

CRYSTALLIZATION PARAMETERS OF NON-CRYSTALLINE ANTIMONY CHALCOGENIDES

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The results of studying the kinetics of non-isothermic crystallization of Sb–S–I glasses are given. By DTA and DerTA methods the characteristic temperatures of thermal effects T_g , T_c , T_m have been investigated. The activation energies of originating nuclei of crystals ΔG_{A0} and their growth ΔG_{AM} have been calculated from temperatures beginning at T_{C0} and maximum T_{CM} of the crystallization effect as a function of the heating rate q . The critical radii for nuclei of crystals r_c and amorphization radii r_a are calculated. The crystallizability of melts depending on the composition has been studied. The compositions from the regions of eutectics have been shown to possess a minimal crystallizability, and those ones in the vicinity of Sb_2S_3 and $SbSI$ stoichiometric compounds possess a maximal one. The results obtained are being discussed proceeding from the peculiarities of the structure of studied materials.

Key words: chalcogenide glass, crystallization, activation energy.

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I. INTRODUCTION

The unique combination of diverse properties in chalcogenide glassy semiconductors conditions a wide range of their practical application. Non-crystalline antimony chalcogenides and chalcogenides (Sb–S(Se)–I(Br) systems) are very promising in this aspect. Due to high photoconductivity and light sensitivity, specific optical properties, the existence of a polar state the glasses of these systems can serve as the initial material for creating the media of optical information recording, radiation indicators, optical elements of IR technique, high-voltage supply sources, ferroelectric glass-ceramics [1–5]. However, preparing these materials in a glassy state is connected with some difficulties because of a high crystallization ability of their melts. As the calculations and experiments have shown the majority of glasses in Sb–S(Se)–I(Br) systems may be prepared under the conditions of hard quenching (at cooling rates of melts equal to 100–300 K/s [4, 6]). The crystallization of the glasses of indicated systems is very specific, too. That is why it is necessary to study the mechanisms and kinetics of “melt–glass” and “glass–crystal” phase transitions. The study of crystallization processes of glasses allows one to qualitatively connect relaxation and kinetic parameters with critical cooling rates of the melt in the glass-formation process, to develop technological regimes of preparing glasses with reproducible parameters, high stability and thermal resistance, to define optimal regimes of preparing ferroelectric glass-ceramics.

In the present report the results of studying the kinetics of non-isothermic crystallization of Sb–S–I glasses (Sb–S and Sb_2S_3 – SbI_3 sections) are given.

II. EXPERIMENTAL METHODS

The glasses under study were synthesized by the method of vacuum fusion of purity elements in ac-

cordance with the methods given in [4, 6, 7]. Different methods of quenching melts allowed us to prepare Sb_xS_{1-x} alloys with antimony content up to 35–45 at.% and $(Sb_2S_3)_y(SbI_3)_{1-y}$ alloys with iodine content up to 33.3 at.% in a glassy state.

By the DTA method [8] at heating rates $q = 0.08$; 0.17; 0.25 and 0.33 K/s the characteristic temperatures of thermal effects of glasses were studied (temperatures of glass-formation T_g , crystallization T_c , melting T_m). The crystallization process is characterized by temperatures of the exothermic effect beginning of crystallization T_{CO} and maximal growth rate of a crystalline phase T_{CM} . In many cases it is very difficult to unambiguously define these temperatures by the DTA method.

That is why while studying the non-isothermic crystallization of Sb_xS_{1-x} and $(Sb_2S_3)_y(SbI_3)_{1-y}$ glasses the DerTA method [9] was used by us which possesses more expressed singularities in thermograms and allows one to determine temperatures of thermal effects with a larger accuracy. The accuracy of temperature determination made up ± 0.5 K.

III. RESULTS AND DISCUSSION

In Fig. 1 DTA and DerTA thermograms of some glassy alloys of Sb–S–I system (typical for all studied materials) at heating rates of 0.08 K/s are given. Softening, crystallization and melting effects of a crystallized phase are observed in these curves. The concentrational dependences of characteristic temperatures T_g , T_c and T_m are given in Fig. 2. The value of T_c corresponds to the maximum of crystallization. It should be noted that the composition trend of a curve T_c agrees well with the liquidus curve of a stable phase diagram of Sb_2S_3 – SbI_3 system [10]. The similar situation is observed in Sb–S system [11]. With increasing the iodine content in the composition of glasses the crystallization and melting effects get noticeably

complicated. While introducing a small amount of SbI_3 additional crystallization and melting effects appear in DTA and DerTA curves (Fig.1, curves 3, 3'). With increasing the iodine content these effects increase in amplitude. At this the decrease in T_g and T_c (Fig. 2) is observed.

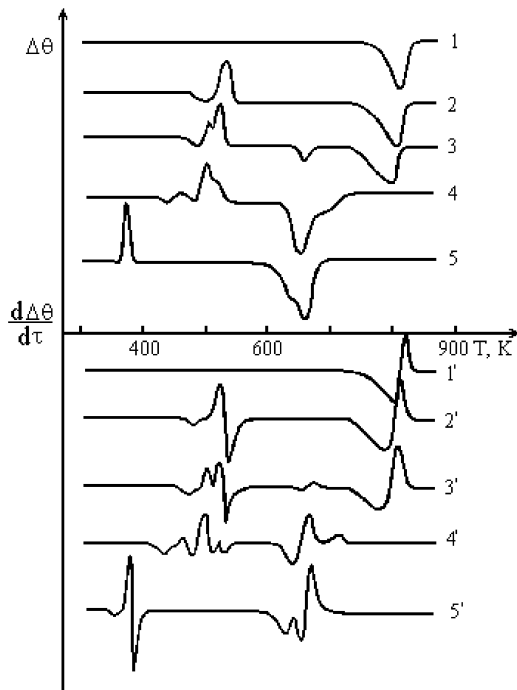


Fig. 1. DTA (1–5) and DerTA (1'–5') curves of glasses in Sb–S–I system. 1, 1' – crystalline Sb_2S_3 ; 2, 2' – $\text{Sb}_{0.40}\text{S}_{0.60}$; 3, 3' – $\text{Sb}_{0.39}\text{S}_{0.59}\text{I}_{0.02}$; 4, 4' – $\text{Sb}_{0.37}\text{S}_{0.48}\text{I}_{0.15}$; 5, 5' – $\text{Sb}_{0.33}\text{S}_{0.33}\text{I}_{0.33}$.

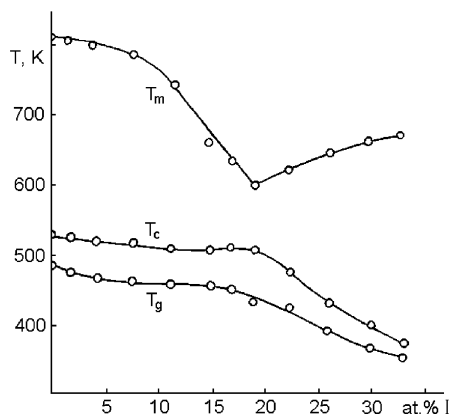


Fig. 2. Dependences T_g , T_c , T_m of $(\text{Sb}_2\text{S}_3)_y(\text{SbI}_3)_{1-y}$ glasses vs composition.

A complex character of thermograms speaks in favour of a microheterogenic model of the structure of glasses of Sb–S–I system. The structure of $\text{Sb}_x\text{S}_{1-x}$ glass-

es is determined by a random two-dimensional network structure whose main element is $\text{SbS}_{3/2}$ trigonal pyramid [5]. The presence of excess antimony and iodine promotes the formation of a complicated spacially branched quasiaeutectic structure [12]. At high temperatures in $(\text{Sb}_2\text{S}_3)_y(\text{SbI}_3)_{1-y}$ glasses the activated complexes with the structure close to that of a crystalline SbSI may appear. The formation of such high-polarized complexes was revealed while studying dielectric properties and IR-spectra of glassy SbSI [3, 7].

The availability of some structural units promotes the glass-formation in Sb–S–I system. However, in the region of a ternary compound (SbSI) it sharply decreases due to suppression of relaxation and kinetic factors by the processes that result in the thermodynamic balance. The indirect proof of increasing the crystallization ability of glasses with $y > 0.25$ is a considerable increase in their T_g and T_c (Fig. 2). The crystallization ability of glasses may be estimated with the help of the parameter introduced by Hruby [13]

$$K_G = \frac{T_c - T_g}{T_m - T_c} \quad (1)$$

The larger the difference $T_c - T_g$ and the smaller the temperature interval $T_m - T_c$, the less is the probability of the fact that when heating the glass it will crystallize. The dependences of K_G vs composition are given in Fig. 3. It is seen that the maximal value of this parameter ($K_G = 0.60$) in Sb_2S_3 – SbI_3 system is for the alloy of eutectic composition ($y = 0.25$). The glasses of stoichiometric composition Sb_2S_3 (0.15) and SbSI (0.10) possess minimal values of K_G . In Sb–S system the parameter K_G varies within the limits of 0.15–0.20 and non-stoichiometric glassy $\text{Sb}_x\text{S}_{1-x}$ alloys ($x \neq 0.40$) have larger values of K_G .

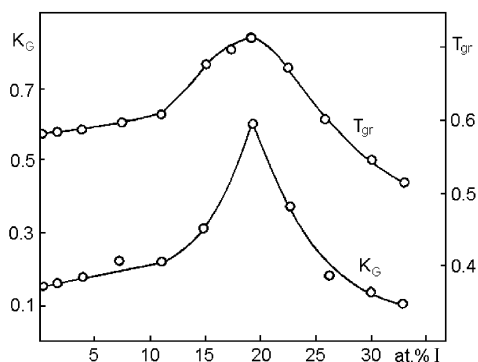


Fig. 3. Dependences of parameters K_G and T_{gr} of $(\text{Sb}_2\text{S}_3)_y(\text{SbI}_3)_{1-y}$ glasses vs composition.

It should be noted that for the majority of glass-forming alloys of different chalcogenide systems a good correlation of the parameter K_G with the reduced temperature of glass-formation $T_{gr} = T_g/T_m$ exists [14]. The glasses having a low crystallization ability are charac-

terized by high values of K_G and T_{gr} . In Sb–S system the value of T_{gr} while varying the composition does not practically change and is within the limits of 0.59–0.60. In Sb_2S_3 – SbI_3 system the glass of eutectic composition possesses the maximal value of T_{gr} (iodine content makes up 19 at.%) (Fig. 3) The data obtained testify to the fact that the glasses from the regions of eutectics possess the minimal crystallization ability in Sb–S–I system, and the glasses near stoichiometric Sb_2S_3 and SbSI compounds have a maximal crystallization ability.

The kinetics of any phase transition is determined by the nucleation rate (I) and the rate (U) of subsequent growth of the size of the inhomogeneities of composition and structure. If the centres of crystallization are absent in the glass, it is necessary to take into account the rate of their spontaneous formation. In this case the inhomogeneities are nucleated by a fluctuation way. Because of the formation of the phase interface this nucleation is accompanied by a small time increase in the free energy of the system. The increase in the free energy may sometimes exceed its decrease connected with the crystallization that is the nuclei may be unstable. Stable nuclei are formed with a noticeable rate at certain overheating, which depends on relative magnitudes of the free energy of the phase interface and that of crystallization.

The behaviour of the nucleus depends on its size. It can grow or dissolve as both processes are accompanied by the decrease in the thermodynamic potential. The nucleus will grow if its radius is larger than some critical one. The radius of a critical nucleus r_c may be determined from the relationship [15]

$$r_c = \frac{2\sigma T_m V}{\Delta H_m \Delta T}, \quad (2)$$

where σ is the free energy on the interface crystal|glass, V is a molar volume, ΔH_m is a molar enthalpia of melting, $\Delta T = T_m - T$.

The specific free energy of surface tension σ in accordance with the empiric approach of Skopski–Turnbull

[16] may be estimated from the formula

$$\sigma = \frac{\beta \Delta H_m}{N_A^{1/3} V^{2/3}}. \quad (3)$$

Here β is constant, for chalcogenides ≈ 0.2 [6], N_A – Avogadro’s number.

If the nucleus radius of a crystalline phase is within the limits of $r_c < r < r_a$, the growth of nucleus is more favourable, though its presence in the system remains not energetically favourable, on the whole. The dimension of the nucleus with which the ordering process becomes favourable is given by the expression [15]:

$$r_a = \frac{3\sigma T_m V}{\Delta H_m \Delta T}. \quad (4)$$

The magnitude r_a may be considered to be the smallest radius of stable crystals. It is often called the “amorphization radius”. The nuclei formed begins to grow with the rate to be determined by the diffusion rate of atoms necessary for the crystal surface growth. The initial data and calculated radii r_c and r_a of some alloys of Sb–S–I system are given in Table 1. For comparison the similar data for $\text{As}_{0.40}\text{Se}_{0.60}$ alloy are given here. The data r_c obtained for this glass correlate well with those determined earlier ($r_c = 9 \text{ \AA}$) [17]. As a kinetic barrier of the crystallization the activation energy of viscous flow was used. As it is seen from Table 1, the alloy, which corresponds to stoichiometric SbSI has the smallest values of r_c and r_a . It testifies to a very high crystallization ability of the given material and explains well an exclusive difficulty of preparing it in a glassy state.

Since the nucleation and growth of a new phase bear an activation character one should consider the process flow and matter of the activation energy of crystallization in accordance with the statements of the general theory for absolute reaction rates [18].

Parameter	$\text{Sb}_{0.40}\text{S}_{0.60}$	$\text{Sb}_{0.36}\text{S}_{0.45}\text{I}_{0.19}$	$\text{Sb}_{0.33}\text{S}_{0.33}\text{I}_{0.33}$	$\text{As}_{0.40}\text{Se}_{0.60}$
T_g , K	483	433	349	453
T_c , K	525	505	369	579
T_m , K	808	599	673	638
ΔH_m , kJ/mol	29.7	23.5	17.8	35.3
$\sigma \cdot 10^3$, J/m ²	56	49	45	43
$r_c \cdot 10^{10}$, m	6.4	6.8	4.4	8.5
$r_a \cdot 10^{10}$, m	9.6	10.2	6.5	12.8
ΔG_{A0} , kJ/mol	131	188	90	158
ΔG_{AM} , kJ/mol	114	176	82	146

Table 1. Thermodynamic and crystallization parameters of glasses.

The following equation is the basis for the experimental determination of kinetic parameters of the crystallization of glasses [19]

$$\frac{d\alpha}{d\tau} = f(\alpha, T) . \quad (5)$$

Here $f(\alpha, T)$ is the quantity function of the matter α which changed into a crystalline state and temperature T at the moment of time τ . The rate of given off heat $dQ/d\tau \sim da/d\tau$ may be recorded in the form of peaks in thermal analysis curves. Though the kinetic equation (5) depends on a definite mechanism of the reaction, one of its most used variants for the majority of processes has the form [20]

$$\frac{d\alpha}{d\tau} = A(1 - \alpha)^n \exp\left(-\frac{\Delta G_A}{RT}\right) . \quad (6)$$

Here A is a pre-exponential factor (frequency factor), n is the ‘‘order’’ of the reaction, ΔG_A is the activation energy of the process. Its essence is transforming a structural complex into an activated state along the direction of crystallization reaction.

Since the dependence of the characteristics upon heating rates is peculiar for kinetic flowing processes (with increasing q the values of T_g and T_c increase), for definite points of DTA and DerTA curves of glasses one may estimate the activation energies of processes that take place in them with sufficient approximation [21].

In case of the first-order reaction ($n = 1$) by studying the reaction (6) for the extremum and taking the stationarity of the process into account Kissinger [22] got the relation

$$\frac{d(\ln(q/T_{\text{cmax}}^2))}{d(1/T_{\text{cmax}})} = -\frac{\Delta G_A}{R} , \quad (7)$$

where R is an universal gas constant; T_{cmax} is the extremum temperature in thermal analysis curve. By solving the equation graphically (7), we found the activation energy ΔG_A of the process under study.

In practice a somewhat modified variant of defining the activation energies is used [23]. Constructing the dependences of temperatures T_{CO} and T_{CM} of onset and maximum of crystallization thermal effect upon the rate of programmed heating q , we obtained the activation energies of crystallization from the relationship of the following kind:

$$\frac{1}{T_{CO}} = C_0 - \frac{R}{\Delta G_{A0}} \ln q , \quad (8)$$

$$\frac{1}{T_{CM}} = C_M - \frac{R}{\Delta G_{AM}} \ln \frac{q}{T_{CM}^2} . \quad (9)$$

Here C_0 and C_M are the constants which depend on the nature of a material and conditions of the experiment. The activation energies ΔG_{A0} and ΔG_{AM} were determined according to the inclination of dependences $1/T_{CO}$ of $\ln q$ and $1/T_{CM}$ of $\ln(q/T_{CM}^2)$. The results of calculations are shown in Fig. 4.

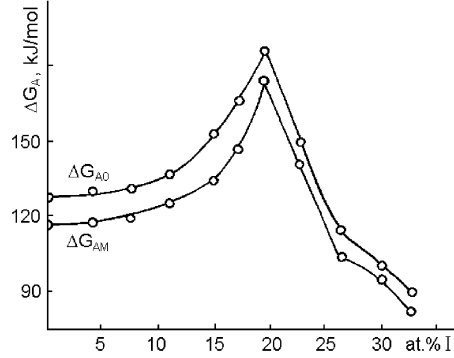


Fig. 4. Dependences of activation energies ΔG_{A0} and ΔG_{AM} of $(\text{Sb}_2\text{S}_3)_y(\text{SbI}_3)_{1-y}$ glasses vs composition.

It is evident that at temperatures of the crystallization beginning of glasses T_{CO} the part of activation energy, which forms crystal nuclei prevails in ΔG_{A0} . It includes the process of diffusion or reorientation of molecules into a right unit. At T_{CM} the activation energy of the crystalline phase growth in ΔG_{AM} prevails.

As it is seen from Fig. 4 and Table 1, the activation energies of crystallization in Sb_2S_3 – SbI_3 system greatly depend on the composition of glasses. Maximal values of ΔG_{A0} and ΔG_{AM} are observed for the glass of eutectic composition ($y = 0.25$). Either with the increase or decrease of iodine content in the composition of glasses of Sb – S – I system these parameters greatly decrease and their crystallization ability increases. A stronger concentrational dependence of ΔG_{A0} and ΔG_{AM} for glasses from $\text{Sb}_{0.36}\text{S}_{0.45}\text{I}_{0.19}$ – $\text{Sb}_{0.33}\text{S}_{0.33}\text{I}_{0.33}$ region than for glasses with smaller iodine content should be mentioned. In Sb – S system the values of activation energies are within a considerably narrower interval ($\Delta G_{A0} = 123.2 \div 130.6$ kJ/mol, $\Delta G_{AM} = 105.3 \div 110.8$ kJ/mol) and the maximum of ΔG_{A0} and ΔG_{AM} is observed for the glass of stoichiometric composition ($x = 0.40$). Such behaviour of crystallization parameters of glasses may be explained on the basis of their local structure. As it was mentioned earlier, in the region of stable bulk glasses with $y < 0.25$ the structure of $(\text{Sb}_2\text{S}_3)_y(\text{SbI}_3)_{1-y}$ glasses is quasieutectic and capable of forming polar structural units. In glasses depleted in iodine the main structural element is $\text{SbS}_{3/2}$ trigonal pyramid. It is evident that regrouping of spacially coordinated $\text{SbS}_{3/2}$ pyramids is more complicated. This results in more higher values of ΔG_{A0} and ΔG_{AM} for the glasses close to Sb_2S_3 by the composition than for those ones with high iodine content. The results obtained correlate well with the results of calculating r_c and r_a (Table 1). It is seen that the

glasses with the smallest crystallization ability have the largest values of r_c , r_a , ΔG_{A0} , ΔG_{AM} .

The analysis of preparing and crystallization conditions of the system under study has shown that the surface crystallization is typical for them. The free surface of the glass has larger probability of forming a thermally activated nucleus than the fluctuation origin of the nucleus in the glass bulk. In the process of non-isothermic heating the transition from surface to volume crystallization takes place. The given conclusion is confirmed by the results of studying chalcogenide glasses in a dispersed state [24]. While decreasing the sizes of grains both critical sizes of nuclei and activation energies of crystallization ΔG_{A0} and ΔG_{AM} decrease, too.

IV. CONCLUSION

As a result of this study and the conducted calculations it is established that the glasses of stoichiometric compositions (Sb_2S_3 and SbSI) possess minimal values of activation energies of crystal nuclei origin ΔG_{A0} and their growth ΔG_{AM} in Sb-S-I system. These compositions have the smallest critical radii of crystalline nuclei. The change in the composition of glasses is accompanied by the essential changes in thermodynamic and crystallization parameters. The glasses from the region of eutectics possess the smallest crystallization ability. Such a behaviour of parameters of the crystallization of Sb-S-I system is connected with the peculiarities of their structure.

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ПАРАМЕТРИ КРИСТАЛІЗАЦІЇ НЕКРИСТАЛІЧНИХ ХАЛЬКОГЕНІДІВ СУРМИ

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Подано результати дослідження кінетики неізотермічної кристалізації стекол системи Sb-S-I . Методами ДТА і ПТА вивчено характеристичні температури теплових ефектів T_g , T_c , T_m . Із залежностей температур початку T_{C0} і максимуму T_{CM} ефекту кристалізації від швидкості нагрівання q розраховано енергії активації виникнення кристалічних зародків ΔG_{A0} і їх росту ΔG_{AM} . Визначено критичні радіуси кристалічних зародків r_c і радіуси аморфізації r_a . Досліджено кристалізаційну здатність сплавів залежно від складу. Показано, що мінімальну кристалізаційну здатність мають склади з ділянок евтектик, а максимальну — склади поблизу стехіометричних сполук Sb_2S_3 і SbSI . Отримані результати обговорено на основі особливостей структури вивчених матеріалів.