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On the Determination of the Concentration of Crystal Nuclei in Glasses by DSC

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An interesting technique was proposed by Ray *et al.* over a decade ago to determine the number density of nucleation sites, N_q, or the nucleation rate, $I(T)$, in glasses that exhibit internal nucleation. Their approach is based on the measurement of the areas under the differential scanning calorimetry (DSC) crystallization peaks of partially crystallized glass samples. In this study, we review their method and test a modified equation recently proposed by some of us, which also takes into account the crystal morphology and impingement. We compare N_q obtained with both methods for a $Li_2O \cdot 2SiO_2$ glass. Small glass monoliths were treated at 620°C for different time periods for crystal growth, without any nucleation treatment, and subsequently analyzed by DSC up to 800°C. We thus estimated N_q from the area under the DSC crystallization peaks. The corrected approach resulted in N_q values which were not affected by the pair of growth times chosen, as expected, but the obtained values were two- to fivefold lower than those calculated with the Ray model. Taking into account previously reported nucleation rates and the corresponding induction periods as a function of temperature (for specimens of the same glass batch), we estimated the number of nuclei formed during the DSC heating/cooling steps, and also measured them by optical microscopy (OM). Finally, we compared the obtained values from OM with the N_q values determined by the DSC method. The N_q resulting from the original and new equations were approximately two orders of magnitude larger than those experimentally determined for the same glass using optical microscopy. This difference is attributed to the formation of new nuclei during the heating and cooling paths of the DSC runs and to surface crystallization, which are not taken into account in the DSC expressions.

I. Introduction

THE knowledge of any parameter that influences glass crystallization kinetics is of great scientific and practical interest. For example, the temperature-dependent crystal nucleation and growth rates, $I(T)$ and $u(T)$, respectively, and the number density of "athermal" crystallization sites per unit volume, N_q, are parameters under constant study. However, the direct procedures to determine $I(T)$, $u(T)$, and N_q require measuring the number and size of crystals embedded within a known volume of glass after a given heat treatment by microscopy, which requires a large set of samples and laborious and time-consuming experiments.

Over a decade ago, Ray *et al.*[1] proposed a practical method to determine the $I(T)$ or N_q of glasses that exhibit internal nucleation using a differential scanning calorimetry (DSC) or differential thermal analysis (DTA) technique that is, in principle, much simpler and faster than the traditional microscopy method. In their method, the glass samples are first heated to a nucleation temperature, T_N, and maintained at that temperature for a certain period of time, t_N. In the next step, to foster crystal growth, the samples are further heated to a temperature T_G for different periods of time, t_G. In the sequence, regular DTA or DSC runs are carried out to detect a crystallization peak that should be affected by the previous nucleation and growth treatments. It is assumed that the heating rate is fast enough to avoid the precipitation of new nuclei on the heating path.

In this study, we review the derivation of Ray *et al.*[1] and an alternative equation recently published by Fokin *et al.*, including some of us.[2] We test the assumption that the DSC heating rate is fast enough to avoid the precipitation of new nuclei during the DSC run and then compare the results for N_q from the two DSC methods with values directly obtained using optical microscopy.

In the next section, we detail the careful treatments that one must follow to correctly evaluate crystallization kinetics by DSC, taking into account the crystal morphology, nucleation, and growth rates and the nucleation induction time.

II. Theory

In the late 1930s, Johnson–Mehl–Avrami–Kolmogorov–Yerofeeyev[3–8] independently developed a classical model (JMAKY model) that can be used to describe the time dependence of the fraction of a new phase formed after an isothermal transformation process controlled by nucleation and growth. In the case of a volumetric transformation, the JMAKY model has the following form:

$$\alpha(t) = \frac{V_c(t)}{V_o} = 1 - \exp[-\alpha'(t)] \tag{1}$$

where V_o is the volume of the sample before transformation, $V_c(t)$ is the volume transformed, and $\alpha'(t)$ is the transformed fraction without taking into account the overlapping of the growing particles, often denominated the "extended volume", which can be calculated by knowing the crystal morphology and crystallization parameters.

In the present case, we are interested in glass crystallization. For the special case of spherical crystals simultaneously nucleating and growing in the interior of a glass sample that

is isothermally treated at a temperature T, the $I(T)$ and $u(T)$ curves overlap to some extent, and the "extended volume" is given by

$$\alpha'(t) = \frac{4\pi}{3}\int_0^t I(T)\left[\int_{t'}^t u(T)\mathrm{d}t'\right]^3 \mathrm{d}t \tag{2}$$

where t' is the time for the nucleation of each new nucleus and t is the total treatment time (nucleation and growth).[9] Assuming that the nucleation and growth rates are time independent at a given temperature, Eq. (2) becomes

$$\alpha'(t) = \frac{\pi}{3}Iu^3t^4 \tag{3}$$

For double-stage heat treatments, i.e., an isothermal treatment for nucleation at a temperature T_N followed by an isothermal treatment for growth at a higher temperature T_G, such that no significant nucleation occurs during the growth step and no significant growth takes place in the nucleation step, one can write Eq. (2) as follows:

$$\alpha'(t) = \frac{4\pi}{3}\int_0^{t_n} I(T)\mathrm{d}t\left[\int_0^{t_G} u(T)\mathrm{d}t'\right]^3 \tag{4}$$

Assuming time-independent rates, after integration, Eq. (4) becomes

$$\alpha'(t) = \frac{4\pi}{3}(I.t_n)(u.t_G)^3 \tag{5}$$

In the common case, in which the glass contains some initial concentration of preexisting[†] nuclei per unit volume (N_q) before the isothermal treatment at the temperature of interest T, Eq. (5) must be modified to give

$$\alpha'(t) = \frac{4\pi}{3}(I.t_n + N_q)(u.t_G)^3 \tag{6}$$

Ray et al.[1] proposed that in a DTA/DSC scan of a stoichiometric glass that has been previously treated for partial crystallization, the glassy phase remaining in the sample crystallizes, and the area A under the crystallization peak detected by DTA/DSC is linearly proportional to the volume, V_g, of such residuals of glass as follows

$$A(t) = k.V_g(t) = k.(V_o - V_c(t)) = k.V_o.(1 - \alpha(t)) \tag{7}$$

where k is a proportionality constant that depends on the instrumental conditions.

Ray et al.[1] further assumed $\alpha(t) = \alpha'(t)$ throughout the crystallization process, from 0% to 100% crystallized volume fraction, and obtained the following expression

$$\alpha(t) = \alpha'(t) = -\frac{\pi}{3}(I.t_n + N_q)(u.t_G)^3 \tag{8}$$

We will show later in this study that this second assumption may lead to significant errors in some cases because Eq. (8) is strictly valid for small crystallized volume fractions

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[†]In this study, we refer to N_q as the sum of quenched-in nuclei existing in the original glass, from the melting and forming procedure, plus the nuclei that arise during all the process of heating and cooling in the DSC. In contrast, in their publication, Ray et al.[1] defined N_q only as the nuclei formed on the cooling path in the glass after melting.

(approximately for $\alpha(t) < 0.10$), i.e., before the crystals impinge. In addition, this equation cannot be applied to the present experiments because significant nucleation is not expected during the growth step. As crystallization occurs via crystal growth from a fixed number of nuclei, the extended volume should be described by Eq. (6) instead of Eq. (8).

By executing regular (nonisothermal) DTA/DSC runs of two samples of different masses, m_1 and m_2, previously treated for different times, t_{G1} and t_{G2}, at T_G for crystal growth with all other experimental conditions remaining the same, one obtains crystallization peaks with different areas of A_1 and A_2, respectively. These areas should be related to the amount of residual glass in each sample. From Eqs. (7) and (8), using $V_o = m_o/\rho_g$, where ρ_g is the glass density and m_o is the initial mass (which does not differ from the mass after transformation), Ray et al.[1] concluded that

$$I.t_n + N_q = \frac{3(A_1m_2 - A_2m_1)}{\pi u^3(A_1m_2t_{G2}^3 - A_2m_1t_{G1}^3)} \tag{9}$$

One can thus obtain N_q for each glass using Eq. (9), if the samples are not submitted to any nucleation heat treatment ($I.t_N = 0$). N_q corresponds to the number of homogeneous nuclei formed while cooling the melt, in addition to the heterogeneous nuclei associated with impurities, defects, surfaces and interfaces. This quantity must be constant for samples obtained from a single batch, for which the melting, forming, and sample preparation procedures were the same. Nevertheless, to yield the correct values of N_q, the values calculated from Eq. (9) must be divided by four because crystallization occurs via growth from a fixed number of nuclei, as expressed by Eq. (6).

However, neglecting effects due to the limited thermal conductivity of the glass samples, the area under a DSC crystallization peak should be proportional to the mass of the residual glass in the sample, m_g, and not to its volume, as stated before. Therefore, one may write

$$A(t) = k.m_g(t) = k.(m_o - m_c(t)) \tag{10}$$

where m_o is the sample mass before transformation and $m_c(t)$ is the mass transformed by crystallization.

Following a similar approach to that proposed by Ray et al.,[1] we replaced $m_c(t)$ in Eq. (10) by a function of the transformed mass fraction, $\alpha_m(t)$, and the initial mass

$$A(t) = k.(m_o - m_o.\alpha_m(t)) = k.m_o.(1 - \alpha_m(t)) \tag{11}$$

by definition

$$\alpha_m(t) = \frac{m_c(t)}{m_o} = \frac{V_{cristal}(t).\rho_c}{V_o.\rho_g} \tag{12}$$

A relationship between the volume of the crystal phase present in the sample, $V_{cristal}(t)$, and the volume of the glass transformed, $V_c(t)$, is given by a mass balance, where $m_{cristal}(t)$ is the mass of the crystal phase present in the sample.

$$m_c(t) = m_{cristal}(t)$$
$$V_c(t).\rho_g = V_{cristal}(t).\rho_c \tag{13}$$
$$V_{cristal}(t) = \frac{V_c(t).\rho_g}{\rho_c}$$

substituting Eq. (13) into Eq. (12), one has:

$$\alpha_m(t) = \alpha(t) \tag{14}$$

substituting Eq. (14) into (11), it follows that:

$$A(t) = k.m_0.(1 - \alpha(t)) \tag{15}$$

Eq. (15) is a slightly modified version of Eq. (7). However, when one follows the approach of Ray et al. to make the quotient between the expressions for two different areas (A_1 and A_2), both V_o and m_o are canceled.

Regarding Eq. (8), one should recall that $\alpha(t) = \alpha'(t)$ is only valid for small crystallized fractions, i.e., before crystal impingement. This occurs approximately when $\alpha(t_G) \approx 0.1$ after the previous treatment for partial crystallization (i.e., before the final DSC run). Thus, one should use the more general Eq. (1) to correctly express the crystallized volume fraction, combined with the extended volume given by Eq. (6). By following the same experimental procedure suggested by Ray et al.[1] and using Eqs. (1), (6) and (15), Fokin et al.[2] derived the following equation as a substitution for Ray's Eq. (9):

$$I.t_n\, N_q = \frac{3}{4\pi}\left(\frac{1}{u^3(t_{G2}^3 - t_{G1}^3)}\right) \ln\left(\frac{A_1 m_2}{A_2 m_1}\right) \tag{16}$$

One can now calculate N_q from Eqs. (9) and (16). In this study, we compare the results of these two equations, i.e., the values experimentally measured by optical microscopy in Ref. [2] and the values measured and calculated in this work, as we will discuss later.

III. Experimental Procedure

To compare the values of N_q obtained from Eqs. (9) and (16), seven cuboid samples (2 mm × 2 mm × 3 mm) of a practically stoichiometric lithium disilicate (LS$_2$) glass (~33.2 mol% of Li$_2$O) were heat treated in the furnace of a NETZSCH STA 449C thermal analyzer (NETZSCH-Geratebau GmbH, Selb, Germany). Table I shows the mass of the DSC samples. The heat treatments included the following steps: (1) from room temperature to 620°C at 20°C/min; (2) an isothermal dwell at 620°C for a variable period of time t_G (growth treatment); (3) cooling to 380°C at 20°C/min, sustained for 5 min; (4) heating at 15°C/min to 800°C (above the crystallization peak, which is approximately $T_p = 685$°C); and (5) repetition of all the previous steps for different samples, varying the time of crystal growth (t_G): 10, 15, 20, 30, 35, and 40 min. One totally glassy sample, without a previous heat treatment for crystal growth, was also submitted to a DSC analysis. For this last sample, $t_G = 0$.

To make use of Eqs. (9) and (16), one must know the crystal growth rate u at T_G. To determine u, we measured the crystal size as a function of time in samples that were first nucleated at 480°C for 40 min and then heat treated at 620°C for 5, 10, 15, and 20 min for crystal growth to reach a visible size in an optical microscope. The glass specimens were treated in a tubular electrical furnace and the temperatures

were measured with a calibrated thermocouple located just above the sample; the temperature records showed a fluctuation of ±1°C around the desired temperatures. After heat treatment, the samples were ground with silicon carbide sandpaper and polished with an aqueous solution of cerium oxide dispersed on a cloth; this procedure was performed on both sides of the sample. The microstructure analysis was performed with a Leica DM 2500M (Wetzlar, Geramny) optical microscope under transmitted light. The number of crystals was counted with a magnification of 2.5X, allowing visualization of the entire sample. Several images were captured by a CCD camera focusing from the bottom to the upper surface for the visualization of all the crystals within the sample volume. The images were analyzed with the free software ImageJ,[‡] using a special feature that overlays the images and marks the crystals.

IV. Results

Figure 1(a) and (b) shows the DSC trace from the heating of LS$_2$ samples previously crystallized at different times t_G. One must observe that Ray et al.[1] previously treated samples for crystal growth at 600°C, whereas in the present work the samples were treated at 620°C. Nevertheless, the same heating/cooling rates and crystal growth times employed in Ref. [1] were used here. It must be emphasized that the samples were not submitted to any nucleation heat treatment (i.e., $I.t_N = 0$). Table I shows the areas under the crystallization peaks obtained from the DSC traces.

A micrograph with typical LS$_2$ prolate ellipsoidal crystals is shown in Fig. 2. The values of the crystal growth rates for the ellipse major and minor axes, u_M and u_m, respectively, were equal to 2.6 and 1.6 µm/min, as observed in Ref. [2]. The value of u_M is close to those obtained by Deubener et al.[10] (3.4 µm/min) and Gonzalez-Oliver et al.[11] (2.4 µm/min) at 619°C.

To take into account the ellipsoidal shape of LS$_2$ crystals, Eq. (6) must be further corrected to consider such morphology. Following Zanotto and Leite,[12] one obtains the following:

$$\alpha'(t) = -\frac{4\pi}{3}(I.t + N_q)u_M u_m^2 t^3 \tag{17}$$

Therefore, Eqs. (9) and (16) must be rewritten as follows, respectively:

$$I.t_n + N_q = \frac{3(A_1 m_2 - A_2 m_1)}{\pi u_M u_m^2(A_1 m_2 t_{G2}^3 - A_2 m_1 t_{G1}^3)} \tag{18}$$

$$I.t_n + N_q = \frac{3}{4\pi}\left(\frac{1}{u_M u_m^2(t_{G2}^3 - t_{G1}^3)}\right)\ln\left(\frac{A_1 m_2}{A_2 m_1}\right) \tag{19}$$

thus, using our crystal growth data for the ellipsoidal crystals, the results obtained from both equations can be compared.

Figure 3 shows the resulting N_q plotted for the different pairs of t_G. The values of N_q estimated by the approach of Ray et al.[1] presented a systematic variation depending on the chosen pair of growth times. However, the values of N_q estimated by our approach are approximately constant, as one should expect. The average value and the value of the 95% confidence interval of N_q, assuming Student's t-distribution, obtained from Eq. (18) is $(240 \pm 40) \times 10^{10}$ m^{-3}, while our approach using Eq. (19) gives $(93 \pm 8) \times 10^{10}$ m^{-3}, as observed in Table II.

Table I. Values of t_G at 620°C, Mass, and Area Under the Crystallization Peaks of the Corresponding DSC Paths

Sample	t_G (min)	m (mg)	A (a.u.)
0	0	41.9	215.5
1	10	41.4	211.5
2	15	41.5	192.4
3	20	40.4	173.7
4	30	42.5	102.9
5	35	40.2	77.0
6	40	37.3	41.7

a.u., arbitrary units.

Fig. 2. Typical micrograph of a partially crystallized LS_2 sample showing prolate ellipsoid crystals after a heat treatment at 480°C for 40 min (nucleation step) and at 620°C for 15 min (crystal growth stage).
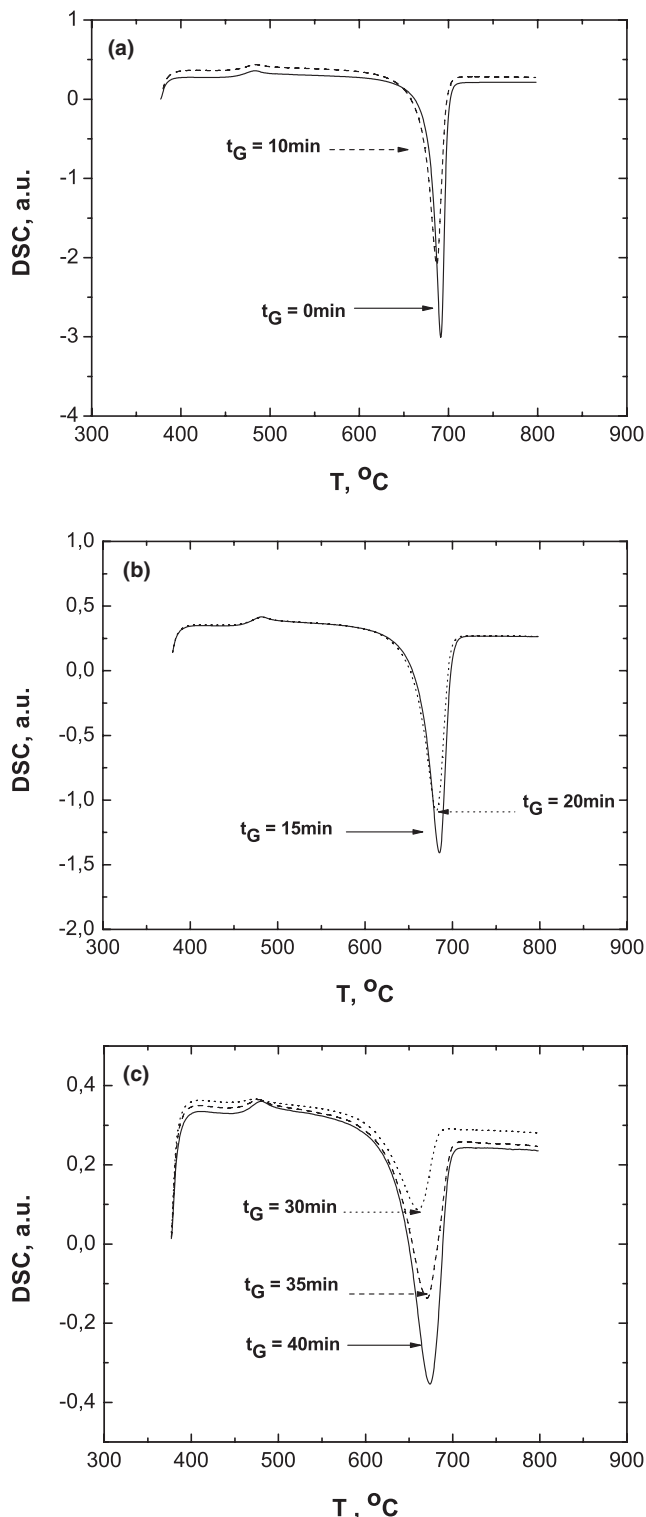

Fig. 1. DSC runs of samples previously heat treated at different periods of time for crystal growth: (a) $t_G = 0$–10 min; (b) $t_G = 15$–20 min; (c) $t_G = 30$–40 min.

V. Discussion

It is well-known that the nucleation rates and the number of preexisting nuclei in glasses that present homogeneous nucleation increase as the water content dissolved in the glass (which depends on the procedure of glass synthesis) increases.[13] To avoid this problem, in the present work, all the experiments, including the N_q determined by DSC by the approach of Ray *et al.*, were carried out with samples from a single LS_2 glass, obtained from one single batch, thus, the
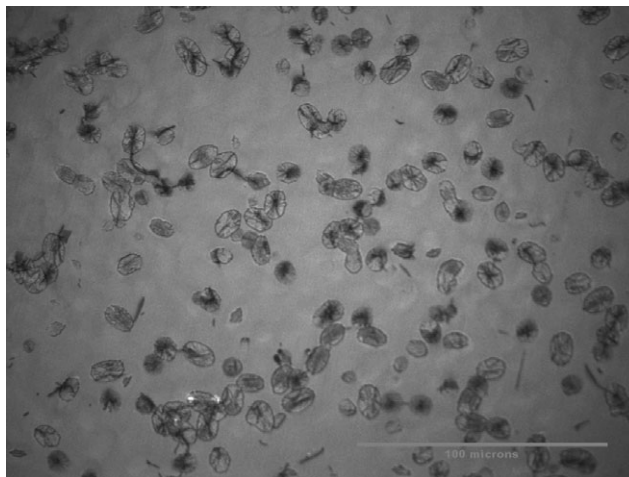
water content can be considered constant and its effect neglected. However, the comparison with results from the literature is hampered.

Based on the approach of Ray *et al.*,[1] Ranasinghe *et al.*[14] used Eq. (9) to determine N_q for two silicate glasses that undergo homogeneous nucleation: $Li_2O \cdot 2SiO_2$ (LS_2) and $Na_2O \cdot 2CaO \cdot 3SiO_2$ ($N_1C_2S_3$). The samples were previously heat treated for partial crystallization in a DSC furnace at different periods of time ($t_G = 10$, 15, and 20 min) using the following temperatures for crystal growth: 600°C for LS_2 and 670°C for $N_1C_2S_3$. They obtained an approximately constant value of N_q for the LS_2 glass, $(4.4 \pm 0.3) \times 10^{12}$ m^{-3}, independent of the chosen pair of t_G. However, the values of N_q obtained for the $N_1C_2S_3$ glass varied drastically, $(32 \pm 22) \times 10^{13}$ m^{-3}, where the intervals correspond to the standard deviation; not to the confidence interval. The behavior of the $N_1C_2S_3$ glass was attributed to an appreciable overlapping of the crystal nucleation and growth for this glass. Nevertheless, even the LS_2 glass presents considerable overlapping of the crystal nucleation and growth rate curves, as proved by Rodrigues *et al.*[15] Therefore, the constant value of N_q obtained for this composition cannot be related to the nonexistence of the overlapping of the $I(T)$ and $u(T)$ curves.

The average N_q obtained by the DSC method of this study is approximately half the value obtained by the original equation of Ray *et al.*,[1] for the same glass. However, when calculated by Eq. (18), the individual values largely depend on the chosen pair of t_G, as one can see in Fig. 3. If, for discussion, we make a partial correction of Eq. (18) with a dividing factor of four, i.e., considering the extended volume given by Eq. (6), the new results shown as open triangles in Fig. 3 present much less variation. In addition, one can see that the results are closer to those calculated by Eq. (19) when the growth time periods are shorter, for example, for up to 20 min, i.e., for low crystallized fractions, as expected.

Nevertheless, the N_q values resulting from Eqs. (18) and (19) are still far too high when compared with the experimental values obtained for specimens of the same glass batch. Fokin *et al.*[2] measured by microscopy the N_q of samples from the same LS_2 glass batch used here. They heated one sample in the DSC furnace from room temperature to 620°C at 20°C/min, kept it at this temperature for 20 min to allow the crystals to grow to a size detectable in the optical microscope, and cooled it at 20°C/min. They found $N_q = 2 \times 10^{10}$ m^{-3} (we will use the unity 10^{10} m^{-3} for N_q from now for an easier comparison of values). Those authors also measured the N_q of another sample, which was almost instantly heated by dropping it in the treatment chamber of
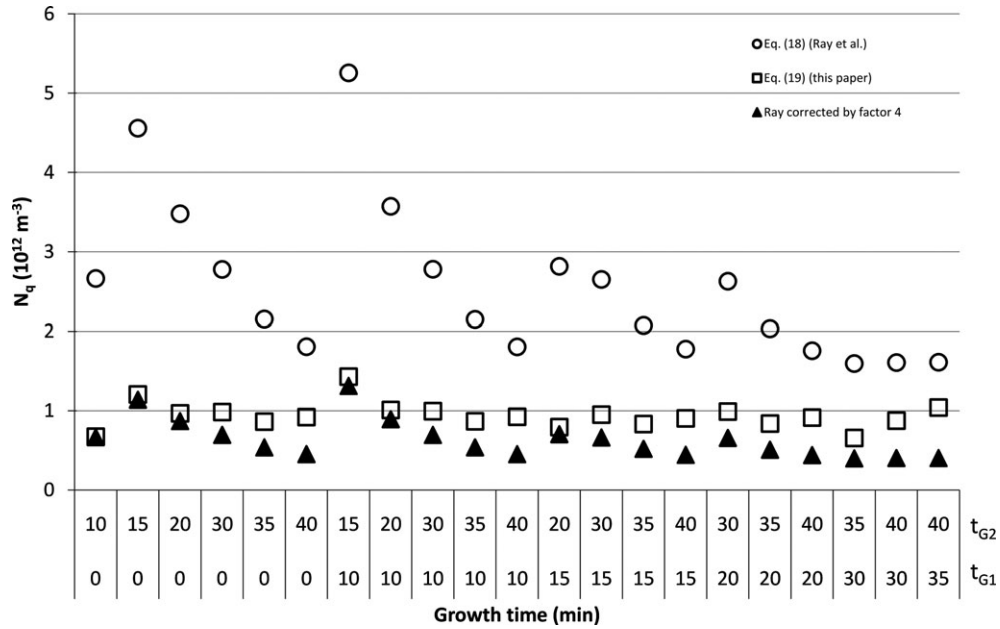
Fig. 3. N_q-calculated values through Eqs. (18) and (19) for different pairs of crystal-growth times.

Table II. N_q Values Determined Directly by Optical Microscopy[2] and Indirectly by DSC Runs [from Eqs. (18) and (19)]

		N_q (10^{10} m^{-3})	
		Microscopy	DSC
Ray *et al.* Eq. (18)		–	240 ± 40
This work; Eq. (19)		–	93 ± 8
Experimental Ref. [2]	20°C/min to 620°C + 20 min	2	–
	Dropped at 600°C + 40 min	0.2	–
Experimental [this work]	20°C/min to 620°C + 20 min	1	–
	Dropped at 600°C + 40 min	0.1	–

a vertical furnace at 600°C, where it was left for 40 min for crystal growth. In this case, the measured value of N_q was 0.2×10^{10} m^{-3}, i.e., one order of magnitude lower than that of the sample treated in the DSC furnace. In this work, we checked the repeatability of these results in samples from the same batch following the same thermal schedules, and our results were very close to the former. Fokin *et al.*[2] proposed that part of the observation of so called "quenched-in" nuclei after heating to 620°C at 20°C/min is actually due to nucleation in the heating path. A comparison between the experimental values determined by Fokin *et al.*[2] and those obtained in this work (experimental and DSC) is shown in Table II.

To estimate the contribution of each step of a heat treatment to N_q, one can proceed as it was made for the BS$_2$ glass by Silva *et al.*[16] The heat-treatment schedule proposed by Ray *et al.*[1] and approximately followed in this work embraces five different steps: (1) a nonisothermal heating from room temperature to 620°C at 20°C/min; (2) an isothermal dwell for crystal growth at 620°C for different t_G; (3) a nonisothermal cooling from 620°C to 380°C at 20°C/min; (4) an equilibrating isothermal dwell for 5 min; and (5) a nonisothermal ramping from T_g to 800°C at 15°C/min. The number of nuclei formed during these steps can be estimated with Eq. (20):

$$N_q = \frac{\int_{653}^{893} I_{N1}.dT}{q_1} + I_{G1}.t_{G1} + \frac{\int_{893}^{653} I_{N2}.dT}{q_1} + I_{G2}.t_1$$
$$+ \frac{\int_{653}^{1073} I_{N3}.dT}{q_2} \tag{20}$$

where the temperatures are given in Kelvin (K). The terms $I_{N1}.dT/q_1$, $I_{N2}.dT/q_1$ and $I_{N3}.dT/q_2$ are the number of nuclei formed during each nonisothermal step with rates of $q_1 = 20$°C/min and $q_2 = 15$°C/min. $I_{G1}.t_{G1}$ and $I_{G2}.t_1$ contribute to N_q from the isothermal steps, where t_1 is 5 min. We assumed an integration limit of 380°C (653 K) instead of room temperature in the first heating for simplicity; it is the same temperature of the intermediate isothermal dwell, and no nucleation is expected to occur below this temperature. The movement of cooperative units (atoms or molecules) toward crystallization is almost negligible at temperatures below the glass transition temperature (T_g), which is ~455°C (728 K) for LS$_2$, due to its long induction time for nucleation. The same behavior is expected in the cooling step $I_{N2}.dT/q_1$.

The first and second integrals in Eq. (20) yield identical values with opposite signs because they are related to opposite paths, i.e., heating and cooling in the DSC. Thus, for accuracy, their modulus was taken into account. It is important to emphasize that the N_t values provided by Eq. (20) do not take surface crystallization into account.

Experimental values of nucleation rates are not available over the whole temperature range needed in Eq. (20). However, it is well-known that the classical nucleation theory describes very well the temperature dependence of steady-state nucleation rates $I_{st}(T)$ with some fitting parameters. The values of I_G at 620°C and 380°C were estimated using the following equation[17]:

$$\ln\left(\frac{I_{st}.\eta}{T}\right) = A'.\exp\left(\frac{B}{T.\Delta G^2}\right) \tag{21}$$

where T is the absolute temperature, η is the viscosity, A' and B are empirical (fitting) constants, and ΔG corresponds to the free energy change per mole. According to Eq. (21)

plots of $\ln(I_{st}.\eta/T)$ versus $1/(T.\Delta G^2)$ using experimental data for I_{st}, η, and ΔG should produce a straight line of slope B and intercept A'. Using experimental data taken from Ref. [18], we obtained I_G at 380°C and 620°C as approximately equal to 4.1×10^5 m^{-3}/s and 6.2×10^{-4} m^{-3}/s, respectively. Replacing these values in Eq. (20), N_q in the isothermal step at 620°C varies from 0 to 1.5 m^{-3}, depending on t_G, what is insignificant compared with other effects.

In addition, the time periods in the nonisothermal steps of the crystal growth treatments (heating up to 620°C and cooling down to 380°C) are much lower than the induction time for the nucleation of the LS$_2$ glass. Even at temperatures larger than 470°C, the time required for the nucleation rate to attain the steady-state regime is not negligible, as shown in Ref. [19]. This means that the terms $I_{N1}.dT/q_1$, $I_{N2}.dT/q_1$, and $I_{N3}.dT/q_2$ in Eq. (20) must be evaluated assuming non-steady-state nucleation. According to the theory of nonstationary nucleation,[20] the crystal nucleation rate as a function of time can be estimated by

$$I = I_{st}.\exp\left(-\frac{\tau}{t}\right) \qquad (22)$$

where I_{st} is the steady-state nucleation rate as given by Eq. (21) and τ is the induction time. The N_q calculated by Eq. (20) for each step of the heat-treatment schedule was thus obtained using Eq. (22), and the experimental data for τ were taken from Ref. [18]. The results are summarized in Table III and compared with values of N_q calculated without taking the induction time into account, i.e., using I_{st} from Eq. (21). Their sums are also presented. By taking the induction time into account, the number of nuclei produced during the DSC runs, i.e., 0.4×10^{10} m^{-3}, is more than two orders of magnitude smaller than that calculated when not taking such time into account, 93×10^{10} m^{-3}. However, these results show that a significant number of nuclei form during the heat treatment performed in the DSC, which is of the same order of magnitude of the number of nuclei measured in Ref. [2] $(0.2 \times 10^{10}$ m$^{-3})$ and in this study $(0.1 \times 10^{10}$ m$^{-3})$ after dropping a sample in a previously heated furnace. This result is in an agreement with that of Davis[21,22] using numerical simulations that demonstrated that the nuclei density in LS$_2$ glass is strongly sensitive to the heating rate conditions. Hence, the technique of measuring N_q by DSC would show this artifact at the levels of the heating/cooling rates considered here.

Nevertheless, the N_q provided by our DSC method, $(93 \pm 8) \times 10^{10}$ m^{-3}, is still much higher than the best values measured experimentally $(0.1–0.2 \times 10^{10}$ m$^{-3})$. This result is due to the formation of extra nuclei on the heating

and cooling path during the DSC experiments plus the effect of the surface crystallization of the samples, which are not considered in the DSC methods. This problem was also discussed in Ref. [2].

VI. Conclusions

We used an expression derived by Fokin et al.[2] to estimate the concentration of preexisting nuclei in a glass that undergoes internal crystallization using DSC experiments. We have accounted for the crystal morphology, the crystal impingement at relatively large volume fractions transformed, and transient nucleation effects. The number density of crystallization sites, N_q, that arise during each heat-treatment step in the DSC was estimated for LS$_2$ glass by two DSC equations and compared with measured microscopy values.

We demonstrate that significant nucleation occurs in LS$_2$ glass in the heating and cooling paths in DSC runs carried out at 15°C/min–20°C/min, as some nuclei may reach the critical size at the temperatures used for crystal growth. An excellent agreement was found between the calculated values of N_q (which also took into account the induction times for nucleation) and the measured values by DSC. Nevertheless, the N_q values provided by both DSC expressions are much higher than the experimental values directly obtained by microscopy. This result is due to the formation of new nuclei during the heating and cooling paths of the DSC runs plus the effect of surface crystallization, which are not considered in the DSC methods.

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Table III. N_q-Calculated Values from Eq. (20) Using Experimental Data of Viscosity and Nucleation Induction Times

Heat-treatment step	Calculated N_q (10^{10} m^{-3}) [Eq. (20)]	
	Without transient effects (Eq. 21)	With transient effects (Eq. 22)
20°C/min from 380°C to 620°C	28	0.1
Isothermal at 620°C ($t_G = 0$–40 min)	0–1.5 × 10^{-10}	0–1.5 × 10^{-10}
20°C/min from 620°C to 380°C	28	0.1
Isothermal at 380°C (5 min)	0.012	0.012
15°C/min from 380°C to 800°C	37	0.19
Total	93	0.4

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