

PECULIARITIES OF PREPARATION AND PROPERTIES OF GLASSY ANTIMONY CHALCOGENIDES

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The calculations of melt cooling critical rates and studies of physical and chemical parameters for Sb-S and Sb-Se system glasses are reported. The glass stability range is obtained within 35 to 50 at.% Sb for Sb-S system and below 25 % Sb in Sb-Se system. The activation energies for viscous flow and the glass crystallization are calculated.

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The characteristic feature of glassy semiconductors consists in the possibility of their properties to be controlled by variation of composition. However, each time the property variation limits are restricted by the glass-forming region in the system, whose boundaries are rather vague. The glass formation process is determined by the melt cooling rate which is limited by its amount and volume.

In this view non-crystalline antimony chalcogenides (Sb-S and Sb-Se systems) are of certain interest. The glasses of these systems are not enough studied due to considerable difficulties in their preparation. This is probably related to high crystallizability of the alloys and the existence of a separation region in the state diagrams of Sb-S and Sb-Se systems [1].

In the present paper the glass formation ranges, physico-chemical and thermodynamical parameters of the glasses in Sb-S and Sb-Se systems are reported.

The ability of the melt to form glass can be characterized by the critical cooling rate (Q), i.e. the rate, at which the crystallization process is suppressed. The kinetics of any phase transition is determined by the homogeneous nucleation rate I and the rate U of subsequent growth of the size of the inhomogeneities of composition and structure. In the assumption of the spherical shape of nuclei and the kinetic barrier of nucleation being close to the viscous flow potential barrier, the fluctuation in the nucleation rate and the growth rate for the normal mechanism are given by [2, 3]

$$I = \frac{nRT}{3\pi a_0^3 \eta} \exp\left(-\frac{16\pi\alpha^3}{3RT^3} \frac{\Delta H_m T_m^4}{\Delta T^2}\right) \quad (1)$$

$$U = \frac{RT}{3\pi a_0^3 \eta} \left[1 - \exp\left(-\frac{\Delta H_m \Delta T}{TRT_m}\right)\right] \quad (2)$$

Here n is the amount of atoms per unit volume, a_0 – elementary displacement of crystal-glass boundary, i.e. kinetic unit hopping distance, ΔH_m – molar enthalpy of melting, α – a constant (for chalcogenides $\alpha \sim 0.2$), T_m – melting temperature, $\Delta T = T_m - T$ – the liquid overcooling, η – viscosity of a non-associative liquid with spherical particles of a diameter a_0 .

Temperature dependences of I and U for glassy Sb_2S_3 are shown in Fig. 1. I value sharply increases in a relatively narrow temperature interval. Nucleation rate decrease at strong overcooling, i.e. at temperatures close to the glass-forming temperature T_g , is caused by the decreases of frequency of attachment of molecules to a critical nucleus due to the increase of the melt viscosity. If the overcooling is small, I also decreases due to the high values of thermodynamical barrier of nucleation.

Only in the range of medium overcooling the nucleation rate achieves maximal values. Below the melting temperature T_m the crystallization rate U reaches high values in the range of small overcooling and decreases to an extremely small value in the range of the glass-forming temperature T_g . Meanwhile the maximum of I is shifted to higher overcooling values and at the temperature, being characterized by the maximal nucleation frequency, the growth rate U is very small. For the phase transition of the melt to the crystalline state the overlap range of I and U curves is kinetically the most convenient.

The condition of non-crystalline solidification can be determined by solving the Kolmogorov-Avrami kinetic equation [4]

$$z = \pi I U^3 \tau^4 / 3 \quad (3)$$

Here τ is the exposure time, for which at the temperature T the crystalline phase fraction reaches the value z . In [4] a criterion of "absolute" suppression of crystallization is proposed, requiring the crystalline phase fraction in the investigated volume not to exceed 10^{-6} during the whole cooling process, the stationary nucleation frequency and the crystal growth rate being constant over a period of τ .

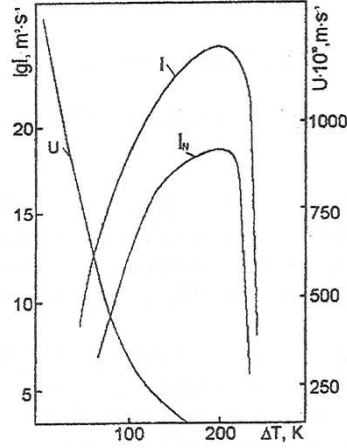


Fig. 1. Temperature dependences of I , I_N and U for Sb_2S_3 .

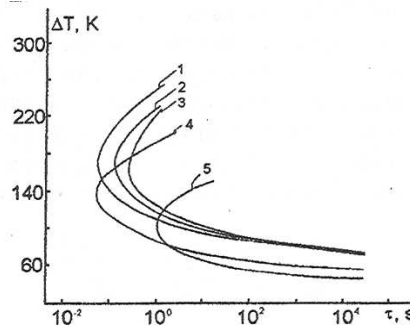


Fig. 2. T-T-T diagrams for the alloys of Sb-S and Sb-Se systems: 1 - $Sb_{0.40}S_{0.60}$; 2 - $Sb_{0.36}S_{0.64}$; 3 - $Sb_{0.43}S_{0.57}$; 4 - $Sb_{0.20}S_{0.80}$; 5 - $Sb_{0.10}Se_{0.90}$.

When the highly viscous melt is cooled, the stationary nucleation rate can be achieved with a considerable delay. In this case for the non-stationary nucleation process

$$I_N(\tau) = I \exp(-\tau_0/\tau) \quad (4)$$

The retardation time τ_0 of reaching the stationary nucleation rate is determined by the expression

$$\tau_0 = 3\pi a_0^3 N_A \eta n^{4/3} / 4RT \quad (5)$$

The temperature dependences of the non-stationary nucleation rate I_N for Sb_2S_3 are shown in Fig. 1.

To determine the critical cooling rates the calculation of Eq. (3) for stationary and non-stationary nucleation was performed in accordance with the method proposed in [5]. Based on it, time-temperature-transformation (T-T-T) diagrams were constructed for the alloys in Sb-S and Sb-Se systems (Fig. 2), their inflection points enabling the Q values to be determined:

$$Q = \Delta T_{\min} / \tau_{\min} \quad (6)$$

The initial data and the calculation results are listed in Tables 1 and 2.

The results of Q calculations for the melts have shown that in Sb-S system the composition, corresponding to stoichiometric Sb_2S_3 , possesses the minimal glass-forming capability ($Q = 255 \text{ K/s}$). The variation of the alloy composition on both sides of $\text{Sb}_{0.40}\text{S}_{0.60}$ towards the eutectic concentrations results in the Q decrease. However, the compositional positions of the Q minima absolute values are shifted with respect to the equilibrium eutectic alloys ($\text{Sb}_{0.37}\text{S}_{0.63}$ and $\text{Sb}_{0.43}\text{S}_{0.57}$ [1]) towards the increase of S and Sb concentrations and are determined for the compositions $\text{Sb}_{0.35}\text{S}_{0.65}$ and $\text{Sb}_{0.45}\text{S}_{0.55}$.

In the Sb-Se system Q increases continuously with the antimony content in the alloy, for this system Q_{ns} values, calculated for the non-stationary nucleation process, being applicable. This is probably related to the higher values of the alloy viscosity at the temperatures close to T_g .

Table 1.

Composition	ΔH_{\min} , kJ/mol	$a_0 \cdot 10^{10}$, m	I_{\max} , $\text{m}^{-3} \cdot \text{s}^{-1}$	τ_{ns} , s	Q , K/s	Q_{ns} , K/s
$\text{Sb}_{0.35}\text{S}_{0.65}$	27.5	8.7	$6.2 \cdot 10^{18}$	3.8	124	210
$\text{Sb}_{0.37}\text{S}_{0.63}$	28.6	8.7	$5.6 \cdot 10^{18}$	9.2	155	320
$\text{Sb}_{0.40}\text{S}_{0.60}$	29.7	8.8	$3.9 \cdot 10^{18}$	32.8	255	720
$\text{Sb}_{0.43}\text{S}_{0.57}$	29.0	8.8	$5.3 \cdot 10^{18}$	2.9	49	91
$\text{Sb}_{0.45}\text{S}_{0.55}$	29.1	8.8	$6.1 \cdot 10^{18}$	8.9	40	90
$\text{Sb}_{0.50}\text{S}_{0.50}$	31.1	8.9	$8.2 \cdot 10^{18}$	0.1	280	290
$\text{Sb}_{0.05}\text{S}_{0.95}$	19.5	8.6	$8.9 \cdot 10^{18}$	310	1480	30
$\text{Sb}_{0.15}\text{S}_{0.85}$	20.8	8.7	$3.8 \cdot 10^{18}$	28	1150	95
$\text{Sb}_{0.20}\text{S}_{0.80}$	22.1	8.7	$4.2 \cdot 10^{18}$	1.0	515	235
$\text{Sb}_{0.25}\text{S}_{0.75}$	26.5	8.8	$7.3 \cdot 10^{18}$	0.1	325	295
$\text{Sb}_{0.40}\text{S}_{0.60}$	32.1	8.9	$9.7 \cdot 10^{18}$	0.05	1420	1200

The high values of Q for the Sb-S (Se) system alloys are the evidence for the possibility of the glasses in this system to be obtained only in the hard quenching regime.

Table 2.

Composition	ρ , $\text{kg} \cdot \text{m}^{-3}$	H, Pa	T_g , K	T_c , K	T_m , K	E_n , kJ/mol	E_{CM} , kJ/mol
$\text{Sb}_{0.35}\text{S}_{0.65}$	$3.86 \cdot 10^3$	$130 \cdot 10^{-6}$	460	500	778	97.2	126.5
$\text{Sb}_{0.37}\text{S}_{0.63}$	$3.92 \cdot 10^3$	$160 \cdot 10^{-6}$	472	504	793	99.5	128.2
$\text{Sb}_{0.40}\text{S}_{0.60}$	$4.14 \cdot 10^3$	$170 \cdot 10^{-6}$	483	506	808	99.8	130.6
$\text{Sb}_{0.43}\text{S}_{0.57}$	$4.04 \cdot 10^3$	$160 \cdot 10^{-6}$	477	494	803	97.4	125.6
$\text{Sb}_{0.45}\text{S}_{0.55}$	$4.12 \cdot 10^3$	-	475	483	798	97.8	123.2
$\text{Sb}_{0.01}\text{S}_{0.99}$	$4.22 \cdot 10^3$	$45 \cdot 10^{-7}$	315	409	496	51.9	92.0
$\text{Sb}_{0.03}\text{S}_{0.97}$	$4.30 \cdot 10^3$	$60 \cdot 10^{-7}$	324	419	512	53.9	87.1
$\text{Sb}_{0.05}\text{S}_{0.95}$	$4.40 \cdot 10^3$	$75 \cdot 10^{-7}$	336	420	552	57.7	82.8
$\text{Sb}_{0.10}\text{S}_{0.90}$	$4.51 \cdot 10^3$	$110 \cdot 10^{-7}$	348	429	643	62.7	75.1
$\text{Sb}_{0.15}\text{S}_{0.85}$	$4.63 \cdot 10^3$	$150 \cdot 10^{-7}$	357	440	687	68.2	70.2
$\text{Sb}_{0.20}\text{S}_{0.80}$	$4.78 \cdot 10^3$	-	372	448	716	73.6	60.1
$\text{Sb}_{0.25}\text{S}_{0.75}$	$4.94 \cdot 10^3$	-	392	456	749	-	-

The glasses were synthesized from elements in evacuated quartz ampoules. The initial mixture was prepared in the amount of 10 g at homogenization temperature, exceeding the liquidus temperature by $30 \div 50 \text{ K}$ for of $\sim 20 \text{ h}$. Thereafter, the obtained mixture was packed in thinwalled quartz ampoules in the amount of $0.5 \div 2 \text{ g}$. The melt was quenched from the homogenization temperature to overcooled salt solutions, thus high cooling rate of the melt being achieved. The application of this synthesis technique allowed to get glassy $\text{Sb}_x\text{S}_{1-x}$ ($0.35 \leq x \leq 0.50$) and $\text{Sb}_x\text{Se}_{1-x}$ ($0 \leq x \leq 0.25$) alloys. X-ray phase analysis and microstructural analysis have shown the absence of crystalline inclusions in the materials. The

characteristic temperatures of thermal effects T_g , T_c (crystallization temperature) and T_m (melting temperature) were determined by differential thermal analysis (DTA) at the heating rate $q = 5$ K/min. These parameters, as well as the density ρ and microhardness H are listed in Table 2.

It should be noted that for the glasses of Sb-Se system in the 0.05-0.15 at.% range of Sb content the physical and chemical parameters considerably depend on the synthesis conditions. In case the melt homogenization temperature exceeds the melting temperature for the corresponding compositions by 150-200 K, the values of ρ , H , T_g , T_c and T_m of the glassy alloys are considerably lower with respect to those listed in Table 2. The similar results were obtained in [6]. The DTA curves for such glasses are characterized by the presence of two or three endothermic softening effects, this being the evidence for their phase non-uniformity.

As a result of the comparison of DTA curves, measured at various q ($q = 5, 10, 20, 30$ K/min), T_g and T_c of the glasses in Sb-S and Sb-Se systems are shown to depend essentially on the heating rate. T_m is practically independent of q .

The dependence of T_g on q is described by [7]

$$q = q_0 \exp\left(-\frac{E_\eta}{RT_g}\right), \quad (7)$$

and the dependence of T_M temperature, corresponding to the maximum of crystallization effect in the DTA curve is given by [8]:

$$\frac{1}{T_M} = C_M - \frac{R}{E_{CM}} \ln \frac{q}{T_M^2}. \quad (8)$$

In (8) C_M is a composition-dependent constant, E_η and E_{CM} – “visible” activation energies of viscous flow and crystallization, respectively. The plots of $\ln q$ on $1/T_g$ and $1/T_M$ on $\ln(q/T_M^2)$ dependences are straight lines, and from their slope E_η and E_{CM} values can be found. The determined activation energy values E_η and E_{CM} for Sb_xS_{1-x} glasses are listed in Table 2.

In the Sb-S system E_η and E_{CM} values are maximal for $Sb_{0.40}S_{0.60}$ glass. The maxima for the concentration dependences of ρ and H correspond to the same composition. This is the evidence for the fact that Sb_2S_3 is the glass-forming compound in the Sb-S system. The glassy Sb_2S_3 matrix is built mostly by SbS_3 trigonal pyramids, linked by two-fold coordinated sulphur atoms [5]. The quoted parameters decrease with the deviation of the composition from $Sb_{0.40}S_{0.60}$ both in favour of sulphur or antimony content. This is related to the increase of the amount of structural groupings with homopolar S-S and Sb-Sb bonds in the glass matrix and, as a result, the loosening of its structural core.

In the Sb-Se system the increase of antimony content in the glass composition is accompanied by the strengthening effect of antimony on the glass-forming selenium core. This is confirmed by the increase of ρ and H with Sb concentration. We may suppose that the very first admixtures of antimony lead to the formation of $SbSe_{3/2}$ structural groups in Sb_xSe_{1-x} glass matrix and the increase of their amount with x . The energy E_{CM} of the glasses of this system decreases with x . The selenium-rich alloys with low antimony concentration possess the lowest crystallizability since the energy barrier of their structural transformation is higher. The decrease of E_{CM} and, accordingly, the glass-forming ability of Sb-Se alloys with antimony concentration is caused by the decrease of selenium chains content and the influence of the $SbSe_{3/2}$ structural groups.

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