



# Crystallization in glass-forming liquids: Effects of fragility and glass transition temperature



Jörn W.P. Schmelzer<sup>a,\*</sup>, Alexander S. Abyzov<sup>b</sup>, Vladimir M. Fokin<sup>c,d</sup>, Christoph Schick<sup>a</sup>, Edgar D. Zanotto<sup>d</sup>

<sup>a</sup> Institut für Physik der Universität Rostock, Wismarsche Strasse 43–45, 18057 Rostock, Germany

<sup>b</sup> National Science Center, Kharkov Institute of Physics and Technology, 61108 Kharkov, Ukraine

<sup>c</sup> Vavilov State Optical Institute, ul. Babushkina 36–1, 193 171 St. Petersburg, Russia

<sup>d</sup> Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, UFSCar, 13565–905 São Carlos, SP, Brazil

## ARTICLE INFO

### Article history:

Received 16 June 2015

Received in revised form 19 July 2015

Accepted 27 July 2015

Available online xxxx

### Keywords:

Nucleation;

Crystal growth;

Overall crystallization;

Fragility;

Glass transition

## ABSTRACT

The relevance of the concepts of fragility,  $m$ , of the liquid and of the reduced glass transition temperature,  $T_g/T_m$  ( $T_g$ : glass-transition temperature,  $T_m$ : melting or liquidus temperature) for the understanding of crystal nucleation and growth in glass-forming liquids is explored. Based on the analysis of crystallization processes in glass-forming melts, it is shown that classical fragility can be relevant for the understanding of the crystallization behavior only if several severe conditions are fulfilled that are rarely met. By this reason, a new definition of liquid fragility is introduced. This new definition does not involve the commonly utilized temperature ratio  $T_g/T$  ( $T$ : actual temperature). Instead, we employ the reduced variable  $T_m/T$  and do not restrict the computation of  $m$  to the glass transition temperature,  $T_g$ , as in the standard approach. Moreover, we specify the fragility index by computing it for the temperature appropriate for the particular kinetic process being analyzed. With this modified definition of fragility applied to both the diffusion coefficient controlling crystallization and viscosity, fragility becomes one of the main factors determining the temperatures and magnitudes of the maxima of nucleation, growth, and overall crystallization rates. In addition, the origin of the previously reported correlations between reduced glass transition temperatures and intensity of crystallization processes is specified.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

To control the features of the newly evolving crystal phases in an undercooled liquid and the characteristics of the resulting material, a detailed understanding of the mechanisms of nucleation and crystal growth is required [1–3]. However, measurements of crystal-nucleation rates in glass-forming liquids are both difficult to perform and time-consuming. Therefore the knowledge of correlations between the rate of crystallization processes and easily measurable properties of glasses is highly desirable.

By this reason, as a starting point for detailed investigations, it is useful to devise general criteria allowing one to estimate the rate of crystallization processes. For example, long ago, Tammann addressed some factors affecting the crystallization of glass-forming melts, stating “the higher the melt viscosity at the melting temperature, the lower its crystallizability” [4]. Another empirical correlation exhibited by nucleation data for several silicate glasses is the relationship between reduced glass transition temperature and the magnitudes of crystal nucleation and growth rates. For example, James [5] and Zanotto & Weinberg [6,7] connected the intensity of nucleation with the reduced

glass transition temperature. These researchers stated that, on laboratory time/size scales, glasses having a reduced glass transition temperature  $T_{gr}$  ( $T_{gr} = T_g/T_m$ ,  $T_g$  is the glass transition temperature and  $T_m$  is the melting temperature) higher than  $\approx 0.58 - 0.60$  display only surface (mostly heterogeneous) nucleation, whereas glasses showing volume (homogeneous) nucleation have  $T_{gr} < 0.58 - 0.60$ .

These conclusions have been corroborated and further advanced by Fokin et al. [8,9]. Assuming that the Stokes–Einstein–Eyring (SEE) relation holds and that the viscosity of undercooled liquids is governed by the Vogel–Fulcher–Tammann (VFT) equation, it was demonstrated in [8] that an increase of  $T_{gr}$  results in: (i) an increase of the temperature  $T_{max}^{(nucl)}$  where the steady-state nucleation is maximal, (ii) a decrease of the magnitude of the maximum nucleation rate, (iii) a decrease of the ratio  $T_{max}^{(nucl)}/T_{gr}$ , and (iv) an increase of the nucleation time-lag at  $T_{max}^{(nucl)}$ .

In [9], experimental data for the maximum growth rate,  $u_{max}$ , as a function of the reduced glass transition temperature,  $T_{gr}$ , were given (Fig. 2 and Table 1 in [9]) and analyzed. Employing similar assumptions as those utilized in [8] for the analysis of nucleation, the following results were obtained: (i) with increasing values of the reduced glass transition temperature,  $T_{gr}$ , the temperature  $T_{max}^{(growth)}$  of the crystal growth maximum shifts to higher values and (ii) the maximum growth rate,  $u_{max}(T_{max}^{(growth)})$ , decreases with increasing  $T_{max}^{(growth)}$ . This analysis has been recently extended by Gallo et al. [10] and Orava & Greer [11].

\* Corresponding author.

E-mail address: [juem-w.schmelzer@uni-rostock.de](mailto:juem-w.schmelzer@uni-rostock.de) (J.W.P. Schmelzer).

Another parameter that is frequently supposed to give some information on the nucleation-growth tendencies is the fragility index,  $m$  [10,12–17]. Its possible relevance to understand crystallization processes has been widely discussed in recent decades and different points of view in this respect can be found in the literature. By this reason, the analysis of the problem whether fragility can give such insights is of current interest.

A quantitative theoretical understanding of the crystallization behavior of glass-forming liquids requires appropriate models for the kinetics of nucleation, growth, and overall crystallization. In the resolution of the problem, which parameters determine the rate of crystallization, in particular, the temperatures and magnitudes of the maxima of nucleation, growth, and overall crystallization rates and the parameters affecting them must be known. For that purpose, in a preceding paper [18] general relations for the specification of locations and magnitudes of these maxima have been derived. This analysis was performed in terms of the classical theory of nucleation and growth without introducing additional assumptions for the derivation of the general relations. In particular, in deriving and analyzing these general relations, we did not use any specific equations for the diffusion coefficient or the viscosity, such as, e.g., the VFT equation, and also did not assume validity of the SEE equation. This relation is frequently employed in the description of crystal nucleation and growth, allowing one to replace the effective diffusion coefficients,  $D$ , governing nucleation and growth by the inverse of the Newtonian viscosity,  $\eta(T)$ . Only for analytical estimates and numerical computations, commonly employed models for the specification of the thermodynamic properties of the crystallites are utilized. These theoretical predictions have been applied successfully in [18] for an interpretation of a variety of crystal nucleation and growth experiments.

Based on the theoretical results derived in [18], in the present paper we analyze whether, why, and how the locations and magnitudes of the maximum rates of nucleation, growth, and overall crystallization are correlated with certain properties of liquids, such as the reduced glass transition temperature [5–9,11] and fragility index [10,12–17]. In this analysis, we demonstrate that classical fragility can be relevant for the understanding of the crystallization behavior only if several severe conditions are fulfilled that are rarely met. By this reason, we introduce here a modification of the classical definition of fragility. This modification contains three new elements: (i) Fragility is defined for both diffusion coefficient (controlling nucleation and growth) and viscosity. (ii) We do not utilize the commonly employed ratio of the glass transition temperature to the actual temperature,  $T_g/T$ , for the description of the temperature dependence of diffusion coefficient or viscosity, instead we use the ratio,  $T_m/T$ , of the melting (or liquidus) temperature,  $T_m$ , to the actual temperature,  $T$ . (iii) Finally, we do not connect fragility with the properties of the liquid at the glass transition temperature (as done in the classical approach). Instead, we compute the values of fragility at the temperatures of maximum nucleation, growth, and overall crystallization rates, respectively, i.e. we specify the fragility index by computing it for the temperature appropriate for the particular kinetic process being analyzed. We show that, employing this modified definition, fragility becomes one of the main parameters determining the maximum rates of crystal nucleation, growth, and overall crystallization in undercooled liquids. In addition, the basic origin of previously reported correlations between reduced glass transition temperatures and intensity of crystallization processes is clarified in a general model-independent way.

The paper is structured as follows: In Section 2, basic relations derived in [18] allowing one to determine the temperatures and magnitudes of the maximum nucleation, growth, and overall crystallization rates are summarized. Based on these results, correlations between the reduced glass transition temperature, fragility, and crystal nucleation and growth kinetics are established and analyzed in Section 3. A summary and discussion of the results and possible developments (Section 4) complete the paper.

## 2. Temperatures and magnitudes of maxima of nucleation, growth, and overall crystallization rates

In a preceding analysis [18], we derived conditions for the location and magnitudes of the maximum crystal nucleation, growth, and overall crystallization rates. The main equations employed in the analysis and the results are briefly summarized in the present section as the basis for the analysis of possible interrelations between crystallization intensity, fragility, and reduced glass transition temperature.

The steady-state nucleation rate,  $J$ , is expressed as

$$J = c \sqrt{\frac{\sigma}{k_B T}} \left( \frac{D}{d_0} \right) \exp\left(-\frac{W_c}{k_B T}\right), \quad W_c = \frac{1}{3} \sigma A_c, \quad A_c = 4\pi R_c^2. \quad (1)$$

Here,  $\sigma$  is the specific interfacial energy,  $k_B$  the Boltzmann constant,  $T$  the absolute temperature,  $d_0$  a characteristic size parameter that is determined by the particle number density,  $c = (1/d_0^3)$ , of the basic units of the ambient phase,  $W_c$  is the work of critical cluster formation which can be expressed via the surface area,  $A_c$ , of the critical cluster or its radius,  $R_c$ , assuming spherical shape [3],  $D$  is the effective diffusion coefficient determining the processes of aggregation of ambient phase particles to the crystal clusters,

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right), \quad (2)$$

where  $E_D = E_D(T)$  is the activation energy for diffusion,  $D_0$  a kinetic prefactor that depends only slightly on temperature as compared with the exponential term.

For the macroscopic linear growth rate,  $u$ , we use the commonly employed relation [19,20]

$$u = f \frac{D}{4d_0} \left[ 1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right) \right] \quad (3)$$

that describes well the crystal growth kinetics in most oxide glass-formers.  $f$  ( $0 < f \leq 1$ ) is a parameter that depends on the growth mechanism and temperature. For analytical estimates and numerical illustrations, we express the thermodynamic driving force,  $\Delta\mu$ , for nucleation and growth in its simplest form as

$$\Delta\mu = q \left( 1 - \frac{T}{T_m} \right), \quad q = T_m \Delta s_m, \quad (4)$$

where  $q$  ( $q > 0$ ) is the latent heat of crystallization per particle and  $\Delta s_m$  is the melting entropy per particle at the equilibrium melting temperature,  $T_m$ . The specific surface energy,  $\sigma$ , is estimated by the Stefan-Skapski–Turnbull relation [3] as

$$\sigma = \alpha \frac{q}{v^{2/3}}, \quad v = \frac{1}{c} = d_0^3. \quad (5)$$

Employing this relation, surface effects enter the description via the parameter  $\alpha$ , which is considered to be constant.

The maximum of the nucleation rate is found at a temperature  $T_{max}^{(nucl)}$  given by [18]

$$\frac{T_{max}^{(nucl)}}{T_m} = \frac{1}{T_m} \left( \frac{W_c + E_D}{\frac{d(W_c + E_D)}{dT}} \right) \Bigg|_{T=T_{max}^{(nucl)}}. \quad (6)$$

Based on the analysis of this relation it can be shown [18] that the maximum steady-state nucleation rate decreases with increasing values of  $T_{max}^{(nucl)}$ . Employing Eq. (4), Eq. (6) can be transformed to

$$\frac{T_{max}^{(nucl)}}{T_m} = \left( \frac{W_c + E_D^{(eff)}(T)}{3W_c + E_D^{(eff)}(T)} \right) \Bigg|_{T=T_{max}^{(nucl)}}. \quad (7)$$

The effective activation energy for diffusion,  $E_D^{(eff)}$ , in Eq. (7) is defined as

$$E_D^{(eff)}(T) = \left( E_D(T) - T \frac{dE_D(T)}{dT} \right). \quad (8)$$

The temperature  $T_{max}^{(growth)}$  of maximum growth rate is determined by calculating the derivative ( $du/dT = 0$  in Eq. (3)). We then obtain [18]

$$E_D^{(eff)}(T_{max}^{(growth)}) = - \frac{\Delta\mu}{\exp\left(\frac{\Delta\mu}{k_B T}\right) - 1} \left( \frac{T}{\Delta\mu} \frac{d\Delta\mu}{dT} - 1 \right) \Bigg|_{T=T_{max}^{(growth)}}. \quad (9)$$

Employing Eq. (4), Eq. (9) can be simplified to give

$$\exp\left(\frac{\Delta\mu}{k_B T}\right) \Bigg|_{T=T_{max}^{(growth)}} = 1 + \frac{q}{E_D^{(eff)}} \Bigg|_{T=T_{max}^{(growth)}}. \quad (10)$$

Resolving this relation with respect to  $T_{max}^{(growth)}/T_m$ , we obtain

$$\frac{T_{max}^{(growth)}}{T_m} = \frac{1}{1 + \frac{k_B T_m}{q} \ln\left(1 + \frac{q}{E_D^{(eff)}}\right)} \Bigg|_{T=T_{max}^{(growth)}}. \quad (11)$$

The dependence of the maximum growth rate on temperature can be approximately expressed as

$$u_{max}^{(growth)}(T_{max}^{(growth)}) \cong f \frac{D_0}{4d_0} \left( \frac{q}{E_D^{(eff)}} \right) \exp\left(-\frac{1}{1 - \left(\frac{T_{max}^{(growth)}}{T_m}\right)}\right) \Bigg|_{T=T_{max}^{(growth)}}. \quad (12)$$

It is demonstrated in [18] that the maximum growth rate decreases with increasing values of the ratio  $T_{max}^{(growth)}/T_m$ . Consistent with experimental results, we observe that the growth rate maxima are located as a rule at higher temperatures than the maxima of the homogeneous nucleation rates. This conclusion holds provided the system is characterized by normal values of the specific interfacial energy. For homogeneous nucleation in systems with a very small surface energy and for heterogeneous nucleation, an opposite behavior is also possible.

The temperature  $T_{max}^{(overall)}$  of the maximum of the overall crystallization rate is given by

$$\frac{T_{max}^{(overall)}}{T_m} = \frac{1 - \Upsilon}{3 - \Upsilon} \Bigg|_{T=T_{max}^{(overall)}}, \quad (13)$$

$$\Upsilon(T_{max}^{(overall)}) = (n+1) \frac{E_D^{(eff)}(T_{max}^{(overall)})}{W_c(T_{max}^{(overall)})} \times$$

$$\times \left\{ \frac{nq}{(n+1)E_D^{(eff)}\left(\exp\left(\frac{\Delta\mu}{k_B T}\right) - 1\right)} - 1 \right\} \Bigg|_{T=T_{max}^{(overall)}}.$$

The temperature of the maximum overall crystallization rate is located in between the temperatures of the maxima of the nucleation and growth rates.

### 3. Glass transition temperature, fragility, and nucleation – growth kinetics

#### 3.1. Diffusion fragility and viscosity fragility: Extension of the classical definition

In the aforementioned analysis [18], we derived general relations for the maximum nucleation, growth, and overall crystallization rates without any reference to concepts such as the glass transition temperature or fragility. However, already in the introduction to the present paper, several studies were briefly reviewed that correlate the glass transition temperature and fragility with some essential features of nucleation-growth processes and the glass forming ability. The question thus arises whether such correlations indeed exist and how they can be explained.

The concept of fragility, introduced by Angell (cf. [3,11,15,16]), has been widely discussed in the analysis of the behavior of glass-forming systems, including their glass-forming ability. The fragility index,  $m$ , was originally computed based on viscosity data and defined as

$$m_\eta^{(c.d.)} = m\{\eta, (T_g/T), T = T_g\} = \frac{d \log \eta}{d\left(\frac{T_g}{T}\right)} \Bigg|_{T=T_g}, \quad (15)$$

where the viscosity is given by

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{k_B T}\right). \quad (16)$$

The activation energy for viscosity,  $E_\eta$ , is, in general, a function of temperature, while the pre-exponential term,  $\eta_0$ , depends only weakly on it.

In the definition of fragility, expressed by Eq. (15) and specified here by the superscript (c.d.), (i) the fragility parameter,  $m$ , is computed based on the knowledge of the temperature dependence of the viscosity, (ii) temperature is expressed in terms of the ratio ( $T_g/T$ ), and (iii)  $m$  is calculated at the glass transition temperature,  $T = T_g$ , defined (as discussed here later) in a particular way. These three elements of the definition are expressed in the above equation by the subscript  $\eta$  in  $m_\eta^{(c.d.)}$  and are also summarized in a mathematical form as  $m\{\eta, (T_g/T), T = T_g\}$ .

However, when considering the temperature and magnitude of the maxima of nucleation and growth rates, primarily it is not viscosity but the diffusion coefficient that defines the rates of crystal nucleation and growth (cf. also [18,21] for a detailed analysis). By this reason, Angell's fragility index may be relevant only for cases when the diffusion coefficient can be replaced by the inverse of the Newtonian viscosity, i.e., in cases when the SEE relation holds. This is one of the principal limitations of the classical definition of the fragility index in application to crystallization. In order to overcome it, in the modified definition of fragility proposed here, (i) we rely primarily on the diffusion coefficient controlling nucleation and growth and not on viscosity. In addition, we take into account that it is not  $T_g$  that determines the nucleation-growth behavior, but the melting or liquidus temperature,  $T_m$ , employing the reduced variable  $T_m/T$  instead of  $T_g/T$ .

Also another factor stimulated such attempt to replace  $T_g/T$  by  $T_m/T$  in the definition of fragility: the glass transition temperature,  $T_g$ , is not a well-defined property of a given glass-forming material like  $T_m$ .  $T_g$  also depends on the cooling and heating rates [3,22–24]. This dependence is especially relevant if wide ranges of rates of change of temperature are involved in the experiments. Such considerations provide additional support to the viewpoint that it would be appropriate to introduce and employ a modified definition of the fragility parameter, (ii) selecting as the reference temperature not the glass transition temperature (respectively, the reduced variable  $T_g/T$ ) but the melting (or liquidus) temperature (respectively, the reduced temperature  $T_m/T$ ). Such choice turned out to be very fruitful in the analysis of

thermodynamic properties of glass-forming melts and glasses [3,25–27] and also of viscosity (cf. e.g. [14]). For example, Laughlin and Uhlmann [14] presented viscosity data for different systems as functions of these two reduced variables. Mentioned authors classified the presentation of viscosity in terms of  $T_m/T$  as a “superior normalization” of viscosity data but went over then to  $T_g/T$  considering it as “difficult to rationalize a priori the dependence of liquid flow on characteristics other than those of the liquid phase alone.” For the analysis of nucleation and growth processes the latter restriction becomes irrelevant and the description of the temperature dependence of diffusion and viscosity in terms of  $T_m/T$  is preferable in any respect.

These are the two primary reasons, which led us to search for a modification of the original concept of fragility that could then be directly applicable to crystal nucleation and growth. As will be demonstrated here shortly, this modified fragility parameter, computed for temperatures corresponding to the maxima of crystal nucleation, growth, and overall crystallization rates, determines to a large extent both the location of these maxima and their magnitudes. Consequently, the third modification in the definition of fragility advanced by us consists of the fact that (iii)  $m$  is not strictly connected with the glass transition temperature,  $T_g$ . In contrast, it is defined first as a function of temperature. The specific temperature at which the fragility is computed is then selected in accordance with the particular application. As will be shown shortly, if the modified fragility is computed with respect to viscosity at  $T = T_g$ , the classical and new versions lead to widely equivalent results, i.e., they are proportional to each other.

As a consequence of above given considerations, we introduce here (similarly to Eq. (15)) a modified definition of fragility. In application to the diffusion coefficient, we call it the *modified diffusion fragility* and define it as follows:

$$m_D^{(m.d.)}(T) = m\{D, (T_m/T), T\} = -\frac{d \ln D}{d\left(\frac{T_m}{T}\right)}. \quad (17)$$

The above discussed three elements of the modified definition of fragility (specified by the superscript (m.d.) in Eq. (17) and distinguishing it from the classical one) can be expressed similarly to Eq. (15) by the subscript  $D$  in  $m_D^{(m.d.)}$  and are summarized in Eq. (17) in a mathematical form as  $m\{D, (T_m/T), T\}$ . With the same approximations employed earlier (considering  $D_0$  in the expression for the diffusion coefficient (cf. Eq. (2)) as a constant), we arrive at

$$m_D^{(m.d.)}(T) = \frac{\left(E_D(T) - T \frac{dE_D(T)}{dT}\right)}{k_B T_m} = \frac{E_D^{(eff)}(T)}{k_B T_m}. \quad (18)$$

The modified diffusion fragility turns out to be proportional to the effective activation energy for diffusion as defined by Eq. (8).

In addition, we may also introduce the new definition of fragility for the viscosity. We define the *modified viscosity fragility* as

$$m_\eta^{(m.d.)}(T) = m\{\eta, (T/T_m), T\} = \frac{d \ln \eta}{d\left(\frac{T_m}{T}\right)}. \quad (19)$$

Equivalently to Eqs. (8) and (18), we obtain

$$m_\eta^{(m.d.)}(T) = \frac{E_\eta^{(eff)}(T)}{k_B T_m}, \quad E_\eta^{(eff)}(T) = \left(E_\eta(T) - T \frac{dE_\eta}{dT}\right). \quad (20)$$

The modified viscosity fragility is proportional to the effective activation energy for viscosity as defined by Eq. (20). We would like to stress again that in the above definitions, we did not specify the temperature at which the fragility is computed. Such specification depends on the application to the particular problem of interest.

The modified fragility indices  $m_D^{(m.d.)}(T)$  and  $m_\eta^{(m.d.)}(T)$  are shown in Fig. 1 for four glass-forming melts as a function of the reduced temperature ( $T_m/T$ ). Open circles specify the particular values of the modified viscosity fragility,  $m_\eta^{(m.d.)}$ , for the respective glass transition temperatures,  $T_g$ , obtained at typically employed cooling or heating rates. Full circles give the values of the fragility,  $m_\eta^{(c.d.)}$ , if the classical definition is employed (cf. Eqs. (15) and (33)).

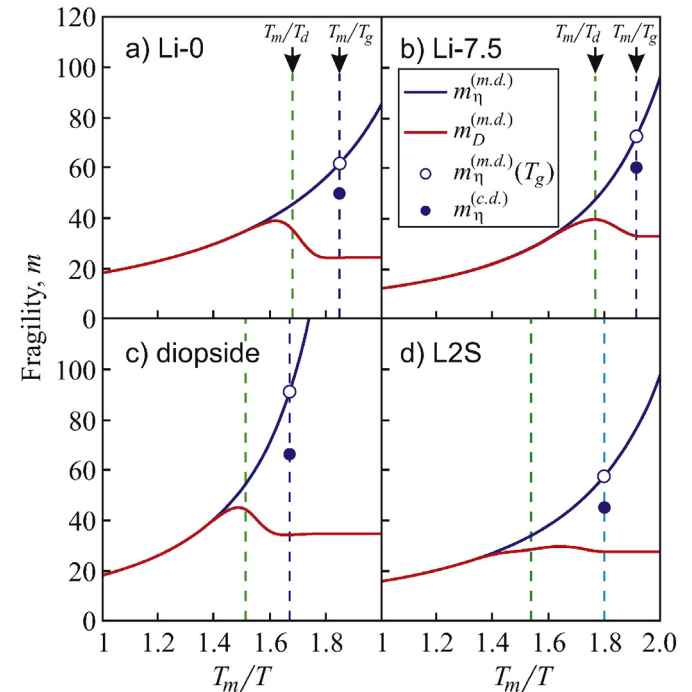
Provided the SEE equation holds, we then arrive as a special case at

$$m_\eta^{(m.d.)}(T) = m_D^{(m.d.)}(T) \equiv m^{(m.d.)}(T) = \frac{E^{(eff)}(T)}{k_B T_m}. \quad (21)$$

The effective activation energy ( $E^{(eff)}(T)$ ) can then be determined either via the knowledge of the diffusion coefficient (its activation energy,  $E_D^{(eff)}(T)$ ) or the viscosity (its activation energy,  $E_\eta^{(eff)}(T)$ ) as a function of temperature. In such cases, the effective activation energy divided by  $k_B T_m$  is equal to the modified fragility independently of the way it is determined (either via the diffusion coefficient or the viscosity). Indeed, as shown in Fig. 1, the values of the new fragility parameter computed based on the diffusion coefficient and viscosity coincide for temperatures in the range above the decoupling temperature,  $T_d$  (i.e. for  $T \geq T_d$ ). For temperatures below  $T_d$ , however, the diffusion fragility and the viscosity fragility have quite different values.

### 3.2. Diffusion fragility, glass transition temperature, and crystal nucleation-growth kinetics

We will demonstrate now that the fragility, when defined in this new way, is one of the main parameters determining the location and



**Fig. 1.** Modified fragility parameters,  $m_\eta^{(m.d.)}$  and  $m_D^{(m.d.)}$ , as a function of the reduced temperature  $T_m/T$  for four glass-forming systems (compositions in mol%): 16.4Na<sub>2</sub>O · 33.3CaO · 50.3SiO<sub>2</sub> (Li-0), 14.8Na<sub>2</sub>O · 29.0CaO · 48.7SiO<sub>2</sub> · 7.5Li<sub>2</sub>O (Li-7.5), lithium disilicate (L2S), and diopside (CaO-MgO-2SiO<sub>2</sub>). Open circles give the particular values of  $m_\eta^{(m.d.)}$  for the respective glass transition temperatures,  $T_g$ , obtained at typical cooling and heating rates. Full circles show the values of the classical fragility  $m_\eta^{(c.d.)}$  (cf. Eqs. (15) and (33)). The values of viscosity were taken from [10,31–33]. The method of specification of the diffusion coefficient determining nucleation and growth is discussed in detail in an accompanying paper [21].

magnitude of the maxima of nucleation, growth, and overall crystallization rates. With respect to nucleation, another main parameter is the work of critical nucleus formation, which can be expressed in terms of the so-called Gibbs number.

Conventionally, the Gibbs number is defined as  $Gi(T) = W_c(T)/k_B T$  [28,29]. We introduce here a modification of this definition denoting the Gibbs' number as

$$Gi(T, T_m) = \frac{W_c(T)}{k_B T_m}, \quad (22)$$

i.e., relating it to the melting temperature. Employing Eqs. (6) and (22), the ratio  $T_{max}^{(nucl)}/T_m$  can then be written generally as

$$\frac{T_{max}^{(nucl)}}{T_m} = \frac{1}{T_m} \left( \frac{Gi(T, T_m) + (E_D/k_B T_m)}{\frac{d(Gi(T, T_m) + (E_D/k_B T_m))}{dT}} \right) \Bigg|_{T=T_{max}^{(nucl)}}. \quad (23)$$

Similarly, Eq. (7) may be reformulated in such terms as

$$\frac{T_{max}^{(nucl)}}{T_m} = \left( \frac{Gi(T, T_m) + m_D^{(m.d.)}(T)}{3Gi(T, T_m) + m_D^{(m.d.)}(T)} \right) \Bigg|_{T=T_{max}^{(nucl)}}. \quad (24)$$

It is evident that the temperature of the maximum steady-state nucleation rate is determined by Gibbs' number (defined by Eq. (22)) and reduced activation energy for diffusion,  $(E_D/k_B T_m)$ , respectively, Gibbs' number and modified diffusion fragility. All parameters must be computed for the temperature  $T = T_{max}^{(nucl)}$ . Consequently, the fragility index in the proposed by us modified definition is one of the main (kinetic) factors determining the location and magnitude of the nucleation rate maximum. In particular, if, at given values of the Gibbs' number, the fragility index,  $m_D^{(m.d.)}$ , is increased then the ratio,  $T_{max}^{(nucl)}/T_m$ , increases and the value of the nucleation rate at  $T_{max}^{(nucl)}/T_m$  decreases (cf. [18] for a proof of the latter statement).

The next problem we analyze now is how the glass transition temperature enters the description of nucleation-growth processes. The key to the understanding of such interdependence consists of the following. In many cases, when the cooling or heating rates are varied within a restricted range, correlations between the melting and glass transition temperatures are observed experimentally. For example, for large classes of inorganic glass-forming melts at normal cooling rates, frequently  $T_g \cong (2/3)T_m$  has been observed [3,26,27]. This relation corresponds to the maximum of the frequency distribution of  $T_g$  data, which varies from approximately 0.4 to 0.8 for oxide glass formers [3]. It is known from experiments with oxide systems that only glasses with  $T_g \leq (3/5)T_m$  exhibit homogeneous bulk nucleation with experimentally detectable rates [6]. This experimental result has been corroborated in [8] employing certain assumptions concerning the properties of the glass-forming systems under consideration. Here we give this result a general interpretation (not employing any particular assumptions concerning the temperature dependence of the diffusion coefficient or the viscosity) because we have shown in [18] that the maximum nucleation rate decreases with increasing  $T_{max}^{(nucl)}/T_m$ . Employing, in addition, the abovementioned correlations between  $T_g$  and  $T_m$ , we can reformulate the above derived relations, Eqs. (23) and (24), in terms of the ratio  $T_{max}^{(nucl)}/T_g$ .

For example, assuming that  $T_g \cong (2/3)T_m$ , Eq. (24) may be rewritten as

$$\frac{T_{max}^{(nucl)}}{T_g} \cong \frac{3}{2} \left( \frac{Gi(T, T_m) + m_D^{(m.d.)}(T)}{3Gi(T, T_m) + m_D^{(m.d.)}(T)} \right) \Bigg|_{T=T_{max}^{(nucl)}} \quad \text{at} \quad T_g = \frac{2}{3}T_m. \quad (25)$$

Similarly to Eq. (24), we arrive at a relation connecting the temperature of the maximum nucleation rate and the glass transition temperature. With an increase of  $T_{max}^{(nucl)}/T_g$  the maximum steady-state nucleation rate decreases, confirming the aforementioned results

concerning glass transition temperature and nucleation kinetics. For metallic glass-forming systems,  $T_g = (1/2)T_m$  is frequently observed [3,12], resulting in

$$\frac{T_{max}^{(nucl)}}{T_g} = 2 \left( \frac{Gi(T, T_m) + m_D^{(m.d.)}(T)}{3Gi(T, T_m) + m_D^{(m.d.)}(T)} \right) \Bigg|_{T=T_{max}^{(nucl)}} \quad \text{at} \quad T_g = \frac{1}{2}T_m. \quad (26)$$

Consequently, in cases when the rate of change of temperature is varied in sufficiently small intervals,  $T_g$  can be uniquely correlated to the melting or liquidus temperature, and the consequences of the general relations derived in the preceding sections in terms of the reduced temperature  $T_{max}^{(nucl)}/T_m$  can also be expressed in terms of the ratio  $T_{max}^{(nucl)}/T_g$ . Alternatively, we may express these correlations via the reduced variables  $T_{max}^{(nucl)}/T_m$  and  $T_{gr} = (T_g/T_m)$ , resulting in dependencies between temperatures and magnitudes of maximum nucleation rates and reduced glass transition temperature, as reviewed in the Introduction.

Similar considerations can be applied to the temperature of maximum growth rate. For that purpose, we rewrite Eq. (11) as

$$\frac{T_{max}^{(growth)}}{T_m} = \frac{1}{1 + \left( \frac{k_B T_m}{q} \right) \ln \left( 1 + \frac{q/(k_B T_m)}{m_D^{(m.d.)}(T)} \right)} \Bigg|_{T=T_{max}^{(growth)}}. \quad (27)$$

Hence the temperature of the maximum growth rate is determined by the interplay between the reduced latent heat of crystallization,  $(q/k_B T_m)$ , and the fragility  $m_D^{(m.d.)}$  at  $T = T_{max}^{(growth)}$ .

For systems where the relation  $T_g = (2/3)T_m$  holds, we obtain a relation determining the ratio of temperature of maximum crystal growth rate and the glass transition temperature in the form

$$\frac{T_{max}^{(growth)}}{T_g} = \frac{3}{2} \frac{1}{1 + \left( \frac{k_B T_m}{q} \right) \ln \left( 1 + \frac{q/(k_B T_m)}{m_D^{(m.d.)}(T)} \right)} \Bigg|_{T=T_{max}^{(growth)}} \quad \text{for} \quad T_g \cong \frac{2}{3}T_m. \quad (28)$$

This result is consistent with the findings of Orava and Greer [11] that experimental values of this ratio are located in the range  $(T_{max}^{(growth)}/T_g) \cong 1.48 \pm 0.15$ . Replacing in Eq. (12) and its generalizations the ratio  $T_{max}^{(growth)}/T_m$  by the relation

$$\frac{T_{max}^{(growth)}}{T_m} = \frac{2}{3} \frac{T_{max}^{(growth)}}{T_g} \quad (29)$$

we may conclude that the maximum growth rate decreases with increasing values of  $T_{max}^{(growth)}/T_g$ . This result is confirmed by numerous experiments [9]. Similar considerations can be performed for the case that the glass transition temperature and melting temperature are correlated via  $(T_g/T_m) = 1/2$ .

Finally, in terms of the Gibbs number (Eq. (22)), the parameter  $q/(k_B T_m)$ , and the diffusion fragility,  $m_D^{(m.d.)}$ , the parameter  $T$  in Eq. (14) can be written as

$$T \left( T_{max}^{(overall)} \right) = (n+1) \frac{m_D^{(m.d.)} \left( T_{max}^{(overall)} \right)}{Gi \left( T_{max}^{(overall)}, T_m \right)} \times \left\{ \frac{n(q/(k_B T_m))}{(n+1)m_D^{(m.d.)}(T) \left( \exp \left[ \left( \frac{q}{k_B T_m} \right) \left( \frac{T_m}{T} - 1 \right) \right] - 1 \right)} - 1 \right\} \Bigg|_{T=T_{max}^{(overall)}}. \quad (30)$$

These three parameters uniquely determine the temperature of the maximum overall crystallization rate.

### 3.3. Limits of applicability of the classically defined fragility index to nucleation-growth kinetics

Various attempts have been made to correlate the conventionally defined fragility with the crystallization kinetics and, in particular, with the maxima of nucleation and growth rates (cf. e.g. [10–12,30]). From the standard definition of fragility, Eq. (15), we obtain (similarly to Eqs. (18) and (21))

$$m_{\eta}^{(c.d.)} = (\log e) \left( \frac{E_{\eta}^{(eff)}(T_g)}{k_B T_g} \right), \quad (31)$$

i.e., the conventionally determined fragility index is proportional to the effective activation energy for viscosity computed at the glass transition temperature,  $T_g$ . However, in formulating Eqs. (24)–(30), the modified diffusion fragility index,  $m_D^{(m.d.)}$ , enters the relations determining the location and magnitude of the maximum rates of nucleation, growth, and overall crystallization. This modified fragility parameter is defined based on the diffusion coefficient (Eq. (17)) and is proportional to the effective activation energy for diffusion (Eq. (18)). Moreover, not the diffusion fragility at  $T_g$  enters Eqs. (24)–(30) but its value computed for the temperatures  $T_{max}^{(nucl)}$ ,  $T_{max}^{(growth)}$ , and  $T_{max}^{(overall)}$  corresponding to the maxima of nucleation, growth, and overall crystallization rates, respectively. When posing the question of whether the classically defined fragility index is relevant for nucleation-growth processes, we must specify the conditions at which the diffusion fragility (Eq. (17)) can be replaced by the viscosity fragility in both the classical and modified definitions (Eqs. (15) and (19)), and at which the fragility index at the temperatures  $T_{max}^{(nucleation)}$ ,  $T_{max}^{(growth)}$ , or  $T_{max}^{(overall)}$  can be approximated sufficiently accurately by the fragility index at  $T_g$ . Only if such replacement is possible then the classically defined fragility can be relevant for the understanding of crystal nucleation and growth processes. As a rule, these conditions are not fulfilled.

Indeed, as demonstrated in Fig. 1, at least for the systems analyzed there, the nucleation kinetics is governed by diffusion, not by viscosity. Therefore, in this case, the SEE equation is not applicable to the description of nucleation. It holds only for growth at sufficiently high temperatures above the decoupling temperature,  $T_d$  (quite frequently located in the range  $1.15 - 1.25T_g$ ). For example, according to [6,8], homogeneous nucleation in oxide glass formers is observable in laboratory time and size scales only for reduced glass transition temperatures below  $(T_g/T_m) \approx (3/5)$ . For the systems under consideration in Fig. 1, in this temperature range, diffusion is decoupled from viscosity. This result is valid for several oxide glass-formers and also for other classes of glass-forming liquids (cf. also [21]).

Provided that the SEE relation holds, the diffusion fragility parameter  $m_D^{(m.d.)}$  can be replaced by the newly defined modified viscosity fragility coefficient,  $m_{\eta}^{(m.d.)}$  (cf. Eq. (21)). Similarly to the conventional definition of fragility, Eq. (15), resulting into Eq. (31), from Eq. (20), we similarly arrive then at

$$m_{\eta}^{(m.d.)}(T) = \frac{E_{\eta}^{(eff)}(T)}{k_B T_m}. \quad (32)$$

Computed for  $T = T_g$ , the modified definition of fragility is proportional to the classical definition, i.e.,

$$m_{\eta}^{(m.d.)}(T_g) = \left( \frac{T_g}{T_m \log(e)} \right) m_{\eta}^{(c.d.)} \quad (33)$$

holds (cf. Fig. 1). But this proportionality is valid only in such limiting case. As also shown in Fig. 1, in the range of validity of the SEE equation, the fragility index  $m_{\eta}^{(m.d.)}(T)$  is a function of temperature. Its values at  $T_{max}^{(nucl)}$ ,  $T_{max}^{(growth)}$ , or  $T_{max}^{(overall)}$  are not identical to the respective values at  $T = T_g$ . Therefore, also from such considerations it cannot be expected that the classical fragility index can be quantitatively

correlated with the location and magnitude of the maxima of nucleation, growth, and overall crystallization rates.

The nucleation, growth, and overall crystallization rates depend primarily on the activation energy,  $E_D(T)$ , and not on the effective activation energy,  $E_D^{(eff)} = E_D - T(dE_D/dT)$ , of diffusion (or of viscosity if the SEE equation holds). As demonstrated in [18] and advanced in the present paper, the effective activation energy and its substantial part  $[-T(dE_D/dT)]$  (correlated with deviations from the Arrhenius-type temperature dependence of viscosity) both affect the location and magnitude of the maxima of the nucleation and growth rates. Given that the classical fragility is a measure of deviations from the Arrhenius-type temperature dependence of viscosity, one could (in the case that the SEE equation holds) expect under certain conditions some qualitative correlation between classical fragility and nucleation-growth behavior (cf. also [10,12]). However, in order that the classical fragility index can be considered as such measure of deviations from the Arrhenius-type temperature dependence of viscosity, a particular definition of  $T_g$  has to be chosen. Following Tammann [25],  $T_g$  has to be identified with  $T_g^{(12)}$  defined by  $\eta(T_g^{(12)}) = 10^{12}$  Pa s, i.e.,  $T_g$  is defined by assigning a particular value to the viscosity at  $T_g$ . Only for such choice, classical fragility can be treated as a measure of deviation from an Arrhenius type temperature dependence. However, the glass transition temperature is not a material property, it also depends strongly on cooling or heating rates [22–24]. By this reason, the glass transition temperature is, as a rule, different from the temperature  $T_g^{(12)}$ , the fragility at the experimentally determined glass transition temperature is different from the fragility at  $T_g^{(12)}$  and  $m_{\eta}^{(c.d.)}(T_g)$  is, as a rule (if  $T_g \neq T_g^{(12)}$  holds), not a measure of deviations from Arrhenius-type temperature dependence of the viscosity. These considerations have to be also taken into account in attempts to correlate classical fragility with nucleation-growth and glass transition processes.

## 4. Summary of results and discussion

The main results of the present analysis can be summarized as follows: (i) Fragility, in the classical definition, employs viscosity as the parameter reflecting the properties of the liquid. However, primarily, it is not viscosity, but diffusion that governs nucleation and growth in deeply supercooled liquids. Consequently, the classical fragility concept can be relevant for the understanding of nucleation-growth processes only when the Stokes–Einstein–Eyring (SEE) relation holds, i.e. when the diffusion coefficient is inversely proportional to viscosity. (ii) The fulfillment of the SEE relation is a necessary but not sufficient requirement for applicability of the fragility concept to crystallization. The classical definition of fragility involves the ratio  $T_g/T$  to compute the derivative of viscosity with respect to temperature. Moreover, the value of  $T_g$  is chosen in accordance with Tammann's definition of the glass transition temperature [25] identifying it with  $T_g^{(12)}$ , defined by  $\eta(T_g^{(12)}) = 10^{12}$  Pa s, i.e., assigning a definite value of the viscosity to  $T_g$ . Only for such choice, the classical fragility can be treated as a measure of deviation from an Arrhenius type temperature dependence. (iii) Crystallization processes depend primarily not on the ratio  $T_g/T$ , but on  $T_m/T$ . This fact stimulated us to introduce here a modification of the fragility index employing in its definition not the reduced temperature  $T_g/T$ , but  $T_m/T$ . As we have shown, in particular, the maxima of the nucleation, growth, and overall crystallization rates can be expressed in terms of the modified diffusion fragility at the respective temperatures  $T_{max}^{(nucl)}$ ,  $T_{max}^{(growth)}$ , and  $T_{max}^{(overall)}$ . Only when the SEE equation holds, the diffusion fragility can be replaced by viscosity fragility in the modified definition. As a rule, the modified viscosity fragility computed at these temperatures  $T_{max}^{(nucl)}$ ,  $T_{max}^{(growth)}$ , and  $T_{max}^{(overall)}$  differs considerably from classical fragility computed in terms of  $T_g/T$  and taken at  $T = T_g = T_g^{(12)}$ . Thus, the classical fragility is expected to correlate with typical features of the nucleation-growth processes only in exceptional cases. (iv) For different classes of glass-forming melts vitrified or heated up within a limited range of cooling or heating rates, well-defined correlations

between the glass transition temperature and melting temperature such as  $(T_g/T_m) \approx 2/3$  or  $(T_g/T_m) \approx 1/2$  may exist. In such cases, the melting temperature can be replaced by the glass transition temperature in the relations derived here (cf. Eqs. (13), (25)–(30)). This fact allows us to develop a general, model-independent interpretation of correlations between nucleation-growth characteristics and the glass transition temperature or the reduced glass transition temperature, respectively. Based on the above summarized results, we reconfirm the experimental finding that homogeneous nucleation in silicate glass-forming melts is observed only at reduced temperatures below  $(T_g/T_m) \approx 0.58 - 0.60$ . For higher reduced glass transition temperatures, the nucleation induction times are too long and the nucleation rate is too low to yield measurable results in laboratory time scales.

## 5. Conclusions

Possible correlations of fragility index and reduced glass transition temperature with the crystallization kinetics are analyzed. The location and magnitude of the maxima of nucleation, growth, and overall crystallization rates can be interpreted in terms of a newly defined fragility index, which is proportional to the effective activation energy of diffusion at the temperatures corresponding to these maxima. By this reason, one of the restrictions of applying the classical fragility concept to crystallization consists in the decoupling of diffusion and viscosity at deep undercoolings. With respect to both the applicability of fragility concepts and the description of nucleation-growth processes it is, therefore, of considerable interest to establish for a given system the temperature range where the SEE equation breaks down. This topic is addressed in detail in an accompanying paper [21]. Moreover, even in cases when the SEE equation holds, the maximum rates of crystal nucleation and growth depend primarily on the effective activation energy or the newly defined fragility index computed at the temperature corresponding to these maxima, and not at the glass transition temperature  $T_g = T_g^{(12)}$ . This is a second factor limiting the applicability of the classical fragility index to crystallization. Based on the abovementioned theoretical results concerning the location and magnitude of the maxima of nucleation and growth rates, and dependencies between glass transition temperature and melting temperature, the origin of the previously reported correlation between reduced glass transition temperatures and the magnitudes of nucleation and growth rates is clarified.

## Acknowledgments

Financial support from the German Academic Exchange Council (DAAD, Project No. A/14/02369) and the Heisenberg-Landau program of the German Ministry of Science and Technology (BMBF) is highly acknowledged. Generous and continuous funding by the Brazilian

agencies CAPES, CNPq and São Paulo Research Foundation, FAPESP (CEPID grant No. 13/07793-6) is greatly appreciated as well.

## References

- [1] W. Höland, G.H. Beall, *Glass-ceramic Technology*, Second edition Wiley, New Jersey, 2012.
- [2] K.F. Kelton, A.L. Greer, *Nucleation in Condensed Matter: Applications in Materials and Biology*, Pergamon, Amsterdam, 2010.
- [3] I.S. Gutzow and J.W.P. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization* (First edition, Springer, Berlin, 1995; Second enlarged edition, Springer, Heidelberg, 2013).
- [4] G. Tammann, *Z. Elektrochem.* 10 (1904) 532.
- [5] P.F. James, *Volume nucleation in silicate glasses*, in: M.H. Lewis (Ed.), *Glasses and Glass-ceramics*, Chapman and Hall, New York, 1989.
- [6] E.D. Zanotto, *J. Non-Cryst. Solids* 89 (1987) 361.
- [7] E.D. Zanotto, M.C. Weinberg, *Phys. Chem. Glasses* 30 (1989) 186.
- [8] V.M. Fokin, E.D. Zanotto, J.W.P. Schmelzer, *J. Non-Cryst. Solids* 321 (2003) 52.
- [9] V.M. Fokin, M.L.F. Nascimento, E.D. Zanotto, *J. Non-Cryst. Solids* 351 (2005) 789.
- [10] L.S.A. Gallo, T.M. Mosca, B.H. Teider, I.G. Polyakova, A.C.M. Rodrigues, E.D. Zanotto, V.M. Fokin, *J. Non-Cryst. Solids* 408 (2014) 102.
- [11] J. Orava, A.L. Greer, *J. Chem. Phys.* 140 (2014) 214504.
- [12] G. Wilde, *Early stages of crystal formation in glass-forming metallic alloys*, in: J.W.P. Schmelzer (Ed.), *Glass: Selected Properties and Crystallization*, de Gruyter, Berlin 2014, pp. 95–136.
- [13] W. Oldekop, *Glastech. Ber.* 30 (1957) 8.
- [14] W.T. Laughlin, D.R. Uhlmann, *J. Phys. Chem.* 76 (1972) 2317.
- [15] C.A. Angell, *Science* 267 (1995) 1924.
- [16] L.-M. Martinez, C.A. Angell, *Nature* 410 (2001) 663.
- [17] S.V. Nemilov, *Thermodynamic and Kinetic Aspects of the Vitreous State*, CRC Press, Boca Raton, 1995.
- [18] J.W.P. Schmelzer, A.S. Abyzov, V.M. Fokin, C. Schick, E.D. Zanotto, *Crystallization in glass-forming liquids: maxima of nucleation, growth, and overall crystallization rates*, *J. Non-Cryst. Solids* (2015) (submitted for publication).
- [19] J.W.P. Schmelzer, E.D. Zanotto, I. Avramov, V.M. Fokin, *J. Non-Cryst. Solids* 352 (2006) 434.
- [20] I. Markov, *Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy*, World Scientific, Singapore, 2002.
- [21] J.W.P. Schmelzer, A.S. Abyzov, V.M. Fokin, C. Schick, E.D. Zanotto, *Crystallization in glass-forming liquids: effects of decoupling of diffusion and viscosity on crystal growth*, *J. Non-Cryst. Solids* (2015) (submitted for publication).
- [22] J.W.P. Schmelzer, *J. Chem. Phys.* 136 (2012) 074512.
- [23] O.V. Mazurin, *Glas. Phys. Chem.* 33 (2007) 22.
- [24] T.V. Tropin, J.W.P. Schmelzer, C. Schick, *J. Non-Cryst. Solids* 357 (2011) 1291 (1303).
- [25] G. Tammann, *Der Glaszustand*, Leopold Voss Verlag, Leipzig, 1933.
- [26] W. Kauzmann, *Chem. Rev.* 43 (1948) 219.
- [27] J.W.P. Schmelzer, I.S. Gutzow, *Glasses and the Glass Transition*, Wiley-VCH, Berlin-Weinheim, 2011.
- [28] V.G. Baidakov, *Explosive Boiling of Superheated Cryogenic Liquids*, Wiley-VCH, Berlin-Weinheim, 2007.
- [29] V.G. Baidakov, *Crystallization of undercooled liquids: results of molecular dynamics simulations*, in: J.W.P. Schmelzer (Ed.), *Glass: Selected Properties and Crystallization*, de Gruyter, Berlin 2014, pp. 481–520.
- [30] M.D. Ediger, P. Harrowell, L. Yu, *J. Chem. Phys.* 128 (2008) 034709.
- [31] S. Reinsch, M.L.F. Nascimento, R. Müller, E.D. Zanotto, *J. Non-Cryst. Solids* 354 (2008) 5386.
- [32] M.L.F. Nascimento, E.B. Ferreira, E.D. Zanotto, *J. Chem. Phys.* 121 (2004) 8924.
- [33] D.R. Cassar, *Crystal Nucleation, Growth, Relaxation and Viscous Flow in Diopside and Lithium Diborate Glasses* (PhD thesis) Federal University of São Carlos (UFSCar), São Carlos, Brazil, 2014.