Crystal growth and viscous flow in barium disilicate glass

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\textbf{A B S T R A C T}

Decoupling between the diffusion coefficients that control crystal growth ($D_c$) and viscous flow ($D_\eta$) 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 $D_c$ and $D_\eta$, 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. Another is to calculate or predict at which cooling rates a given composition can be vitrified. Still another drive is to understand deeply 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 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\textsubscript{2}O\textsubscript{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].

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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 ($\eta$) via the SEE relation. The crystal growth rate in supercooled glass-forming liquids can be written as [15]:

$$U = \frac{j}{4d} \left[ 1 - \exp \left( -\frac{dG_{v}d}{k_{B}T} \right) \right]$$

(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 $d = (V_{M}/N_{A})^{1/3}$; $D_{U}$ is the effective diffusion coefficient determining the kinetics of attachment of structural units with size $d$ to the crystalline phase; $\Delta G_{v}$ is the thermodynamic driving force for crystallization per unit volume of crystal, and $j$ 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 BaO·2SiO$_2$ crystal is $2.62$R (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].

$$f \cong \frac{(T_{m} - T)}{2k_{B}T_{m}}$$

(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]:

$$\log_{10}(\eta) = A + \frac{B}{T - T_{0}}$$

(3)

where $A$, $B$, and $T_{0}$ are fit parameters. Then to estimate the diffusion coefficient, $D_{U}$ from viscosity data we employed the SEE relation.

$$D_{U} = \gamma \frac{k_{B}T}{\eta}$$

(4)

where $\gamma$ 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 $D_{U}$ 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 $D_{\eta}$ was proposed in [5] (see also [6]) as the decoupling parameter $\Pi_{dec}$ characterizing the difference between the mechanisms controlling diffusion and viscous flow.

$$\Pi_{dec} = \frac{D_{U}}{D_{\eta}} = \frac{4d^{2}}{\eta k_{B}T \left[ 1 - \exp \left( -\frac{dG_{v}d}{k_{B}T} \right) \right]} U \eta.$$  

(5)

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

$$\Pi_{dec}^{red}(T) = \frac{\Pi_{dec}(T)}{\Pi_{dec}(T_{red})},$$

(6)

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

$$\Pi_{dec}^{red} \cong \left[ \frac{U(T)\eta(T)}{U(T_{red})\eta(T_{red})} \right] \frac{T_{red}f(T_{red})}{f(T)}.$$  

(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

$$\Pi_{dec}^{red} \cong \left[ \frac{U(T)\eta(T)}{U(T_{red})\eta(T_{red})} \right].$$  

(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 $\Pi_{dec}^{red}$ should increase with decreasing temperature, starting at one at temperatures close to $T_{red}$.

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 66.7SiO$_2$ (mol%) from melting SiO$_2$ (Vitrovita, Brazil $\geq 99.99\%$) and BaCO$_3$ (Vetc, 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 $T_{m}$ (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 glass 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·2SiO$_2$).

3.2. Viscosity measurements

We used the micro penetration (close to $T_{m}$) and rotation (around $T_{c}$) 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
(300, 400, 600, and 1200 grit), polished with a colloidal suspension of CeO₂ (3 μm), and chemically attacked for 15/20 s by an acid solution with concentration 0.6HF/0.2HCl (vol%).

We obtained similar micrographs to that shown in Fig. 1 (left side) from the cross sections using a DMRX optical microscope coupled with a Leica DFC490 CCD camera. We measured the radius, R, of the largest crystal traces and the thickness h of the crystalline layer for each sample. We then plotted R and h against the treatment time at each temperature. It should be noted that this radius is the real size of crystals growing in the interior of the glass at temperatures where the nucleation rate is negligible low (please compare the micrographs obtained in transmitted and reflected light shown in Figs. 1a,b), and hence the crystal size distribution is approximately monodispersed. When the nucleation rate cannot be neglected (at low temperatures approaching the glass transition temperature), the R of the largest crystal traces is equal to the real size of the largest crystals, i.e. the first nucleated grains.

The growth rates of the internal and surface nucleated crystals (growing toward the sample center) were estimated by computing U_R = dR/dt and U_h = dh/dt, respectively. Two stable polymorphic forms of barium disilicate—monoclinic and orthorhombic structure—are known [11,23,24]. According to the equilibrium phase diagram [25], the low-temperature crystalline form (orthorhombic) reveals slowly reversible transformation into the high-temperature crystalline form (monoclinic) at T_{f/m} about 1623 K. Nevertheless, at the temperatures/times studied in this paper (983–1198 K), the internally nucleated crystals have the monoclinic structure. Hence they are metastable at these temperatures. According to [24], the monoclinic structure fully transforms to the orthorhombic structure in non-isothermal DSC experiment during heating with a rate 10 K/min to the temperatures above 1293 K. The exothermal effect detected in the DSC curve (Fig. 2) accompanying this transformation corroborates that a transformation from the metastable to a stable phase occurs. Fig. 2 gives a good illustration of Ostwald’s rule of stages: supercooled liquid, metastable crystalline phase, and stable crystalline phase.

4. Results

The analyzed composition of the resulting glass - 32.6BaO + 67.4SiO₂ (mole%) - is very close to the desired nominal stoichiometry: 33.33BaO 66.67SiO₂. As we will show, this minor compositional shift was not enough to cause differences in the kinetic properties measured in this work, i.e. when compared with results published by other authors that worked with glasses of the same nominal composition. Our DSC analysis revealed the solidus at T_s ~ 1660 K and liquidus T_l ~ 1683 K, marked in Fig. 2, which are consistent with the equilibrium phase diagram of the BaO-SiO₂ system [26]. The glass transition temperature, T_g = 963 K, marked on the DSC curve is also in good agreement with literature data [11,12,14,27,28].

4.1. Viscosity

Fig. 3 shows the viscosity, η(T), data of the barium disilicate liquid versus temperature obtained in this work along with η(T) data published by others authors [29–31]. Due to the fast crystallization in the intermediate temperature range, we limited the measurements to two temperature ranges: 997–1075 K and 1590–1781 K, which are close to T_s and T_m, respectively. The full line refers to a fit by the Vogel–Fulcher–Tammann (VFT) equation (Eq. (3)) for the viscosity data obtained in this work, with the following free parameters: A = -3.07 (0.01), B = 3734(12)K, and T_B = 718.3 (0.7)K; viscosity given in Pcs. Our data is very close to the literature data. The value of the fragility index, m ~ 59, calculated by the Angel equation [32], indicates that barium disilicate can be classified as a fragile liquid.

4.2. Crystal growth rates

Figs. 4 and 5 show the R(t) and the h(t) dependencies at several temperatures. After some induction period, t_{ind}, these dependencies are linear with a slope corresponding to the crystal growth rates. We list the values of U_R, U_h Table 1 for different temperatures. Similar induction periods, which greatly exceed the induction periods for nucleation, were reported and discussed for lithium disilicate and sodium calcium silicate glasses [33,34], and in [11] for a BS2 glass. These t_{ind} are not related to the classical nucleation induction times; instead, they are likely related with the smaller (than the macro) growth rates of nanosize nuclei, which are just larger than the critical nucleus size, and (or) with the possible formation of metastable phases in the early stages of crystallization [32,33].

5. Discussion

The primary objective of this paper is to analyze the decoupling phenomenon between the diffusion coefficients controlling crystal growth and viscous flow in barium disilicate (undercooled) liquid. To evaluate this phenomenon we employed the reduced decoupling parameter introduced in [6] which we described in Section 2.

Fig. 6 shows the reduced decoupling parameter (estimated using viscosity and crystal growth rates U_R and U_h, see Eq. (8)) versus temperature. The decoupling analysis was performed using only the “clean” crystal growth and viscosity experimental data obtained in this work using samples of the same batch. As expected, Π_{dec} red strongly depends
on the temperature. We estimated the decoupling temperature \( T_d \) as suggested in [6], via the following condition:

\[
\Pi^{\text{red}}_{\text{dec}}(T_d) = e.
\]

This definition of \( T_d \), discussed in [6], allows one to normalize the estimation of the decoupling temperature. For instance for the current glass, this method gives an estimated \( T_d \approx 1060 \text{ K} \). One could also use a “naked eye” analysis of Fig. 6, which would give an estimated \( T_d \) of \( \approx 1140 \text{ K} \). Hence the decoupling temperatures estimated by different authors vary substantially and that is why we use the suggestion of [6].

The decoupling temperature determined in such a way is marked in Fig. 6 by a solid arrow. The reduced decoupling parameter reflects a deviation of the diffusion coefficient controlling crystal growth from that estimated from viscosity. It should be noted that the diffusion and viscous flow processes do not depend on crystal growth. Therefore one could expect an equality of the reduced decoupling parameter estimated using the growth rates of different crystal phases (e.g., a polymorphic phase) in the same melt, i.e. the same diffusion coefficient determines the growth of different crystals. To our knowledge, such equality is experimentally shown here (Fig. 6) for the first time.

The similarity of the temperature dependences of \( U_h \) and \( U_R \) gives additional evidence for this conclusion (see Fig. 7) since, at deep supercoolings, diffusion is the key factor that determines the temperature dependence of crystal growth rates. Because we performed the crystal growth measurements in a temperature range where the growth kinetics practically does not depend on the thermodynamic driving force for crystallization, the later cannot explain the small, but well defined difference between the growth rates of the crystalline surface layer and the crystals nucleated in the bulk of glass, illustrated by the onset in Fig. 7. Thus, this difference likely reflects the difference in crystal growth rates due to (often reported) texture of the crystalline layer, \( h \), versus random orientation of the internal crystals.

Still, about Fig. 7, it is possible to compare crystal growth measurements obtained in this work with measurements by other authors [10,12,35]. It is important to note that \( U_v \) values reported in the literature for barium disilicate glass were measured for internally nucleated crystals; and our results are very close to them.

Based on an empirical correlation observed between the melting temperature and the viscosities at the glass transition temperature and the decoupling temperature

\[
\log_{10} \frac{\eta(T_g)}{\eta(T_d)} = C(T_m) = a + bT_m,
\]

the following relation between \( T_g \), \( T_d \) and liquid fragility \( m \) was derived in [6] and corroborated by experimental data for several compositions

\[
\frac{T_g - T_d}{T_d} = \frac{C(T_m)}{m}.
\]

Here we replaced \( T_g \) by \( T_{12} \) (\( T_{12} \) corresponds the temperature at which \( \log_{10} \eta = 10^{12} \text{ Pa}\cdot\text{s} \)) because the glass transition temperatures estimated from DSC curves with moderate heating rates (10–20 K/min) correspond to viscosity \( \sim 10^{12} \text{ Pa}\cdot\text{s} \). Then, we replotted Fig. 8 using data reported in Ref. [6]. The point marked by a black star in Fig. 8 corresponds to the BaO-2SiO2 glass. It agrees with the general trend. Thus, knowing the melting temperature of the system and the temperature dependence of viscosity (and hence the values of \( T_{12} \) and \( m \)) one can estimate the temperature of decoupling between diffusion and viscosity.

It should be stressed again that the decoupling between diffusion...
and viscosity does not depend on the crystallization process. However, the latter strongly depends on the diffusivities of elements controlling crystal formation. In the case of non-stoichiometric crystallization, the evaluation of the decoupling via the determination of the effective diffusion coefficient of crystal growth rate is a complex procedure since, in the advanced stages of phase transformation, one has to take into account the evolution of the residual melt composition, which could result in a change of both diffusion coefficient and liquid viscosity. Thus, different decoupling parameters and decoupling temperatures can be expected for different compositions of the residual melt. However, the general approach to decoupling problem remains the same as in the case of stoichiometric crystallization.

### 6. Conclusions

We measured the viscosity and crystal growth rates of supercooled barium disilicate liquid in a wide temperature range using samples of the same batch. Our results show the expected decoupling of crystal...
growth and viscous flow at deep undercoolings. Most important, for the first time, we show that the decoupling parameter and the decoupling temperature are characteristics of the system and do not depend on the crystal growth mechanism (Normal versus Screw Dislocation). Finally, temperature are characteristics of the system and do not depend on the decoupling parameter.

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