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Nucleation and Crystal Growth in Phase Separated Glasses in the Lithium Silicate System

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1. Introduction

The glass forming systems may be regarded as model systems for technical glass ceramics. Many papers on investigation of nucleation in oxide glasses are known. Table 1 shows the compound glass-forming systems, for which the temperature dependence of the steady and unsteady crystal nucleation in the bulk nucleation were studied.

As can be seen from Table 1, the greatest attention was paid by researchers to the system $\text{Li}_2\text{O}-\text{SiO}_2$ [1-68] because of its practical importance. A specific feature of the system $\text{Li}_2\text{O}-\text{SiO}_2$ is that, in the region of compositions from 0 to 32 mol % Li_2O , the glasses have a tendency towards the phase separation. Many authors [1, 2, 3, 4] have believed that the process of phase separation of glasses into two vitreous phases favors a homogeneous crystallization of a glass with the formation of small crystals. As follows from [5, 6] the role of the phase separation is reduced to the appearance of phase boundaries that serve as a particular catalyst of the crystallization. According to [93], the crystallization of phase separated glasses cannot be referred to as catalytic. It is necessary to speak about the influence of the phase separation on a further crystallization process rather than about catalysis. Actually, a review of a number of experimental works [7, 8, 9, 10, 81, 11] demonstrates that the liquid-liquid phase separation before crystallization affects the crystal structure of glass-ceramic materials through at least three different ways.

1. The boundary between phases plays a role of an initiating agent.
2. Since, after the phase separation, the composition of a matrix or dispersed phase becomes closer to that of a crystallizing phase, the formation and growth of crystals progress more easily.
3. In one of the phases, the metastable phase precipitates and plays a role of a catalyst for the main crystalline phase.
4. The purpose of this work is to investigate the phase separation and its effect on the crystallization process in lithium silicate glasses that serve as a basis for the preparation of glass ceramic materials.

| Nucleated compound | System | № References |
|--|--|--|
| The system $\text{Li}_2\text{O}-\text{SiO}_2$ [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78] | | |
| Glasses of the stoichiometric composition | | |
| $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ | $\text{Li}_2\text{O}-\text{SiO}_2$ | [15, 16, 17, 20, 21, 22, 23, 24, 27, 28, 32, 35, 39, 46, 52, 79] |
| $\text{Li}_2\text{O}\cdot \text{SiO}_2$ | $\text{Li}_2\text{O}-\text{SiO}_2$ | [40] |
| $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ | $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ | [80, 81] |
| $2\text{Na}_2\text{O}\cdot \text{CaO}\cdot 3\text{SiO}_2$ | $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ | [82, 83] |
| $\text{BaO}\cdot 2\text{SiO}_2$ | $\text{BaO}-\text{SiO}_2$ | [84, 85, 86] |
| $\text{CaO}\cdot \text{SiO}_2$ | $\text{CaO}-\text{SiO}_2$ | [87] |
| Glasses of the compositions close to stoichiometric ones | | |
| $\text{Na}_2\text{O}\cdot \text{SiO}_2$ | $\text{Na}_2\text{O}-\text{SiO}_2$ | [88, 89, 90, 91] |
| $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ | $\text{Na}_2\text{O}-\text{SiO}_2-\text{Cr}_2\text{O}_3$ | [56] |
| $\text{BaO}\cdot 2\text{SiO}_2$ | $\text{Na}_2\text{O}-\text{BaO}-\text{SiO}_2$ | [92] |
| $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ | $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ | [93, 94, 95] |
| Glasses of the non-stoichiometric compositions | | |
| $\text{Li}_2\text{O}\cdot \text{SiO}_2$ | $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ | [96] |
| MgCr_2O_4 | $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ | [97] |
| $\text{CaO}\cdot \text{MgO}\cdot 2\text{SiO}_2$ | $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ | [86] |
| $\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ | $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ | [98] |
| $2\text{SnO}\cdot \text{P}_2\text{O}_5$ | $\text{SnO}-\text{SnO}_2-\text{ZnO}-\text{P}_2\text{O}_5$ | [99] |
| $\text{Na}_2\text{O}\cdot \text{ZnO}\cdot \text{P}_2\text{O}_5$ | $\text{Na}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5$ | [100] |
| $\text{BaO}\cdot \text{B}_2\text{O}_3\cdot \text{P}_2\text{O}_5$ | $\text{BaO}-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3$ | [101] |

Table 1. Compound of glass-forming systems, for which the temperature dependences of the steady and unsteady crystal nucleation in the bulk nucleation were studied.

2. Sample preparation and experimental technique

The rates of nucleation and growth of crystals and phase separated inhomogeneities were studied in glasses of the analyzed compositions $x\text{Li}_2\text{O}\cdot (100 - x)\text{SiO}_2$ (where $x = 23.4, 26.0, 29.1$ and 33.5 mol % Li_2O). Since it was established earlier that the crystal nucleation parameters are strongly affected by water [35] and bubbles formed in the course of glass synthesis [102], 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 lithium disilicate crystals and increase a number of crystals to 20% [103]. As the water content increases, the stationary nucleation rate increases and the position of the maximum shifts toward lower temperatures [35]. 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 [49]. Bubbles were removed by performing the synthesis at a high temperature. The glasses were synthesized according to the technique described in [103]. 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, 200 ml) in a Globar-heater furnace with silicon carbide heaters (synthesis temperature, 1550 °C; synthesis time, 5 h). 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 2.

| Glass no. | Li ₂ O | SiO ₂ |
|-----------|-------------------|------------------|
| 1 | 23.4 | 76.6 |
| 2 | 26.0 | 74.0 |
| 3 | 29.1 | 70.9 |
| 4 | 33.5 | 66.5 |

Table 2. Chemical compositions under investigation (mol %)

X-ray powder diffraction analysis was performed on a DRON-2 diffractometer (CuK α radiation; operating voltage 30 kV; current 20 mA; detector rotation rate, 2 deg/min). Differential thermal analysis (DTA) was carried out on a MOM derivatograph (heating rate, 10 K/min; sample weight, 1 g; 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). Electron microscopy studies were carried out on an EM-125 transmission electron microscope (accelerating voltage, 75 kV). Samples were prepared using the method of celluloid-carbon replicas. The viscosity was measured by the bending method on a Klyuev viscometer. The temperature dependence data on the viscosity was processed by the least squares technique with the conventional computer program for determining the coefficients A , B , and T_0 in the approximation according to the Vogel-Fulcher-Tammann equation [104]. The nucleation and growth rates of phase separated inhomogeneities and 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 $T_{\text{dev}} > T$ bringing to sizes that can be fixed in an optical microscope. The crystal growth rate was measured by quenching the samples. The samples in the form of small glass pieces were held at a specified temperature for different times and were used to prepare polished plane parallel disks 0.5 mm thick. Crystals with a maximum size were found in the bulk of a sample, and their radius R_{max} was measured using the JenaVal optical microscope. The radius R_{max} of the phase separated droplet or crystal was taken to be equal to the average value over ten maximum radii of crystals or phase separated droplets. This requires the explanation. If some number of phase separated droplets or crystals in the shape of spheres with the same radius R are randomly distributed in the glass bulk (their number per unit volume is designated as N), certain crystals or phase separated droplets will be cut by the plane when preparing the cleavage or cross section of the sample. This holds true only for crystals or phase separated droplets with the centers located at a distance that is not larger than R from the cut plane. Therefore, all crystals or phase separated droplets with the centers located in the layer of thickness $2R$ leave a trace on the cut plane. It is clear that the maximum radius of the trace of the crystal or phase separated droplet will correspond to the real radius of these particles.

3. Temperature dependence of the nucleation and growth rate of phase separated in homogeneities in lithium silicate glasses of the compositions $23.4\text{Li}_2\text{O}\cdot 76.6\text{SiO}_2$ (1), $26\text{Li}_2\text{O}\cdot 74\text{SiO}_2$ (2), and $29.1\text{Li}_2\text{O}\cdot 70.9\text{SiO}_2$ (3)

In the $33.5\text{Li}_2\text{O}\cdot 66.5\text{SiO}_2$ glass with the composition closest to the stoichiometric composition of the lithium disilicate, excess SiO_2 is absent and, therefore, no phase separation is observed. The compositions of the glasses containing 23.4 mol % Li_2O (no. 1), 26 Li_2O (no. 2), and 29.1 Li_2O (no. 3) lie in the metastable phase separation region of the lithium-silicate system. The samples of glasses no. 1, no. 2, no. 3 and no. 4 were subjected to preliminary heat treatment at temperatures in the range 370–560 °C for different times. Then, they were held at a development temperature of 600 °C for 10 min. If glass no. 1, no. 2 or 3 is held at the temperature $T = 600^\circ\text{C}$ for a time in the range 0–10 h, it remains transparent without visible opalescence in visual examination. If the glass is heat treated for $t = 2\text{ h } 40\text{ min}$ at temperatures of 400–560°C, it remains visually transparent and does not become opalescent. After additional heat treatment at 600 °C for 10 min, the glass acquires bright blue (yellow in transmission) going to milky opalescence. The electron microscopic images of the glasses preliminarily heat treated at temperatures in the range 400–560 °C and developed at 600 °C for 10 min are displayed in Figs. 1a–1c.

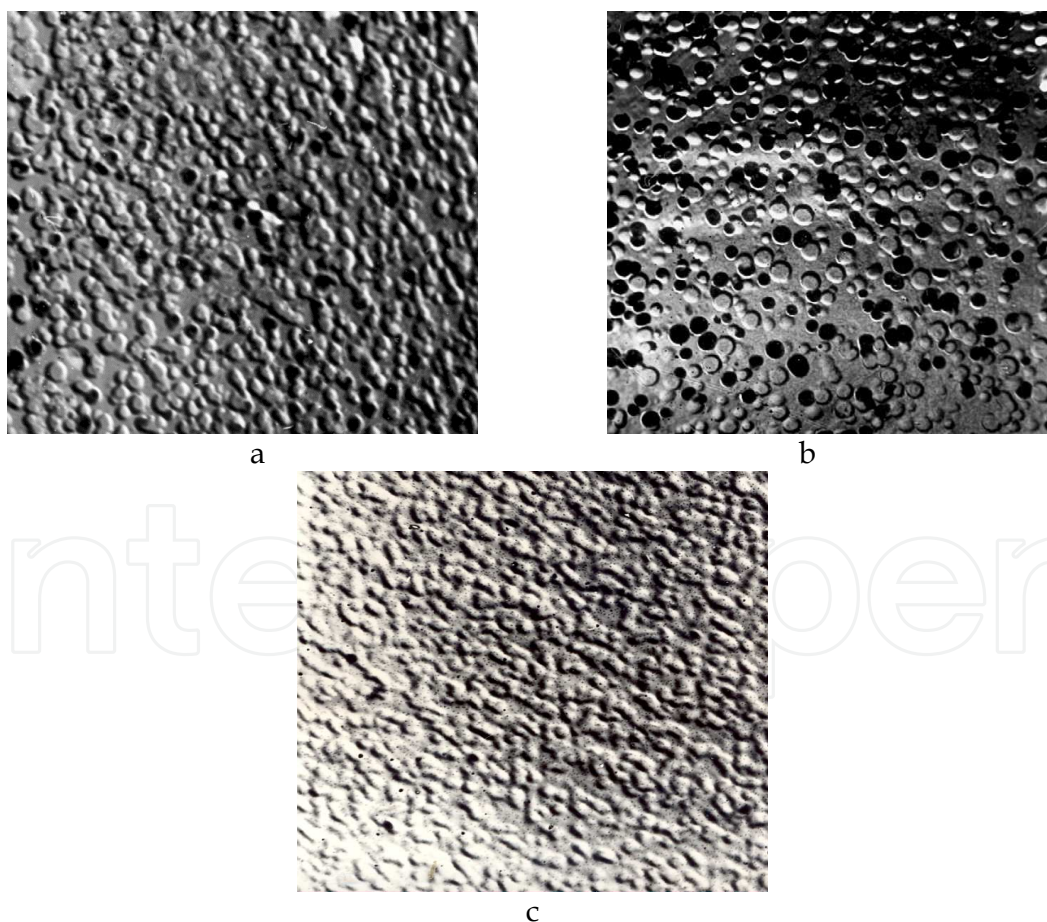


Fig. 1. Electron microscopic images of glasses (a) no. 1, (b) no. 2 and (c) no. 3 preliminarily heat treated at temperature 460 °C for 2 h 40 min and developed at 600 °C for 10 min (magnification, 28800).

We counted the number of traces of particles per unit area in the electron microscopic image N_S/S_0 and determined the sizes of the maximum traces of particles R . The corresponding results for glass no. 1 are listed in Table 3.

| $T, ^\circ\text{C}$ | $N_S, \mu\text{m}^{-2}$ | $R, \text{\AA}$ |
|---------------------|-------------------------|-----------------|
| 370 | 90 | 103 |
| 390 | 108 | 150 |
| 400 | 112 | 160 |
| 420 | 120 | 190 |
| 460 | 134 | 250 |
| 464 | 131 | 260 |
| 490 | 118 | 300 |
| 520 | 94 | 335 |
| 540 | 74 | 375 |
| 560 | 60 | 408 |
| 580 | 48 | 440 |

Table 3. Numbers of traces of particles per unit area in electron microscopic images N_S/S_0 and their sizes in glass no. 3 after heat treatment at T for 160 min and development at 600 °C for 10 min.

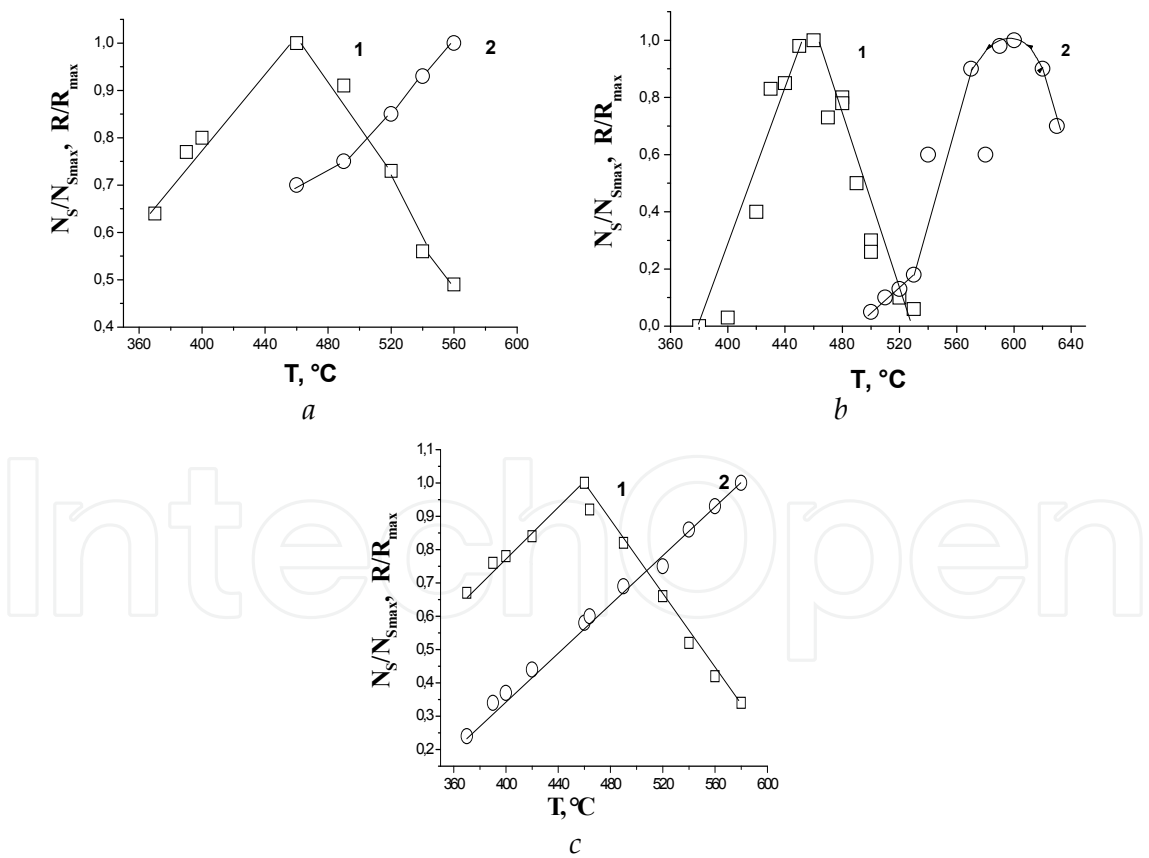


Fig. 2. Quantitative characteristics of the phase separation structure in glasses (a) no. 1, (b) no. 2 and (c) no. 3 as a function of the temperature: (1) ratio of the number of traces to the maximum number of traces $N_S/N_{S_{\max}}$ and (2) ratio of the radius of the particle trace to the maximum radius R/R_{\max} .

Figure 2 presents the quantitative characteristics of the phase separation structure in glasses no. 1 and no. 2 as a function of the temperature, namely, the ratio of the number of traces to the maximum number of traces $N_S/N_{S_{\max}}$ and the ratio of the radius of the particle trace to the maximum radius R/R_{\max} .

Here, we assume that the dependence of the number of traces of phase separated droplets per unit area of the sample surface on the heat treatment temperature (at a constant heat treatment time) obeys the same function law as the temperature dependences of the stationary nucleation rate of droplets. Strictly speaking, in order to determine the stationary nucleation rate $I(T)$, initially, it is necessary to determine the number of droplets per unit volume of the glass by the number of traces per unit area with the use of stereological formulas. Then, it is required to determine a variation in the number of droplets per unit volume as a function of the heat treatment time. Thereafter, it is necessary to check that the nucleation rate is stationary and to determine its value. This is not a simple problem, which is complicated by the fact that the droplets in the volume of the glass can have different sizes. The obtained dependence of the number of traces on the temperature for a fixed heat treatment time can differ substantially from the dependence of the stationary nucleation rate of droplets. However, we used a simpler method to approximately evaluate the temperature dependence of the nucleation rate of droplets. Instead of the dependence $I(T)$, we constructed the dependence $N_S(T)$ of the number of traces of particles developed for the same specified time of development t_{dev} at T_{dev} after preliminary heat treatment for the same specified time t at all temperatures T . Since the quantities I and N_S are approximately proportional to each other, the curves $I(T)/I_{\max}$ and $N_S(T)/N_{S_{\max}}$ are very close to each other and, in order to evaluate the temperature of the maximum nucleation rate, it is sufficient to measure the dependence of the number traces of crystals N_S without regarding for their shape and sizes [77, 80]. It can be seen from Fig. 2 that these dependences exhibit maxima. The maximum values of the number of traces and sizes correspond to temperatures of 460 and 600 °C, respectively. On the whole, the results obtained can be explained as follows. The nucleation rate of a new phase (phase separated or crystalline) I has the form [68]

$$I = A \exp[-(\Phi_A + \Phi^*)/kT], \quad (1)$$

where Φ^* is the increment of the thermodynamic potential of the glass due to the appearance of a critical (in composition and size) inhomogeneity nucleus, Φ_A is the thermodynamic potential of diffusion jumps and transformations during the phase separation, and A is the factor that, like the quantities Φ_A and Φ^* , depends on the glass composition and temperature more weakly than an exponential function. If the glass composition c_0 belongs to the bimodal region at a given temperature, the thermodynamic potential Φ^* is relatively high because the inhomogeneities that do not reach some limiting concentration c_1 appear to be energetically unfavorable irrespectively of their sizes. When the glass composition belongs to the spinodal region, inhomogeneities with an arbitrarily small difference $|c - c_0|$ and, correspondingly, with negligible Φ^* can be energetically favorable if only their size exceeds the critical size. As a consequence, there is an increase in the nucleation rate of inhomogeneities I (expression (1)). By using the notion of the concentration wave length λ introduced by Cahn, in the spinodal region, the

value $|c - c_0|$ most rapidly increases in amplitude and, hence, the inhomogeneities with the size λ_m that is larger than the critical size λ_{cr} by a factor of $\sqrt{2}$ nucleate most rapidly. The wave amplitude λ_m increases as $\exp(t/\tau_m)$; in this case, the magnitude $1/\tau_m$ can be considered not only as the measure of the nucleation rate of the amplitude but also as the measure of the nucleation rate of inhomogeneities by taking $I = B/\tau_m$. As a result, we have (2)

$$I = \frac{B}{\tau_m} = c(T_S - T)^2 \exp\left(-\frac{\Phi_A}{kT}\right) \quad (2)$$

where B and c are temperature independent constants and T_S is the spinodal temperature. From the condition $dI/dT = 0$, we find that the maximum of the rate is located at the temperature T_{max} satisfying the equation (3).

$$T_S - T_m = \frac{2RT_m^2}{E_A(T_m)}, \quad E_A(T) = \Phi_A(T) - T \frac{\partial \Phi_A(T)}{\partial T} \quad (3)$$

By assuming that the thermodynamic potential Φ_A does not depend on the temperature T , i.e., $\Phi_A = E_A$, and setting $\Phi_A = 83$ kcal/mol (activation energy of oxygen diffusion), at $T_m \cong 973K$, Eq. (3) takes the form

$$T_S - T_m \cong T_m(2RT_m / \Phi_A) \cong 25K \quad (4)$$

Under the assumption that the thermodynamic potential Φ_A is equal to the activation energy of lithium self diffusion, we obtain

$$T_S - T_m \cong 60K \quad (5)$$

Therefore, the maximum of the ratio N_S/N_{Smax} in Fig. 2 reflects the maximum of the nucleation rate of droplets with a diameter $\lambda=200-400$ Å. This reflection is rather indirect because the number of inhomogeneities n' nucleated for the time t' $n' = \int I(t)dt$ can differ significantly (and differs) from the number n of large particles growing in the course of the development. The reason is that, after the increase in the temperature to 600 °C, the inhomogeneities with the composition and size that reach critical values at 600 °C are predominantly retained and will develop. The inhomogeneities with the composition that approaches the binodal composition at the corresponding temperature during low temperature heat treatment go beyond the binodal with the increase in temperature to 600 °C and should dissolve in the glass located between inhomogeneities. A number of inhomogeneities can merge together when reaching the critical sizes for a temperature of 600 °C. This dissolution and merging of small inhomogeneities can lead to the formation of larger and stable inhomogeneities with a composition close to the binodal composition at the temperature of 600 °C.

Although the relation between the quantities n and n' is complex, the maximum of the ratio N_S/N_{Smax} in Fig. 2 reflects the rate of nucleation and development of phase separated inhomogeneities. Then, the temperature of its left boundary T_S can be identified with the

spinodal temperature T_S and the difference between this temperature and the temperature of the maximum T_{\max} is appropriately identified by the difference $T'_S - T_{\max}$, which was estimated above as 25–60 °C. It is difficult to accurately determine the spinodal temperature. In our experiment, we determined this temperature from the appearance of pronounced phase separated droplets in the electron microscopic images. Experimental data on the determination of the spinodal are absent in the literature.

Haller et al. [105] calculated the spinodal for glasses in the lithium silicate system. A comparison of our data with those obtained in [105,105] leads to the following results. According to [105], the spinodal temperature T_S amounts to approximately 600 °C for glass no. 1 (23.4 mol % Li_2O) and is in the vicinity of 500 °C for glass no. 2 (26.0 mol % Li_2O). Below 500 °C, data in [105] are absent. However, if the curve is extrapolated to 400 °C, the spinodal temperature T_S for glass no. 2 appears to be 400 °C. In our work, the maximum of the ratio $N_S/N_{S\max}$ in Fig. 2 lies in the temperature range 350–570°C for glass no. 1 and \approx 400–650°C for glass no. 2. Therefore, the experimental and calculated data for glass no. 2 (26.0 mol % Li_2O) are in good agreement, whereas, for glass no. 1 (23.4 mol % Li_2O), the calculated value is by 200 °C higher than the experimental. For glasses no. 1 and no. 2, the difference $T'_S - T_{\max} \cong 40\text{--}50$ °C actually lies in this range. The maximum of the rate of nucleation and development of inhomogeneities is located at the glass transition temperature T_g .

In order to compare more rigorously the theory with the experiment, it is necessary to know the spinodal temperature T_S . This temperature was evaluated as follows. Quenched glasses no. 1 and no. 2 (without low temperature heat treatments) were held in the gradient furnace at temperatures in the range 300–800 °C for 2 h. This led to the appearance of the opalescent band along the sample length, which was stable with respect to a further increase in the holding time. This band had a higher intensity in the central part and weaker intensities toward higher and lower temperatures up to its complete visual disappearance. The temperature of the upper edge of the visible opalescence (770 °C for glass no. 1) coincided with the phase separation temperature T_l (770 °C for glass no. 1) determined as the temperature of the disappearance of the visible opalescence after the opalescent part of the rod was displaced in the range of temperatures a priori higher than T_l . The analysis of the electron microscopic images demonstrates that, in going from the high temperature edge of the band to the low temperature edge, the number of particle traces per unit area (or the relative area occupied by particle traces) increases linearly. Initially, this process goes slowly and then accelerates. It is clear because the nucleation rate is minimum in the vicinity of the phase separation temperature T_l and increases as the spinodal temperature T_S is approached as a result of the decrease in the thermodynamic potential Φ^* in expression (1). When the traces of inhomogeneities begin to cover a larger part of the replica area and to merge together, the increase in the relative area S/S_0 occupied by particles at T_S is retarded sharply. The temperature of this kink in the curve S/S_0 is naturally identified by the spinodal temperature T_S corresponding to the beginning of fast nucleation of inhomogeneities occupying the volume of the glass. This temperature almost absolutely coincide with the low temperature edge of the visible opalescence. The temperature width of the opalescent band ΔT_{op} corresponds to the difference $T_l - T_S \cong \Delta T_{\text{op}}$.

3.1 Effect of displacement of the glass composition from the stoichiometric lithium disilicate composition toward an increase in the SiO₂ content on the nucleation of lithium disilicate crystals

In order to accelerate the search for the temperature range of crystal nucleation, we used the DTA curves and the temperature dependences of the viscosity, because it was previously shown [68] that the maximum of the crystal nucleation rate is located in the range of the endothermic effect in the DTA curve at the temperature corresponding to a viscosity of 10¹³ P. The temperature dependences of the viscosity for glasses no. 1–no. 3 are plotted in Figs. 3a–3c. The inset to Fig. 3 presents the coefficients *A*, *B*, and *T*₀ in the approximation according to the Vogel-Fulcher-Tammann equation [104]. It can be seen from Fig. 3 that the glass transition temperature determined as the temperature corresponding to a viscosity of 10¹³ P is equal to 453 °C for glass no. 1, 458 °C for glass no. 2, 457 °C for glass no. 3 and 450 °C for glass no. 4. The slope of the temperature dependence of the natural logarithm of the viscosity on the reciprocal of the temperature (Fig. 3d) was used to determine the activation energies of the viscous flow $E_{\eta} = R d \ln \eta / d(1/T)$, which were equal to 148, 149, 150 and 152 kcal/mol for glasses no. 1–no. 4, respectively.

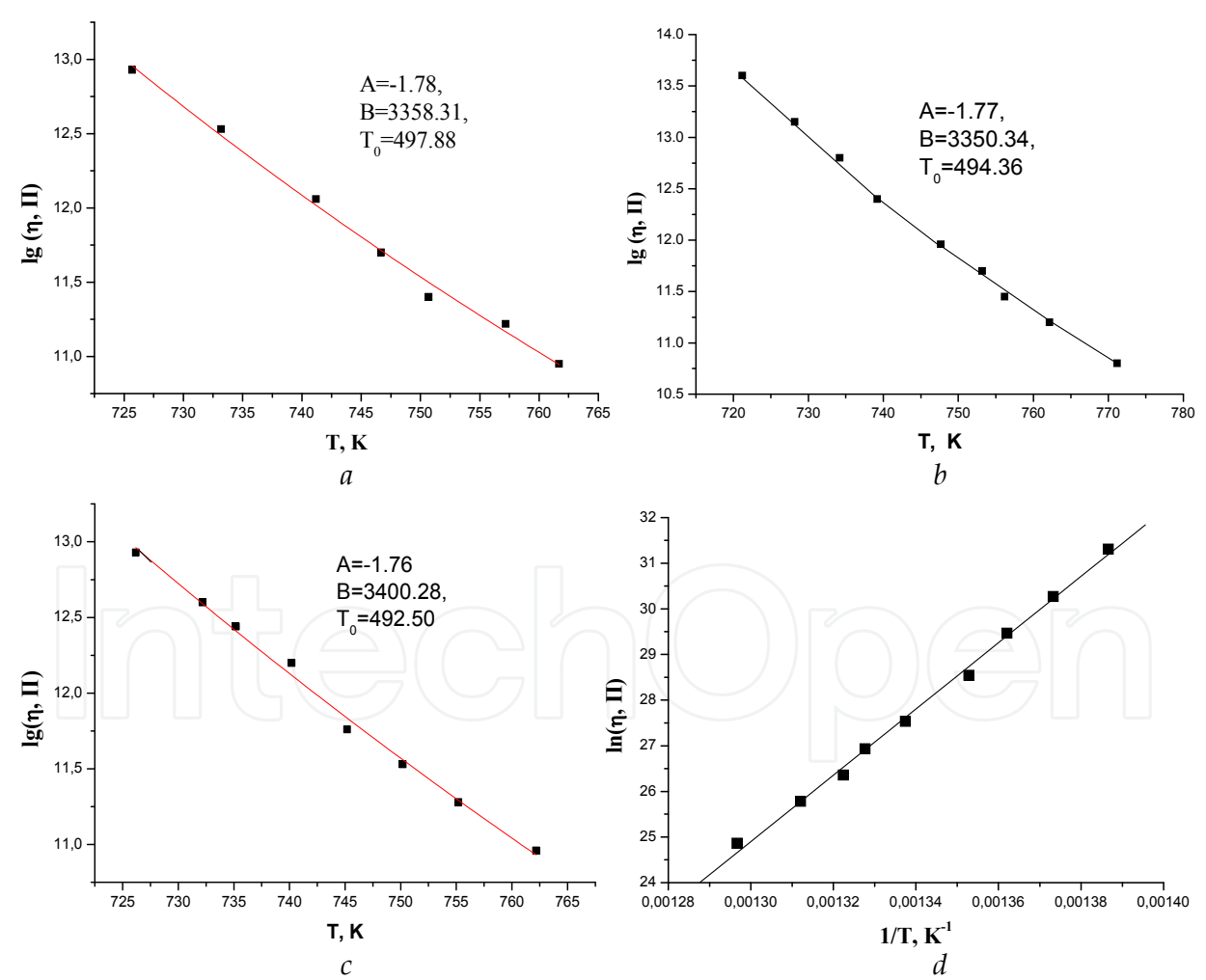
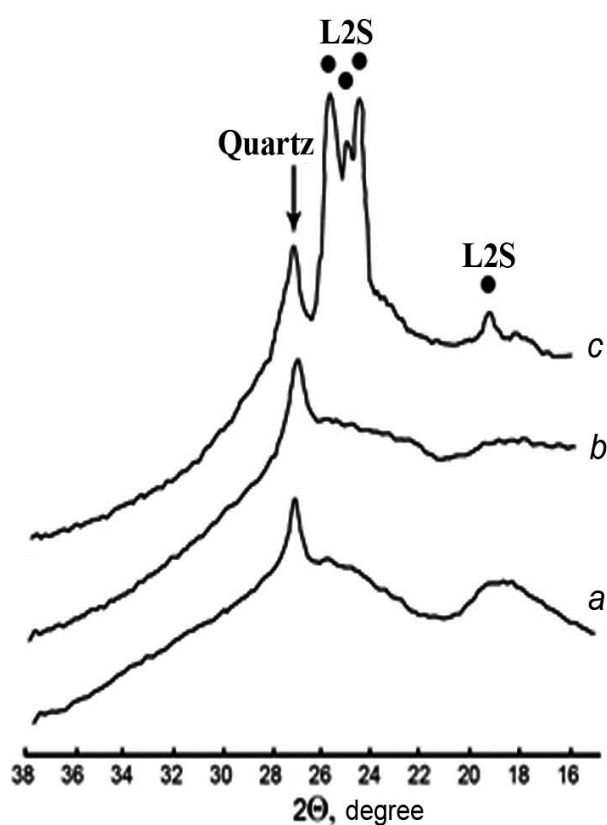


Fig. 3. Temperature dependences of the decimal logarithm of the viscosity for glasses (a) no. 1, (b) no. 2, and (c) no. 3 and (d) temperature dependence of the natural logarithm of the viscosity for glass no. 2 (used for determining the activation energy of viscous flow in the glass).

The X-ray powder diffraction data (Fig. 4) demonstrate that the initial glasses are X-ray amorphous. The lithium disilicate crystals nucleated at temperatures of preliminary heat treatments in the range 420–520 °C for all times cannot be revealed using X-ray diffraction analysis. This is associated with the fact that the lithium disilicate nuclei are extremely small and their total weight is insignificant and, hence, insufficient for identifying by X-ray diffraction analysis, because its sensitivity is equal to a few weight percent of a compound. After heat treatments, lithium disilicate $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (PCPDFWIN no. 80-1470; orthorhombic structure; unit cell parameters $a = 5.687 \text{ \AA}$, $b = 4.784 \text{ \AA}$, and $c = 14.640 \text{ \AA}$) crystallizes in glasses no. 1–no. 3 at a development temperature of 600 °C for 10 min.



Intensity, arb. units

Fig. 4. X-ray diffraction patterns of initial and heat treated glasses no. 2: (a) initial glass, (b) glass heat treated at 450°C for 5 h, and (c) glass preliminarily heat treated at 450°C for 5 h and developed at 600°C for 10 min.

It can be seen from the images obtained using the optical microscope in reflected and transmitted light (Fig. 5) that the lithium disilicate grows in the form of ellipsoids of revolution with an axial ratio of 1.0 : 1.6 in glass no. 4 (with the composition closest to the stoichiometric lithium disilicate composition), with an axial ratio of 1.0 : 2.0 in glass no. 3 and in the shape of regular spheres in glass no. 2. The number of crystals increases with an increase in the holding time during preliminary heat treatment.

In order to nucleate lithium disilicate crystals, the samples of initial glasses no. 1–no. 4 were held at temperatures in the range 420–520 °C (range of the endothermic effect in the DTA

curves). Then, the nucleated crystals were developed (to sizes visible in the optical microscope) at 600 °C for 10 min, i.e., at the temperature corresponding to the ascending branch of the exothermic peak in the DTA curve. The kinetics of homogeneous crystal nucleation was described using the stationary nucleation rate I_{st} , nonstationary nucleation time τ , and temperature dependences of these quantities.

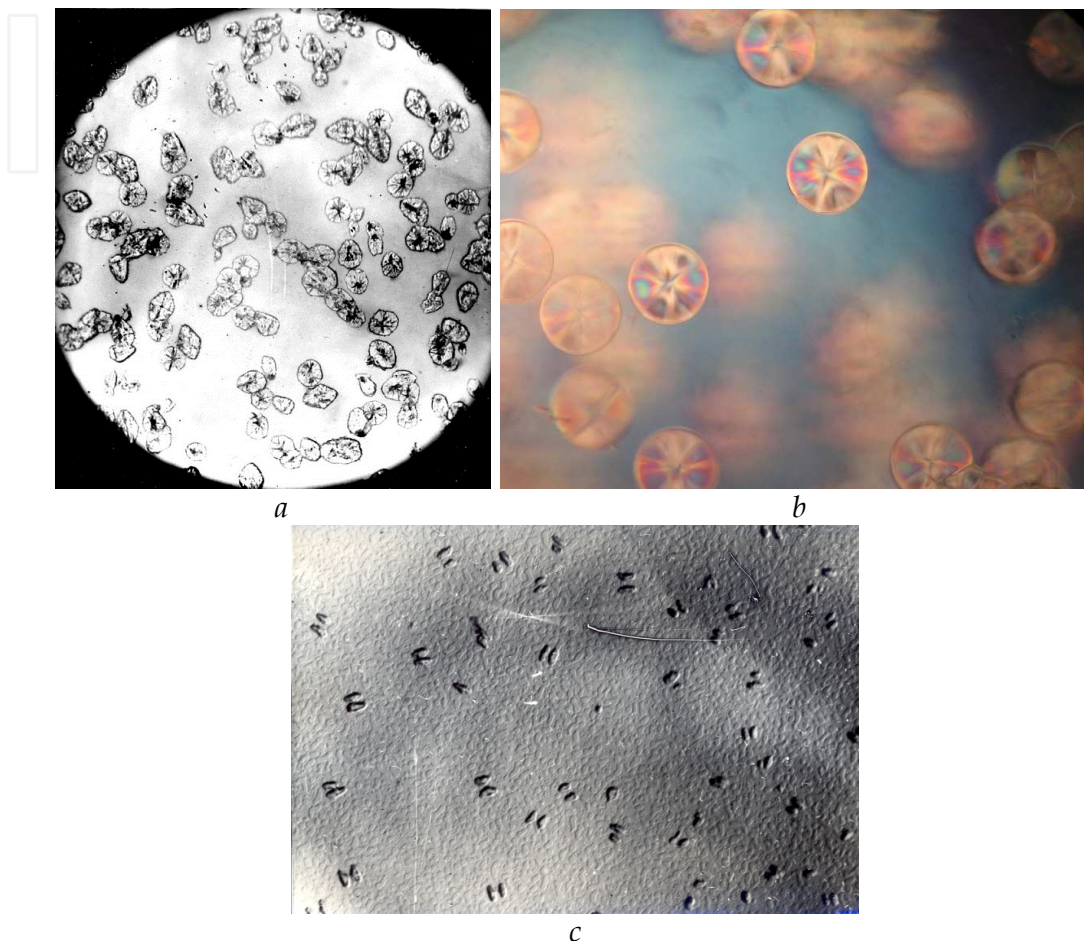


Fig. 5. Shape of lithium disilicate crystals in: (a) glass no. 4 after preliminary heat treatment at the temperature 420 °C for 4 h; (b) glass no. 2 after preliminary heat treatment at the temperature 400 °C for 4 h; (c) glass no. 3 after heat treatment at the temperature 440 °C for 8 h. All samples were developed at the temperature 600 °C for 10 min. Image (a) was obtained in reflected light with the use of the Neophot 32 optical microscope at a magnification of .150. Image (b) was obtained in transmitted light with the use of the Jenaval optical microscope at a magnification of .200. Image (c) was obtained in reflected light with the use of an EM-125 transmission electron microscope at a magnification of .28000.

3.2 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 holding time 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 the 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 0.01 M HF solution for 10 s. 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 nonstationary nucleation time τ was evaluated 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. Then, we constructed the temperature dependences of all the aforementioned quantities.

4. Experimental results on crystal nucleation and their discussion

The nucleation of the lithium disilicate was observed in all glasses. The dependences of the number of developed crystals n in the nucleation temperature range 400–520 °C (development at 600 °C for 10 min) were used to determine the stationary nucleation rate and the nonstationary nucleation time at each specific temperature. The induction period t_{ind} decreases monotonically with an increase in the temperature. The temperature dependence of the induction period $t_{ind}(T)$ allows us to determine the activation energies for nucleation of lithium disilicate crystals E_τ from the formula $E_\tau = R d \ln t_{ind} / d(1/T)$. The corresponding activation energies are equal to 129, 128, 127 and 126 kcal/mol for glasses no. 1–no. 4, respectively. The temperature dependences of the stationary nucleation rate of lithium disilicate crystals $I_{st}(T)$ for the glass with the stoichiometric lithium disilicate composition and glasses with displaced compositions are shown in Fig. 6. It can be seen from this figure that the nucleation rate of lithium disilicate crystals $I_{st}(T_{max})$ at the maximum decreases from 160 to 60 mm⁻³ min⁻¹; in this case, the position of the maximum T_{max} is shifted toward higher temperatures by 12 °C. This relatively small change in the quantity $I_{st}(T_{max})$ can be explained by the fact that the glasses with displaced compositions correspond to the phase separation region in the Li₂O–SiO₂ system, 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. The shift in the maximum T_{max} 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 [106,107] enriched by SiO₂ as compared to the lithium disilicate composition, which provides an increase in the temperature T_{max} according to the relationship for the maximum of the nucleation rate

$$T_{max} = \frac{T_{melt}}{3} \frac{1 + H_A / \Delta \Phi_K^*}{1 + H_A / 3 \Phi_K^*}, \quad H_A = \Phi_A + T S_A \quad S_A = -\frac{\partial \Phi_A}{\partial T} \quad (6)$$

where T_{melt} is the melting temperature and the enthalpy H_A , activation entropy S_A , and the nucleation barrier correspond to $T = T_{\text{max}}$. It can be seen from Fig. 6 that the temperature T_{max} 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_{max} 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 $I_{\text{st}}(T)$ according to relationship (6) toward higher temperatures ($T_{\text{max}} = T_g = 2/3T_{\text{melt}}$) as compared to its position $T_{\text{max}} = 1/3T_{\text{melt}}$ that would be observed at $H = 0$.

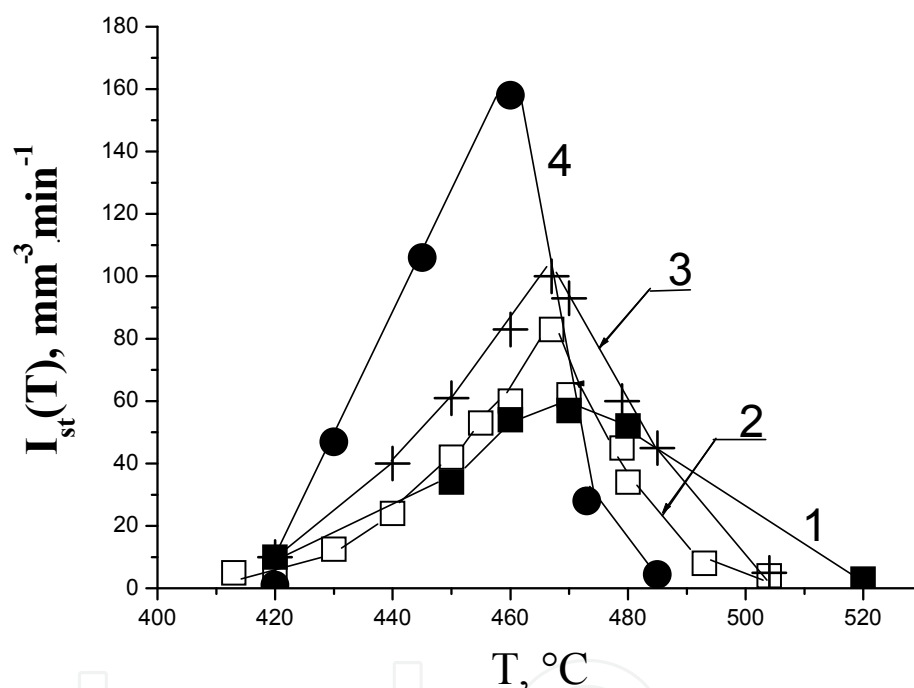


Fig. 6. Temperature dependences of the stationary nucleation rate of lithium disilicate crystals $I_{\text{st}}(T)$ for the glasses (1) no. 1, (2) no. 2 and (3) no. 3 with displaced compositions of the glasses and (4) with the stoichiometric lithium disilicate composition.

5. Crystal growth rate

Before proceeding to the discussion of the results of the experiment on the determination of the growth rate of lithium disilicate crystals in glasses no. 1–no. 3, let us consider the main notions used when determining the crystal growth. The crystal growth occurs as a result of accidental attachments and detachments of structural units from the surface of a supercritical nucleus (the supercritical nucleus is a nucleus with the size exceeding a critical size). The growth of the super-critical nucleus is thermodynamically favorable because this

is accompanied by a decrease in the free energy of the system $\Delta\Phi$. The linear growth rate of the nucleus is determined by the equation

$$(U = \frac{dr}{dt} = l(\beta_+ - \beta_-), \quad (7)$$

where l is the thickness of the monomolecular layer growing on the crystal for some time interval, equal to the linear size of the structural unit), and β_+ and β_- are the probabilities of attachment and detachment of one structural unit from the crystal surface per unit time:

$$\beta_+ = \frac{1}{\tau_0} \exp\left(-\frac{\Phi_A}{kT}\right), \quad \beta_- = \beta_+ \exp\left[\frac{\left(\frac{\partial \Delta\Phi}{\partial a}\right)}{kT}\right] \quad (8)$$

Here, τ_0 is the time of the order of the period of vibrations of atoms in a chemical bond, whose switching provides the transition of the structural unit to the ordered state of the crystal structure of the nucleus; $\Delta\Phi$ is the change in the free energy of the system; and a is the linear size of the structural unit. Substitution of these expressions into formula (7) gives

$$U = \frac{1}{\tau_0} \exp\left(-\frac{\Phi_A}{kT}\right) \left\{ 1 - \exp\left[-\frac{\Delta\varphi}{kT} \left(1 - \frac{r^*}{r}\right)\right] \right\}, \quad (9)$$

where $\Delta\varphi$ is the difference between the free energies of the glass and nucleus per unit volume of the nucleus and r^* is the radius of the critical nucleus. It follows from this relationship that the growth rate of the critical nucleus is equal to zero. Since the critical nucleus is in an unstable equilibrium state, both the increase and decrease in its size is accompanied by a decrease in the difference $\Delta\varphi$ and is equally probable. With an increase in the size of the supercritical nucleus, the growth rate increases and becomes constant when the nucleus radius is larger than the critical radius ($r \gg r^*$).

Now, we consider the temperature dependence of the stationary growth rate. Under the assumption that $\Delta\varphi \approx q(1 - T/T_{melt})$, where q is the specific heat capacity, we have

$$U(T) \approx \exp\left(-\frac{\Phi_A}{kT}\right) \left\{ 1 - \exp\left[-\frac{q(1 - T/T_{melt})}{kT}\right] \right\} \quad (10)$$

According to expression (10), the growth rate is equal to zero at $T \rightarrow 0$ and $T \rightarrow T_{melt}$. At some temperature ($0 \ll T_{melt}$), the growth rate is maximum. This temperature can be evaluated. We assume that $\exp[-q(1 - T/T_{melt})/kT] \approx 1 - q(1 - T/T_{melt})/kT$ and substitute into expression (10). After the differentiation with respect to the temperature, we obtain

$$\frac{dU}{dT} \approx \frac{1}{T^2} \exp\left(-\frac{\Phi_A}{kT}\right) \left[\frac{H_A}{k} \left(\frac{T_{melt}}{T} - 1 \right) - T_{melt} \right] \quad (11)$$

From the extremum condition

$$\left[\frac{H_A}{k} \left(\frac{T_{melt}}{T} - 1 \right) - T_{melt} \right] \Big|_{T=T_{U_m}} = 0 ,$$

we find that

$$T_{U_m} = \frac{T_{melt}}{1 + kT_{melt} / H_A} \quad (12)$$

The quantity kT_{melt}/H_A in formula (12) usually does not exceed 1/10. Therefore, the temperature of the maximum growth rate is close to the melting temperature, and it is very difficult to experimentally determine this temperature. This inference is very important for experimenters.

6. Experimental results on the crystal growth and their discussion

6.1 Crystal growth rate: Dependence on the temperature

There is a large number of works on the rate of crystal nucleation (see Table 1) in lithium silicate glasses, whereas investigations of the concentration dependences of the growth rate are absent. There exist works in which the results are presented only for specific compositions of glasses in this system [108, 99]. The photographs of characteristic lithium disilicate crystals grown at a development temperature of 600 °C in glasses no. 1–no. 3 are displayed in Fig. 5. In order to determine the growth rate U , the dependences $R_{max}(t)$ were constructed for a series of samples held for different times t at a specified temperature. It was revealed that these dependences exhibit a linear behavior, which allows us to determine the crystal growth rate from their slope. In the case of spherical particles, their growth rate U is determined from the expression $U = dR_{max}/dt'$, where t' is the time of holding of the glass at the development temperature. In the case of ellipsoids of revolution, the growth rate U is determined from the change in their average radius defined as the half sum of the major and minor radii of the ellipsoid. The crystal growth rates were studied at temperatures of 570, 590, 600, 640, 685, 718, 720, and 730 °C. The growth rates $U(T)$ of lithium disilicate crystals in glasses no. 1–no. 4 as a function of the temperature are given in Table 4. Figure 7 shows the temperature dependences of the growth rate U for glasses no. 1–no. 3. The data presented in Fig. 7c allow us to compare the growth rates U determined in our work with those obtained in [109]. As can be seen from Fig. 7c, Burgner et al. [109] performed investigations at higher temperatures. We more thoroughly studied the growth rate at low temperatures. In the temperature range 575–600 °C, the results of both studies are in good agreement. It can be seen from Fig. 7 that the growth rate $U(T)$ increases with an increase in the temperature. In the temperature range 640–718 °C, the growth rate increases linearly. It is difficult to judge the accurate position of the maximum of the growth rate $U(T)$, because the error in the measurement of the size at temperatures above 720 °C can increase in an uncontrollable manner due to the fact that the time of heat treatment of the sample (1–2 min) is comparable to the time of its heating to a specified development temperature and we cannot state with assurance that crystals grew accurately at this temperature. Therefore, although the temperature dependence of the growth rate should have a maximum, we cannot argue that its true position is recorded. It is quite probable that the maximum of the growth rate is located at higher temperatures. The maxima of the nucleation rates are located at lower temperatures than the maxima of the growth rates. Theoretically, they can either be located at a large

distance from each other or overlap. Since the accurate position of the maximum of the growth rate is not known, we can only to make the inference that, for the compositions under investigation, the positions of the temperature maxima of the nucleation and growth rates are spaced along the temperature scale by an uncertain value no less than 260 °C (720–460 °C).

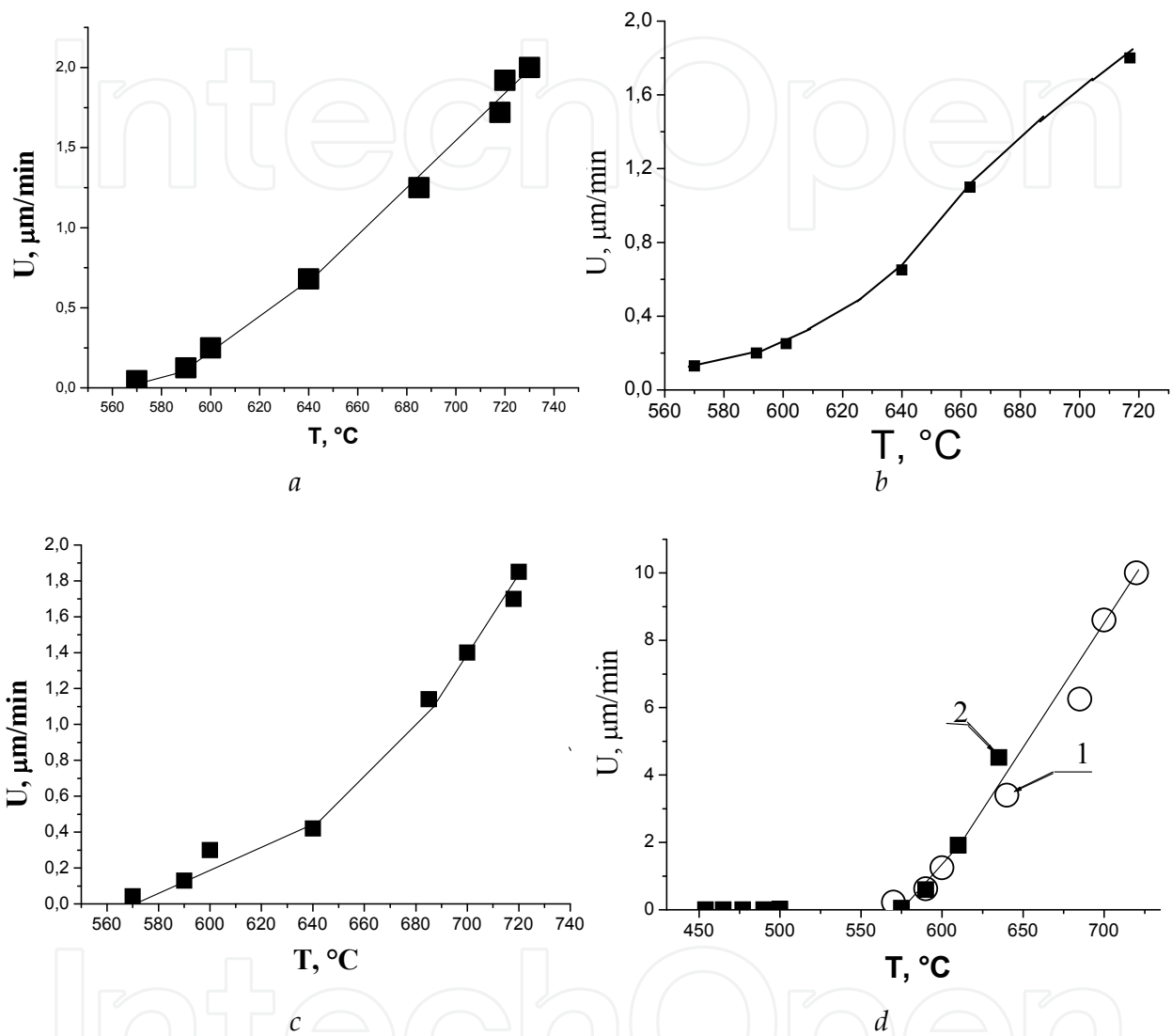


Fig. 7. Temperature dependences of the growth rate U for glasses (a) no. 1, (b) no. 2, (c) no. 3, and (d) no. 4 according to the data (1) obtained in this work and (2) taken from [109].

6.2 Crystal growth rate: Dependence on the time of holding of the glasses at the temperature of 450 °C

The growth rates of lithium disilicate crystals as a function of the holding time glasses at a constant temperature were investigated at the temperature of 450 °C. The results of the measurements are presented in Fig. 8. It can be seen from this figure that the dependence of the growth rate of lithium disilicate crystals in glasses no. 1, no. 2 and no. 3 on the time of low-temperature heat treatment exhibit an oscillatory behavior with a gradual decay of the oscillation amplitude and a retardation of the growth process. In the framework of the existing theories of nucleation and growth, it was demonstrated for metal alloys [110] that the

retardation of the growth process is caused simultaneously by nucleation, growth, and dissolution of particles.

| Glass no. | Growth temperature, °C | | | | | | | | |
|-----------|---|-------|------|------|------|------|------|------|-----|
| | 570 | 590 | 600 | 640 | 685 | 700 | 718 | 720 | 730 |
| | Growth rate $U(T)$, $\mu\text{m}/\text{min}$ | | | | | | | | |
| 1 | 0.045 | 0.125 | 0.25 | 0.68 | 1.25 | - | 1.72 | 1.92 | 2.0 |
| 2 | 0.036 | 0.125 | 0.31 | 0.44 | 1.12 | - | 1.66 | 1.58 | - |
| 3 | 0.042 | 0.130 | 0.40 | 0.42 | 1.14 | 1.40 | 1.70 | 1.85 | - |
| 4 | 0.225 | 0.625 | 1.25 | 3.4 | 6.25 | 8.6 | - | 10.0 | - |

Table 4. Growth rates $U(T)$ ($\mu\text{m}/\text{min}$) of lithium disilicate crystals in glasses no. 1–no. 4 as a function of the temperature

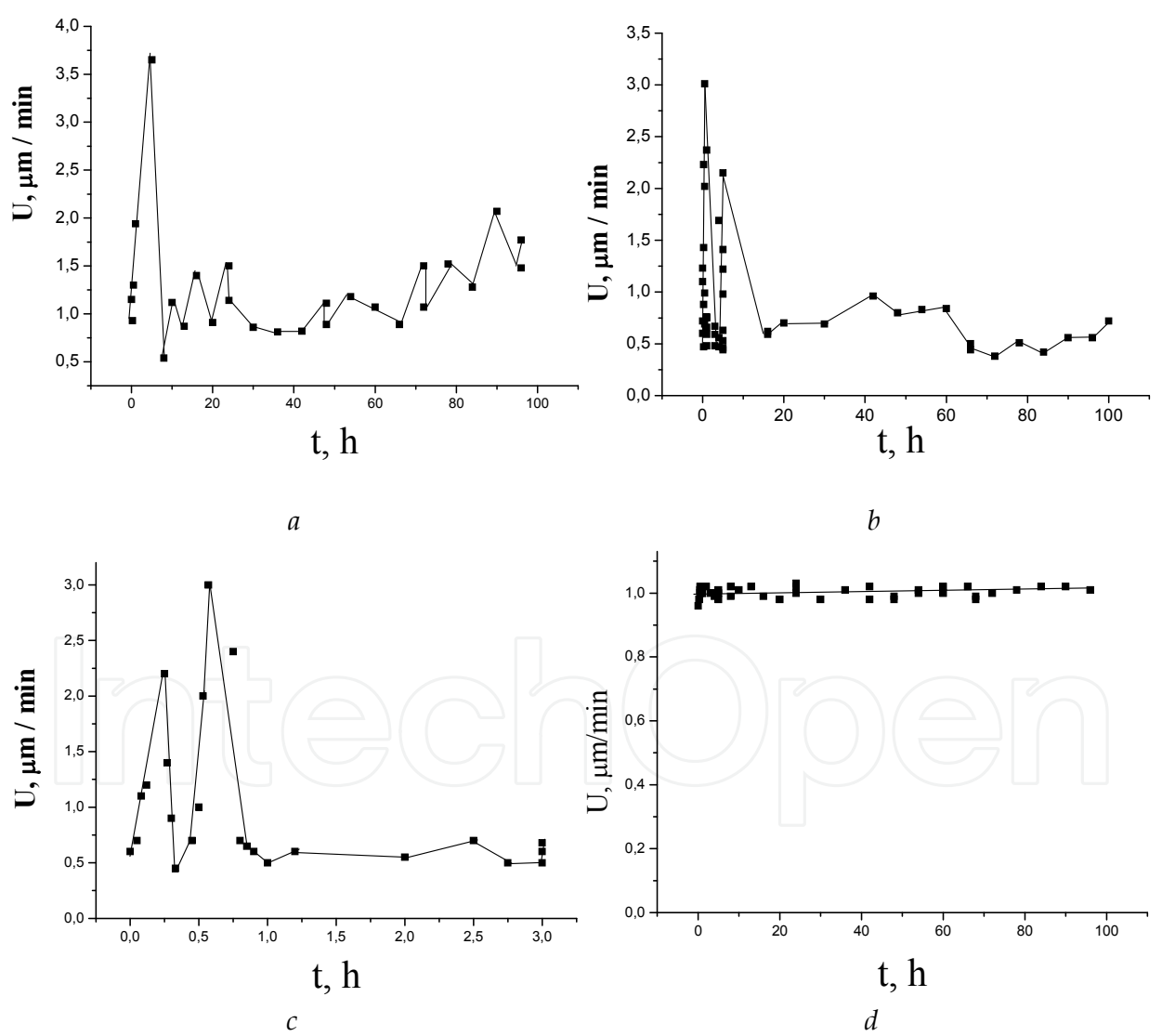
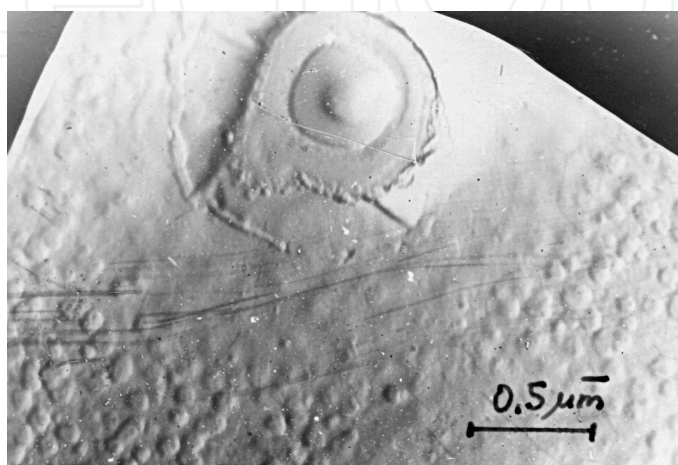


Fig. 8. Dependences of the growth rate U on the time of heat treatment at 450 °C for glasses (a) no. 1, (b) no. 2, (c) no. 3 and (d) no. 4. Samples were developed at the temperature of 600 °C for 10 min.

For glass no. 4 (with the stoichiometric lithium disilicate composition), the crystal growth rate does not depend on the time of low-temperature heat treatment (Fig. 8c).

The gradual decrease in the crystal growth rate with an increase in the time of holding of the glass at a temperature of 450 °C for glasses no. 1, no. 2 and no. 3 (Figs. 8a, 8b, 8c) can be explained by the fact that the crystals grow in the glass with the composition lying in the metastable phase separation region. A part of the material is spent for forming the crystal layer, and the growing crystal appears to be surrounded by the region depleted in the building material (the so-called diffusion zone) (Fig. 9).



a



b

Fig. 9. Electron microscopic images of glasses (a) no. 1 and (b) no. 2 preliminarily heat treated at the temperature of 440 °C for 2 h and developed at 600 °C for 10 min.

The formation of the next crystal layer requires the time it takes for phase separated droplets to come to the crystal growth region. In this case, the phase separated droplets consist predominantly of SiO₂. When the droplets come closer to the growing lithium disilicate crystal, they will block its growth, which manifests itself in the dependences (Figs. 8a, 8b, 8c) as a decrease in the crystal growth rate.

7. Conclusions

Thus, we have investigated the kinetics of phase separation in three lithium silicate glasses containing 23.4, 26.0 and 29.1 mol % Li_2O with the compositions lying in the phase separation region in the Li_2O - SiO_2 system. It has been found that the temperature dependences of the ratio of the number of traces to the maximum number of traces $N_s/N_{s\max}$ and the ratio of the radius of the particle trace to the maximum radius R/R_{\max} exhibit maxima. 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. 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 $I_{st}(T_{\max})$ and T_{\max} is explained by the fact that the glasses with the displaced composition correspond to the phase separation region in the Li_2O - 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.

Variations in the crystal growth rate have been investigated as a function of the temperature and time of heat treatment. It has been shown that the temperature dependences of the crystal growth rate tend to an extremum. It has been found that the crystal growth rate depends substantially on the heat treatment time for phase separated glasses and that the growth rate is constant for the glass with the stoichiometric lithium disilicate composition. The dependence of the crystal growth rate on the heat treatment time in phase separated glasses exhibits a damped oscillatory behavior, which is explained by the depletion of the building material for crystals and the necessity of some time for its supply. Therefore, the performed investigations allow us to draw the following conclusion. Unlike the universally accepted opinion, the phase separation not only does not facilitate the conditions for the formation and growth of crystals but, in some cases (see, for example, the dependences of the crystal growth rate on the time of low-temperature heat treatment), even retards the crystal growth process. The data obtained on the nucleation and growth of crystals help to find optimum compositions and temperature-time conditions for the preparation of many glass-ceramic nanomaterials in lithium silicate system, including photostructured materials.

8. References

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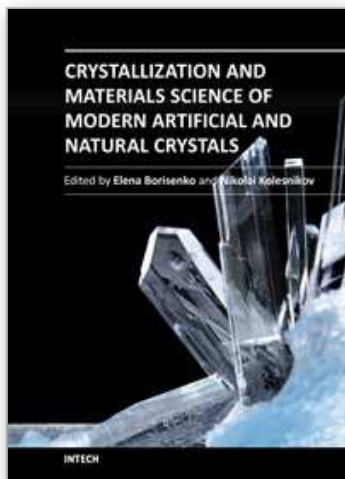
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