

# Sol–Gel Synthesis and Crystal Nucleation of Photosensitive Au/Ag-Containing Glasses of Lithium Silicate System

Galina A. Sycheva\*

*Institute of Silicate Chemistry Named by I.V. Grebenshchikov, Russian Academy of Sciences, Makarova 2, St. Petersburg, 199034 Russia*

**Abstract:** A sol–gel method has been proposed for obtaining the sintering mixture used in the preparing of a photosensitive Au/Ag-containing glasses of the  $\text{Li}_2\text{O} - \text{SiO}_2$  system. It has been established that the use of sol–gel method for the production of the batch for synthesizing photosensitive Au/Ag-containing glasses gives more homogeneous distribution of Au/Ag metals in the bulk of the glass. Crystal-nucleation main characteristics have been defined in a large area of compounds of photo-structured compositions of a lithium–silicate system (23.4–46.0  $\text{Li}_2\text{O}$  mol % by analysis) both for spontaneous and catalyzed nucleations. The spontaneous (homogeneous) nucleation happened in the samples without any photosensitive metals and with photosensitive gold–silver additives (0.05 wt % above 100%) without irradiation; the catalyzed (heterogeneous) nucleation happened in the samples with photosensitive silver ore gold additives under x-ray  $\text{CuK}_\alpha$  irradiation. The ranges of the compositions of the glasses in which the effect of catalyzing irradiation is reversed (suppressing nucleation in accordance with the autocatalytic mechanism) under certain conditions. The spontaneous and catalyzed nucleation of crystals in the glasses of  $\text{Li}_2\text{O} - \text{SiO}_2$  system caused by the addition of photosensitive impurities and X-ray irradiation was analyzed in glasses with a very wide range of compositions in  $\text{Li}_2\text{O} - \text{SiO}_2$  system. Composition ranges with positive (+) and negative (-) differences in the rates of catalyzed and spontaneous steady-state nucleation were established. This finding point is favorable for obtaining photostructured (photosensitive) materials. The concentration limit was determined to be 37.98 mol %  $\text{Li}_2\text{O}$ . About this value, we observe a modification of the mechanism of nucleation of crystals. The behavior of crystal nucleation in photostructured glasses under X-ray irradiation changes to the reverse: autocatalytic nucleation is suppressed rather than induced by x-ray  $\text{CuK}_\alpha$  irradiation. These peculiarities of crystallization mechanism in glasses under study give one the possibility to choose the correct composition range depending on the problems facing researchers.

**Keywords:** Photosensitive glasses, stages of preparation of crystallized photosensitive glass, sol–gel method for producing the batch, parameters of crystal nucleation in photosensitive glass, catalyzed nucleation on photosensitive Ag and Au impurities, effect of X-rays  $\text{CuK}_\alpha$  on crystal nucleation.

## INTRODUCTION

The trend toward miniaturization and complication of technical components in information processing and communication systems for optical schemes and devices [1] calls for microelements less than 1 mm in size. These elements cannot be fabricated conventionally (mechanically). Photosensitive glasses and photo-glass-ceramics on their basis have provided new opportunities in this field [2]. The possibility of obtaining components with different configurations is due to the fact that  $\text{CuK}_\alpha$  irradiation and heat treatment lead to the growth of crystals of the base nonmetallic phase of lithium disilicate ( $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ) or metasilicate ( $\text{Li}_2\text{O} \cdot \text{SiO}_2$ ), which nucleate on photosensitive metal particles. In this case, the crystalline phase is more soluble than the mother glass. Comparison of spontaneous and catalyzed nucleation in photosensitive glasses is also of fundamental scientific interest for the theory of nucleation in condensed systems: it expands the experimental database in the sphere of reciprocal influence of phases [3-7]. Crystal

nucleation in glasses of  $\text{Li}_2\text{O} - \text{SiO}_2$  system is a manifestation of one of the crystallization features of complex glasses and melts (the cooperative character of composite nucleation of crystals of several different phases). In this paper, we report the results of studying the crystal-nucleation rate for a wide range of compositions of lithium–silicate glasses (23.4–46.00 mol %  $\text{Li}_2\text{O}$ ), both pure and doped with gold–silver impurities. The effect of X-ray  $\text{CuK}_\alpha$  irradiation on the nucleation kinetics was analyzed.

## EXPERIMENTAL

### Sample Preparation and Procedure for the Study of the Kinetics of Spontaneous Nucleation in Glasses

#### Synthesis of Glasses

The charge for the glasses with Ag and Au impurities was prepared by the sol-gel method [8, 9]. The batch for conventional melting was prepared from the following reactants: lithium carbonate (chemically pure reagent) and amorphous silica (analytical grade). For a more smooth distribution in the batch, the photosensitive metal admixture of Au was added as the form of an aqueous solution  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ . After that, the dried batch was mixed in a rattler and melted in a

\*Correspondence Address to this author at the Institute of Silicate Chemistry Named by I.V. Grebenshchikov, Russian Academy of Sciences, Makarova 2, St. Petersburg, 199034 Russia; Tel: 8(812)351-08-29; Fax: 8(812)328-22-41; E-mail: sycheva\_galina@mail.ru

platinum crucible placed in a Globar-heater furnace with silicon carbide heaters. The melt temperature was of 1460 °C, time - for 8 h. Glasses from the charge prepared by sol-gel method were synthesized as follows. Ethyl alcohol was added first to as-distilled tetraethoxysilane under vigorous stirring, followed by the drop wise addition of the water acidified with nitric acid. Then, a mixture of the aqueous solutions of lithium nitrate ( $\text{LiNO}_3$ ) and hydric gold chloride ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was added to the resulting solution with rapid vigorous stirring. To obtain the silver containing glasses as a starting reagent  $\text{AgNO}_3$  was used. Mixture prepared in the manner described above, was heated at 30 °C for 30 days. Then the temperature increased to 800 °C at a rate of 1 K/min with isothermal treatment for 4 h in each heating stage at temperatures of 200, 400, 600, 700, 750, and 800 °C. The glass melting was carried out under the following way: 900 °C, 2 h; 1100 °C, 2 h; and 1450 °C for 1 hour. The glass produced into graphite ore steel forms volume  $2 \times 2 \times 5 \text{ mm}^3$ . The gold-containing glasses were slightly ruby color. Glass samples were kept performed in SShOL electric shaft furnaces and in a gradient furnace designed at the laboratory during 693-773K. The temperature was maintained accurate to within  $\pm 1$  °C. The results of the chemical analysis of the synthesized glasses are presented in Table 1.

The crystalline phases were identified by X-ray diffraction analysis with a DRON-2 diffractometer ( $\text{CuK}\alpha$  radiation). X-ray diffraction analysis showed the absence of any crystalline phases in the initial glasses, except for the traces of  $\alpha$ -quartz, which had no effect on the kinetics of catalyzed ore spontaneous crystal nucleation of lithium disilicate (metasilicate). The crystal-nucleation rate was identified by the development method. The method consists: 1) in first keeping the glass under study at low temperatures of  $T=693\text{-}773\text{K}$  for different time spans to bring about crystal nucleation; 2) then the nucleated crystals were allowed to grow at a development temperature for 10 min to size visible in an optical microscope. No nucleation of new crystal was observed at a development temperature  $T_{dev}=873\text{K}$ . The prepared polished micro sections of glass samples were examined in the reflected light with a Neophot-32 microscope. The number of visible traces of crystals,  $N_s$ , was counted on a micro section of area  $S$ . The number of crystals,  $n$ , nucleated per unit volume of the glass was calculated by the formula  $n = N_s / (SD_{av})$ , where  $D_{av} = (D_1 + D_2) / 2$ . ( $D_1$  and  $D_2$  are the minimal and maximal sizes of crystal traces on the section). Here it should be noted that in order to count the crystals, we used only those samples in which the crystals do not fuse with each other. The dependences

**Table 1: Compositions of the Glasses under Study and Steady-State Rates of Spontaneous and Catalyzed Crystal Nucleation in Them**

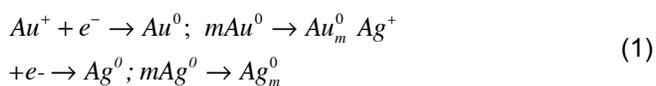
Glass no.	Composition according to synthesis, mol %		Composition according to analysis, wt %		Composition according to synthesis, mol %		$I_{st. hom}(T_{max}), \text{mm}^{-3} \text{min}^{-1}$	$I_{st. het}(T_{max}), \text{mm}^{-3} \text{min}^{-1}$
	$\text{Li}_2\text{O}$	$\text{SiO}_2$	$\text{Li}_2\text{O}$	$\text{SiO}_2$	Au	Ag		
1	23.00	77.00	13.15	86.85	0.03		80	70000
2	23.80	76.20	13.47	86.53	-	0.03	84	68000
3	26.00	74.00	14.87	85.13	0.03	-	90	70000
4	29.00	71.00	16.88	83.12	0.03	-	110	70000
5	33.50	66.50	20.03	79.97	0.03	-	150	70000
6	33.50	66.50	20.03	79.97	-	0.03	150	68000
7	34.72	65.28	20.91	79.09	0.03	-	300	68000
8	36.20	63.80	22.01	77.99	0.03	-	1850	70000
9	37.00	63.00	22.61	77.39	0.03	-	4300	70000
10	37.98	62.02	23.35	76.65	0.03	-	5600	70000
11	39.00	61.00	24.12	75.88	0.03	-	270000	70000
12	41.15	58.85	25.80	74.20	-	0.03	512220	68000
13	44.11	55.89	28.19	71.81	0.03	-	520000	70000
14	46.00	54.00	30.51	69.49	0.03	-	525000	70000

Note: The data for heterogeneous nucleation are given for the depth  $x = 0.5 \text{ mm}$ .

of the number  $n$  of nuclei per glass unit volume on the nucleation time were obtained by development method [2]. The nucleation rate  $I = dn/dt$  was varied from zero to the stationary value  $I_{st}$ . The differential-thermal analysis (DTA) was used to estimate the temperature range of the first stage of heat treatment as the region of the endothermic effect in the DTA curves near the glass-formation effect. The optimum corresponded to the middle of the ascending phase of the crystallization exothermic peak in the DTA curve. The dependences  $n(t)$  first went through a region where an increase in the number of crystals was nonlinear and then, when a certain moment of time was achieved, they became linear. The nonstationary crystal nucleation can be characterized in terms of the induction period,  $t_{ind}$ , determined as the point where the extension of the linear portion of the kinetic curve intersects the time axis. The value of  $t_{ind}$  decreases with an increase in temperature. The steady-state rate of crystal nucleation  $I_{st} = dn/dt$  was determined from the slope of linear portion of the kinetic curve  $n(t)$ . The temperature dependence of the stationary crystal nucleation,  $I_{st}$ , has the form of an symmetric peak with a maximum.

#### METHOD FOR STUDYING THE KINETICS OF CATALYZED NUCLEATION IN PHOTOSENSITIVE GLASSES

The photosensitive glass samples intended for the study of the catalyzed nucleation kinetics was prepared as follows. The technique for studying the kinetics of catalyzed crystallization in photosensitive glasses (with photosensitive impurities) was considered in detail in [2, 7]. The samples had two well polished surfaces, which were perpendicular to one another. One of the faces was irradiated, and another one was used for measuring the number of particles at the depth  $x$  of sample. The irradiation was performed on the X-ray system (operating voltage 30 kV, current 20 mA) for 10 min. The irradiated area was 0.57 cm<sup>2</sup>. The photosensitive glass sample was placed directly in front of the X-ray tube window. It was assumed [1] that the Au or Ag metal crystals, on which the main non-metallic phase (in our case Li<sub>2</sub>O·2SiO<sub>2</sub> or Li<sub>2</sub>O·SiO<sub>2</sub>) nucleates afterwards, are formed according to the scheme



where  $m$  is the number of photosensitive metal atoms in the  $Au_m^0$  and  $Ag_m^0$  conglomerates.

The attenuation of the irradiation intensity  $i$  in the course of passing through the substance is described by the following relationship

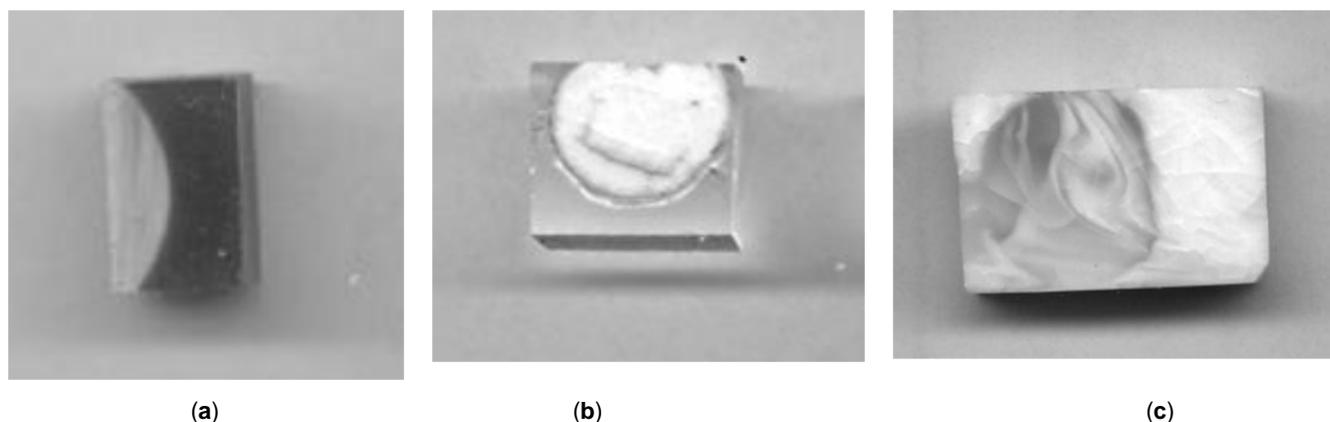
$$i = i_0 \exp\left(-\mu_m / \rho \cdot x\right) \quad (2)$$

where  $\mu_m$  - is the mass attenuation factor,  $\rho$  - is the density of the substance, and  $x$  - is the depth of layer.

During X-ray irradiation, the layers of irradiated samples located at different depths ( $x$ ) absorb different radiation doses. This is reflected in the amount of the formed metallic crystals. The maximum number of crystals is formed in the near-surface layer with a thickness from  $x=0$ –0.1 mm. The number of gold (silver) crystals decreases away from the surface deep into the sample with decreasing radiation intensity  $i$  by an exponential dependence (2). To compare the catalyzed nucleation rates of crystals in glasses of vary different compositions, the numbers of crystals per unit sample volume were counted at the depths  $x$  characterized by the same irradiation dose. These depths were found by calculating the mass X-ray attenuation factors, linear ( $\mu_L$ ) X-ray attenuation factors, and the half-attenuation lengths  $\Delta$  [2, 7-10]. These attenuation factors are similar for the compositions under study; therefore, the half-attenuation lengths  $\Delta$  differ slightly only in the second decimal place. So you could take that for all glasses under consideration, the half-attenuation length is  $\sim 0.1$  mm. The number of crystals in the glasses was calculated at the depth  $x = 0.50$  mm. The sample layer between an irradiated surface and a depth of 0.3 mm is completely crystallized out. In the layer from a depth of 0.6 mm and more, the crystallization process is controlled by a spontaneous mechanism, because  $n(x)$  becomes independent of irradiation dose.

#### RESULTS AND DISCUSSION OF RESULTS

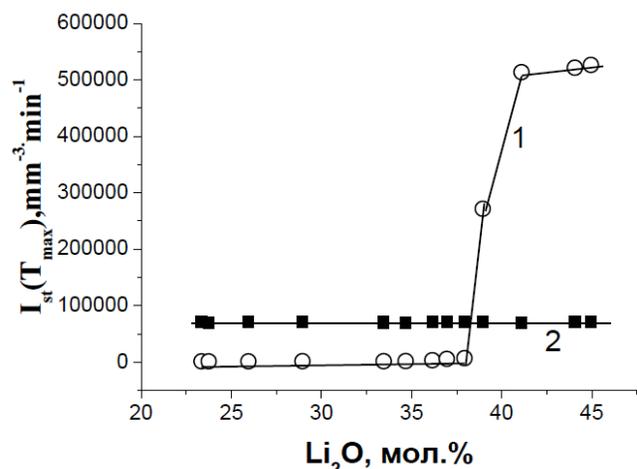
Figure 1 indicates the appearance of irradiated and crystallized glass samples 5, 6, and 12 (see the Table 1). As can be seen, for the stoichiometric lithium disilicate glasses (samples 5 and 6), the irradiated areas were completely crystallized during preliminary heat treatments with subsequent development, whereas the areas without irradiation were remained transparent. Glass sample 12 exhibited the opposite pattern: the area without irradiation was completely crystallized, whereas the unirradiated area remained without crystallization. Effect of the X-rays becomes the reverse: the irradiated areas (the central spot)



**Figure 1:** Appearance of the irradiated and crystallized glass samples: (a) 6 + 0.05 wt % Au, (b) 6 + 0.05 wt % Ag, and (c) 12 + 0.05 wt % Ag. Heat treatment: 450 °C for 24 h (nucleation) + 600 °C for 10 min (development).

remained amorphous after the heat treatment, whereas the area without irradiation was completely crystallized.

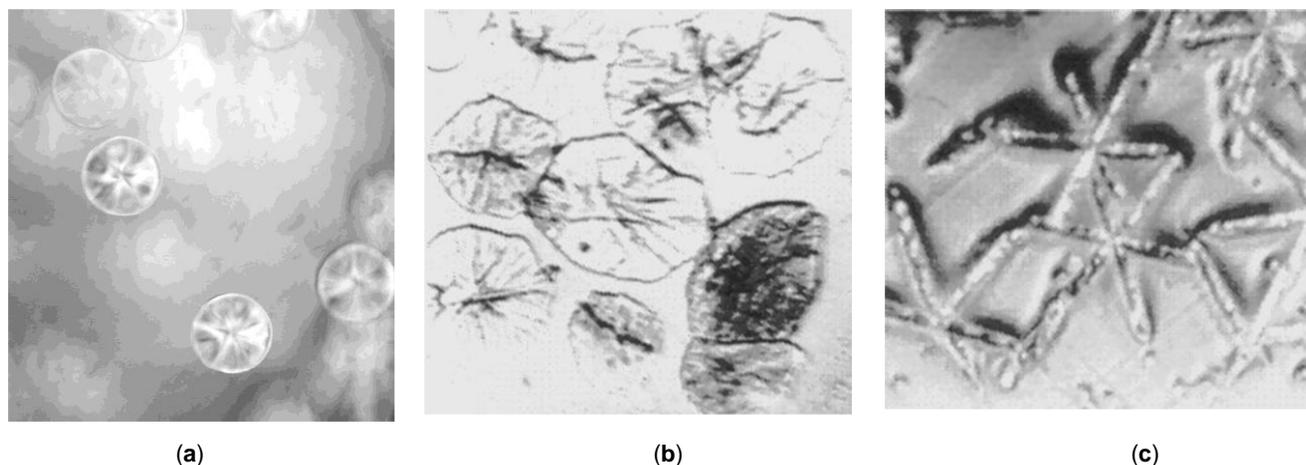
Figure 2 shows the dependence of the steady-state nucleation rate  $I_{st}(T_{max})$  on the  $\text{Li}_2\text{O}$  content.  $T_{max}$  is the temperature corresponding to the maximum nucleation rate of  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  and  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystals in lithium–silicate glasses without impurities (1) and with photosensitive impurities and under irradiation (2).



**Figure 2:** Dependence of the steady-state nucleation rate  $I_{st}(T_{max})$  on the  $\text{Li}_2\text{O}$  content in lithium–silicate glasses (1) without photosensitive-metal impurity and (2) with 0.05 wt % Au impurity and under X-ray irradiation.

First, we consider the behavior of curve 1 in Figure 2. It's obviously that the nucleation rate of crystals in  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  system changes slightly with an increase in the  $\text{Li}_2\text{O}$  content from 23.00 to 36.20 mol % (glasses 1–8) and then sharply increases. As was shown in [4] lithium disilicate spherulites are transformed into two-phase aggregates composed of complex lithium disilicate and lithium metasilicate. The nucleation rate of these complex mixed crystals increases with a

further increase in the  $\text{Li}_2\text{O}$  content (especially at the transition from glass 12 to glass 13). As can be seen from Figure 3, the shape of the crystals also varies with the glass composition. For the formulations 1-4 (Figure 3a) is characteristic spherical shape. For glasses 5-11 (Figure 3b) shape becomes ellipsoidal crystals with different ratio of diameters. In the compositions of 13-14 (Figure 3c) nucleate and grow crystals of lithium metasilicate acicular shape. The sharp increase in the nucleation rate observed in the glass with a  $\text{Li}_2\text{O}$  content 36.20 mol%. This phenomenon was observed previously [3, 6] and has been called autocatalytic nucleation in the system from the outside is not introduced catalytic impurities. This means that catalytic impurities were not introduced into the system from outside but arose in the glass due to the formation of lithium metasilicate. Apparently, the 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 5-11. During heat treatment at the nucleation temperature, the main process occurring in glasses 1–4 is the spontaneous nucleation of lithium disilicate; the nucleation rate changes only slightly with a change in the glass composition. With an increase in lithium oxide content, the simultaneous crystallization of lithium disilicate and lithium metasilicate occurs, and the nucleation of lithium metasilicate and, additionally, catalyzed nucleation of lithium disilicate crystals on metasilicate crystals (autocatalytic nucleation of lithium disilicate crystals on metasilicate) becomes possible. Thus it can be assumed that lithium disilicate crystals nucleate on lithium metasilicate crystals, the acceleration at the



**Figure 3:** Photographs of crystals in glasses (a) 1–4, (b) 5–11, and (c) 13–14 (magnification  $\times 300$ ).

disilicate nucleation being promoted by the closeness of unit cell parameters of lithium disilicate (database Pcpdwin, No. 80-1470, orthorhombic structure, parameters of elementary cells:  $a=5.687$ ,  $b=4.784$ ,  $c=14.64\text{\AA}$ ) and lithium metasilicate (database Pcpdwin, No. 80-1470, orthorhombic structure, parameters of elementary cells:  $a=9.396$ ,  $b=5.396$ ,  $c=4.661\text{\AA}$ ). Finally, crystals of lithium metasilicate are spontaneously nucleated and grow in glasses of compositions 12–14.

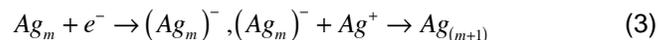
Now let us consider the curve 2 in Figure 2. This is the dependence of the steady-state nucleation rate of crystals formed according to the catalyzed mechanism on specially introduced photosensitive Au and Ag impurities subjected to X-ray irradiation. The latter stimulates the nucleation of crystals of the main nonmetallic phase of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  or  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  on the photosensitive metal particles. In this case the number of crystallization centers depends on the amount of introduced impurity of Au or Ag and dose of X-ray irradiation. The number of crystals was counted in the glass samples at depths characterized by the same irradiation dose for all compositions. The number of introduced impurity was also the same for all glasses, so the steady-state rate of the catalyzed crystal nucleation was independent of the composition to within the measurement error. In this case, the nucleation catalysis is mainly determined by the large number of very small silver or gold particles with the radii  $R$  smaller than the critical radius  $r^*$  of crystalline lithium di- or metasilicate nuclei. According to [3], the catalyzed-nucleation rate is higher than the spontaneous-nucleation rate by the factor

$\frac{N_{\text{cat}}}{N} \exp\left(\frac{4\pi R^3 q}{3kT_{\text{melt}}}\right)$ , where  $N_{\text{cat}}$  is the number of lithium disilicate crystals nucleated according to the catalyzed mechanism (on photosensitive gold impurity),  $N$  is the number of lithium disilicate crystals nucleated

according to the homogeneous mechanism,  $R$  is the radius of lithium disilicate crystal,  $q$  is the melting heat ( $q = 0.24 \text{ kcal/cm}^3$  for lithium disilicate),  $k$  is Boltzmann's constant, and  $T_{\text{melt}}$  is the melting temperature ( $T_{\text{melt}} = 1306 \text{ K}$  for lithium disilicate).

The numerical value of this factor can be estimated. Let us assume that silver or gold is completely segregated from glass in the form of particles containing, for example, 100 atoms; then, at a concentration of silver or gold photosensitive impurity of  $10^{-2} \text{ mol } \%$ , the factor  $N_{\text{cat}}/N$  is about  $10^6$ . Thus, to increase the crystal nucleation rate by a factor of 1000, the catalyzing particles should contain at least 0.001 of all silver or gold impurity atoms that are present in the system. In principle, the same effect can be obtained by introducing a photosensitive impurity smaller in amount by a factor of 1000, provided that the introduced impurity is entirely involved in catalysis.

As can be seen in Figure 2, X-ray irradiation in glasses with a  $\text{Li}_2\text{O}$  content  $>36.20 \text{ mol } \%$  and photosensitive metal impurities suppresses the autocatalytic crystal nucleation on lithium metasilicate. This fact can visually be interpreted as the absence of crystals on the irradiated areas (Figure 1c). The photographic process can be explained in terms of the following mechanism of formation of silver nanoparticles:



This mechanism may also be valid for photosensitive glasses. The occurrence of negative particles  $(\text{Ag}_m)^-$  may affect crystallization in glasses. For example, along with mobile  $\text{Ag}^+$  ions, glass contains alkaline  $\text{Li}^+$  ions, whose mobility (diffusivity) depends on the temperature and composition. Then,

on the assumption that a charged particle ( $\text{Ag}_m^-$ ) is a crystallization center, alkaline ions can be accumulated near this particle to facilitate crystallization. At a high  $\text{Li}_2\text{O}$  content (~38%) negative photosensitive metal particles cause depletion of the basic glass with  $\text{Li}^+$  ions, thus changing the glass composition. This may lead to suppression of autocatalysis.

## CONCLUSIONS

The spontaneous (homogeneous) and catalyzed (heterogeneous) nucleation of crystals in the lithium–silicate glass system caused by the introduction of photosensitive impurities Ag/Au and X-ray irradiation was studied in glasses with a wide range of compositions. Composition ranges with positive and negative differences in the rates of spontaneous and catalyzed steady-state nucleation were established. This finding is favorable for obtaining photosensitive materials. The concentration limit was found to be 37.98 mol %  $\text{Li}_2\text{O}$ . Above this value, the behavior of crystal nucleation in photosensitive glasses under X-ray irradiation changes to the reverse: autocatalytic crystallization is suppressed rather than induced by x rays. These features of crystallization in photosensitive glasses allow one to choose the correct composition range depending on the problem at hand.

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