with long laser impulses. At the time of the erasing process, the amorphized areas get back to a crystalline state. During these photostructural changes, the main optical characteristics of the ChG, as the reflection, transmission, ex-

inction and refraction coefficients, the optical band gap, etc. are changed.

To erase the recorded information, laser impulses with duration of a few hundred nanoseconds are used, i.e. the glass  $\leftrightarrow$  crystal transition should pass very quickly. In that sense, studying the kinetics of this transition is a main task when determining the applicability of a new ChG.

As a rule, two methods are used for studying the crystallisation kinetics – an isothermal one and a non-isothermal one [1]. In the first case, the sample is subjected to a thermal treatment at  $T \approx T_{\text{crystallization}}$  for a short time and the physicochemical properties are studied as a function of time. According to the second method, the sample is heated with a constant rate and the investigated characteristics are measured as a function of the temperature.

The thin films based on Se and Te are promising materials for devices, which use the transition amorphous  $\leftrightarrow$  crystalline state [2]. The addition of a

third component to the binary  $\text{Se}_x\text{Te}_{1-x}$  chalcogenide glasses leads to the increase of their stability.

The crystallization kinetics is an object of many studies [3 - 10]. Different methods for its determination (DSC or DTA), based on investigation of the exothermal peaks obtained by heating are used.

The glass forming region in the  $\text{As}_2\text{Se}_3$ - $\text{As}_2\text{Te}_3$ - $\text{Sb}_2\text{Te}_3$  system (Fig. 1), outlined on the basis of the results from visual, x-ray and electron microscopic analyses, was drawn to the area rich of  $\text{As}_2\text{Se}_3$ , which lied fully on the  $\text{As}_2\text{Se}_3$ - $\text{As}_2\text{Te}_3$  side (from 0 to 100 mol %  $\text{As}_2\text{Se}_3$ ) and partially on the  $\text{As}_2\text{Se}_3$ - $\text{Sb}_2\text{Te}_3$  side (from 0 to 38 mol %  $\text{Sb}_2\text{Te}_3$ ) [11]. Glasses were not obtained in the  $\text{As}_2\text{Te}_3$ - $\text{Sb}_2\text{Te}_3$  side.

The aim of the present work is to investigate the crystallization kinetics of glasses from the  $\text{As}_2\text{Se}_3$ - $\text{As}_2\text{Te}_3$ - $\text{Sb}_2\text{Te}_3$  system and to define the thermodynamic parameters characterizing this process.

## EXPERIMENTAL

Five chalcogenide glasses from the  $(\text{As}_2\text{Se}_3)_x(\text{As}_2\text{Te}_3)_y(\text{Sb}_2\text{Te}_3)_z$  system, corresponding to points 1 to 5 in the Gibbs concentration triangle (Fig. 1), have been synthesized for conduction of the investigations. Dialuminium trioxide (preliminary tempered at 800 - 1000°C) and selenium (with known thermodynamic pa-

rameters of crystallization) were used as standard substances. The investigated compositions in powder form with particles size 63-125  $\mu\text{m}$ , together with the standard substances, were placed in quartz Stepanov's pots, vacuumed and sealed under residual pressure of  $1.33 \times 10^{-2}$  Pa.

## RESULTS AND DISCUSSION

### Thermal characteristics

One of the methods for quantitative determination of the phase transitions parameters (heat and temperature) is DTA [12]. From the heating curves at a given rate (b), the characteristic temperatures for the crystallisation process were obtained: temperatures of the beginning ( $T_{st}$ ) and the end ( $T_{end}$ ), as well as the maximal crystallization temperature ( $T_{cr}$ ). The results are presented in Table 1.

### Activation energy

Four different approaches (equations), using the thermal characteristics in Table 1, were used for determination of the activation energy ( $E_a$ ) of the crystallization process. The obtained  $E_a$  values, as well as the parameters needed for the calculation are systematized in Table 2.

• *Activation energy by Mamedov's model.*  $E_a$  is calculated using data for the temperature of the beginning of crystallization,  $T_{st}$  [13]:

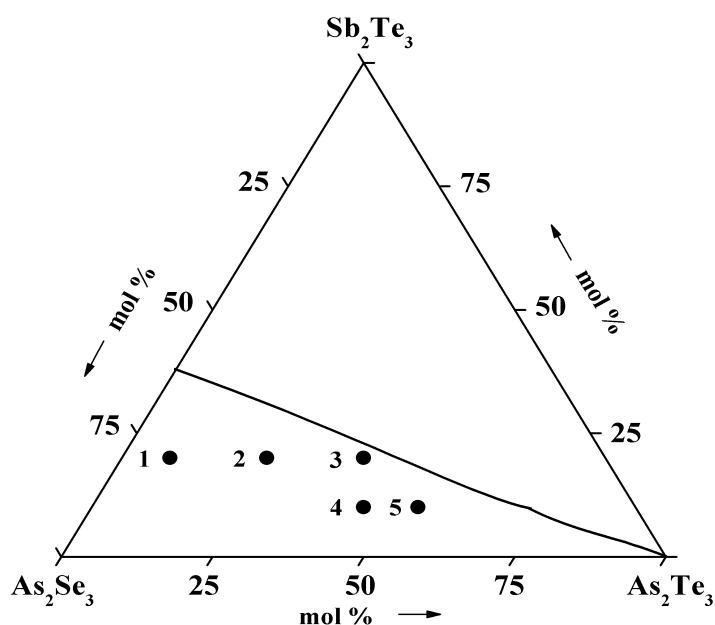


Fig. 1. Glass forming region in the  $\text{As}_2\text{Se}_3$ - $\text{As}_2\text{Te}_3$ - $\text{Sb}_2\text{Te}_3$  system.

Table 1. Temperatures of the beginning ( $T_b$ ), the maximum ( $T_{max}$ ) and the end ( $T_{end}$ ) of the exothermal effect of crystallization for ChG with composition  $(As_2Se_3)_x(As_2Te_3)_y(Sb_2Te_3)_z$ .

№	Composition	b, K min <sup>-1</sup>	T <sub>st</sub> , K	T <sub>cr</sub> , K	T <sub>end</sub> , K
1	$(As_2Se_3)_{72}(As_2Te_3)_8(Sb_2Te_3)_{20}$	10	498	526	569
		15	487	525	531
		25	479	536	604
		36	479	526	612
2	$(As_2Se_3)_{56}(As_2Te_3)_{24}(Sb_2Te_3)_{20}$	10	469	488	541
		15	466	483	536
		25	464	483	531
		36	462	498	617
3	$(As_2Se_3)_{40}(As_2Te_3)_{40}(Sb_2Te_3)_{20}$	10	416	433	526
		15	420	450	522
		25	422	450	526
		36	429	463	612
4	$(As_2Se_3)_{45}(As_2Te_3)_{45}(Sb_2Te_3)_{10}$	10	440	463	536
		15	440	469	536
		25	445	479	541
		36	455	493	579
5	$(As_2Se_3)_{36}(As_2Te_3)_{54}(Sb_2Te_3)_{10}$	10	422	444	531
		15	426	458	607
		25	432	464	560
		36	435	474	560

$$E_a = \frac{R \cdot T_{st}^2}{b \cdot \tau}, \quad (1)$$

where R is the universal gas constant, b - the heating rate;  $\tau$  - the time for passing of the phase transition (during our investigations  $\tau$  changed in the range from 1 to 3 minutes and decreased when the heating rate was raised).

The lower values for the activation energy, calculated by Eq. 1, most probably are connected to a certain inaccuracy of the starting ( $T_{st}$ ) and ending ( $T_{end}$ ) temperatures of crystallization, as well as of the time for passing of the phase transition ( $\tau$ ). Due to these rea-

Table 2. Activation energy of ChG from the  $As_2Se_3$ - $As_2Te_3$ - $Sb_2Te_3$  system.

№	$E_a$ , kJ mol <sup>-1</sup>			
	Eq.			
	(1)	(2)	(3)	(4)
1	61.21	767.05	75.56	74.33
2	56.07	309.75	73.62	71.39
3	45.97	82.27	62.90	59.17
4	51.16	83.07	72.21	69.59
5	47.09	80.07	69.12	65.83

sons, the data for  $E_a$  obtained by the Mamedov's model does not appear to be very reliable.

• *Activation energy by Piloyan's model* [14]. It is based on the Arrhenius equation inscribed as:

$$\frac{1}{T_{cr}} = A' - \frac{R}{E_a} \ln b \quad (2)$$

where  $A'$  is a constant  $A' = (\frac{R}{E_a} \ln V_0)$ , in which  $V_0$  is the pre-exponential multiplier from the Arrhenius equation. In this model

$$E_a = \frac{R}{|\operatorname{tg} \alpha|}, \quad \text{where } \operatorname{tg} \alpha = \frac{\Delta(1/T_{cr})}{\Delta(\ln b)}.$$

The calculated values of  $E_a$  by this model are very different (larger) compared to those obtained by the Mamedov's model. This is most likely due to the fact that this equation does not assume a dependence of  $V_0$  on  $T_{cr}$ . For this reason we used other models (of Kissinger and of Augis & Bennett), which account for this dependency.

• *Activation energy by Kissinger's model* [15]:

$$\ln \frac{b}{T_{cr}^2} = -\frac{E_a}{RT_{cr}} + \operatorname{const} \quad (3)$$

• *Activation energy by Augis & Bennett's model* [16]:

$$\ln \frac{b}{T_{cr} - T_o} = -\frac{E_a}{RT_{cr}} + \text{const} \quad (4)$$

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

According to the Kissinger's model, the pre-exponential multiplier  $V_o = f(T_{cr}^2)$ , and according to this of Augis & Bennett –  $V_o = f(T_{cr} - T_o)$ . To eliminate the influence of  $T_{cr}$  on the pre-exponential multiplier  $V_o$ , it is multiplied by:  $T_{cr}^{-2}$  in Eq. 3 and by  $(T_{cr} - T_o)^{-1}$  in Eq. 4. This approach seems reasonable, since the values obtained for  $E_a$  are comparable. On the other hand, the dependencies  $E_a = f(z)_{m_{AT}=\text{const}}$  and  $E_a = f(m_{AT})_{z=\text{const}}$  possess identical trends. The index  $m_{AT}$  is defined as:  $m_{AT}=y/(x+y)$ .

### Thermodynamic characteristics

It is known [17], that the area of the exothermal peak of the differential curve, corresponding to the heat effect of the glass  $\leftrightarrow$  crystal transition, depends on multiple factors:

- i. the nature of the investigated substance;
- ii. the mass of the probe, the heat conductivity coefficients, the heat capacity and the granulometric composition of the investigated and the standard substances;
- iii. the conditions of leading the process (heating rate, shape, material and filling degree of the pots, location of the thermocouples' solders, the characteristics of the furnace area), etc.

If the influence of the factors from the ii- and iii-group is not taken into account, the area (s) of the differential peak is proportional to the value of the heat effect (Q), i.e.  $s = kQ$ , where k is a proportional coefficient.

For determination of the value of the coefficient k, a standard solution with known heat of the phase transition is used [18].

The following dependencies are used for definition of the phase transition heat [19]:

$$\frac{\Delta H_A}{\Delta H_B} = X \frac{m_B}{m_A} \cdot \frac{M_A s_A}{M_B s_B},$$

$$\Delta H_A = X \frac{Q_A}{Q_B} \cdot \frac{m_B}{m_A} \cdot \frac{M_A}{M_B} \cdot \Delta H_B, \text{ as} \quad (5)$$

$$\Delta H = Q \left( \frac{m}{M} \right);$$

$$\frac{Q_A}{Q_B} = \frac{s_A}{s_B}, \quad (6)$$

where  $\Delta H_A$ ,  $\Delta H_B$  are the phase transition heats of the investigated (A) and the standard (B) substances,  $m_A$ ,  $m_B$  - the mass of the two materials,  $M_A$ ,  $M_B$  - the molecular masses and X is 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 ( $\Delta H_b$ ) of crystallization to the selenium is calculated by Eq. 6, as the heat of this element is known ( $Q = 68.66$  J/mol) [20].

The entropy alternation ( $\Delta S_b$ ) of the crystallization process is defined by Eq. 7:

$$\Delta S_B = \frac{\Delta H_B}{T_{cr}} \quad (7)$$

The results from the calculation of the thermodynamic parameters (enthalpy and entropy alternation) of the crystallization process for samples from the  $As_2Se_3$ - $As_2Te_3$ - $Sb_2Te_3$  system are presented in Table 3. Their composition was selected so as to follow its influence on these parameters.

Table 3. Alternation of the enthalpy ( $\Delta H$ ) and the entropy ( $\Delta S$ ) of the crystallization process of glasses from the  $As_2Se_3$ - $As_2Te_3$ - $Sb_2Te_3$  system.

substance	$T_{cr}$ , K	s, $cm^2$	M	m, g	$\Delta H$ , $kJ mol^{-1}$	$\Delta S$ , $J mol^{-1} K^{-1}$
Se	422	3.5853	78.96	0.4	13.55	-
1	482	1.6307	446.18	0.4	37.98	78.80
2	470	1.4579	469.56	0.4	35.49	75.51
3	450	3.9633	497.33	0.5	80.84	179.64
4	469	3.4125	476.26	0.4	84.22	179.57
5	458	2.3434	489.41	0.4	59.06	128.95

A decrease of  $\Delta H$ , when increasing the  $\text{As}_2\text{Te}_3$  content (at constant concentration of  $\text{Sb}_2\text{Te}_3$ ) and respectively of the  $\text{Sb}_2\text{Te}_3$  content (at  $m_{\text{AT}} = \text{const}$ ), is observed for all investigated compositions. The compositions with  $m_{\text{AT}} = 0.5$  (equimolar ratio of the components  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{Te}_3$ ) are an exception, for them were observed abnormally high values of  $\Delta H$ . These abnormal values could be explained on the basis of the investigations led by Kotkata et al. [21].

According to these authors, the structure of  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3$  is a superposition of two structures ( $\alpha$  and  $\gamma$ ). The  $\alpha$ -phase is solid solution of Te in  $\text{As}_2\text{Se}_3$  (rich of Se) and the  $\gamma$ -phase – solid solution of Se in  $\text{As}_2\text{Te}_3$  (rich of Te). Near to the composition  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3$ , the homogeneity of the glasses is disturbed, as the crystallization of the ChG is embarrassed. The probability for formation of new solid solutions, when  $\text{Sb}_2\text{Te}_3$  is introduced, increases. These solid solutions between  $(\text{As}_2\text{Se}_3)_{1-x}(\text{Sb}_2\text{Te}_3)_x$  and  $(\text{As}_2\text{Te}_3)_{1-x}(\text{Sb}_2\text{Te}_3)_x$ , together with the above-mentioned, would even more complicate the structure of ChG, which leads to impediment of the crystallization to a certain degree. On the other hand, the disturbed homogeneity of the glasses, situated around the  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  section, is a reason for the increase of  $\Delta S$ . Probably, these are the reasons for the “abnormally” high values of  $\Delta S$  and  $\Delta H$  for the compositions lying around this section.

The enthalpy of the phase transition glass!crystal is a criterion about the detached heat during this process. For the glasses lying on the  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  section and near it (points 3, 4 and 5), the lowest activation energy values are observed, but  $\Delta H$  is the highest. Most probably it is due to the fact that for these compositions the crystallization process passes through an intermediate stage (transition glass  $\leftrightarrow$  solid solution). For the compositions corresponding to points 1 and 2 such an intermediate transition is not known.

## CONCLUSIONS

The crystallization kinetics of glasses from the  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  system was investigated by DTA. The activation energy of the crystallization process was determined using four independent models. The obtained results were discussed and an explanation for the differences in the activation energy values, calculated by

these models, was given. The alternation of the enthalpy ( $\Delta H$ ) and the entropy ( $\Delta S$ ) for the process of crystallization was determined. The dependencies of the activation energy,  $\Delta H$  and  $\Delta S$  on the glass composition were analyzed. An explanation of the observed anomaly in the alternation of the thermodynamic properties for the compositions lying upon and around the  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  section was presented. The appearance of this anomaly is most probably connected to a superposition to three intermediate structures, which disturb the homogeneity of the glasses.

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## REFERENCES

1. N. Mehta, M. Zulfequar, A. Kumar, *JOAM*, **6**, 2, 2004, 441.
2. A.H. Moharram, A.A. Abu-Shely, M. Abu El-Oyoun, A. S. Soltan, *Physica B*, **324**, 1-4, 2002, 344.
3. S. Sahay Satyam, Karthik Krishnan, *Physica B*, **348**, 1-4, 2004, 310.
4. M.M. Wakkad, *J. Thermal Anal. Cal.*, **63**, 2001, 533.
5. M.N. Abdel-Rahim, A. Y. Abdel-Latif, A. S. Soltan, *Physica B*, **291**, 2000, 41.
6. J. Málek, *Thermochimica Acta*, **355**, 1-2, 2000, 239.
7. M. Abu El-Oyoun, *J. Phys. Chem. Solids*, **61**, 10, 2000, 1653.
8. J. Málek, *J. Therm. Anal. Cal.*, **56**, 1999, 763.
9. V. Pamukchieva, E. Savova, M. Baeva, *Phys. Chem. Glass.*, **39**, 6, 1998, 328.
10. M. Abu El-Oyoun, *J. Phys. D: Appl. Phys.*, **33**, 2000, 2211.
11. T. Hristova-Vasileva, V. Vassilev, L. Aljihmani, S. Boycheva, *J. Phys. Chem. Solids*, in press.
12. M.E. Brown, *Introduction to Thermal Analysis Techniques and Applications*, 2<sup>nd</sup> edn., Kluwer Academic Publishers, Dordrecht, 2001.
13. K.N. Mamedov, Z.I. Sulejmanov, E.I. Zamanova, S.O. Iskanderov, *Neorganicheskie Materialii*, **15**, 7, 1979,

- 1165, (in Russian).
14. G.O. Piloyan, *Vvedenie v teoriu termicheskogo analiza*, Nauka, Moskva, 1962, (in Russian).
15. H.E. Kissinger, *Anal. Chem.*, **29**, 1957, 1702.
16. J.A. Augis, J.E. Bennett, *J. Thermal Anal.*, **13**, 1978, 283.
17. L.G. Berg, T.E. Yasnikova, *J. Neorg. Himii*, **11**, 4, 1966, 886, (in Russian).
18. V. Vassilev, T. Hristova-Vasileva, L. Aljihmani, V. Parvanova, Crystallization kinetics of chalcogenide glasses from the  $\text{As}_2\text{Se}_3$ - $\text{Ag}_4\text{SSe}$ - $\text{SnTe}$  system, V<sup>th</sup> International Scientific Conference UNITECH'05, Gabrovo, 25-25.11.2005, Proceedings, Vol I, pp. I-380, (in Bulgarian).
19. E.N. Verhoturov, I.N. Odin, A.A. Sher, *Neorgan. Mater.*, **16**, 9, 1980, 1688, (in Russian).
20. K.P. Mamedov, Z.I. Suleimanov, V.Z. Zajnalov, *Azarbeidz. Him. J.*, **4**, 1965, 84, (in Russian).
21. M.F. Kotkata, H.H. Labib, S.A. Rahman, *J. Thermal Anal.*, **34**, 1998, 93.