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Crystal growth and viscous flow in barium disilicate glass

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ABSTRACT

Decoupling between the diffusion coefficients that control crystal growth (D_U) and viscous flow (D_η) in deeply supercooled glass-forming liquids is one of the most celebrated, still unsolved, phenomena in glass science because it strongly impacts the analysis and prediction of crystallization kinetics. To further understand the decoupling phenomenon, we measured viscosity and crystal growth rates (of the crystalline surface layer growth and internally nucleated crystals) of a supercooled liquid with barium disilicate composition. We performed all measurements using glass samples from the same batch, a rare case that we call a “clean” experiment. This type of analysis is uncommon, and its aim is to minimize the uncertainty due to the composition variation that is inherent in laboratory glass production. The decoupling temperature (T_d), the glass transition temperature (T_g), the melting point (T_m), and the liquid fragility index were obtained and successfully used to test a recently derived relationship which allows one to estimate T_d by knowing only T_m and the viscosity curve. We also show, for the first time, that the reduced decoupling parameter, which gauges the degree of deviation between D_U and D_η , does not depend on the crystal growth mechanism for the cases of Normal or Screw Dislocation growth.

1. Introduction

Systematic studies of crystal nucleation and crystal growth kinetics in supercooled glass-forming liquids are relevant for several reasons. One is to compute, simulate, and understand the kinetics of crystallization. Another is to calculate or predict at which cooling rates a given composition can be vitrified. Still another drive is to understand deeply enough about these kinetic phenomena to be able to design and control the crystallization process for the development of innovative glass-ceramics [1,2].

Crystal growth kinetics depends on an effective diffusion coefficient, D_U , governing the aggregation process of the structural units of the liquid phase to the growing crystals. At deep undercoolings, the diffusion coefficient is the main factor that determines both the temperature dependence of crystal growth rates and their absolute values. Unfortunately, in the case of complex liquids, such as oxides, the community does not know what is the nature and size of the “structural units” that control this diffusion coefficient; hence one can only make some reasonable assumptions. Therefore, D_U is often replaced by the inverse of the viscosity via the Stokes–Einstein–Eyring (SEE) relation. This method works quite well at low or moderate undercoolings [3]. However, for deep supercooling near the glass transition temperature (T_g), it leads to what is known as the “decoupling” between crystal

growth and viscous flow, or the breakdown of the SEE relation [4–7]. The temperature that marks this phenomenon is denoted as the decoupling temperature, which T_d lies between $1.10 - 1.25 T_g$ [5,6]. The breakdown of the SEE relation is typical for “fragile” liquids and has been ascribed to spatially *dynamic heterogeneities* (see e.g. [8,9]).

The primary objective of this paper is to investigate the decoupling phenomenon for a glass-forming liquid with barium disilicate (BaSi_2O_5) composition, for which no such analysis has been done. We report and use new measurements of crystal growth rates and the viscosity measured for samples of the same glass batch. This glass-forming liquid is relevant because it is one of the very few that undergoes internal crystal nucleation when heated around T_g and has been the basis of some important fundamental studies about crystal nucleation and growth processes [10–14]. Moreover, as a second objective, we test a relation, recently derived in [6], between T_d and easily measured parameters, such as T_g and the liquid fragility index, m . Finally, we test for the first time if the decoupling parameters and the corresponding decoupling temperatures estimated from different growth mechanisms in the same glass-forming melt are equal.

2. Basic equations

Here we collect the main equations used to estimate the effective

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diffusion coefficient for crystal growth, D_U . We will then compare D_U 's temperature dependence with that evaluated from viscosity (D_η) via the SEE relation. The crystal growth rate in supercooled glass-forming liquids can be written a [15]:

$$U = \frac{f}{4d} D_U \left[1 - \exp\left(-\frac{\Delta G_V d^3}{k_B T}\right) \right], \quad (1)$$

where U is the crystal growth rate; k_B is the Boltzmann constant; T is the absolute temperature; d is the characteristic size of the “structural units”, which is usually estimated from the molar volume, V_M , and Avogadro number, N_A , as $d \approx (V_M/N_A)^{1/3}$; D_U is the effective diffusion coefficient determining the kinetics of attachment of structural units with size d to the crystalline phase; ΔG_V is the thermodynamic driving force for crystallization per unit volume of crystal, and f is a parameter that has different values for different growth mechanisms. According to Jackson's model of crystal growth based on the description of the crystal/melt interface structure [16], we assume that the screw dislocation growth mechanism prevails for this composition since the melting entropy of the $\text{BaO}\cdot 2\text{SiO}_2$ crystal $\Delta S_m = 2.62R$ (between $2R$ and $4R$, R is the gas constant). For this growth model, the fraction of sites on the interface where the structural units can be added or removed is the number density of screw dislocations, which is given approximately by Uhlmann [17].

$$f \approx \frac{(T_m - T)}{2\pi T_m}, \quad (2)$$

where T_m is melting point. As we will show later, to evaluate the decoupling phenomenon in the way proposed in [6], there is no need to specify the mechanism of crystal growth.

The measurements of viscosity were performed in a wide temperature interval and fitted using the VFT equation [18–21]:

$$\log_{10}(\eta) = A + \frac{B}{T - T_0}, \quad (3)$$

where A , B , and T_0 are fit parameters. Then to estimate the diffusion coefficient, D_η , from viscosity data we employed the SEE relation.

$$D_\eta = \gamma \frac{k_B T}{d\eta}, \quad (4)$$

where γ is a constant which depends on the theoretical approaches employed in the derivation, and d is assumed to be the same as in Eq. (1). If the Eq. (4) holds and D_η is equal to D_U , the latter can be written as a function of the viscosity in Eq. (1).

The ratio between D_U and D_η was proposed in [5] (see also [6]) as the decoupling parameter Π_{dec} , characterizing the difference between the mechanisms controlling diffusion and viscous flow.

$$\Pi_{\text{dec}} = \frac{D_U}{D_\eta} = \frac{4d^2}{\gamma f k_B T \left[1 - \exp\left(-\frac{\Delta G_V d^3}{k_B T}\right) \right]} U \eta, \quad (5)$$

To avoid the uncertainty in the definition of the crystal growth mechanism, a reduced decoupling parameter was introduced in [6] as:

$$\Pi_{\text{dec}}^{\text{red}}(T) = \frac{\Pi_{\text{dec}}(T)}{\Pi_{\text{dec}}(T_{\text{ref}})}, \quad (6)$$

The reference temperature T_{ref} was chosen in such a way that, for all temperatures, $T \leq T_{\text{ref}}$ the exponential term in Eq. (5) is much less than unity, hence the term in brackets in Eq. (5) could be omitted. Also at $T \geq T_{\text{ref}}$, the SEE relation holds. Thus, for $T \leq T_{\text{ref}}$, Eq. (6) could be expressed in the following form:

$$\Pi_{\text{dec}}^{\text{red}} \approx \left[\frac{T_{\text{ref}} f(T_{\text{ref}})}{T f(T)} \right] \cdot \left[\frac{U(T) \eta(T)}{U(T_{\text{ref}}) \eta(T_{\text{ref}})} \right]. \quad (7)$$

Since the temperature dependence of f (see Eq. (2)) is rather weak as compared with that of viscosity, we can rewrite Eq. (7) as

$$\Pi_{\text{dec}}^{\text{red}} \approx \left[\frac{U(T) \eta(T)}{U(T_{\text{ref}}) \eta(T_{\text{ref}})} \right]. \quad (8)$$

This equation is equivalent to Eq. (5), but allows us to estimate the decoupling parameter as a function of temperature by knowing only experimental data of $U(T)$ and $\eta(T)$. Hence knowledge of the growth mechanism and the size parameter, d , is not needed. The value of $\Pi_{\text{dec}}^{\text{red}}$ should increase with decreasing temperature, starting at one at temperatures close to T_{ref} .

It should be noted that the above described procedure is not valid for the case of Two-Dimensional (2D) Secondary Nucleation growth, since in this case, the thermodynamic driving force at deep undercooling cannot be neglected (as done for Normal and Screw Dislocation mechanisms) because the latter influences the crystal growth rates for all undercooling. However, this 2D growth mechanism is rare for silicate glasses.

3. Experimental procedures

3.1. Glass preparation

We prepared a glass with nominal stoichiometric composition 33.3BaO and 66.7SiO₂ (mol%) from melting SiO₂ (Vitrovita, Brazil $\geq 99.99\%$) and BaCO₃ (Vetec, Brazil $\geq 99\%$). We dried the chemicals for 12 h at 393 K, then weighed and mixed them. The mixture was placed in a platinum crucible and calcined in an electric furnace at 1623 K for 36 h. This procedure was performed to remove the carbonate and to promote the formation of the barium disilicate crystal phase [13,14]. After the calcination stage, the temperature was slowly raised to 1823 K and maintained for 30 min to allow for complete fusion. We then poured and pressed the liquid between two stainless steel plates. To improve its chemical homogeneity, the glass was crushed and then re-melted three times, following the same temperature ramp described above. After casting small cylindrical pieces in a metallic mold, the glass was annealed for 6 h at 90 K below T_g (at 10 K/min by DSC) to avoid significant crystal nucleation. This treatment was enough to relieve the internal stresses and allowed us to cut samples for differential scanning calorimetry and crystal growth experiments. The chemical analysis was determined via wet chemical analysis in the Institute of Silicate Chemistry, Russian Federation. The analyzed composition of the glass is very close to the desired stoichiometry (BaO·2SiO₂).

3.2. Viscosity measurements

We used the micro penetration (close to T_g) and rotation (around T_m) methods to measure the viscosity. The micro penetration measurements were done by the late Dr. V.P. Klyuev from the Silicate Chemistry Institute of the Russian Academy of Sciences; details about the employed technique and data analysis can be found elsewhere [22]. The Rotation measurements were performed in the Vitreous Materials Laboratory (LaMaV) using a Brookfield Model DV-III rotational rheometer. For this technique, approximately 60 g of glass were remelted in a platinum crucible. Then the glass filled crucible was heated up to 1733 K and stabilized at this temperature for thirty minutes. Then the liquid was cooled at a rate of 10 K/min in 15 K steps with simultaneous data acquisition. Before each datum acquisition, an isothermal stop of 15 min was performed to stabilize the temperature of the liquid.

3.3. Crystal growth rate measurements

To measure the crystal growth rates, we subjected small pieces of glasses to isothermal treatments in the temperature range between 983 and 1198 K during different periods. A preliminary heat treatment for nucleation was not performed because some crystals nucleated during glass preparation and heating up to the growth temperature. We mounted the treated samples in Epoxy Resin, ground with SiC paper

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