

AUTOCATALYTIC NUCLEATION IN THE SYSTEM $\text{Li}_2\text{O-SiO}_2$

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Abstract

The nucleation in phase separated and no phase separated glasses of the lithium silicate system in wide region of compositions has been investigated. The glasses of $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where $x = 23.4, 26.0, 29.1, 32.5, 32.97, 33.5, 33.85, 34.72, 36.2, 37.0, 37.98, 39.0, 41.15, 44.11,$ and 46.00 mol% Li_2O) compositions have been homogenized by using the previously established special temperature-time conditions, which make it possible to provide a maximum dehydration and removal of bubbles from the glass melt. The parameters of crystal nucleation have been determined. The absolute values of the stationary nucleation rates I_{st} of lithium disilicate crystals in the $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where $x = 23.4, 26.0,$ and 29.1 mol% Li_2O) glasses with the compositions lying in the metastable phase separation region have been compared with the corresponding rates I_{st} for the $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where $x = 32.5, 32.97, 33.5, 33.85, 34.72, 36.2, 37.0, 37.98, 39.0, 41.15, 44.11,$ and 46.00 mol% Li_2O).

Keywords and phrases: $\text{Li}_2\text{O-SiO}_2$ system, the glasses of $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where $x = 23.4, 26.0, 29.1, 32.5, 32.97, 33.5, 33.85, 34.72, 36.2, 37.0, 37.98, 39.0, 41.15,$ and 44.11 mol% Li_2O) compositions, lithium disilicate crystal, lithium metasilicate crystal, crystal nucleation, stationary nucleation in phase separated and no phase separated glasses.

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The character of crystallization in glasses with the compositions lying in the phase separation region of the $\text{Li}_2\text{O-SiO}_2$ system is compared with that in the glass of the stoichiometric lithium disilicate composition. The inference has been made that the phase separation weakly affects the nucleation parameters of the lithium disilicate.

1. Introduction

As was shown [5, 7], in shifting of the composition of lithium silicate glass from lithium disilicate to metasilicate, the nucleation rate of spherulites practically composed only of lithium disilicate increases sharply. In this work, this phenomenon has been studied more systematically and interpreted in a most probable way.

2. Sample Preparation and Experimental Technique

The rates of nucleation were studied in glasses of the analyzed compositions $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where $x = 23.4, 26.0, 29.1, 32.5, 32.97, 33.5, 33.85, 34.72, 36.2, 37.0, 37.98, 39.0, 41.15, \text{ and } 44.11$ mol% Li_2O). Since it was established earlier that, the crystal nucleation parameters are strongly affected by water [4] and bubbles formed in the course of glass synthesis [9, 10], the glasses were homogenized to a maximum extent under specially established temperature-time conditions of synthesis. As was previously shown, bubbles can play a role of initiators of nucleation of crystals [8] and increase a number of lithium disilicate crystals to 20% [10]. As the water content increases, the stationary nucleation rate increases and the position of the maximum shifts toward lower temperatures [4]. In this respect, all cares were taken in order to prepare glasses homogenized to a maximum extent. Water was removed by bubbling glass melts with argon for 20 min. Bubbles were removed by performing the synthesis at a high temperature. The glasses were synthesized according to the technique described in [11]. A batch was prepared from lithium carbonate (analytical grade) and dehydrated silicon dioxide (analytical grade) by mixing in a drum. The glasses were synthesized in a platinum crucible (volume, 200ml) in a Globar-heater furnace with silicon carbide heaters (synthesis temperature, 1550°C ; synthesis time, 5h). Heat treatments were performed in SShOL electric shaft furnaces and a gradient furnace designed at a laboratory. The temperature was maintained accurate to within $\pm 1^\circ\text{C}$. The results of the chemical analysis of the synthesized glasses are presented in Table 1.

Table 1. Chemical compositions under investigation (mol and mass %)

Glass no.	Mol%		Mass%	
	Li ₂ O	SiO ₂	Li ₂ O	SiO ₂
1	23.40	76.60	11.62	88.38
2	26.00	74.00	13.14	86.84
3	29.10	70.90	15.02	84.98
4	32.50	67.50	17.17	82.83
5	32.97	67.03	17.47	82.53
6	33.50	66.50	17.82	82.18
7	33.85	66.15	18.05	81.95
8	34.72	65.28	18.63	81.37
9	36.20	63.80	19.63	80.37
10	37.00	63.00	20.18	79.82
11	37.98	62.02	20.86	79.14
12	39.00	61.00	21.58	78.42
13	41.15	58.85	23.14	76.86
14	44.11	55.89	25.36	74.64
15	46.00	54.00	26.83	73.17

X-ray powder diffraction analysis was performed on a DRON-2 diffractometer (CuK α radiation; operating voltage, 30kV; current, 20mA; detector rotation rate, 2deg/min). Differential thermal analysis (DTA) was carried out on a MOM derivatograph (heating rate, 10K/min; sample weight, 1g; galvanometer sensitivity, 1/5; reference sample, Al₂O₃; platinum crucible). Optical microscopy investigations in transmitted and reflected light were performed on Carl Zeiss JenaVal and Neophot 32 microscopes (Germany). The viscosity was measured by the bending method on a Klyuev viscometer. The nucleation rates of crystals were determined by the development method: Preliminary heat treatment of the glass at a low temperature T , followed by the development at a higher temperature $T_{dev} > T$ bringing to sizes that can be fixed in an optical microscope.

3. Determination of the Crystal Nucleation Rate

The stationary nucleation rate I_{st} was determined from the experimental dependences of the number of crystals $n(t)$ as the slope of the stationary portion of these dependences on the time of holding of glasses at each holding temperature. In this work, the rate of stationary homogeneous crystal nucleation was determined by the cross section method (in reflected light) and by direct counting of the number of crystals (in transmitted light). The glass samples were subjected to preliminary heat treatment and rapidly cooled in air to room temperature. Then, the samples were repeatedly heat treated at a development temperature of 600°C for 10 min. With the aim of examining the samples in reflected light, the surface layer was ground off and the prepared surface was polished. In order to increase the contrast of the boundaries between crystals and glass, the sample surface was etched in a 0.01M HF solution for 10s. The number and size of cross sections of crystals per unit surface area were determined from the micrographs with the use of the Neophot optical microscope or directly in the field of vision of the Jenaval microscope.

The number of crystals per unit volume n and the number of cross sections of crystals in the micro section N_S are related by the expression $n = N_S / (SD)$, where S is the micro section area and D is the diameter of a maximum particle in the micro section. The non-stationary nucleation time τ was evaluated by using the induction period t_{ind} , which differs from the time τ by the temperature independent factor.

The induction period t_{ind} was determined as the intersection point between the continuation of the linear portion of the dependence $n(t)$ and the time axis. The time-temperature dependence of the nucleation rate was studied for glasses, whose composition is given in Table 1. $I(T, t)$ was determined by using a method of « development » -the growth at temperatures T_{dev} (see Table 1) of crystals nucleated at a lower temperature $T < T_{dev}$. At T_{dev} , the crystals grew in the form of spherulites.

4. Experimental Results

The kinetic curves of the number of nucleated crystals $n(T, t)$ ($I = dn/dt$) per unit volume of the glass for the time t are of the ordinary shape (Figure 1).

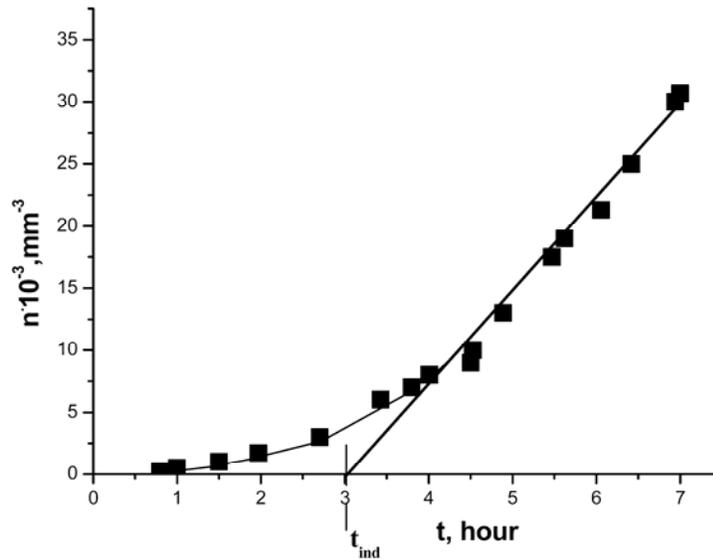


Figure 1. The kinetic curve of the number of nucleated crystals $n(T, t)$ ($I = dn/dt$) per unit volume of the glass $32.97\text{Li}_2\text{O} \cdot 67.04\text{SiO}_2$ for the time t , $T = 460^\circ\text{C}$.

The time of non-stationary nucleation τ was assumed to be proportional to the time t_{ind} (Figure 1), obtained as the point of intersection of the straight line corresponding to the stationary nucleation $I_{st}(T)$ with the time axis.

Given in Figure 2 are the curves of $\ln(t_{\text{ind}})$ versus $1/T$ (they are practically linear), the slope of which permitted to determine the values of activation energy E_τ of the transition of structural units from the glass to the crystal nucleation.

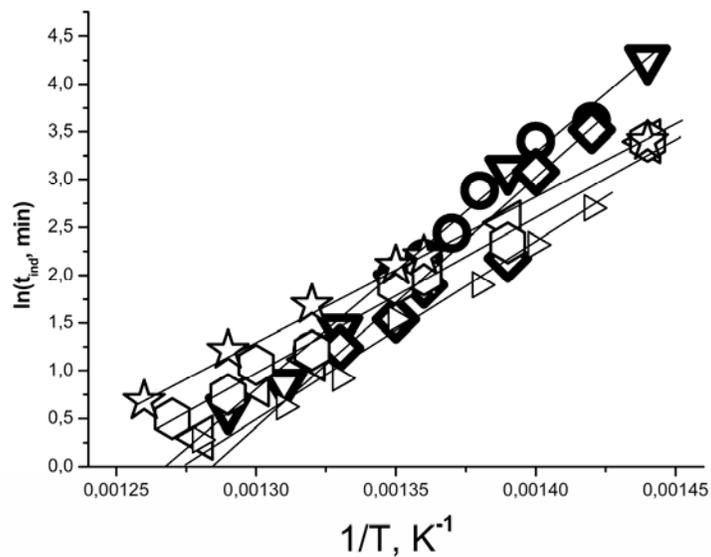
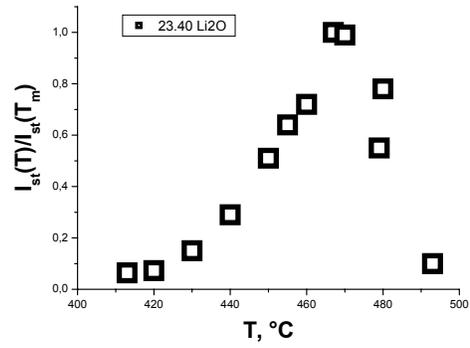
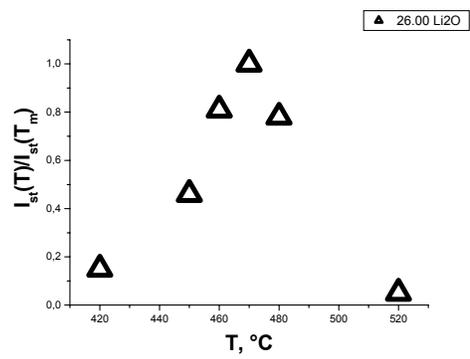


Figure 2. The curves of $\ln(t_{\text{ind}})$ versus $1/T$.

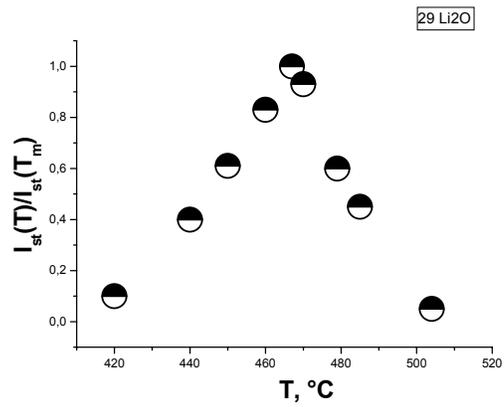
This values are compared in Table 2 with the ones of the viscous flow E_{η} determined from the slopes of straight lines showing the dependence of the logarithm of viscosity coefficient η on $1/T$. It follows from the table that $E_{\eta} > E_{\tau}$, E_{τ} decreasing (almost linearly) with increasing concentration of Li_2O .



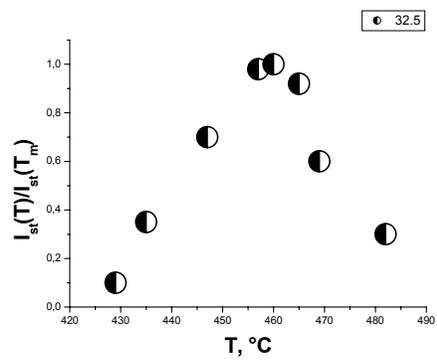
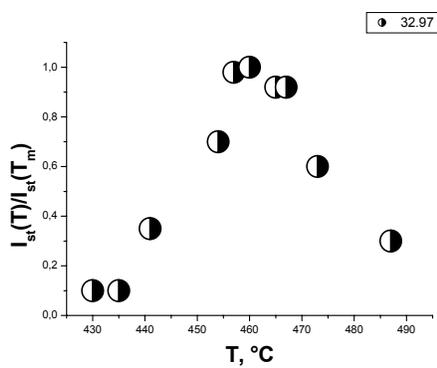
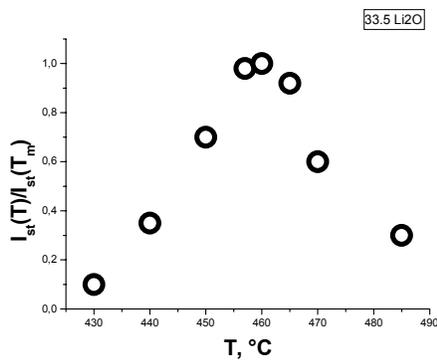
N1. 23.4 Li₂O

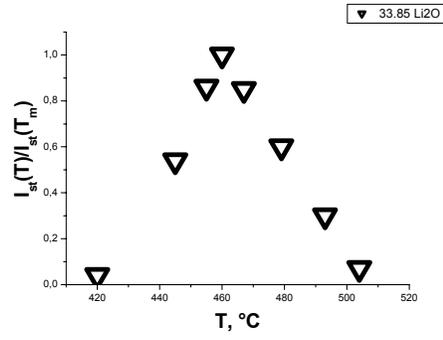


N2. 26.0 Li₂O

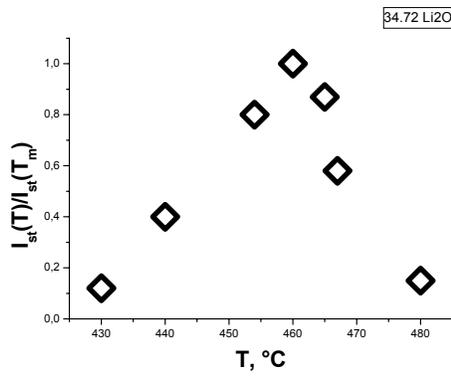


N3. 29.1 Li₂O

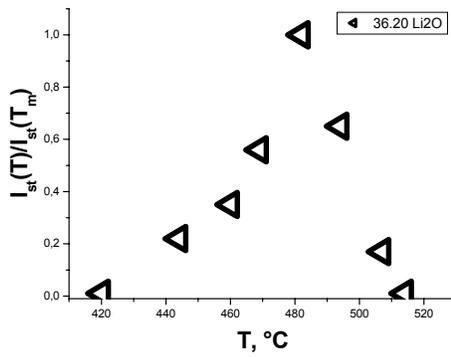
N4. 32.5 Li₂ON5. 32.97 Li₂ON6. 33.5 Li₂O



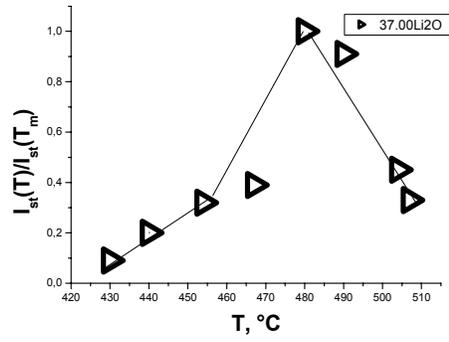
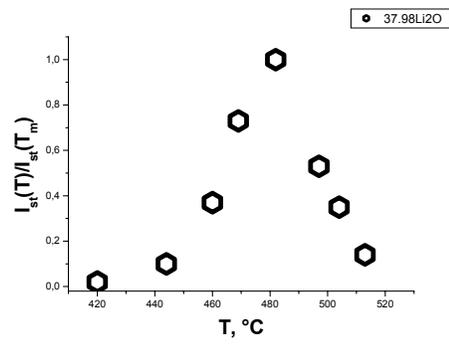
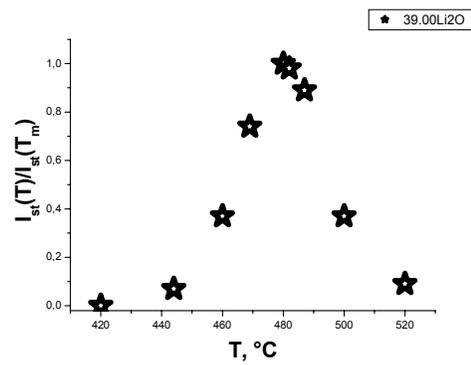
N7. 33.85 Li₂O

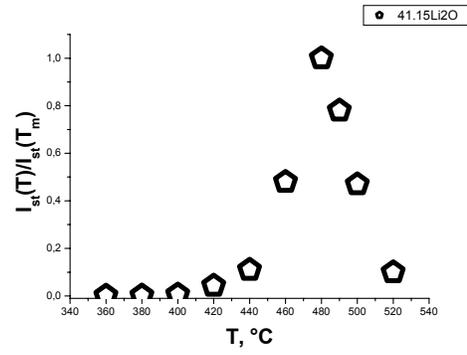


N8. 34.72 Li₂O

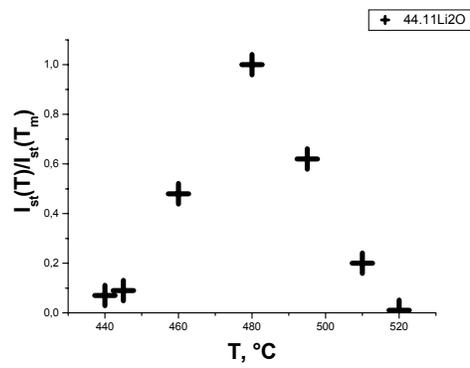


N9. 36.2 Li₂O

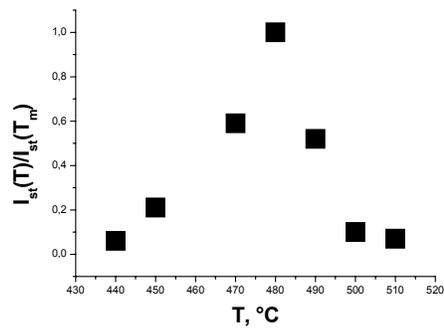
N10. 37.0 Li₂ON11. 37.98 Li₂ON12. 39.0 Li₂O



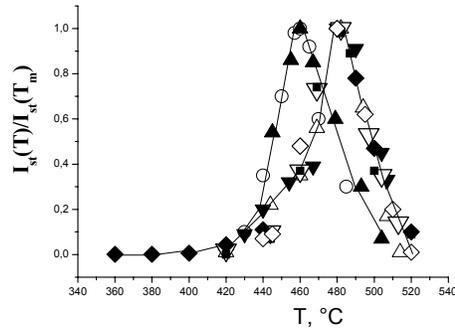
N13. 41.15 Li₂O



N14. 44.11 Li₂O



N15. 46.00 Li₂O



Total curve for N4-15

Figure 3. Stretched curves of stationary nucleation rate of crystals developed in the form of spherulites $I_{st}(T)/I_{st}(T_m)$, depending on the nucleation temperature.

Figure 3 shows the stretched curves of stationary nucleation rate of crystals developed in the form of spherulites $I_{st}(T)/I_{st}(T_m)$, depending on the nucleation temperature T (compositions N 4-15). Figure 4 shows the stretched curves of stationary nucleation rate of crystals, depending on the nucleation temperature T for compositions N 1-4.

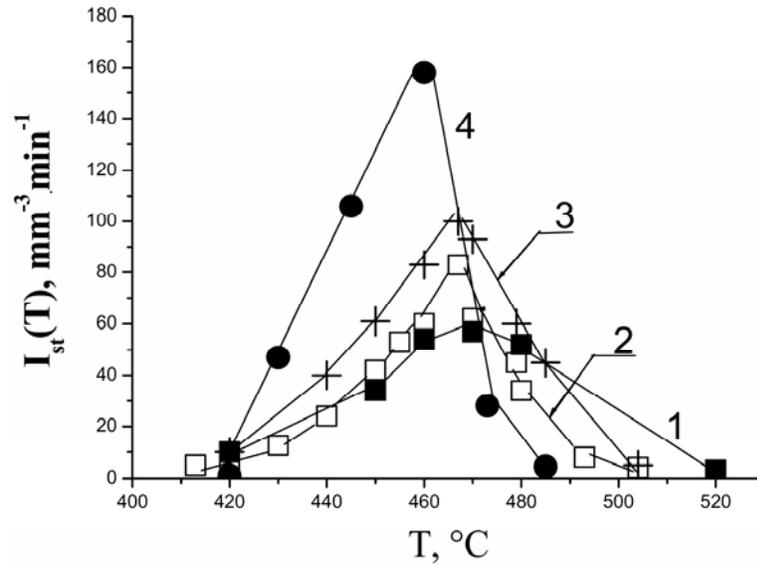


Figure 4. Temperature dependences of the stationary nucleation rate of lithium disilicate crystals $I_{st}(T)$ for the glasses (1) no. 1, (2) no. 2, (3) no. 3 with displaced compositions of the glasses, and (4) with the stoichiometric lithium disilicate composition.

Given in the Table 2 are the values of temperature T_m at which the maximum of nucleation rate is attained as well as values of $I_{st}(T_m)$. It is seen from the table and the Figure 5 that starting from 36 mol% Li_2O , the nucleation rate increases rapidly, in the range of 38 to 39% Li_2O , it grows as many as 50 times. The temperatures of the maximum shifts towards higher temperatures by 20°C on going from glass No. 4 to No. 15.

Table 2. Structure and parameters of crystallization of the investigated glasses

Стекло	Состав, мол. %		$T_g = T_{13}$, °C	E_{τ} , ккал/моль	E_{η} , ккал/моль	$I_{cm}(T_m) \cdot 10^{-3}$, мм ⁻³ · мин ⁻¹	T_m , °C	T_{np} , °C
	Li ₂ O	SiO ₂						
1	23.40	76.60	460	129	148	0.057	467	620
2	26.00	74.00	462	128	149	0.083	470	620
3	29.10	70.90	455	128	149	0.099	470	620
4	32.50	67.50	455	127	149	0.15	460	620
5	32.97	67.03	455	127	149	0.15	460	620
6	33.50	66.50	457	126	152	0.15	460	620
7	33.85	66.15	457	105	155	0.28	460	620
8	34.72	65.28	456	103	–	0.30	460	620
9	36.20	63.80	450	87	141	1.85	480	620
10	37.00	63.00	446	84	151	4.30	480	620
11	37.98	62.02	446	74	151	5.60	480	560
12	39.00	61.00	450	64	147	270.00	480	560
13	41.15	58.85	450	56	–	512.00	480	540
14	44.11	55.89	–	–	–	520.00	480	540
15	46.00	54.00	–	–	–	560.50	480	520

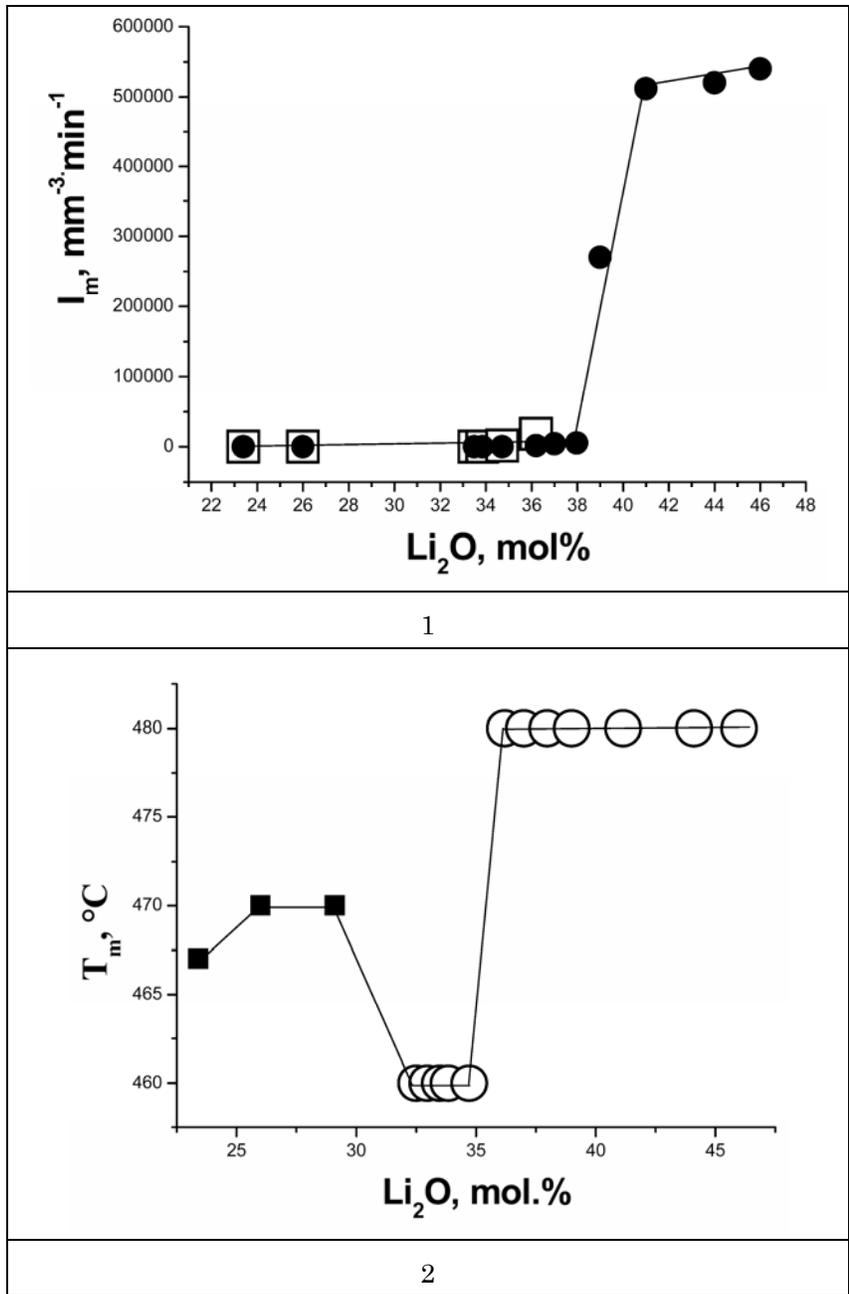


Figure 5. Dependences of the stationary nucleation rate of crystals $I_{st}(T_m) = I_m$ (1) and of T_m (2) on the Li_2O content in lithium-silicate glasses.

5. Discussion of Results

The stationary nucleation rate is determined by the following formula:

$$I_{st}(T) = I_0 \exp\left(-\frac{\Phi_\tau + \Phi^*}{kT}\right), \quad \Phi^* = 16\pi\sigma^3 / 3(\Delta\varphi)^2. \quad (1)$$

There Φ_τ - is the free activation energy of the transition of structural units from the glass to the nucleus (Φ_τ - can be considered similar to the free activation energy of the viscous flow Φ_η [4]), Φ^* - is the increment of the system free energy due to the formation of the critical nucleus of the radius $r^* = 2\sigma / \Delta\varphi$, σ - is the surface energy of the nucleus/glass boundary, $\Delta\varphi = \varphi_g - \varphi_c$ difference between free energies of glass and a crystal counting per unit volume of the nucleus. The values I_0 , $\Delta\varphi$, σ , Φ^* , and Φ_τ depend on the glass composition. For the case of crystallization of stoichiometric glass, the expression for I_0 is given, for example, in [3]. In the case of non-stoichiometric glass model to be considered below, there appears in I_0 the multiplier C_B , which is approximately equal to the concentration in the glass (at small C_B) of structural units B from which the nucleus is formed.

As the viscosity of glass (in Table 1 are given the values of activation energy $E_\eta = \Phi_\eta - T\partial\Phi_\eta / \partial T$ and $E_\tau = \Phi_\tau - \partial\Phi_\tau / \partial T$) decreases insignificant by on going from glass No. 1 to glass No. 15, the sharp increase of $I_{st}(T)$ cannot be explained by a sharp decrease of Φ_τ in Equation (1). The values of $\Delta\varphi$ and σ cannot also change at small (by 12 mol% Li_2O) deviation of the composition from stoichiometry (33.3% Li_2O), if the nucleation of lithium disilicate is assumed to take place. Apparently, the only explanation of such a sharp growth of spherulites nucleation rate composed (in the limits of X-ray phase analysis sensitivity of the crystallized glass) of lithium disilicate is an assumption that the

nucleation of these spherulites is catalyzed by metasilicate crystals, which nucleate and grow with higher rate compared to lithium disilicate crystals in glasses Nos. 8-10. In these glasses, the traces of lithium metasilicate have been rather clearly detected by X-ray diffraction even at short heat treatment times $t < t_{\text{ind}}(T)$, the amount of metasilicate changing further insignificantly even in the case of complete crystallization of the glass. In glasses Nos. 5-7, metasilicate was found only after prolonged exposures of the glass at $t \gg t_{\text{ind}}$, which is evidence of comparatively small amounts and low rates of nucleation and growth of lithium metasilicate crystals.

Thus, it can be assumed that lithium disilicate crystals nucleate on lithium metasilicate crystals, the acceleration at the disilicate nucleation being promoted by the closeness of unit cell parameters of lithium disilicate (database Pcpdfwin, No. 80-1470, orthorhombic structure, parameters of elementary cells: $a = 5.687$, $b = 4.784$, $c = 14.64 \text{ \AA}$) and lithium metasilicate (database Pcpdfwin, No. 80-1470, orthorhombic structure, parameters of elementary cells: $a = 9.396$, $b = 5.396$, $c = 4.661 \text{ \AA}$). The rapid increase of lithium metasilicate crystal nucleation rate can be explained by a rapid growth of $\Delta\phi$ in Equation (1) for lithium metasilicate with shift of the glass composition from lithium disilicate to metasilicate. Actually, let us assume that glass can be represented as composed of structural units of lithium disilicate $\text{O}_{3/2} \equiv \text{Si} - \text{O} - \text{Li}$ (tetrahedron bonded to one lithium atom) and lithium metasilicate $\text{Li} - \text{O} - \text{SiO}_{2/2} - \text{O} - \text{Li}$ (tetrahedron bonded to two lithium atoms) compositions with the concentrations x_A and x_B , respectively; $x_A + x_B = 1$. The chemical potential, for example, of the structural unit B (metasilicate) in the melt or in the glass can be written in the usual form (Equation 2)

$$\mu_B = \mu_B^0 + kT \ln(\gamma_B x_B), \quad (2)$$

where μ_B^O is the chemical potential B in the glass (melt) of the B composition -lithium metasilicate, γ_B is the activity coefficient. Thus, for $\Delta\varphi$ in Equation (1) in terms of Equation (2), we have

$$\Delta\varphi = \Delta\varphi_B = \frac{\mu_B - \mu_{B_c}^O}{v_B} = q_B \left(1 - \frac{T}{T_B}\right) + \frac{kT}{v_B} \ln(\gamma_B x_B), \quad (3)$$

where $\mu_{B_c}^O$ is the chemical potential of the structural unit B in the crystal B (where $x_B = 1$), v_B is the crystal volume per this unit; it is taken into account in Equation (3) that approximately $\frac{\mu_B - \mu_{B_c}^O}{v_B} = q_B \left(1 - \frac{T}{T_B}\right)$, T_B being the melting temperature, q_B is the heat of melting per unit volume of the crystal.

Unlike the value $\Delta\varphi = q(1 - T/T_{melt})$, for glasses of the stoichiometric composition in the Equation (3), there is an additional negative (at small x_B) term $\frac{kT}{v_B} \ln(\gamma_B x_B)$, which decreases the stronger, the lower the value of x_B . This term accounts for the entropy advantage of the accidental distribution of units B within the whole volume of the initial glass of x_B composition and consequently the entropy disadvantage, the small probability of accumulation of $4\pi r^{*3}/3v_B$ pieces of structural units B in the critical nucleus volume $4\pi r^{*3}/3$. The value $\Delta\varphi$ in Equation (3) can also be written in the form (4), where T_B' is the temperature above which at a given x_B , the nucleation of crystals B is impossible, i.e., $\Delta\varphi_B(T_B') = 0$ (T_B' is the temperature of stable or meta-stable subsolidus liquidus for the phase B).

$$\Delta\varphi_B = q_B \left(1 - \frac{T}{T'_B} \right), \quad T'_B = T_B / \left(1 - \frac{kT_B}{q_B v_B} \ln(\gamma_B x_B) \right). \quad (4)$$

The temperature of the maximum of nucleation rate I_B of the phase B , which can be found from the condition $dI_B / dT = 0$ is given by the formula (5) if in Equation (1) one takes $\Delta\varphi$ from Equation (4) and I_0 , $\sigma = \text{const}$.

$$T_m = \frac{T'_B}{3} \frac{1 + E_\tau(T_m) / \Phi^*(T_m)}{1 + E_\tau(T_m) / 3\Phi^*(T_m)}. \quad (5)$$

Thus, at small shifts of glass composition towards lithium metasilicate (small x_B) only lithium disilicate can nucleate. With increasing x_B , the nucleation rate of lithium metasilicate I_B increases rapidly due to the rapid growth of $\ln x_B$ in Equation (3) ($\partial \ln x_B / \partial T = 1 / x_B \rightarrow \infty$ at $x_B \rightarrow 0$). This is a qualitative conclusion taking into consideration roughness of formula (3), incongruent melting of disilicate etc..

The kinetic equation for catalyzed nucleation of crystals A on crystals B was obtained [5] in the following way. Assume that $\Delta N_{AB}(t', t) = I_{AB}(t', t) \Delta t'$ is the number of crystals B nucleated in the moment t' for the time $\Delta t'$ on which by the moment t , the crystal A has nucleated. For the time from t to $t' + \Delta t'$, the number of ΔN_{AB} changes into (6), where $\Delta N_B(t') = I_B(t') \Delta t'$ is the number of crystals B nucleated for the time from t' to $t' + \Delta t'$ with the rate $I_B(t')$; $S_B(t', t)$ is the surface area of crystal B by the moment t ; $I_{S_A}(t)$ - is the rate of surface nucleation of crystals A on crystals B .

$$d\Delta N_{AB}(t', t) = [\Delta N_B(t') - \Delta N_{AB}(t', t)] I_{S_A}(t) S_B(t', t) dt, \quad (6)$$

where $\Delta N_B(t') = I_B(t')\Delta t'$ is the number of crystals B nucleated for the time from t' to $t' + \Delta t'$ with the rate $I_B(t')$; $S_B(t', t)$ is the surface area of crystal B by the moment t ; $I_{S_A}(t)$ - is the rate of surface nucleation of crystals A on crystals B .

When solving Equation (6), one obtains the following equation for the total number of crystals B on which, if only one crystal A nucleated by the moment t , (7).

$$N_{AB}(t) = \int_0^t I_{AB}(t', t) dt' = \int_0^t I_B(t') \left[1 - \exp \left(- \int_{t'}^t I_{S_A}(t'') S_B(t', t'') dt'' \right) \right] dt'. \quad (7)$$

$$\int_{t-\tau_1}^t I_{S_A}(t'') S_B(t - \tau_1, t'') dt'' = 1, \quad \tau_1 = \left(\frac{3}{4\pi c_B^2 I_{S_A}} \right)^{1/3}. \quad (8)$$

Let us introduce the average time of nucleation τ_1 of one crystal A on crystal B by using the formula (8), where it is assumed for the estimation that $I_{S_A} = \text{const.}$, $c_B = \text{const.}$ - is the growth rate of spherical crystal, $S_B(t', t'') = 4\pi c_B^2 (t'' - t')$. Let us also introduce the time t_1 for which the phase B precipitates practically completely (it is assumed that $c_B = 0$ at $t > t_1$) and the time t_0 during which $I_B(t)$ differs significantly from zero ($I_B(t) \cong 0$ at $t > t_0$). It can be assumed that $t_1 \gg t_0$ as $I_B(t)$ decreases much more rapidly than $c_B(t)$ due to a decrease of x_B during precipitation of phase B . If $t_1 \ll \tau$, then assuming $I_{S_A} = \text{const.}$ and $c_B = \text{const.}$ at $t > t_1$, we obtain from Equation (7)

$$N_{AB}(t) \cong N_B(t_0) \left[1 - \exp \left(- I_{S_A} 4\pi c_B^2 t_1^2 t \right) \right], \quad t > t_1, \quad t_1 \ll \tau_1. \quad (9)$$

If on the contrary $t_1 \gg \tau_1$, then from Equation (7), we obtain at $t \gg \tau_1$ (10)

$$N_{AB}(t) \cong \int_0^t I_B(t') dt', \quad I_{AB}(t) \cong I_B(t) \quad t_1 \gg \tau_1, \quad (10)$$

i.e., the rate of catalyzed heterogeneous nucleation A_{S_A} of phase A coincides with that of homogeneous nucleation I_B of phase B .

For glasses Nos. 8-10, we have apparently the case of Equation (9) $t_1 \ll \tau_1$, at sufficiently small values of t ; $I_{AB} = dN_{AB} / dt \cong N_B(t_0) \cdot 4\pi c_B^2 t_1^2 I_{S_A}$, where the values N_B , c_B , t_1 , and I_{S_A} are temperature dependent determining the T_m position of the maximum of I_{AB} (see Table 2).

It should be mentioned that unlike the heterogeneous nucleation of lithium disilicate on silver particles [2], we deal in this case with the nucleation of lithium metasilicate particles, whose size is much greater than the one of at critical radius of lithium disilicate nuclei.

It can be seen from Figure 4 that the nucleation rate of lithium disilicate crystals $I_{st}(T_m)$ at the maximum decreases from 160 to 60mm⁻³ min⁻¹; in this case, the position of the maximum T_m is shifted toward higher temperatures by 12°C. This relatively small change in the quantity $I_{st}(T_m)$ can be explained by the fact that the glasses with displaced compositions (from 33.5Li₂O·66.5SiO₂ to 23.4Li₂O·76.6SiO₂) correspond to the phase separation region in the Li₂O-SiO₂ system (Figure 6), so that the nucleation of the lithium disilicate occurs in phase separated inhomogeneities with the composition that is displaced toward the lithium disilicate composition and depends weakly on the temperature.

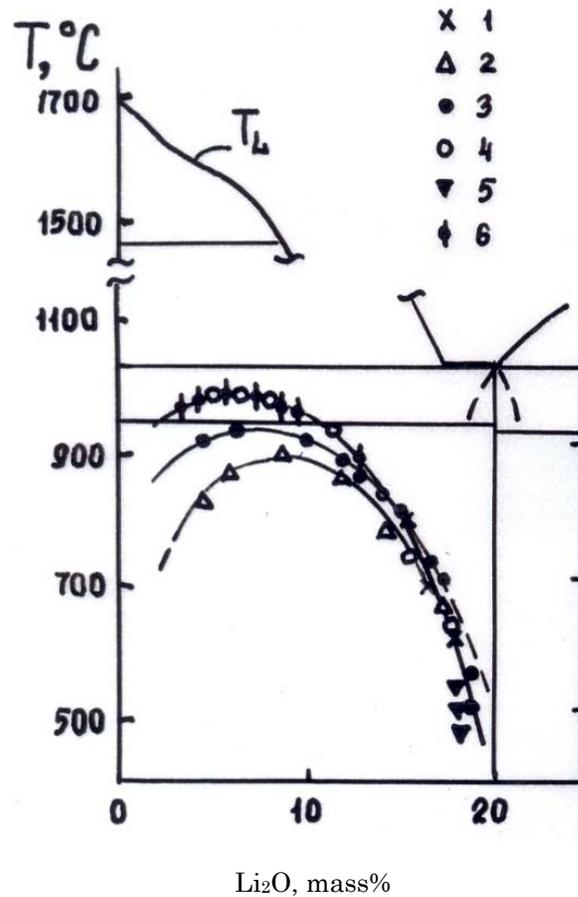


Figure 6. The plot of diagram with the metastable phase separation cupola (1 – 6 – the data by different authors (see [1] and [12])).

The shift in the maximum T_m by 12°C can be explained by the increases in the viscosity and the glass transition temperature of the melt in the phase separated (matrix) region [1, 6] enriched by SiO_2 as compared to the lithium disilicate composition, which provides an increase in the temperature T_m according to the relationship for the maximum of the nucleation rate

$$T_m = \frac{T_{melt}}{3} \frac{1 + H_A / \Delta\Phi_K^*}{1 + H_A / 3\Phi_K^*}, \quad H_A = \Phi_A + TS_A, \quad S_A = -\frac{\partial\Phi_A}{\partial T}, \quad (11)$$

where T_{melt} is the melting temperature and the enthalpy H_A , activation entropy S_A , and the nucleation barrier correspond to $T = T_m$. It can be seen from Table 2 that, the temperature T_m of the maximum nucleation rate of lithium disilicate crystals for all the compositions under investigation is close to the glass transition temperature T_g . The closeness of the temperatures T_m and T_g for the glass of the stoichiometric compositions and the glasses with displaced compositions can be explained as follows. The relative displacements of structural units that are necessary for crystal nucleation and occur through the breaking and switching of chemical bonds become sufficiently fast with an increase in the temperature beginning from the glass transition point T_g . The presence of the viscosity determined by the free activation energy $\Phi_\eta = \Phi_A$ leads to a shift in the maximum of the stationary nucleation rate $I_{st}(T)$ according to relationship (11) toward higher temperatures ($T_m = T_g = 2/3T_{melt}$) as compared to its position $T_m = 1/3T_{melt}$ that would be observed at $H = 0$.

6. Conclusion

Thus, we have investigated the nucleation in phase separated and no phase separated glasses of the lithium silicate system in wide region of compositions. The parameters of crystal nucleation have been determined. The crystal nucleation rate has been studied in glasses with the compositions displaced from the stoichiometric lithium disilicate composition toward an increase in the SiO_2 content ($x = 29.1, 26.0,$ and 23.4 mol% Li_2O) and with the compositions displaced from the stoichiometric lithium disilicate composition toward an increase in the Li_2O content ($x = 32.5, 32.97, 33.5, 33.85, 34.72, 36.2, 37.0, 37.98, 39.0, 41.15, 44.11,$ and 46.00 mol% Li_2O). The absolute values of the stationary nucleation rates I_{st} of lithium disilicate crystals in the $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where

$x = 23.4, 26.0,$ and 29.1 mol% Li_2O) glasses with the compositions lying in the metastable phase separation region have been compared with the corresponding rates I_{st} for the $x\text{Li}_2\text{O} \cdot (100 - x)\text{SiO}_2$ (where $x = 32.5, 32.97, 33.5, 33.85, 34.72, 36.2, 37.0, 37.98, 39.0, 41.15, 44.11,$ and 46.00 mol% Li_2O).

The following features have been revealed:

(i) The absolute values of the crystal nucleation rate in glasses with the lower content Li_2O than that in the glass with the stoichiometric lithium disilicate composition vary insignificantly.

(ii) The position of the temperature maximum of the nucleation rate for the glass with the lower lithium oxide content is shifted on the temperature scale by 12°C . This relatively small change in the quantities $I_{st}(T_m)$ and T_m is explained by the fact that the glasses with the displaced composition correspond to the phase separation region in the $\text{Li}_2\text{O}\text{-SiO}_2$ system, so that the lithium disilicate in glasses with displaced composition nucleates in phase separated inhomogeneities with compositions that are displaced toward the lithium disilicate composition and depend weakly on the temperature.

(iii) The position of the temperature maximum of the nucleation rate for the glasses with the bigger lithium oxide content shifts towards higher temperatures by 20°C on going from glass No. 4 to No. 15. Starting from 33.5 mol% Li_2O , the nucleation rate increases rapidly, in the range of 34.72 to 46.00 mol% Li_2O , it grows as many as 1800 times.

(iv) The temperature T_m of the maximum nucleation rate of crystals for all the compositions under investigation is close to the glass transition temperature T_g .

The data obtained on the nucleation of crystals help to find optimum compositions and temperature-time conditions for the preparation of glass-ceramic nanomaterials in lithium silicate system, including photo-structured materials.

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