Journal

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: $Li_2O \cdot 2SiO_2$ (LS$_2$) and $Na_2O \cdot 2CaO \cdot 3SiO_2$ (N$_1$C$_2$S$_3$).

C RYSTALLIZATION 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, α_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.[1] Nevertheless, a wide range of nucleation rates, from 10 to 10^{17} $(m^3 \cdot s)^{-1}$, have been measured in a number of silicate glasses[1] 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[2–8] 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.[9,10] 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,[9,10] about their potential to estimate crystal nucleation rates, these nonisothermal methods contain serious problems, which are analyzed in great detail in Fokin and colleagues.[11,12]

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 depen-

dencies of T_x and area, S, of the crystallization peak with previously crystallized volume fraction (before a DSC heating run) of $Li_2O \cdot 2SiO_2$ (LS$_2$) and $Na_2O \cdot 2CaO \cdot 3SiO_2$ (N$_1$C$_2$S$_3$) glasses, which were also used in Ray and colleagues.[9,10] In the methods reported in Ray and colleagues,[9,10] 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.
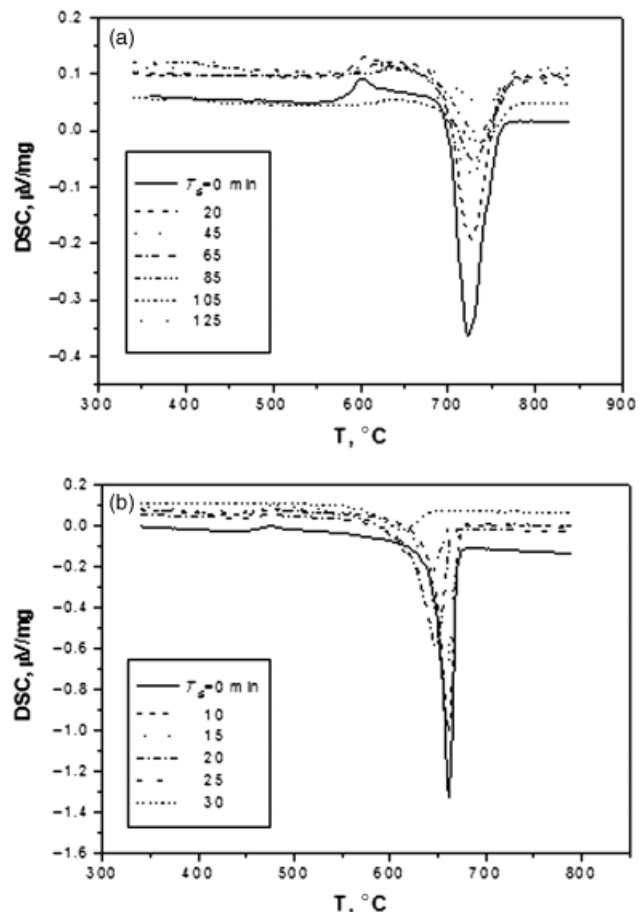

Fig. 1. DSC traces of (a) N$_1$C$_2$S$_3$ partially crystallized samples heat treated at $T_N = 590°C$ for 40 min, and at $T_G = 670°C$ for different times; (b) LS$_2$ partially crystallized at $T_N = 480°C$ for $t_N = 40$ min, and at $T_G = 620°C$ for different times.

The glass samples were heated in a tubular electrical furnace with a precision of $\pm 1°C$ at two temperatures following the Tammann method,[1] 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 $N_1C_2S_3$ glass samples, T_N was 590°C ($t_N = 40$ min) and T_G was 670°C (several t_G, as one can see in Fig. 1(a)); whereas for the LS_2 samples, T_N was 480°C ($t_N = 20$ min) and T_G was 620°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°C/min, kept at 300°C for 5 min, and then at 10°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 $N_1C_2S_3$ 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 $N_1C_2S_3$, the above dependence smoothly departs from linearity at $(1-\alpha_c) \approx 0.8$.

Figure 3 shows that the evolution of T_x in the two glasses is quite different. In the $N_1C_2S_3$ glass, T_x increases with decreasing residual glass volume fraction, while the LS_2 glass shows the opposite behavior.
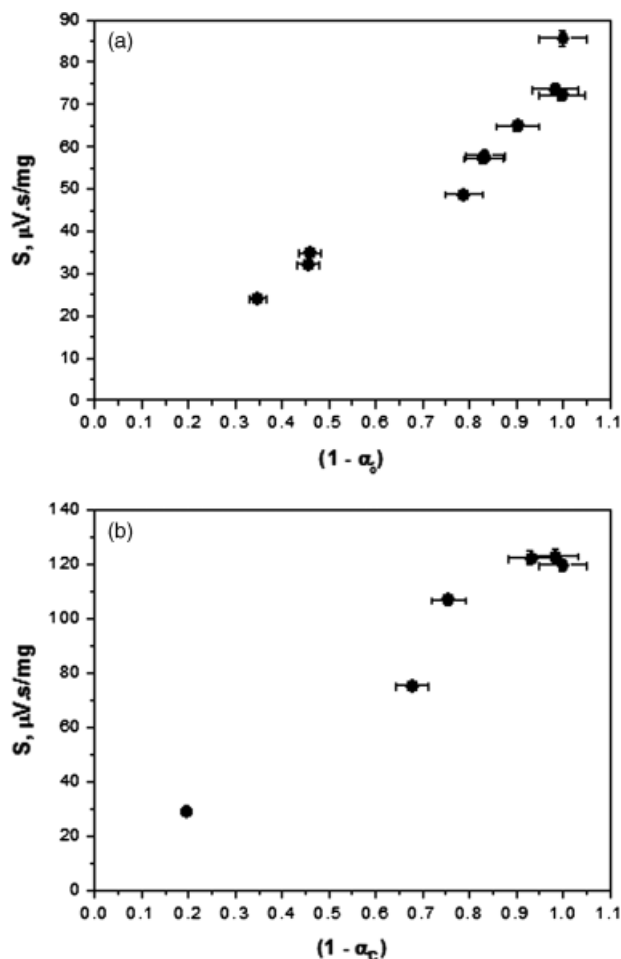

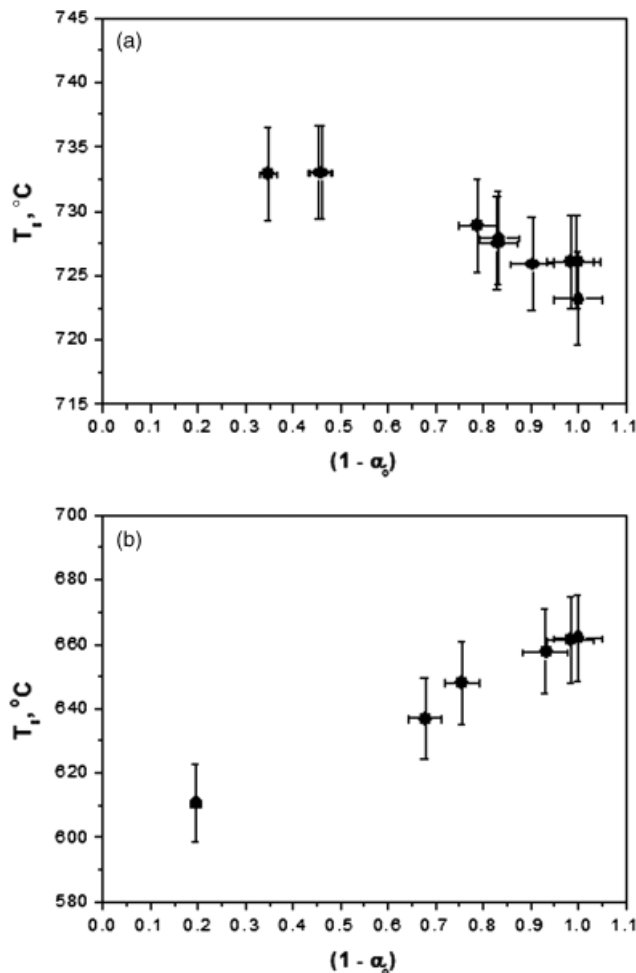**Fig. 2.** S versus residual glass fraction for: (a) $N_1C_2S_3$ and (b) LS_2 glasses. The error bars correspond to 2σ.

Fig. 3. T_x versus residual glass fraction for: (a) $N_1C_2S_3$ and (b) LS_2 glasses. The error bars correspond to 2σ.

The behavior of T_x in the $N_1C_2S_3$ 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 $N_1C_2S_3$ 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.[13,14] 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 $N_1C_2S_3$ glass, for instance, in which crystallization starts via the formation of a solid solution (SS) strongly enriched by sodium oxide.[15,16] Then, during the phase transformation, the composition of the SS continuously approaches on average that of the $N_1C_2S_3$ 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 α_c increases.

The decrease of T_x with increasing α_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 Sdh, 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 ($\Delta T = 15°C$ for the $N_1C_2S_3$ and $\Delta T = -60°C$ for LS_2) and cannot be due to experimental errors.
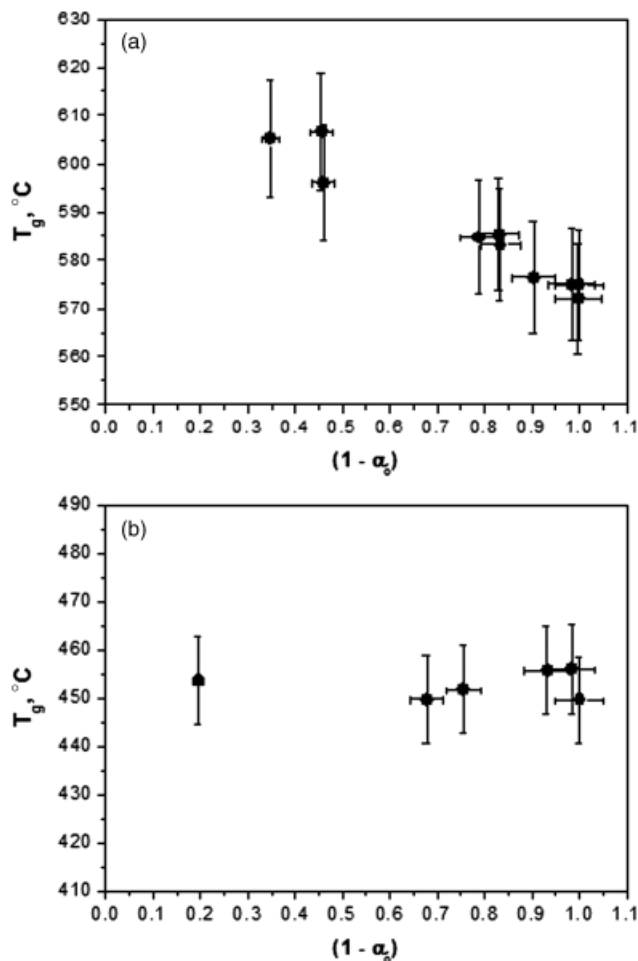
Fig. 4. T_g versus residual glass fraction for: (a) $N_1C_2S_3$ and (b) LS_2 glasses. The error bars correspond to 2σ.

change of the thermodynamic driving force for crystallization and to a deviation from linearity of the S versus $(1-\alpha_c)$ 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 $N_1C_2S_3$ glass crystallization, the value of S depends on the crystal number density.[11] 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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If one follows the changing of T_x for a wide range of $(1-\alpha_c)$, 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_G), because the number of nuclei formed after each treatment is fixed because the other heat treatment parameters $(T_N, t_N,$ and $T_G)$ 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[3–5] 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 $(1-\alpha_c)$ of residual glass, which underpins DTA/DSC methods to estimate nucleation rates,[9–10] is a fact. However, the evolution of crystal and melt compositions during crystallization (as in the case of $N_1C_2S_3$ glass) could lead to a continuous