Glass forming ability (on cooling) and stability (on heating)

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Scientific interest on glass crystallization underwent three stages. Initially the main task was to avoid spontaneous crystallization to prepare good glasses. The second stage begun in the late 60s with an increased interest in induced crystallization to prepare glass- ceramics. Thirty years later the focus reversed again. The era of fiber optics brought the requirement of complete avoidance of crystallization. It now seems that the fourth wave is starting, i.e. controlled formation of nanocrystals with designed size and spatial distribution.

Uhlmann et al. [1] took the nucleation rate, *J*, and the linear growth rate, *G*, into account simultaneously, formulating a kinetic criterion for vitrification. In 1969 Gutzow et al. (see [2]) related glass stability to the non-steady-state time lag. In 1989, Weinberg et al. [3,4] demonstrated that the volume fractions transformed and the resulting critical cooling rates, R_c, are quite sensitive to the method of calculation. The so-called "nose method", for instance, which uses isothermal TTT curves, overestimates R_c by up to one order of magnitude. In a subsequent paper [4],[5], the same authors demonstrated that R_c is highly sensitive to the main physical properties that govern nucleation and growth kinetics: crystal liquid surface energy, thermodynamic driving force and viscosity. Later on, Weinberg [5] integrated the equation of overall crystallization kinetics to estimate and compare criteria for vitrification on cooling and glass stability against crystallization on heating. He compared the trends in computed glass forming ability *(GFA)* and glass stability *(GS)* against melting entropy ΔS_m, and two viscosity parameters: the Kauzmann temperature, T_o, and apparent activation energy, *B*, $\lg\eta = \lg\eta_o + \frac{B}{T-T_o}$. He found that both *GFA* and *GS* increased with an increase of ΔS_m and T_o; however, *GFA* and *GS* moved in <u>opposite</u> directions (decrease of *GFA* and increase of *GS*) with an increase of *B* (in this case, a concomitant <u>decrease</u> in the pre-exponential term $lg\eta_o$ of the viscosity equation was imposed). From these results, Weinberg concluded that *GFA* and *GS* are ill-related concepts.

However Cabral Jr. et al. [7] find found a correlation between GFA and GS. Since these two papers reached contradictory conclusions we decided to check the two approaches; i.e. the theoretical calculations of Ref. [6] and the experimental data and approach of Ref. [7] through further testing. Before integrating the equation of overall crystallization kinetics we carefully examined what are the independent variables according to the experimental data, i.e., whether the activation energy for viscous flow, B, is correlated to the pre-exponential term. We demonstrate that GFA and GS are indeed related quantities, a finding that is corroborated by the experimental results of Cabral Jr. et al. [6].[7].

Theory

Glass-forming ability accounts for the easy vitrification of a melt when cooled from above the liquidus, T_m, to the glass transition, T_g, temperature. This parameter is characterized by the critical cooling rate, $q_{cr}(x_c)$, which is the lowest cooling rate at which the final degree of crystallinity of the frozen liquid will not exceed a given critical value, x_c, normally assumed to be within 10^{-6} to10^{-3} [1]. Glass stability (GS), on the other hand, accounts for the resistance of a glass towards devitrification upon re-heating. Quantitative measurements of glass stability are formulated through T_{cr}, the temperature of maximum crystallization rate observed in non-

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isothermal experiments. T_{cr} is usually taken as the peak crystallization temperature determined by DSC or DTA measurements.

The most popular criteria to access glass stability accounts for the position of the crystallization temperature, T_{cr}, which is always located between the glass transition temperature, T_g, and the melting (or liquidus) temperature, T_m.

$$K_H = \frac{T_{cr} - T_g}{T_m - T_{cr}} \qquad (1)$$

The larger the Hruby parameter K_H, the greater the stability of the glass against devitrification.

The theoretical basis for interpreting overall crystallization kinetics is given by the theory of transformation kinetics long ago proposed by Kolmogorov [8] and Avrami [9,10]. In non-isothermal case, considering the limiting case of homogeneous nucleation with simultaneous growth of spherical crystals, the crystallized fraction, x, depends on the nucleation frequency per unit volume, J(T), on the crystal growth rate, G(T), and on the rate of temperature change *q* as:

$$x(q) = 1 - exp\left\{-\frac{4\pi}{3q}\int_{T_m}^{T} J(T')\left[\frac{1}{q}\int_{T'}^{T} G(T'')dT''\right]^3 dT'\right\} \qquad (2)$$

The critical cooling rate necessary to crystallize a fraction x_c, $q_c(x_c)$, determined from Eq.(2) is, thus

$$q_{cr}(x_c) = \left[-\frac{\frac{4\pi}{3}\int_{T_m}^{T} J(T')\left[\int_{T'}^{T} G(T'')dT''\right]^3 dT'}{ln(1 - x_c)}\right]^{\frac{1}{4}} \qquad (3)$$

The crystal growth rate in silicate glasses is given by (see for instance [10]):[11]):

$$G = W\frac{d_o}{\tau_G}\left[1 - exp\left(-\frac{\Delta\mu}{RT}\right)\right] \qquad (4)$$

where W<1 is the concentration of possible growth sites on the crystal/melt interface, which depends on the growth mechanism, τ_G is the time required by the building units to cross the interface, d_o is the mean intermolecular distance, $\Delta\mu$ is the driving force and R is the gas constant.

The steady-state nucleation rate J(T) is determined as

$$J = \frac{\Gamma}{d_o^3 \tau_J} \exp\left(-\frac{A_k}{k_B T}\right) \qquad (5)$$

where A_k is the work of formation of a critical nucleus, Γ is the Zeldovich parameter, and τ_J is the characteristic time required to cross the melt/nucleus interface.

We use the following assumptions:

i. The driving force, $\Delta\mu(T)$, is approximated through the melting entropy, ΔS_m, and temperature, *T*, by the Turnbull equation.

$$\Delta\mu = \Delta S_m T_m (1 - T/T_m) \qquad (6)$$

This equation is valid at low undercoolings or when the specific heat of glass and isochemical crystal is similar.

ii. The crystal/melt interface energy is expressed using the Scapski-Turnbull equation (see [1,2]):

$$\sigma \approx a_s \frac{\Delta S_m T_m}{N_a d_o^2} \qquad (7)$$

where N_a is Avogadro's number, and a_s is a dimensionless constant, which should vary between $0.30 < a_s < 0.55$. Indeed, in fitting the experimental temperature dependence of *J(T)* for several silicate glasses, Weinberg, Manrich & Zanotto [12] found that a_s varies within $0.40<a_s<0.55$ (under the assumption that σ is temperature and size independent). Therefore, in our calculations we assume $a_s=0.4$

iii. We assume the screw dislocation growth mechanism ($W \approx \frac{1-\frac{T}{T_m}}{4\pi\alpha_s}$) because it is the most typical for silicate glasses. According to Jackson, e.g., [10],[11], normal growth is expected only for materials having a low melting entropy ($\Delta S_m<2R$).

iv. We assume that both characteristic times, τ_G and τ_J, are equal to the characteristic time of viscous flow, τ_η. The latter is related to the shear viscosity, η, by the Maxwell relation.

Expressions for viscosity

We intend to express the crystallization tendency of certain substances in terms of T_g/T_m, ΔS_m and two independent variables that account for their viscosity. It is well known that three parameter equations give the most reliable viscosity dependencies. We do not assume here that it is possible to define a viscosity equation with only two parameters. The trick is to replace one of them with T_g. Here we demonstrate how this is done for the three most popular models: the Adam & Gibbs equation, the Vogel-Fultcher-Tammann (VFT) equation and the "jump frequency" model, analyzing the meaning of the parameters included in these equations.

In general, viscosity is expressed as:

$$\eta = \eta_o \exp\left(\frac{E(T)}{RT}\right) \tag{8}$$

where the effective value of activation energy $E(T)$ depends on temperature, while the pre-exponential constant η_o depends on the mean vibration frequency of the building units, $v_o \sim 10^{12} s^{-1}$ and shear modulus, $H_\infty \sim 9.10^{10} Pa$ (see, e.g., Eq.10) as

$$\eta_o = \frac{H_\infty}{v_o} \approx 10^{-1}\, Pa.s \;\;,\;\; i.e.\; \lg\eta_o = -1 \pm 2 \tag{9}$$

Taking into account the constant value of viscosity η_g at the glass transition temperature, one finds that the ratio of the activation energy at T_g and the glass transition temperature is constant

$$\varepsilon = \frac{E(T_g)}{RT_g} = 2.31 * \left(\lg\eta_g - \lg\eta_o\right) = 32 \pm 5\% \tag{10}$$

Quite frequently the activation energy determined from the slope of Arrhenius plots of viscosity is much larger than the predicted value of

$$\boldsymbol{E(T_g)=\varepsilon RT_g} \approx (0.26 \pm 1) T_g \quad , [kJ/mol] \tag{11}$$

The reason is that activation energy is temperature dependent, therefore the slope accounts for the energy plus its first derivative

*The **jump frequency model*** for viscosity [13,14] takes into account the existence of a distribution of the activation energies for molecular motion in liquids (a distribution of the jump frequencies)

$$\eta = \eta_o exp\left(\varepsilon\left(\frac{T_g}{T}\right)^\alpha\right) \tag{12}$$

The fragility parameter α [12, 13] in Eq. (12) is proportional to the heat capacity of the melt. Typically α varies from *1 to 6* for multi-component silicate glasses and is 1 for pure SiO_2 glass. Low α are typical for "*long*" glasses, while *"short"* glasses are characterized by high α.

Adam & Gibbs [14] correlate viscosity with the configurational entropy of liquid. Within certain approximations their equation can be presented in terms of the *Vogel-Fulcher-Tammann* (VFT) relation

$$\eta = \eta_o exp\left(\frac{B}{T - T_o}\right) \qquad (13)$$

where T_o is the Kauzmann temperature below which configurational entropy vanishes. With Eq. (11) the value of B becomes

$$B = \varepsilon(T_g - T_o) \qquad (14)$$

Therefore the VFT equation can be rewritten as

$$\eta = \eta_o \exp\left(\varepsilon \frac{T_g - T_o}{T - T_o}\right) \qquad (15)$$

Computations given in Ref. [5] follow the crystallization tendencies as depending on B for a fixed T_g and T_o values. However, it follows from Eq. (14) and Eq. (10) that B cannot vary by more than 5% for a fixed T_o. Moreover, it has an upper limit, $E(T_g)/R$, in the case of Arrhenian glasses for which T_0=0.

As we intend to elucidate the role of thermodynamic properties, such as $\Delta S_m/R$, *on* crystallisation it is important to verify whether the viscosity parameters, T_g or α *in Eq. (12),* are related to $\Delta S_m/R$.

Despite the abundance of data on T_g and α (see e.g. [12,13]),[13,14]), there is only a limited amount of $\Delta S_m/R$ data [1,2,15,16]. By plotting the available data $\Delta S_m/R$ *vs* T_g *and* $\Delta S_m/R$ *vs* α, (not shown in this paper) we[1,2,3,15,16]. We proved the absence of correlation between these kinetic and thermodynamic quantities. As the jump frequency model, explicitly contains T_g in its expression, we choose $\Delta S_m/R$, T_g *and* α *as independent variables for the following analysis.*

Results

We integrate Eqs.(2,3) numerically, a procedure similar to that used by Weinberg [5].[6]. Our investigation is confined to the influence of the three dimensionless parameters on q_{cr} (Eq. 5) and K_H (Eq. 1): reduced melting entropy $\Delta S_m/R$, and two viscosity parameters – fragility α, and reduced glass transition temperature T_g/T_m. It is not the purpose of this article to present results for particular compositions. Therefore, unless specified, computations are performed for a typical silicate glass, with T_m=*1500 K*.

Fig.1A illustrates the overall crystallization rates calculated by introducing Eqs.(12-16) into Eq.(4) for a heating rate of q=*0.01 K/min*. The value of $\Delta S_m/R$ is shown on each curve. Fig.1B shows the derivatives of the curves of Fig.1A. The maximum of each peak corresponds to the crystallization temperature, T_{cr} (for instance, in a DSC experiment). It is interesting to note that high $\Delta S_m/R$ shifts the crystallization peak to higher temperatures.

Similar results are obtained upon cooling. It should be noted that the tendency to crystallize is much lower upon cooling than on reheating. For $\Delta S_m/R$=*3*, for instance, the degree of crystallization achieved on cooling is incomplete while, on reheating, crystallization saturates at $T/T_m \sim 0.75$.

We found that K_H increases with melting entropy, according to the empirical expression:

$$K_H = 0.05*10^{0.2\frac{\Delta S_m}{R}} \qquad (16)$$

the dependence of the critical cooling rate on melting entropy is empirically described as:

$$\lg\ q_{cr}(x_c) = 1.35\text{-}0.25\ \lg\ x_c\text{-}1.68\frac{\Delta S_m}{R} \qquad (17)$$

A similar result

$$\lg\ q_{cr}(x_c) = const - 2\frac{\Delta S_m}{R} \qquad (17a)$$

we obtained earlier (see [2]) using the TTT method.Analogous to the critical cooling rate one can formulate a critical heating rate $q_{cr}^{(+)}$, defined as the lowest heating rate at which the sample can be heated from T_g to T_m so that crystallization will not exceed a certain x_c. The critical heating rate is much higher than the critical cooling rate and somewhat less sensitive to melting entropy. The resulting equation is:

$$lg\, q_{cr}^{(+)}(x_c) = 2.81 - 0.25\, lg\, x_c - 1.17\frac{\Delta S_m}{R} \tag{18}$$

Equations (16-18) indicate that, for a given viscosity, in the absence of heterogeneous nucleating centers, substances with higher melting entropy form glasses more readily and are more stable than those with low melting entropy, confirming the results of Uhlmann et al. [4].[5].

The critical cooling rate q_{cr} decays with K_H . Substances with higher K_H are more stable on heating and are better glass formers on cooling from the melt. Fig.2 shows the dependence of the Hruby parameter K_H and of critical cooling rate q_{cr} on the fragility α, in log-lin coordinates. Data for K_H are calculated for a heating rate of $q=1$ *K/min*. K_H and q_{cr} change very rapidly with α, even in logarithmic coordinates. More fragile glasses crystallize easily.

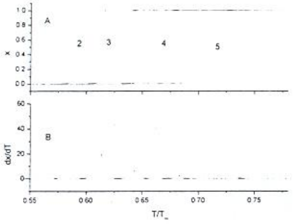

Fig. 1A Overall crystallization rate for heating rate q=0.01 K/min, $\Phi=1$, $\alpha=3$, $T_g/T_m=0.55$ and $\eta_o=0.3$. The curves were calculated by introducing Eqs.(12-16) into Eq.(4). The value of $\Delta S_m/R$ is attached at each curve. The corresponding temperature derivatives are shown in **Fig. 1B**.

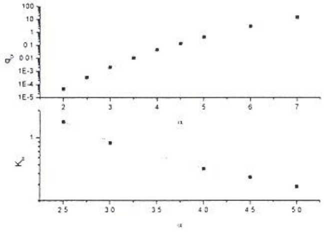

Fig.2 Critical cooling rate, q_{cr}, and Hruby parameter, K_H, versus fragility α, in log-lin coordinates. Data for K_H are calculated for a heating rate of $q=1$ *K/min*

Discussion

In the case of homogeneous crystallization, the tested stability parameter K_H increases (indicating greater stability on heating), while the critical cooling rates decrease with melting entropy. Thus, the tendency to crystallize decreases as $\Delta S_m/R$ increases.

It is interesting to note that, for a given set of parameters, the critical cooling rate is several orders of magnitude lower than the corresponding critical heating rate. Samples that vitrify at a given cooling rate could crystallize completely if heated at the same heating rate. The reason is that, as it cools, the melt first crosses the region of high growth rate with a small number of nuclei, while, on heating, the nuclei first cross the high nucleation rate region. This effect is accounted for by the double integral given in Eq.(2).

The more *fragile* glass-forming substances easily crystallize, as one expects. *Long glasses* are more stable than *short glasses*. The direct correlation between GFA and GS that is demonstrated in the present work was not found in Ref. [5].[6]. We believe that the assumption in Ref. [5] that changes in *B* (with fixed T_g and T_o) accompanied by equivalent changes in η_0 leads to the discrepancy between the results of Ref. [6] and the present findings. Moreover,

$(T_g - T_o)/T_m$ is not a perfect constant, as assumed in Ref. [6]. A summary of existing experimental data indicates that $\frac{T_g - T_o}{T_m} \approx 0.38 - 0.5\frac{T_o}{T_m}$

Our finding that GFA and GS are directly proportional agrees with the results of Cabral Jr et al. [7,18], who have experimentally tested the Hruby parameter vs. q_{cr} for a set of seven selected glasses that undergo homogeneous nucleation.

Among the limitations of the present approach lies the assumption of capillarity often used in the Classic Nucleation Theory, which is limited to rather large nuclei with sharp interfaces. At high supersaturation, however, the nuclei/glass interfaces may be quite diffuse and size dependent. Since there are no independent measurements of surface tension, σ, and any model specifying these dependencies is rather unreliable, for the sake of simplicity we have assumed that σ is temperature and size independent.

Despite these limitations, the present non-isothermal treatment (continuous cooling or heating) is more accurate than the classic TTT-treatment. The main purpose of this investigation: to monitor the trends of crystallization with certain parameters and to test the possible correlation between GFA and glass stability, has thus been achieved.

Conclusions

The approach used here enabled us to evaluate the effect of melting entropy, of glass transition temperature and of fragility parameters on glass stability and glass-forming ability.

Glass-forming ability and glass stability follow the same trend with the three parameters tested here. Namely, when K_H increases, indicating an increase in glass stability, the critical cooling rate decreases, showing an increase of GFA. We have thus demonstrated that glass-forming ability and glass stability are directly related.

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