On the Determination of Nucleation Rates in Glasses by Nonisothermal Methods

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In this short communication, the experimental dependencies of \( T_x \), \( T_g \), and area, \( S \), of the crystallization peak with previously crystallized volume fraction (before a DSC heating run) were investigated for two silicate glasses: \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \) (LS2) and \( \text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2 \) (N1C2S3).

Crystallization is a key phenomenon to understand and control vitrification and to develop glass–ceramics (GC), which are polycrystalline materials produced by controlled internal crystallization of certain glasses. The average crystal number density, \( N_V \), crystal size distribution, \( N_V(R) \), and crystallized volume fraction, \( \alpha_c \), determine, to a great extent, the properties and applications of GCs. To control the above parameters one needs to know the crystal nucleation rate, \( I(T) \), and the growth rate, \( U(T) \).

Optical or electronic microscopy is normally used to accurately determine crystal nucleation rates, but these techniques are time consuming and have limitations. Nevertheless, a wide range of nucleation rates, from 10 to \( 10^{17} \, \text{(m}^3\text{s)}^{-1} \), have been measured in a number of silicate glasses by these techniques. On the other hand, DTA/DSC techniques are very handy because they provide rapid information about characteristic temperatures, such as the glass transition temperature, \( T_g \), the crystallization peak, \( T_x \) (which is connected with the maximum overall crystallization rate), the liquidus, the number of crystalline phases and mechanism of crystallization. In addition, some nonisothermal methods have been developed for the quantitative estimation of crystallization kinetics, which combine preliminary isothermal heat treatments with further heating up to full crystallization of the residual glass. One of these methods serves to estimate the temperature range of maximum nucleation rate, while the other is geared towards the determination of the number of nucleated crystals and nucleation rates. These methods are based on the analysis of the peak position, \( T_x \), or crystallization peak area of a DSC/DTA curve. They are integral methods dealing with overall crystallization. Despite the claimed advantages, for instance in Ray and colleagues, about their potential to estimate crystal nucleation rates, these nonisothermal methods contain serious problems, which are analyzed in great detail in Fokin and colleagues.

Because the relationship between the preliminary heat treatment of vitreous samples and the change in the crystallization peak of the residual glass is a key issue in the above methods, in this short communication we present the experimental dependencies of \( T_x \) and area, \( S \), of the crystallization peak with previously crystallized volume fraction (before a DSC heating run) of \( \text{Li}_2\text{O} \cdot 2\text{SiO}_2 \) (LS2) and \( \text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2 \) (N1C2S3) glasses, which were also used in Ray and colleagues. In the methods reported in Ray and colleagues, a decrease of \( S \) with decreasing mass (and volume fraction, \( 1-\alpha_c \)) of residual glass is reasonably assumed. Also, one usually expects an increase of \( T_x \) with increasing \( 1-\alpha_c \) for the case where the composition of the growing crystals is the same of the parent glass. Therefore, the objective of the present study is to test the validity of these assumptions.

Fig. 1. DSC traces of (a) N1C2S3 partially crystallized samples heat treated at \( T_N = 590 \, ^\circ\text{C} \) for 40 min, and at \( T_G = 670 \, ^\circ\text{C} \) for different times; (b) LS2 partially crystallized at \( T_N = 480 \, ^\circ\text{C} \) for \( t_N = 40 \, \text{min} \), and at \( T_G = 620 \, ^\circ\text{C} \) for different times.
The glass samples were heated in a tubular electrical furnace with a precision of $\pm 1^\circ C$ at two temperatures following the Tammann method. The first treatment (nucleation treatment—$T_N$), was used to form new nuclei and the second (growth treatment—$T_G$) was used to develop such nuclei up to a size large enough to be visible under an optical microscope. For the N$_1$C$_2$S$_3$ glass samples, $T_N$ was 590 $^\circ C$ ($t_N = 40$ min) and $T_G$ was 670 $^\circ C$ (several $t_G$, as one can see in Fig. 1(a)); whereas for the LS$_2$ samples, $T_N$ was 480 $^\circ C$ ($t_N = 20$ min) and $T_G$ was 620 $^\circ C$ (several $t_G$, as shown in Fig. 1(b)). These temperatures are above the maximum nucleation temperatures, thus the nucleation induction times can be neglected. After these heat treatments, the samples were divided into two parts. One part of about 40 mg was introduced in a DSC equipment (NETZSCH—model DSC 404, NETZSCH GERATEBAU, Selb, Germany) and reheated from room temperature at 20 $^\circ C$/min, kept at 300 $^\circ C$ for 5 min, and then at 10 $^\circ C$/min until a crystallization peak was observed. After proper polishing and etching with an HF solution, the other part was analyzed by optical microscopy and standard stereological methods to determine the crystallized volume fraction. Figure 1 shows the DSC heating curves for N$_1$C$_2$S$_3$ and LS$_2$ original glasses and after preliminary double-stage heat treatments for precrystallization. In both glasses, the area of the crystallization peak increases with the increasing volume fraction of residual glass (Fig. 2). However, it should be noted that in the case of N$_1$C$_2$S$_3$, the above dependence smoothly departs from linearity at $(1-\alpha_c)^{0.8}$.

Figure 3 shows that the evolution of $T_x$ in the two glasses is quite different. In the N$_1$C$_2$S$_3$ glass, $T_x$ increases with decreasing residual glass volume fraction, while the LS$_2$ glass shows the opposite behavior.

Fig. 2. $S$ versus residual glass fraction for: (a) N$_1$C$_2$S$_3$ and (b) LS$_2$ glasses. The error bars correspond to 2$\sigma$.

Fig. 3. $T_x$ versus residual glass fraction for: (a) N$_1$C$_2$S$_3$ and (b) LS$_2$ glasses. The error bars correspond to 2$\sigma$.

The behavior of $T_x$ in the N$_1$C$_2$S$_3$ glass is unexpected for crystallization of glasses with a stoichiometric composition. This behavior results from the decrease of sodium in the residual matrix accompanied by an increase in viscosity and $T_g$ (shown in Fig. 4). Because the position of the crystallization peak depends on the rate of overall crystallization, the unexpected increase of $T_x$ with decreasing $(1-\alpha_c)$ for N$_1$C$_2$S$_3$ can be explained by a decrease in the crystal growth rate due to the increased viscosity. The evolution of viscosity and glass transition temperature during the crystallization of highly nonstoichiometric glass is well-known, see for example, Fokin and colleagues. However, a stoichiometric glass composition does not ensure the formation of a crystalline phase with the same composition of the parent glass. And this is the case of the N$_1$C$_2$S$_3$ glass, for instance, in which crystallization starts via the formation of a solid solution (SS) strongly enriched by sodium oxide. Then, during the phase transformation, the composition of the SS continuously approaches on average that of the N$_1$C$_2$S$_3$ crystal. This mismatch between the compositions of the crystalline phase and glass leads to a decreasing content of sodium in the residual glass, and hence to an increase in $T_g$ as $\alpha_c$ increases.

The decrease of $T_x$ with increasing $\alpha_c$ of the starting glass is an expected result that is commonly observed in DSC experiments. This effect is due to the increase of the melt/crystal interface area, $S$, and hence the increased volume of newly formed crystals during the heating run, which is approximately equal to $S_{dh}$, where $dh$ is the thickness of the growing crystalline layer. Figures 1(a) and (b) show that there is a significant shift of the crystallization peak temperature ($T_x$) as the residual glass volume changes. This result is confirmed in Figs. 3(a) and (b). This changing is very pronounced ($\Delta T = -15^\circ C$ for the N$_1$C$_2$S$_3$ and $\Delta T = -60^\circ C$ for LS$_2$) and cannot be due to experimental errors.
If one follows the changing of $T_x$ for a wide range of $(1-\alpha)$, as we did in this work, a shift of $T_x$ should be expected, even for systems where there is no changing of glass composition during crystallization (as for the LS$_2$ glass). In this case, the shift of $T_x$ is related to the larger volume of the sample that was previously crystallized during a longer crystal growth treatment ($t_N$), because the number of nuclei formed after each treatment is fixed because the other heat treatment parameters ($T_N$, $I_N$, and $T_C$) were kept constant. Thus, even in the case of glasses with stoichiometric composition, the formation of phases with compositions unlike those of the parent glass could be expected. However, it should be emphasized that the $T_x$ shift method does not include substantial preliminary crystallization (as we did in the present work), but only preliminary nucleation at low temperatures. Therefore, in the $T_x$ shift method, due to the extremely small volume fraction crystallized after nucleation, the crystallization process cannot change the composition of the melt, regardless of its composition.

The increase of the crystallization peak area, $S$, with increasing volume $(1-\alpha)$ of residual glass, which underpins DTA/DSC methods to estimate nucleation rates, is a fact. However, the evolution of crystal and melt compositions during crystallization (as in the case of N$_1$C$_2$S$_3$ glass) could lead to a continuous change of the thermodynamic driving force for crystallization and to a deviation from linearity of the $S$ versus $(1-\alpha)$ plot.

Moreover other factors may affect the crystallization peak area by reduction of the effective thermodynamic driving force for crystallization: elastic stresses, the contribution of the surface energy to the overall free energy of a polycrystalline sample in the case of nanocrystallization, etc. It should also be emphasized that in the case of the N$_1$C$_2$S$_3$ glass crystallization, the value of $S$ depends on the crystal number density. This result was attributed to the fact that despite being fully crystallized that system did not achieve its most stable state. Thus, in order to apply DTA/DSC methods for a quantitative description of crystallization kinetics, each particular case must be analyzed very carefully!

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**References**


![Fig. 4. $T_x$ versus residual glass fraction for: (a) N$_1$C$_2$S$_3$ and (b) LS$_2$ glasses. The error bars correspond to 2σ.](image-url)