

## Nanocrystallization of fresnoite glass. II. Analysis of homogeneous nucleation kinetics

A.A. Cabral<sup>a,\*</sup>, V.M. Fokin<sup>b,1</sup>, E.D. Zanotto<sup>b,\*</sup>

<sup>a</sup> Department of Exact Sciences, Federal Center for Technological Education – CEFET/MA, 65065-021 São Luis, MA, Brazil

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

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### Abstract

We analyzed internal (homogeneous) nucleation rates in an almost stoichiometric fresnoite ( $2\text{BaO} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$ ) glass using the classical nucleation theory (CNT) with experimental viscosity data and calculated thermodynamic quantities. Assuming, first, that the nucleus-melt surface energy is size and temperature-independent,  $\sigma \equiv \sigma_\infty$ , the CNT offered a good description of the temperature dependence of the steady-state nucleation rate  $I_{\text{st}}(T)$  over a wide temperature range, above and below  $T_g$ , but failed to predict the pre-exponential factor, confirming previous tests performed on other silicate glasses. The congruence between theory and experiment was restored with a (fitted) temperature-dependent  $\sigma$ . The main thermodynamic and kinetic parameters of the CNT were investigated to explain the extremely high nucleation rates measured in this glass:  $I_{\text{max}} \sim 10^{16} \text{m}^{-3} \text{s}^{-1}$  ( $T_{\text{max}} \approx 740^\circ\text{C}$ ,  $T_g \approx 710^\circ\text{C}$ ). The viscosity at  $T_{\text{max}}$  was found to be quite close to that of other silicate glasses that display homogeneous nucleation, such as  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$  and  $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ . Therefore, the lowest thermodynamic barrier for nucleation in fresnoite glass, as compared with other silicate glasses, is responsible for these high crystal nucleation rates.

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### 1. Introduction

In the past two decades, the classical nucleation theory (CNT) has been tested for several silicate glasses that nucleate homogeneously, e.g., James [1], Zanotto and James [2], and Gonzalez-Oliver [3]. All these studies have revealed considerable differences between experimental and theoretical crystal nucleation rates, and several reasons have been put forward to explain this discrepancy. In the last few years, three of these possible reasons have been intensively investigated: the possibil-

ity of metastable phase nucleation in the early stages of phase transformation [4], a likely temperature and size dependence of surface energy [5,6], and the potential role of elastic strain energy [7,8].

In a previous paper, Cabral et al. [9] obtained, for the first time, the homogeneous nucleation rate versus temperature curve in a glass having an almost stoichiometric fresnoite composition ( $2\text{BaO} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2 - \text{B}_2\text{TS}_2$ ). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed to estimate the nucleation rates. A reasonable agreement was found between the steady-state nucleation rates obtained from the number densities of nucleated crystals,  $N(t)$ , estimated directly from SEM micrographs and those calculated by fitting experimental crystal growth rates and overall crystallized fractions – measured via SEM and XRD, respectively, – to the JMAK equation. According to Ref. [9], fresnoite displays a maximum internal nucleation rate,

\* Corresponding authors.

E-mail addresses: [acabraljr@cefet-ma.br](mailto:acabraljr@cefet-ma.br) (A.A. Cabral), [dedz@power.ufscar.br](mailto:dedz@power.ufscar.br) (E.D. Zanotto).

<sup>1</sup> On sabbatical leave from the S.I. Vavilov's State Optical Institute, 36-1 Babushkina 193171, St. Petersburg, Russia.

$I_{\max}$ , of about  $10^{17} \text{ m}^{-3} \text{ s}^{-1}$ , the highest reported so far for inorganic glasses. The last value was obtained from the JMAK equation. However, since this method was only used to estimate  $I_{\text{st}}$  at some temperatures, the experimental nucleation rates measured *directly* from SEM micrographs were used in the present analysis. In this case,  $I_{\max}$  is about  $10^{16.5} \text{ m}^{-3} \text{ s}^{-1}$ .

The nucleation data for fresnoite glass were then combined with viscosity data to examine the predictive power of the CNT. The predicted temperature dependence  $I_{\text{st}}(T)$  was compared with the experimental data and the pre-exponential term of the nucleation rate equation was obtained from the experimental nucleation data and compared with its theoretical value. In addition, we investigated the main parameters of CNT to explain the reasons for the very high nucleation rates in fresnoite glass.

## 2. Theory

The theoretical aspects concerning the CNT are extensively discussed in several papers, so only a brief summary of the main equations used in this paper is given below.

The steady-state homogeneous nucleation rate,  $I_{\text{st}}$ , can generally be written as, see e.g., [1]:

$$I_{\text{st}} = A \exp \left[ - \left( \frac{W^* + \Delta G_{\text{D}}}{kT} \right) \right], \quad (1)$$

where  $A$  is a weakly temperature-dependent term,  $W^*$  and  $\Delta G_{\text{D}}$  are the thermodynamic and kinetic barriers for nucleation, respectively, and  $k$  is the Boltzmann constant.

The pre-exponential term  $A$  is approximately:

$$A = \frac{n_V kT}{h}, \quad (2)$$

where  $n_V$  is the number of formula units per unit volume of glass and  $h$  is Planck's constant.

$W^*$  is given by

$$W^* = g \frac{\sigma^3}{\Delta G_V}, \quad (3)$$

where  $\Delta G_V$  ( $\Delta G_V = \Delta G/V_m$ ) is the free energy change per unit volume of crystal,  $\Delta G$  the free energy change per mole,  $V_m$  the molar volume of the crystalline phase,  $\sigma$  the free energy per unit area of crystal/melt interface, and  $g$  represents the shape factor that corresponds to  $16\pi/3$  in the case of spherical nuclei.

CNT-based tests are often carried out assuming that the surface energy does not vary with temperature and nucleus size. Hereinafter, we will denote the surface energy corresponding to this approach as  $\sigma_{\infty}$ .

The crystal–liquid surface energy,  $\sigma_{\infty}$ , is usually estimated through the semi-empirical Turnbull–Scapski expression [10]:

$$\sigma_{\infty} = \frac{\alpha \Delta H_m}{N_A^{1/3} V_m^{2/3}}, \quad (4)$$

where  $\alpha$  is an empirical adimensional coefficient denominated *reduced surface energy* ( $0.40 < \alpha < 0.55$  for homogeneous nucleation in silicate glasses),  $\Delta H_m$  is the melting enthalpy per mole, and  $N_A$  is Avogadro's number.

Analyses of nucleation rate data using CNT require accurate thermodynamic data. If the difference of specific heat between the crystal and undercooled liquid is negligible,  $\Delta G$  can be estimated by the Turnbull expression:

$$\Delta G = - \frac{\Delta H_m \Delta T}{T_m}, \quad (5)$$

$$\Delta T \equiv T_m - T,$$

where  $T_m$  is the melting temperature. This expression gives an upper bound for  $\Delta G(T)$ . Several other expressions for  $\Delta G(T)$  exist and most of them are directly proportional to  $\Delta T$  (e.g., see Ref. [10]).

Inserting Eq. (5) into Eq. (3), one has:

$$W^* = \frac{16\pi\sigma^3 V_m^2 T_m^2}{3\Delta H_m^2 \Delta T^2}. \quad (6)$$

If one neglects a possible breakdown of the Stokes–Einstein equation at deep undercooling ( $\Delta T/T_m \sim 0.5$ – $0.6$ ) and expresses the kinetic barrier in terms of viscosity, Eq. (1) can be rewritten as:

$$I_{\text{st}} = \frac{A'T}{\eta} \exp \left( - \frac{W^*}{kT} \right), \quad (7)$$

$$A' = \frac{n_V k}{3\pi\lambda^3} = \frac{h}{3\pi\lambda^3 T} A,$$

where  $\lambda$  is the characteristic size parameter of the ‘structural’ units of the melt, which can be approximately estimated by  $\lambda^3 \cong 1/n_V$ . Therefore, if the temperature dependence of the nucleation rate is well described by Eq. (7), plots of  $\ln(I_{\text{st}}\eta/T)$  versus  $1/(T\Delta T^2)$ , traced using experimental data for  $I_{\text{st}}$  and  $\eta$ , should produce straight lines, whose slope and intercept can be used to evaluate  $\sigma_{\infty}$  and  $A'$ , respectively.

Because the Turnbull approximation for the thermodynamic driving force gives an upper bound for  $\Delta G$ , it should be emphasized that using Eq. (5) leads to a minimum calculated pre-exponential value [10,11].

## 3. Results

Fig. 1 summarizes some steady-state crystal nucleation rates measured for silicate glasses that nucleate

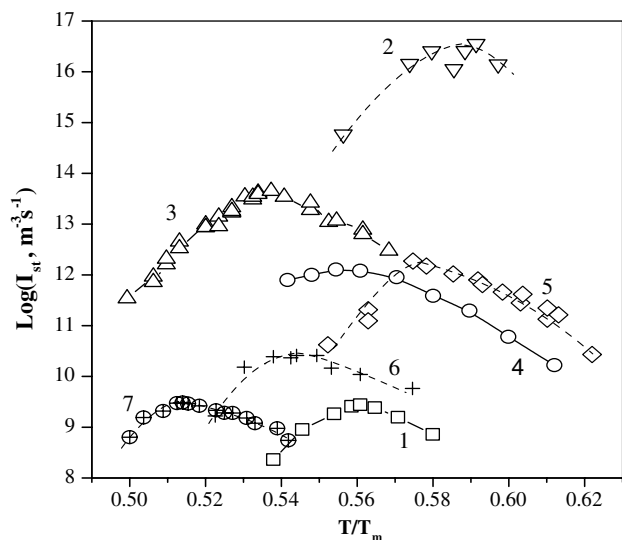


Fig. 1. Experimental steady-state nucleation rates as a function of the reduced temperature for silicate glasses that nucleate internally: (1)  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  [6]; (2)  $2\text{BaO} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$  [9]; (3)  $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$  [13]; (4)  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$  [14]; (5)  $\text{BaO} \cdot 2\text{SiO}_2$  [17]; (6)  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  with 0.2 mol%  $\text{H}_2\text{O}$  [16]; (7)  $44\text{Na}_2\text{O} \cdot 56\text{SiO}_2$  [15]. Lines are placed to guide the eyes.

internally. The nucleation rates of fresnoite glass are several orders of magnitude greater than those obtained for other silicate glasses, being almost 2.5 orders of magnitude higher than that obtained for the stoichiometric  $2\text{Na}_2\text{O} \cdot 1\text{CaO} \cdot 3\text{SiO}_2$  glass – the second best in the plot.

To analyze these nucleation rates in terms of the CNT, one must know the thermodynamic driving force and the viscosity. Klyuev kindly measured the viscosity of stoichiometric fresnoite glass for us in the low temperature range, from 727 to 780 °C, with the special penetration method described in Ref. [12]. These data were then combined with the high temperature measurements of Ref. [9] to fit a Vogel–Fulcher–Tammann equation (VFT) that describes the viscosity in the entire temperature range, as shown in Fig. 2.

To estimate the thermodynamic driving force via Turnbull's approximation, Eq. (5), one must know the melting enthalpy but, to the best of our knowledge, the  $\Delta H_m$  of fresnoite has not yet been determined. This parameter can be roughly estimated from DSC traces since its value is proportional to the melting peak area. We then compared the DSC curves of  $\text{B}_2\text{TS}_2$  and  $\text{NC}_2\text{S}_3$  glasses, using the latter as reference. Two samples having almost the same weight (37.1 and 36.5 mg for  $\text{NC}_2\text{S}_3$  and  $\text{B}_2\text{TS}_2$ , respectively) were used in the DSC runs. To ensure contact with the crucibles was similar, the specimens were ground and polished together to a similar geometrical shape. They were then heated separately at 20 K/min up to 1470 °C in air. Analyses of the respective DSC curves using commercial software yielded the ratio between the heat of melting of the

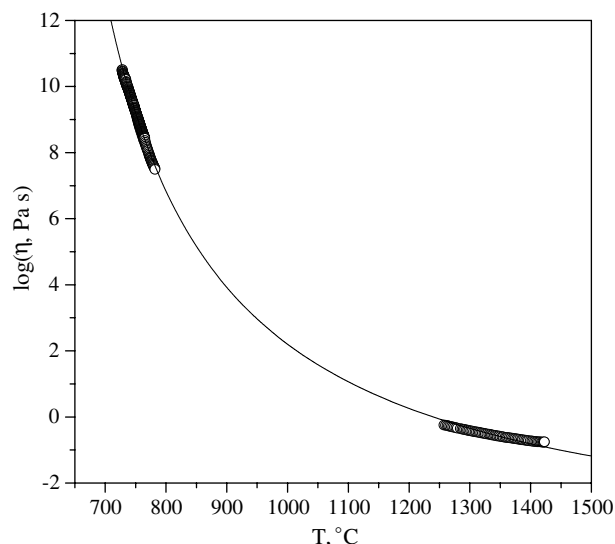


Fig. 2. Viscosity of the  $2\text{BaO} \cdot \text{TiO}_2 \cdot 2\text{SiO}_2$  glass. The line was plotted using the following VFT equation:  $\log(\eta) = -4.50 + 3278/(T - 510.6)$ . ( $T$  (°C),  $\eta$  in Pa s).

reference sample ( $\text{NC}_2\text{S}_3$ ) and that of fresnoite – 1.0:0.8. Then, taking into account the corresponding molar weights and the known melting enthalpy of  $\text{NC}_2\text{S}_3$ ,

$\Delta H_m(\text{NC}_2\text{S}_3) = 91.21 \text{ kJ/mol}$  ( $\cong 7.2 \times 10^8 \text{ J/m}^3$ ), we obtained  $\Delta H_m(\text{B}_2\text{TS}_2) \cong 106 \text{ kJ/mol}$  ( $\cong 9.22 \times 10^8 \text{ J/m}^3$ ).

The steady-state nucleation rates estimated from SEM micrographs (Table 1) and the experimental viscosity were used to plot the  $\ln(I_{st}\eta/T)$  versus  $1/(T\Delta T^2)$  curve shown in Fig. 3. A straight line was fitted over the entire temperature range studied, as predicted by Eq. (7). An intercept equal to  $A' \approx 10^{58} \text{ J/Km}^6$  was obtained. This value corresponded to  $A_{\text{exp}} \approx 10^{68} \text{ m}^{-3} \text{ s}^{-1}$ , which was about 26 orders of magnitude greater than the theoretical one ( $A = 10^{42} \text{ m}^{-3} \text{ s}^{-1}$  calculated by Eq. (2)). The slope of the  $\ln(I_{st}\eta/T)$  versus  $1/T\Delta T^2$  plot yielded  $\sigma_\infty = 0.213 \text{ J/m}^2$ . Using Eq. (4) resulted in  $\alpha = 0.4$ .

The main parameters used to compute the experimental pre-exponential term and the reduced surface energy of fresnoite glass are given in Table 2.

Table 1  
Nucleation rates of fresnoite crystals estimated from SEM [9]

$T$ , K	$I \times 10^{-16}$ , $\text{m}^{-3} \text{ s}^{-1}$
953	0.06
983	1.42
993	2.54
1003	1.13
1008	2.57
1013	3.55

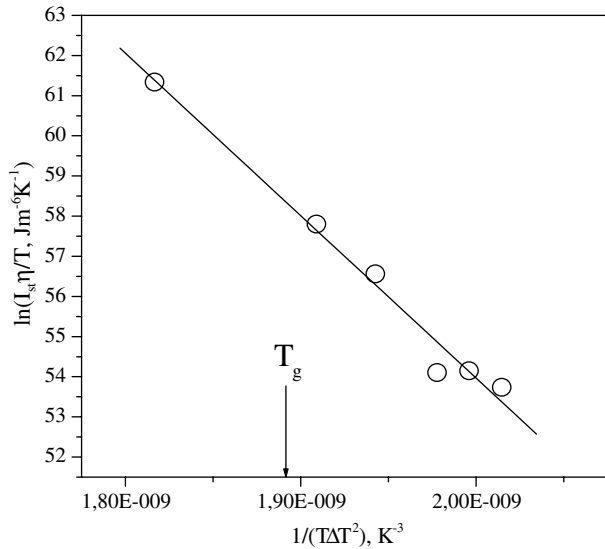


Fig. 3.  $\ln(I_{st}\eta/T)$  versus  $1/T\Delta T^2$  for  $2\text{BaO}\cdot\text{TiO}_2\cdot 2\text{SiO}_2$  glass. Crystal nucleation rates from Cabral et al. [9].

#### 4. Discussion

Fresnoite glass displays the highest nucleation rates so far reported for silicate glasses that nucleate homogeneously (are free of nucleating agents), which are comparable to the nucleation rate of some metallic glasses [10]. According to Eqs. (1) and (7), high crystal nucleation rates are due to small kinetic barriers (estimated through viscosity) or thermodynamic barriers ( $W^*$ ), or both. Hence, to understand these high nucleation rates, we must analyze both barriers, comparing their magnitudes with those of some stoichiometric silicate glasses that nucleate homogeneously:  $2\text{Na}_2\text{O}\cdot\text{CaO}\cdot 3\text{SiO}_2$  ( $\text{N}_2\text{CS}_3$ ),  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$  ( $\text{NC}_2\text{S}_3$ ),  $\text{Ba}_2\text{O}\cdot 2\text{SiO}_2$  ( $\text{BS}_2$ ) and  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  ( $\text{LS}_2$ ).

##### 4.1. Analysis of viscosity

Fig. 4 illustrates the  $\eta(T_r)$  curve obtained for each glass discussed above. The  $\eta(T_{\max})$  of  $\text{B}_2\text{TS}_2$  glass is almost two orders of magnitude lower than that obtained for  $\text{LS}_2$ , while the  $\eta(T_{\max})$  of fresnoite is quite close to that of  $\text{N}_2\text{CS}_3$ . Thus, viscosity is *not* a determining factor to explain the high nucleation rates of fresnoite.

##### 4.2. Analysis of $W^*/kT$

Previous tests carried out by various authors on several glasses [1–3,10,11] have demonstrated that, if one

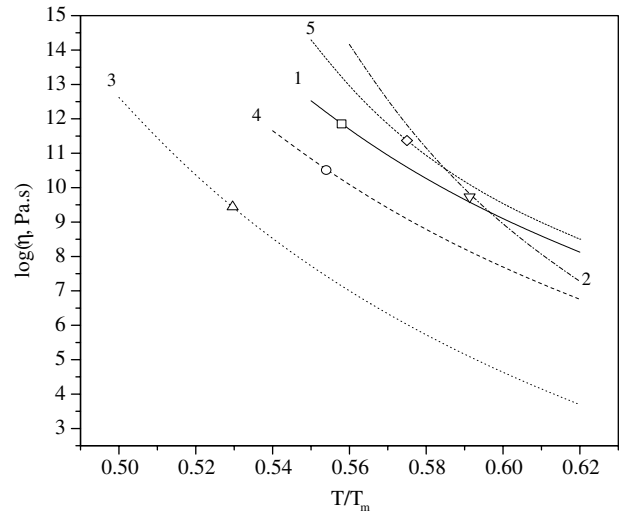


Fig. 4. Viscosity curves for several silicate glasses that nucleate internally. The lines were fitted using the corresponding VFT equations for: (1)  $\text{LS}_2$ ; (2)  $\text{B}_2\text{TS}_2$ ; (3)  $\text{N}_2\text{CS}_3$ ; (4)  $\text{NC}_2\text{S}_3$ ; and (5)  $\text{BS}_2$ . The points denote viscosity at the reduced temperatures of maximum nucleation rates.

assumes that the diffusion process at the nucleus/liquid interface is equal to that of viscous flow *or* to the molecular rearrangement process that controls the nucleation time-lag, and assuming a constant value of  $\sigma_\infty$ , the CNT gives a good description of the temperature dependence of  $I_{st}(T)$ , but *fails* in predicting the pre-exponential factor. These previous findings agree with the results reported here. However, in contrast with previous tests for  $\text{LS}_2$  and  $\text{NC}_2\text{S}_3$  glasses [1–3], Fig. 3 shows that the straight line for fresnoite glass includes temperatures above and below  $T_g$ , which reinforces the statement that, within the present approximations, the CNT can describe the *temperature dependence* of nucleation rates.

For purposes of comparison, the values of  $\sigma_\infty$  and  $\alpha$  for some stoichiometric silicate glasses that display homogeneous nucleation are compiled in Table 3. Fresnoite has the second lowest value of  $\alpha$ . However, the approximation of temperature- and size-independent surface energy results in drastic discrepancies between the theoretical and experimental values of pre-exponential terms for fresnoite glass. Table 3 indicates that the use of similar approximations to calculate the pre-exponential terms for other silicate glasses leads to the same behavior.

This discrepancy can be avoided if one uses the theoretical pre-exponential term given by Eq. (2) and calculated values of  $\sigma(T)$ , see, e.g., [6]. In this case,  $W^*/kT$  can be calculated from Eq. (7) as

Table 2

Parameters used to calculate the experimental pre-exponential term,  $A$ , and the reduced surface energy,  $\alpha$ , of fresnoite glass

$\rho$ (g/cm <sup>3</sup> ) crystal	$V_m$ (m <sup>3</sup> /mol)	$T_m$ (K)	$B^a$	$C^a$ (°C)	$T_0^a$ (°C)	$\Delta H_m$ (kJ/mol)
4.41	$115 \times 10^{-6}$	1713	-4.5	3278	510.6	106

<sup>a</sup> VFT equation:  $\text{Log } \eta = B + C/(T - T_0)$ ;  $\eta$  in Pas and  $T$  (°C).

Table 3

Surface energies, melting enthalpies and ratios between theoretical and experimental pre-factors for several silicate glasses

Glass	$\sigma_\infty$ J/m <sup>2</sup>	Average value of $\sigma(T)$ J/m <sup>2</sup>	$\alpha$	$\Delta H_m \times 10^{-8}$ J/m <sup>3</sup>	$\log(A_{\text{exp}}/A)$
LS <sub>2</sub> [6]	0.200	0.152	0.440	9.36	16
BS <sub>2</sub> [17]	0.130	0.103	0.510	5.11	13
NC <sub>2</sub> S <sub>3</sub> [14]	0.164	0.131	0.385	7.22	15
N <sub>2</sub> CS <sub>3</sub> [13]	0.143	0.096	0.467	5.0	25
B <sub>2</sub> TS <sub>2</sub> [9]	0.213	0.123	0.400	9.22	26

 $\Delta G$  calculated with the Turnbull equation.

$$\frac{W^*}{kT} = -\text{Ln} \left( \frac{I_{\text{st}} \eta}{A' T} \right). \quad (8)$$

Fig. 5 shows  $W^*/kT$  as a function of reduced temperature for different silicate glasses. As expected, fresnoite has the *lowest* thermodynamic barrier, thus favoring high crystal nucleation rates. Such low values of  $W^*/kT$  (compared with other silicate glasses) may be caused by a high thermodynamic driving force or a low surface energy. These parameters will be discussed in the following paragraphs.

#### 4.2.1. Analysis of the thermodynamic driving force

Using the melting enthalpy per unit volume of some glasses that nucleate internally, Fig. 6 was traced to show the temperature dependence of the thermodynamic driving force per unit volume,  $\Delta G_V$ , computed through Eq. (5). As can be seen, the  $\Delta G_V$  of fresnoite and lithium disilicate are higher than those of the other glasses. Thus, the low thermodynamic barrier for the nucleation of fresnoite crystals (as compared with

NC<sub>2</sub>S<sub>3</sub> crystals) may, in principle, be explained by the high thermodynamic driving force for crystallization, which is caused by its large melting enthalpy.

Fig. 5 shows that the  $W^*$  of B<sub>2</sub>TS<sub>2</sub> is 2–4 times lower than that of LS<sub>2</sub> glass. Because these two glasses have similar  $\Delta G_V(T_r)$ , see Fig. 6, the temperature-dependent surface energy also had to be investigated.

#### 4.2.2. Analysis of the surface energy

Fig. 7 indicates that the use of the theoretical pre-exponential term to calculate the crystal/melt surface energy resulted in a slightly *positive* temperature dependence of  $\sigma(T)$  (calculated by fitting  $W^*$  to Eq. (6)). This positive temperature dependence has long been assumed to be caused by an *ordering* of the liquid in front of each nucleus, which could lead to a (local) negative entropy [10]. This is a possible explanation, albeit somewhat speculative. On the other hand, since the surface energy refers to critical nuclei whose diameters increase with temperature, this effective positive temperature dependence of the (force fitted)  $\sigma(T)$  was interpreted in Ref. [6] as resulting from the superposition of its temperature and size dependences. The average value of the

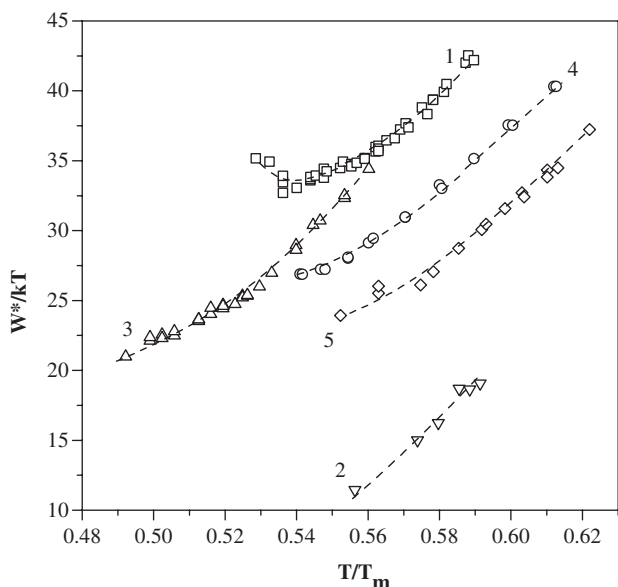


Fig. 5. Work of critical nucleus formation,  $W^*/kT$ , as a function of reduced temperature for the following glasses: (1) LS<sub>2</sub> [6]; (2) B<sub>2</sub>TS<sub>2</sub>; (3) N<sub>2</sub>CS<sub>3</sub> [13]; (4) NC<sub>2</sub>S<sub>3</sub> ( $\eta$  and  $I$  were derived from [3] and [14], respectively); (5) BS<sub>2</sub> [17].

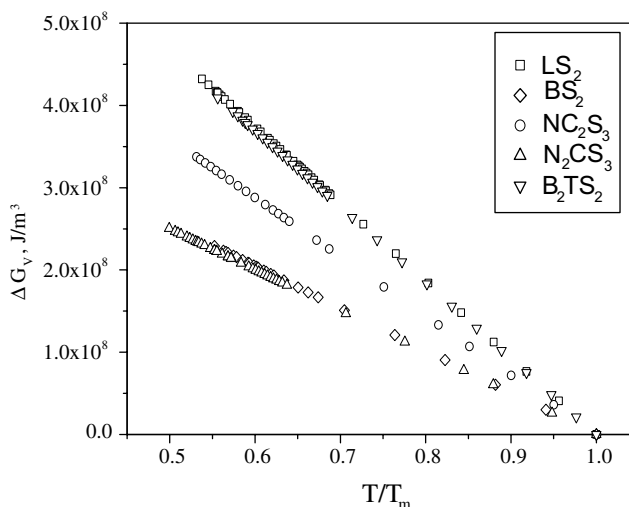


Fig. 6. Thermodynamic driving force per unit volume of crystal versus reduced temperature for stoichiometric silicate glasses that nucleate internally: 2BaO·TiO<sub>2</sub>·2SiO<sub>2</sub>; Li<sub>2</sub>O·2SiO<sub>2</sub>; 2Na<sub>2</sub>O·CaO·3SiO<sub>2</sub>; Na<sub>2</sub>O·2CaO·3SiO<sub>2</sub> and BaO·2SiO<sub>2</sub>.

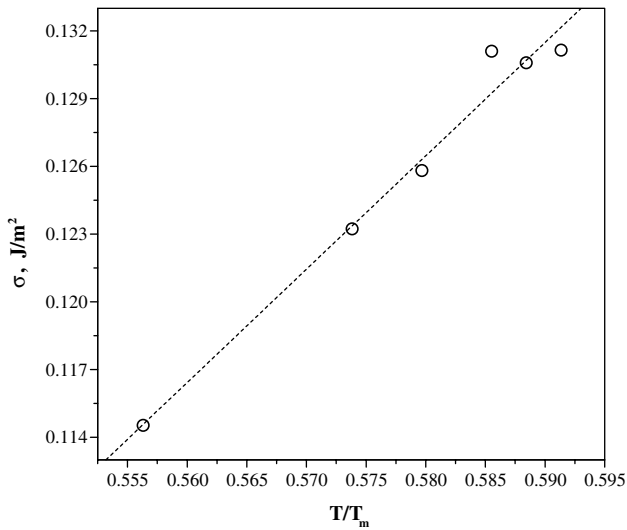


Fig. 7. Calculated nucleus/melt surface energy versus reduced temperature for fresnoite (from a fit of experimental nucleation rates to CNT).

temperature-dependent surface energy  $\sigma(T)$  for fresnoite glass is given, together with similar data for other glasses, in Table 3, which indicates that the relative significance of the surface energy,  $\sigma(T)$ , and of the thermodynamic driving force must be taken into account.

In summary, our analyses of viscosity and thermodynamic barrier data for all the glasses discussed here demonstrated that  $W^*/kT$  is the predominant factor that explains why the crystal nucleation rates of fresnoite glass are the highest so far found in inorganic glasses.

## 5. Conclusions

We analyzed crystal nucleation kinetics in an almost stoichiometric fresnoite glass based on the CNT. Using experimental homogeneous nucleation rates and viscosities, a straight line was fitted over the entire undercooling range studied. Assuming a constant nucleus-melt surface energy, the CNT provided a good description of the temperature dependence of the steady-state nucleation rates both below and above  $T_g$ , but failed in pre-

dicting their actual magnitudes, which is congruent with previous studies for other silicate glasses.

The extremely low thermodynamic barrier for nucleation of fresnoite glass, due to low crystal-melt surface energy and high thermodynamic driving force, is the main factor responsible for the very high homogeneous nucleation rates of this glass compared with those of other stoichiometric silicate glasses that undergo homogeneous nucleation.

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