

# The effect of pre-existing crystals on the crystallization kinetics of a soda–lime–silica glass. The courtyard phenomenon

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## Abstract

New data are presented on bulk crystallization in a glass of composition close to the stoichiometric phase  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ . The effects of pre-existing crystals on the nucleation and growth behavior of secondary crystals are described for the first time. Primary crystals, grown at high temperatures, dramatically *hinder* the formation of new crystals at lower temperatures, in their vicinity (the courtyard effect). The crystal growth velocity decreases with increasing crystal size. Chemical analyses by energy-dispersive X-ray spectroscopy demonstrate that the above-mentioned effects result mainly from compositional changes of the glass matrix, in the neighborhood of the primary crystals. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

All glasses crystallize on their external surfaces when properly heat-treated. On the other hand, glasses of composition close to the stoichiometric phase  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  ( $\text{NC}_2\text{S}_3$ ) are among the few silicate glasses that, in addition to surface nucleation, also exhibit internal nucleation. This is believed to be caused by homogeneous nucleation [1]. Additionally, it is known that the nucleation rate of  $\text{NC}_2\text{S}_3$  crystals in such glasses is very sensitive to their chemical composition [2–4] and that, for a given composition and temperature, the

crystal growth velocity decreases for increasing heat treatment time, i.e. with increasing crystallinity [5].

In this communication, we describe for the first time the effects of pre-existing crystals on the nucleation and crystallization behavior of secondary crystals using a glass of composition close to  $\text{NC}_2\text{S}_3$ . This particular effect has been denominated here as ‘the courtyard effect’.

## 2. Experimental methods

The glass was melted in a platinum crucible for 2 h at 1450°C in an electric furnace. Then the melt was cast on a massive steel plate. Analytical grade carbonates of sodium and calcium, and amorphous silicon dioxide were used for its synthesis.

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The analyzed glass composition (17.0Na<sub>2</sub>O–33.0CaO–49.9SiO<sub>2</sub> mol%) is quite close to the stoichiometric one (16.67Na<sub>2</sub>O–33.33CaO–50.00SiO<sub>2</sub> mol%). The heat-treatments were performed in a vertical electric furnace having an accuracy of 1°C. Optical microscopy and scanning electron microscopy were used to measure the number and size of crystals and the crystallized fraction by an image analysis software. Energy-dispersive X-ray spectroscopy (EDS) was used for semi-quantitative compositional analysis of the crystals and of the glassy matrix.

Two types of heat treatments were used: single-stage heat treatments at 590°C or 720°C, and two-stage treatments, i.e. a previous heating at 720°C followed by a further treatment at 590°C. The second temperature lies in the vicinity of nucleation rate maximum ( $T_{\max} \sim 600^\circ\text{C}$ ) [2–4] and thus, 720°C is much above  $T_{\max}$ . At these temperatures, the high-temperature rhombohedral modification of the NC<sub>2</sub>S<sub>3</sub> phase is formed, but reversibly turns to the low-temperature hexagonal form at 485°C [7]. Indeed, we only detected the latter form with room temperature X-ray analysis of glasses treated at several temperatures. The crystals have a cubic morphology that does not change with the treatment temperature (see, e.g. Fig. 1(a) and (c)). While most silicate glasses that crystallize in the volume display spherulitic morphologies, the crystalline particles in our glass are *single crystals* [2,4,5]. This feature is important for the interpretation of the crystallization behavior of this glass.

### 3. Results

It was shown previously [5] that, despite the fact that the glass composition is quite close to the stoichiometric crystal, the isothermal crystal growth velocity of NC<sub>2</sub>S<sub>3</sub> decreases with heat treatment time. That result was confirmed in this research. Fig. 2 shows the length of the cube edge,  $l$ , of the largest crystals as a function of heat treatment time at 720°C (a) and at 590°C (b). A departure from linearity of the  $l(t)$  plot may be detected even at relatively low crystallinity levels ( $\alpha \sim 4$  vol.%). Thus, Fig. 2 clearly shows that the

growth of the crystals at any temperature slows down with increasing heat treatment time.

The slope of a  $\ln(-\ln(1-\alpha))$  vs.  $\ln(t)$  plot at 720°C is equal to 2.6. In the case of tri-dimensional particles growing with constant growth velocity from a constant number of sites, the slope should be 3.0, e.g. [5]. Hence, this result gives additional evidence for the decrease of the crystal growth velocity with heat treatment time.

Fig. 3 presents the crystal nucleation density vs. nucleation time at  $T = 590^\circ\text{C}$ , obtained by the ‘development’ method (development temperature  $T_d = 690^\circ\text{C}$ ). The steady state nucleation rate can be found from the slope of the linear part of the  $N_v(t)$  curve. The induction period  $t_{\text{ind}}$  is determined as the point of intersection of the linear part extrapolation with the time axis. Fig. 3 demonstrates the nucleation kinetics of the NC<sub>2</sub>S<sub>3</sub> phase in the case when there are no pre-existing crystals.

If the heat treatment at  $T = 590^\circ\text{C}$  is extended up to 26 h, one may observe a large number of crystals in the glass volume without resorting to development (Fig. 1(b)). Thus the crystal nucleation and growth curves for this glass overlap at 590°C. The situation changes when the same heat treatment ( $T = 590^\circ\text{C}$ , 26 h) is preceded by a heating at  $T = 720^\circ\text{C}$ . The crystals grown at  $T = 720^\circ\text{C}$  (pre-existing crystals) *hinder* the nucleation and growth of new crystals at  $T = 590^\circ\text{C}$ , in their vicinity (Fig. 1(c)). This ‘courtyard effect’ is enhanced dramatically when the time of the first heat treatment and thus, the size of the pre-existing crystals increase (Fig. 1(d) and (e)). For instance, if the time of the first heat treatment is 40 min, new crystals are no longer observed, despite the fact that the sample still contains, on an average, about 20% of glass (Fig. 1(f)). Therefore, the pre-existing crystals decrease both the number and size of the secondary crystals.

### 4. Discussion

The following essential features are to be considered for an understanding of the ‘courtyard effect’:

(i) The crystalline particles in the glass volume are *single crystals*. Thus they are not capable of ingesting more than a certain, limited amount of

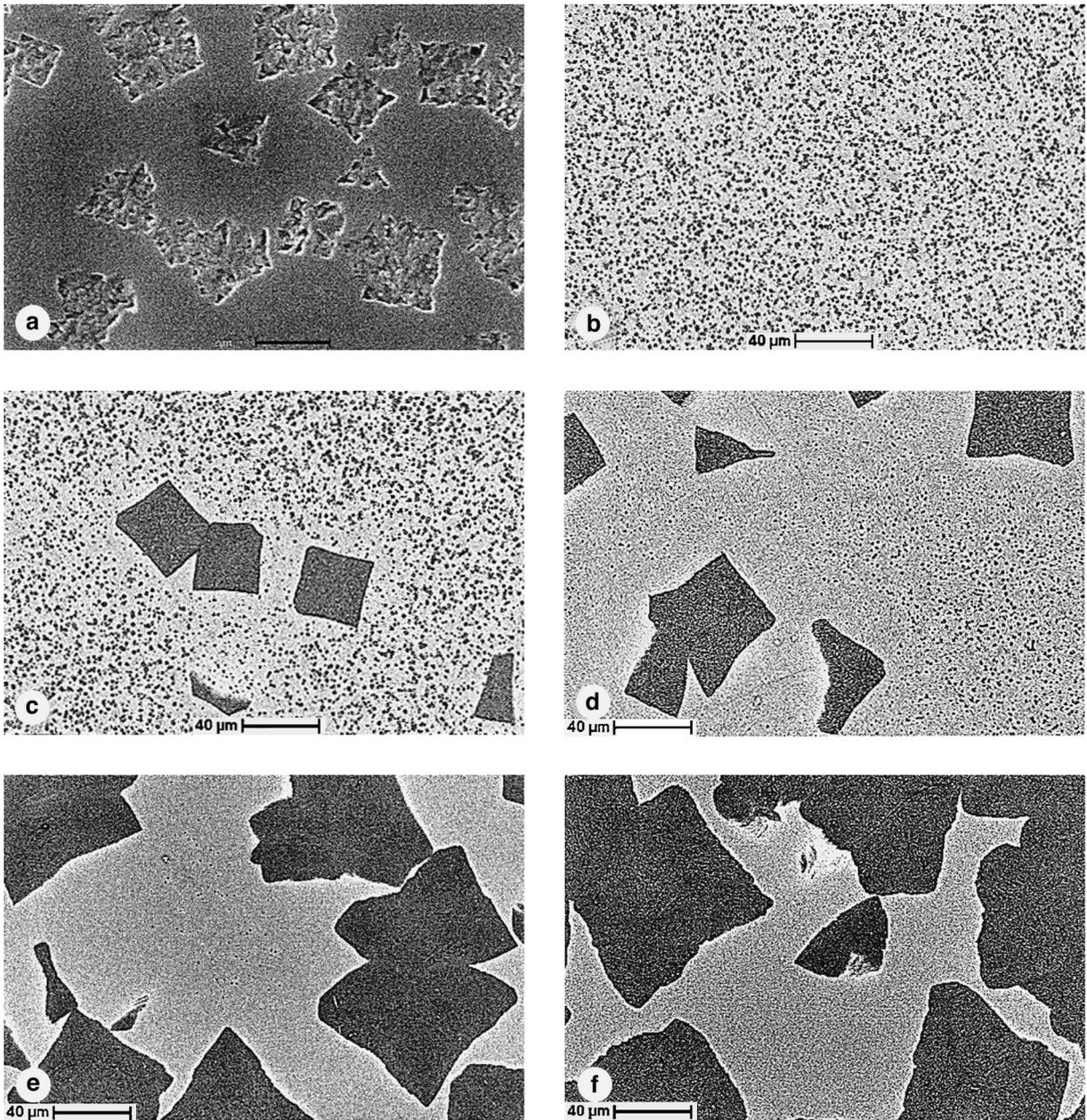


Fig. 1. SEM micrographs of  $\text{NC}_2\text{S}_3$  crystals in glass samples subjected to the following heat treatments: (a, b)  $T = 590^\circ\text{C}$ ,  $t = 26$  h; (c)  $T = 720^\circ\text{C}$ ,  $t = 10$  min +  $T = 590^\circ\text{C}$ ,  $t = 26$  h; (d)  $T = 720^\circ\text{C}$ ,  $t = 20$  min +  $T = 590^\circ\text{C}$ ,  $t = 26$  h; (e)  $T = 720^\circ\text{C}$ ,  $t = 30$  min +  $T = 590^\circ\text{C}$ ,  $t = 26$  h; (f)  $T = 720^\circ\text{C}$ ,  $t = 40$  min +  $T = 590^\circ\text{C}$ ,  $t = 26$  h. The bars denote  $2\ \mu\text{m}$  (a) and  $40\ \mu\text{m}$  (b–f).

Na and Ca in solid solution. The crystallization kinetics of spherulitic and dendritic morphologies are not so sensitive to chemical changes of the glass matrix because these morphologies can engulf

a substantial amount of impurities or excess components among their arms.

(ii) The nucleation rate in this system is very sensitive to the chemical composition of the glass.

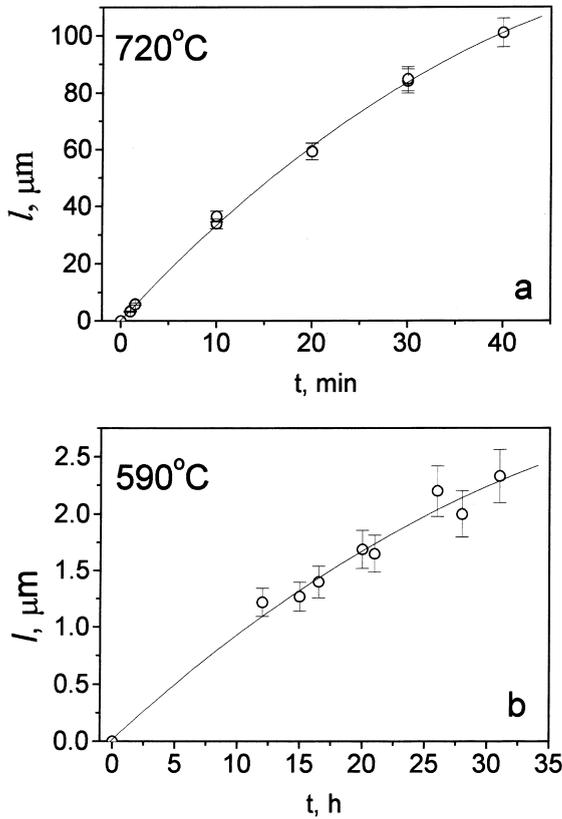


Fig. 2. Length of the cube edges,  $l$ , of the largest crystals as a function of treatment time at 720°C (a) and at 590°C (b). The lines are placed just to guide the eye.

The latter point is illustrated in Fig. 4, where data of different authors are collected. Despite the scatter of the experimental points, it is obvious that the nucleation rate is strongly enhanced when the  $\text{Na}_2\text{O}$  content increases or the  $\text{SiO}_2$  content decreases. The effect of  $\text{SiO}_2$  on the nucleation rate is still a matter of controversy. For instance, this effect was explained by a change in the kinetic barrier for nucleation [2], while in [3] it was attributed mainly to changes in the crystal/liquid interfacial energy.

EDS was used to compare the composition of the glassy matrix with the composition of the crystals, and also to test whether crystallization is accompanied by compositional changes. Fig. 5(a)–(c) show a SEM image and X-ray dot maps (area scan) of a polished surface of the sample heat treated at 720°C for 20 min. The maps give clear

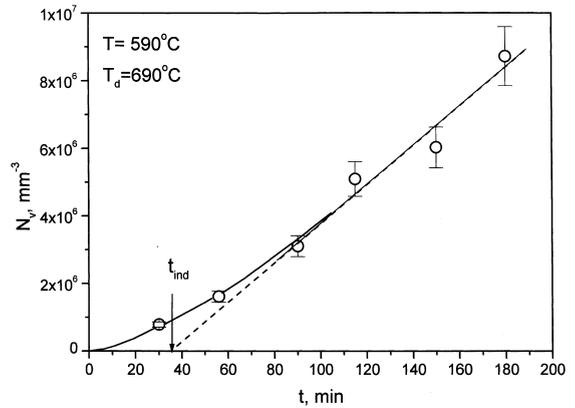


Fig. 3. Number of crystals as a function of nucleation time at 590°C.

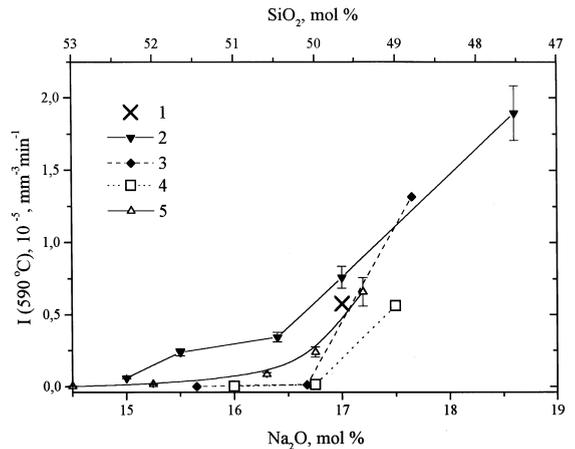


Fig. 4. Crystal nucleation rate at 590°C as a function of  $\text{Na}_2\text{O}$  (1–3) and  $\text{SiO}_2$  (4, 5) content;  $\text{CaO}/\text{SiO}_2 \cong 2/3$  (1–3),  $\text{Na}_2\text{O}/\text{CaO} \cong 1/2$  (4, 5). 1 – this work; 2 – [6]; 3, 4 – [2]; 5 – [3].

evidence for a smaller content of Ca and larger Na content in the crystalline particles than in the glassy matrix. Moreover, it can be noted that the sodium content in the glass increases weakly as one move away from the primary crystals. To eliminate the possibility of sodium leaching during the polishing process, we also studied a fractured surface. The results were similar to those for polished surfaces.

The results of a semi-quantitative EDS analysis of a polished surface are presented in Fig. 6. That figure shows the peak heights of the EDS spectrum corresponding to Na-K<sub>α</sub>, Ca-K<sub>α</sub>, Si-K<sub>α</sub>, and O-K<sub>α</sub> vs. treatment time at 720°C. The open points refer

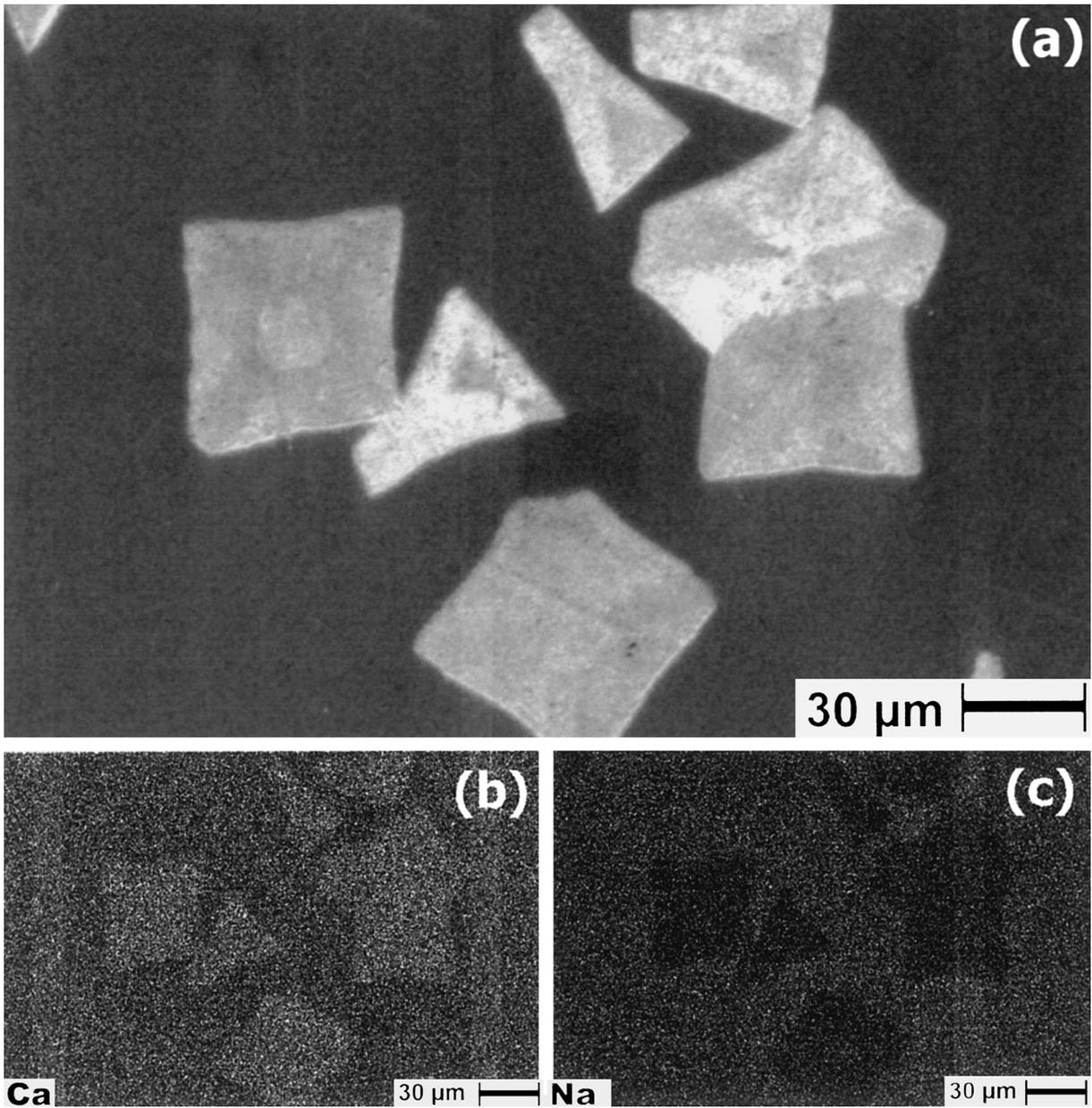


Fig. 5. SEM image (a) and X-ray dot maps of a polished surface of the glass sample heat treated at 720°C for 20 min: (b) Calcium, (c) Sodium.

to measurements of the crystal composition, while solid points refer to the glassy matrix. The zero time data corresponds to the parent glass. The sodium content of the crystals exceeds the content in the glassy matrix, in agreement with the dot

map data, while the glass contains slightly more Ca than the crystalline particles (Fig. 6(a) and (b)). These are only semi-quantitative data, nevertheless we can conclude that the crystals contain more Na than both the glassy matrix and parent glass.

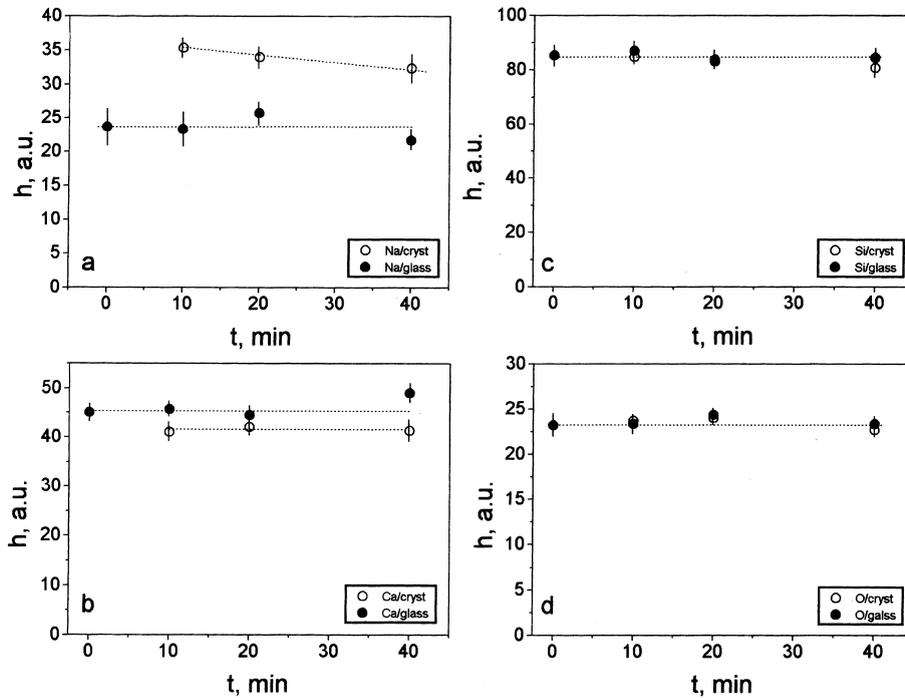


Fig. 6. Peak heights of the EDS spectrum corresponding to Na (a), Ca (b), Si (c), and O (d) vs. treatment time at 720°C.

Hence, one may assume the formation of a solid solution in the crystals, which is commonly observed in silicates.

We should recall that the parent glass composition is close to the stoichiometric composition. Taking into account that the nucleation rate is very sensitive to the glass composition (Fig. 4) we can safely assume a reduction in the sodium content in the vicinity of the pre-existing crystals, resulting in a decrease of the nucleation rate at 590°C. This hypothesis is reinforced by the fact that the crystal growth velocity at 720°C starts to reduce after about 10 min of heat treatment (Fig. 2(a)). At the same time, the pre-existing crystals, grown at 720°C for 10 min, already show a detectable ‘courtyard’ effect at 590°C (Fig. 1(c)).

The proposed chemical effect for the ‘courtyard’ phenomenon deserves further investigation. In particular, the study of this effect in glasses even poorer or richer in Na than the stoichiometric composition is planned. We also plan to study glasses that display spherulitic or dendritic morphologies.

## 5. Conclusions

Primary  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  single crystals, grown at a high temperature in an almost stoichiometric  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  glass, dramatically hinder the nucleation rate of the same crystal phase at lower temperatures, in their vicinity. This phenomenon has been denominated here as ‘the courtyard effect’. A correlation between the courtyard effect and the decrease of the crystal growth velocity with time of isothermal treatment was also given. Experimental evidence demonstrates that the above-mentioned effect results mainly from compositional changes of the glass matrix in the neighborhood of the primary crystals.

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