

Crystal growth and viscous flow in cordierite and other glasses

N. Díaz-Mora, E. D. Zanotto¹ & V. M. Fokin²

Department of Materials Engineering, UFSCar, P.O. Box 676,
13565-905 São Carlos (SP), Brazil

Manuscript received 6 January 1997

Revision received 23 April 1997

Accepted 7 May 1997

We investigated the activation energy and activation enthalpy for crystal growth (ΔG_U , ΔH_u) and viscous flow (ΔG_η , ΔH_η) in a cordierite glass by using experimental growth rates and viscosity data. We found that ΔG_U is similar to ΔG_η in magnitude, however their temperature dependences are not equal leading to different activation enthalpies, $\Delta H_u \neq \Delta H_\eta$. This conclusion was confirmed by an analysis of literature data for six other glasses. The similarity of ΔG_U and ΔG_η indicates that bond breaking and molecular reorientation required for crystallisation is comparable to the atomic transport mechanism involved in viscous flow. Hence, to a first approximation, viscosity data may be used to estimate crystal growth rates in glasses.

In most theoretical analyses of crystal growth kinetics in undercooled melts it is assumed that molecular transport through the crystal melt interface is determined by the shear viscosity η .^(1–3) Based on this assumption the kinetic coefficient for molecular transport is substituted for the viscosity coefficient using the Stokes–Einstein relation. However, it was noted that this suggestion may not be correct due to the peculiar features of the near interface layer.^(4,5) Additionally, it was shown^(6–9) that the activation enthalpies of crystal growth and viscous flow are different for a number of vitreous systems. To get further insight into this problem we determine and compare the activation parameters of crystal growth and viscous flow using experimental data obtained with a cordierite glass and literature data for several other stoichiometric glasses.

Theory

For stoichiometric glass compositions for which there are no compositional changes on crystallisation (no long range diffusion occurs) and in situations where liberation of latent heat does not significantly alter the crystal/melt interface temperature, interfacial rear-

rangements are likely to control the crystal growth processes. In this case the attention of theoretical treatments has been directed to the nature of the interface. The three standard models used to describe the crystal growth process in glasses are based on different views of the nature of the crystal/liquid interface.⁽¹⁾ These models are: (i) the screw dislocation model; (ii) the normal or continuous growth model; and (iii) the two dimensional surface nucleation growth which are summarised in the following paragraphs.

The screw dislocation growth model

The screw dislocation growth model views the interface as smooth, but imperfect on an atomic scale, with growth taking place at step sites provided by screw dislocations intersecting the interface. The crystal growth rate, U is given by

$$U = fav \left[1 - \exp\left(-\frac{\Delta G}{RT}\right) \right] \\ v = v_0 \exp\left(-\frac{\Delta G_u}{RT}\right) \quad (1)$$

where v is the frequency of atomic jumps at the interface, v_0 the vibration frequency of the growth controlling atoms, ΔG_u the activation free energy for diffusion across the interface, a the distance advanced by the interface in a unit kinetic process (usually taken as a molecular diameter), ΔG the motivating free energy per mole and R the gas constant. The fraction of sites on the interface where atoms can preferentially be added or removed, f , is given⁽¹⁾ by

$$f = \frac{a\Delta H_m \Delta T}{4\pi\sigma_E T_m V_m} \approx \frac{\Delta T}{2\pi T_m} \quad (2)$$

where ΔH_m is the molar heat of melting, V_m the molar volume, σ_E the specific edge surface energy of the crystal, T_m the thermodynamic melting point and ΔT ($\Delta T = T_m - T$) is the undercooling.

¹ Author to whom correspondence should be addressed. (e-mail: dedz@power.ufscar.br)

² On sabbatical leave from The Grebenshikov Institute of Silicate Chemistry, Russian Academy of Science, ul. Odoevskogo 24/2, St Petersburg, 199155 Russia

Taking into account that

$$\begin{aligned} \Delta G_U &= \Delta H_U - T\Delta S_U \\ \Delta S &= -\partial G_U / \partial T = (\Delta H_U - \Delta G_U) / T \end{aligned} \quad (3)$$

where ΔH_U and ΔS_U are the enthalpy and entropy of activation, Equation (1) can be expressed by

$$U = f a v_0 \exp\left(-\frac{\Delta H_U}{RT} + \frac{\Delta S_U}{R}\right) \left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right] \quad (4)$$

or

$$\ln \left\{ \frac{U}{a f \left(1 - \exp\left(-\frac{\Delta G}{RT}\right)\right)} \right\} = \ln v_0 + \frac{\Delta S_U}{R} - \frac{\Delta H_U}{RT} \quad (4a)$$

Equation (4a) gives the typical 'Arrhenius' plots frequently used to obtain activation enthalpies in limited temperature ranges. In this paper we use this equation and also another procedure which will be described in a following section.

Normal growth

In the framework of the normal growth model the interface is pictured as rough on atomic scale and all sites on the interface are assumed to be equivalent growth sites ($f \sim 1$). The growth rate is expressed by Equation (1) with $f=1$.

The surface nucleation growth model

According to the surface nucleation growth model the crystal/liquid interface is smooth on an atomic scale and free of intersecting screw dislocations. Thus, crystal growth can take place by (secondary) surface nucleation and lateral spread of two-dimensional nuclei on the interface. This mechanism is presumed to be relatively rare for silicate glasses. The growth rate is expressed⁽¹⁾ by

$$U = C v \exp(-B/T\Delta G) \quad (5)$$

where C and B depend on the time required for the formation of the nucleus relative to that required for its propagation across the interface.

Jackson's model for crystal growth. Jackson^(10,11) has proposed a quite successful approach based on a consideration of the interface morphology and on the entropy of fusion, ΔS_m . In his model, materials with small entropies of fusion ($\Delta S_m < 2R$), such as SiO_2 and GeO_2 , crystallise with nonfaceted interface morphologies, exhibit interface site factors which are independent of undercooling and kinetics of the form predicted by the normal growth model should be observed. In contrast, materials with large entropies of fusion ($\Delta S_m > 4R$), such as most oxide crystals, crystallise with faceted morphologies and exhibit interface site factors which increase with undercooling. In that case two-dimensional surface nucleation or screw dislocation growth should be observed.

In this paper we use Jackson's approach to infer the probable mechanism of crystal growth of the different glasses and then we apply the most appropriate equa-

tion to estimate the activation free energy and enthalpy of crystal growth.

Viscous flow

The temperature dependence of viscosity for most glasses is best described by a Vogel-Fulcher type expression which predicts a variable activation energy. That fact is explained by the temperature dependence of glass structure. However, in limited temperature ranges, the viscosity of typical oxide glass formers such as SiO_2 and GeO_2 with additions of alkali modifiers, R_2O can be approximated by an equation of the form⁽¹²⁾

$$\eta = \frac{RT}{N_A l^3} \tau_0 \exp\left(\frac{\Delta G_\eta}{RT}\right)$$

$$\Delta G_\eta = \Delta H_\eta - T\Delta S_\eta, \Delta S_\eta = -\partial \Delta G_\eta / \partial T \quad (6)$$

where τ_0 is a characteristic time of the order of the period of atomic vibration, l has a value of the order of the Si-O bond length, ΔG_η , ΔH_η and ΔS_η are the activation free energy, enthalpy and entropy of viscous flow, respectively, and N_A is Avogadro's number. Note that Equation (6) is analogous to the equation derived by Frenkel⁽¹³⁾ for the viscosity of a liquid. Equation (6) may also be written

$$-\ln(\eta/T) = -\ln\left(\frac{RT\tau_0}{l^3 N_A}\right) + \frac{\Delta S_\eta}{R} - \frac{\Delta H_\eta}{RT} \quad (6a)$$

Hence, from plots of $\ln(\eta/T)$ vs $1/T$ one can estimate an average activation enthalpy for viscous flow in selected temperature intervals.

Experimental

Crystal growth in a cordierite glass

The cordierite glass used in this work had 52.3SiO₂, 33.2Al₂O₃ and 14.6MgO (wt%). This almost stoichiometric glass (51.3SiO₂, 34.9Al₂O₃, 13.8MgO (wt%)) is the stoichiometric composition) was supplied by Schott Glaswerke, Germany with code GM30870. Specimens with mechanically polished surfaces were prepared using SiC and CeO₂. The crystal growth rates of three different crystal morphologies were determined by heat treating the specimens isothermally in an electric furnace for predetermined times between 820 and 920°C ($T_g \approx 800^\circ\text{C}$).

A detailed investigation of crystal morphologies by x-ray diffraction, infrared and Raman microprobe spectra⁽¹⁴⁾ demonstrated that, depending on the thermal treatment conditions, four different crystal morphologies can be observed at the surface of that cordierite glass: (i) Lozenges, denominated X-phase, which is believed to be a Mg petalite like phase;⁽¹⁴⁻¹⁶⁾ (ii) Regular and elongated hexagons which aggregate to form a compact fully crystallised surface layer with prolonged heat treatment. These crystals belong to the μ -cordierite phase;⁽¹⁴⁾ (iii) Spherical crystals which occur on fully crystallised surfaces and grow at the expense of the hexagons. These crystals constitute the α -cordierite phase;^(17,20) (iv) Square shaped crystals which appear

for high temperature treatments (~1370°C) and also belong to the α-cordierite phase.⁽¹⁴⁾ In this paper the comparative analysis of growth rates will be restricted only to morphologies (i), (ii) and (iii).

In order to measure the growth rates of the type (i) crystals (X-phase) the treated samples were etched with 1 vol% HF solution and observed under reflected light in a Nikon optical microscope equipped with an OPTOMAX-V image analyser. Plots of the largest crystal diagonal versus time were constructed for several temperatures.

The thickness of the crystal layer (type (ii) crystals or μ-cordierite) and the radius of the largest spherical crystals (type (iii) crystals or α-cordierite) were determined by means of a Jenaval Carl Zeiss/Jena optical microscope. The crystal growth rates were obtained by constructing plots similar to those of X-phase crystals.

Viscosity

The experimental viscosity data of the GM30870 glass, determined by the beam bending method at Schott Glaswerke between 800 and 900°C, were fitted to a Vogel–Fulcher–Tamann (VFT) equation, giving

$$\log_{10}\eta = -7.83 + 9488.5 / (T - 323.4) \quad (7)$$

where η is given in Pa s and T in °C.

Results

Crystal growth and viscosity of the cordierite glass

Table 1 shows several kinetic parameters for the GM30870 glass: the growth rates of the lozenge (X-phase) crystals, U_X, the thickness of the μ-cordierite crystallised layer, U_μ, and of the spherical crystals (α-cordierite), U_α, grown within a compact layer of μ-cordierite.**

Table 1 also shows the extrapolated viscosity values (using Equation (7)) to the temperature range at which the crystal growth rates were measured.

The thermodynamic driving force for crystallisation

For a single component system at a temperature T below the melting point, T_m, the motivating free energy per mole, ΔG, is given by

$$\Delta G = -\frac{\Delta H_m}{T_m}(T_m - T) - \int_T^{T_m} \Delta C_p dT' + T \int_T^{T_m} \frac{\Delta C_p}{T'} dT \quad (8)$$

where ΔC_p is the difference in specific heats between the crystalline (C_p^C) and liquid (C_p^L) phases (ΔC_p = C_p^C - C_p^L < 0) at constant pressure at a temperature T.

The thermodynamic driving force for glass–crystal transformation, ΔG is available for some glasses. However, it has not been obtained experimentally for the X-phase because this phase (as well as the μ-cordierite crystals) is metastable.⁽¹⁷⁾ Consequently the specific heats C_p^C and C_p^L, the latent heats of melting, ΔH_m and melting points, T_m are unknown. Thus, some approximations for the values of ΔH_m, T_m and ΔC_p were required to obtain ΔG.

** In the following paragraphs, the comparison of ΔG_c, ΔH_v and ΔG_η, ΔH_η is not concerned with α-cordierite crystals because they grow at the expense of the μ-cordierite crystals.

Table 1. Growth rates and viscosity of the GM30870 cordierite glass

T (°C)	U _α [10 ⁻¹⁰ m/s]	U _μ [10 ⁻¹⁰ m/s]	U _X [10 ⁻¹⁰ m/s]	log η [Pa.s]
819	–	–	0.005	11.3
839	–	–	0.05	10.6
860	1.75	2.7	–	9.8
870	–	–	0.5	9.5
880	9.7	9.2	–	9.2
890	–	–	1.4	8.9
900	29.2	25.6	–	8.6
910	37.8	49.9	3.8	8.3
920	74.5	53.6	6.6	8.1

A value of ΔH_m = 80 kJ/mol was obtained by Müller⁽²¹⁾ for the metastable μ-cordierite phase while Robie *et al*⁽²²⁾ reported that ΔH_m = 345 kJ/mol and T_m = 1740 K for the stable α-cordierite phase. As there is no data for the X-phase we used an estimate of C_p^X, obtained by Sesták⁽²³⁾ based on the Mg petalite formula (MgAl₄Si₈O₂₀) which is presumed to be close to the X-phase⁽²⁴⁾

$$C_p^X = 529.78 + 0.30139T - 13.13566 \times 10^6 T^{-2} \quad (9)$$

where C_p is given in [J/mol K].

The specific heats of cordierite liquid and glass, C_p^L and C_p^g were reported by Richet & Bottinga⁽²⁵⁾

$$C_p^L = 874.406 + 0.047168T \quad (10)$$

$$C_p^g = 582.082 + 0.14369T - 1.4584 \times 10^7 T^{-2} \quad (11)$$

To finalise, an expression for the specific heat of the stable α-cordierite crystal is given by Robie *et al*⁽²²⁾

$$C_p^a = 821.34 + 4.3339 \times 10^{-2}T - 5000.3T^{-0.5} - 8.2112 \times 10^6 T^{-2} \quad (12)$$

Equation (12) was also used for the specific heat of μ-cordierite phase.

There is no previous reference to the X-phase melting temperature, T_m^X. However, specimens heated for a few minutes at ~1623 K still had X-phase crystals. Since one cannot heat the glass for long times, because full crystallisation precludes observation of the X-phase crystals, we took this temperature (1623 K) as a lower bound for T_m. Then, due to these uncertainties in the thermodynamic quantities, ΔG was evaluated using Equation (8) with ΔH_m = 180 kJ/mol, T_m^X ≅ 1623 K and ΔC_p = C_p^X - C_p^L, Equations (12) and (10), respectively.

There is, in fact, no simple way to calculate or measure the heat of fusion ΔH_m for the X-phase, simply because we could not devise a way to crystallise a glass with a significant amount of only that single phase. For severe heat treatments other phases appear. On the other hand for a large number of complex, ternary silicate minerals, ΔH_m vary from 128 to 345 kJ/mol: for instance, it is 128–138 kJ/mol for diopside; 135 kJ/mol for anorthite; 243 kJ/mol for pyrope, 170–190 kJ/mol for μ-cordierite and 345 kJ/mol for α-cordierite. Thus, the value of ΔH_m = 180 kJ/mol used in this work for X-phase can be taken as an average value for complex silicates.

The values of C_p^X are also uncertain since they were estimated using Thermocalc software. However, the ΔG values calculated with C_p^X are bracketed by those estimated using the Hoffman approximation and by using ΔC_p = 0; the usual limits for ΔG. Hence, the use of the calculated C_p^X was justified ‘a posteriori’.

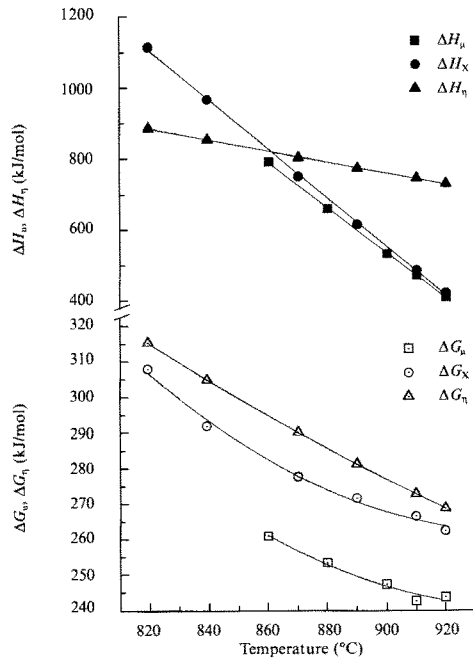


Figure 1. Activation free energies and enthalpies for crystal growth and viscous flow of cordierite glass vs temperature (μ and X correspond to μ -cordierite and X -phase, respectively)

Due to these numerous uncertainties, caused by the very complex crystallisation behaviour and scarcity of thermodynamic data for cordierite, we also determined the activation energies and enthalpies for other, simpler, glasses for which reliable thermodynamic, viscosity and crystal growth data were available.

Determination of the activation parameters

All three crystalline phases of the cordierite glass (α and μ -cordierite, and X -phase) present a faceted interface morphology. Additionally, they have a very large entropy of melting ($\Delta S_m \gg 2R$). Using Jackson's criteria^(10,11) associated to the fact that the 2D-secondary nucleation mechanism is rarely observed for silicates, we suppose that the screw dislocation mechanism of crystal growth should be most appropriate for the three phases.

The activation free energies $\Delta G_U(T)$ and $\Delta G_\eta(T)$, which largely determine the values U and η , were obtained from Equations (1) and (6), respectively. The experimental values of crystal growth rates U and viscosity η , together with $\tau_0 = 10^{-13}$ s, $\nu = 10^{13}$ s⁻¹, $l = 2 \times 10^{-8}$ cm

and $a = 9.34 \times 10^{-8}$ cm for α -cordierite and $a = 5.34 \text{ \AA}$ for μ -cordierite and X -phase were used in the calculations. The temperature dependence of $\Delta G_U(T)$, $\Delta G_\eta(T)$ are shown in Figure 1 and listed in Table 2.

Activation enthalpies ΔH_U and ΔH_η were calculated by Equations (3) and (6) using the values of ΔG_U , ΔS_U and ΔG_η , ΔS_η . Such plots are shown in Figure 1. It is also possible to estimate activation enthalpies from 'Arrhenius' plots, Figure 2: $\ln[U/af(1-\exp(-\Delta G/RT))]$ and $\ln(\eta/T)$ versus $1/T$, see Equations (4a) and (6a). The approximate values obtained in this way were close to those of the previous procedure. Plots of ΔG in Figure 2 are not linear but instead have a positive curvature which decreases with temperature. Thus, it is evident that the activation enthalpies vary with temperature

Comparison of theoretical and experimental crystal growth rates

The calculation of crystal growth rates using the viscosity coefficient is based on the assumption that the activation free energies for the crystal growth and viscous flow are equal. Then, it is possible to replace the kinetic term in Equation (1) by the reciprocal of viscosity, Equation (6) to give

$$U = \frac{\Delta T}{2\pi T_m} a \frac{kT}{l^3 \eta} \left[1 - \exp\left(-\frac{\Delta G}{RT}\right) \right] \quad (13)$$

The comparison of calculated and experimental growth rates, in fact, is similar to that performed in the previous paragraph for the activation energies ΔG_U and ΔG_η , however, it is more illustrative. Figure 3 presents the results of crystal growth rate calculations for X -phase and μ -cordierite using Equation (13) together with the experimental values. In doing these calculations the experimental values of η and ΔG , obtained from Equations (8), (10) and 12, with $a = 5.344 \times 10^{-8}$ cm, $l = 2 \times 10^{-8}$ cm were used.

In the temperature interval under study the experimental values of crystal growth rates are moderately higher than theoretical predictions. The ratio U_{exp}/U_{theor} varies with T but it is not more than 4 for the X -phase and 35 for μ -cordierite in the temperature range studied.

Generalisation for other glasses

Due to the uncertainties in the thermodynamic parameters of cordierite and also to verify if the experi-

Table 2. Activation parameters for growth and viscous flow in cordierite glass GM 30870

	ΔH_m (kJ/mol)	T_m (K)	T (°C)	ΔG_u (kJ/mol)	ΔH_u (kJ/mol)	ΔS_u (J/mol K)	ΔG_η (kJ/mol)	ΔH_η (kJ/mol)	ΔS_η (J/mol K)
α -cordierite	345	1740	860	270	968	616			
			880	258	778	451			
			900	252	595	293			
			910	251	506	215			
			920	246	418	144			
μ -cordierite	190	1740	860	261	792	469	294	817	461
			880	254	662	354	285	787	437
			900	248	536	245	277	761	413
			910	243	474	195	273	748	402
			920	244	414	142	269	732	388
X -phase	180	1623	819	308	1114	738	315	886	523
			839	292	968	608	305	854	494
			870	278	752	414	290	805	450
			890	272	618	297	281	775	424
			910	267	489	188	273	747	400
			920	263	426	137	269	732	388

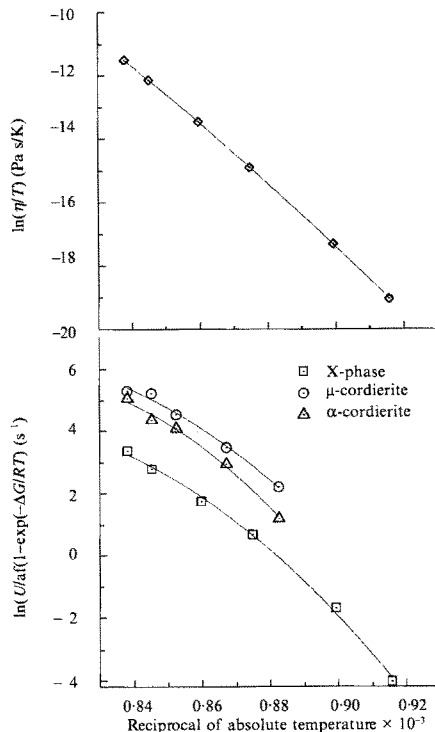


Figure 2. $\ln(\eta/T)$ and $\ln[U/a(1-\exp(-\Delta G/RT))]$ as a function of reverse temperature for a cordierite glass

mental results obtained for that glass could be generalised, literature data on the growth rate, viscosity and thermodynamic parameters for other six stoichiometric glasses were selected from the literature. Table 3 shows several parameters used to obtain ΔG and η for the analysed glasses.

For all compositions, with the exception of the $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass, crystal growth and viscosity data were obtained from the same melt conferring a great reliability to the calculations contrary to the common practice of comparing data from distinct references. The thermodynamic driving force, ΔG was also calculated for these glasses. Similarly to the analysis carried out for the cordierite glass, the activation parameters for viscous flow and crystal growth, ΔG_η , ΔH_η , ΔS_η and ΔG_U , ΔH_U and ΔS_U were estimated. Figure 4 shows ΔG_η , ΔH_η and ΔG_U , ΔH_U as a function of reduced temperature $T_r = T/T_m$ (T and T_m are given in K) for all compositions studied.

Discussion

Cordierite glass

The screw dislocation growth mechanism has been suggested for μ -cordierite by Hübner *et al.*⁽³⁸⁾ Yuritsin

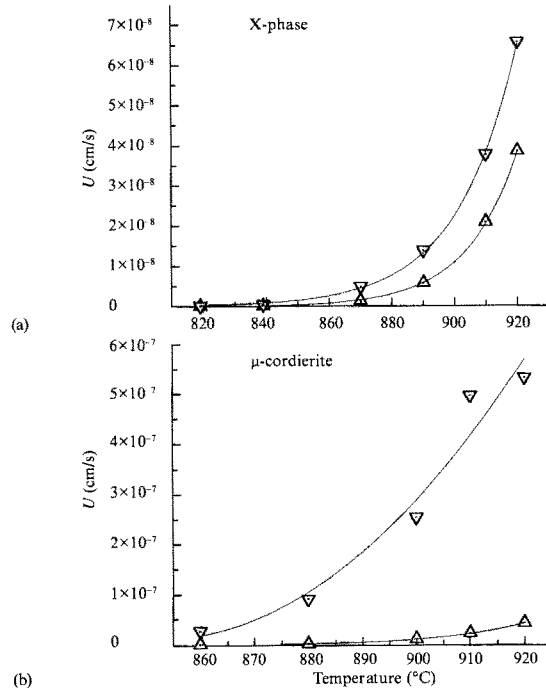


Figure 3. Experimental and calculated, Equation (13), growth rate: (a) X-phase and (b) μ -cordierite as a function of temperature Δ theory ∇ experiment

et al.⁽¹⁵⁾ have measured the growth rates of the X-phase in cordierite; however, they did not propose a growth model. No information was found about the growth kinetics of the spherical crystals of α -cordierite. Hence, based on Jackson's criteria and on the observed (faceted) interface morphologies, we assumed the screw dislocation as the most probable governing mechanism of crystal growth for these three phases of cordierite.

It is interesting to note that $U_\alpha \cong U_\mu$ (Table 1), while in the case of crystals grown in the specimen volume (nucleation catalysed by TiO_2) $U_\alpha \ll U_\mu$.⁽³⁹⁾ Thus, the transition of μ -cordierite to α -cordierite (as in the present case) proceeds more easily than the transformation of glass to α -cordierite. Müller also made similar observations for α -cordierite crystals grown within a compact surface layer of μ -cordierite perpendicular to the sample surfaces.⁽⁴⁰⁾

The values of the activation free-energies [$\Delta G_u(T)$ and $\Delta G_\eta(T)$] listed in Table 2 and plotted in Figure 1 are quite similar. It should be stressed that the uncertainty in the values of v_o , τ_o and l , in Equations (1) and (6), may introduce errors of up to 10% in the activation free energies. However, these errors do not affect the temperature dependence of these free energies.

Table 3. Literature data for thermodynamic parameters and viscosity for six stoichiometric glass forming compositions: (i) $\log_{10}\eta$, (ii) ΔC_p

Glass	ΔH_m (J/mol)	T_m (K)	(i) $\log \eta = A + B/(T - T_0)$ (Pas)			(ii) $\Delta C_p = a + bt + c/T^2$		
			A	B	T_0 (K)	a	$b \times 10^3$	$c \times 10^{-5}$
NS ₂ : $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, Data from Refs 27 & 28	35581	1147	-2.55	3889	437	48.01	-68.9	-37.8
NS ₃ : $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$, Data from Refs 27 & 29	36050	1084	-1.20	2712	563	32.23	-73.3	-15.24
LS ₂ : $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, Data from Refs 26, 27 & 30	57300	1307	-1.44	3370	460	(*)	(*)	(*)
LS ₂ ^F : $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, Data from Refs 26, 27 & 31			-7.52	6259	406	(*)	(*)	(*)
NC ₃ S ₃ : $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$, Data from Refs 27 & 32	87900	1564	-4.86	4893	547	71.41	-103.3	-56.97
N ₂ CS ₃ : $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$, Data from Refs 27, 33 & 34	64883	1448	-8.94	5376	485	71.41	-103.3	-56.55
PbB ₂ : $\text{PbO} \cdot 2\text{B}_2\text{O}_3$, Data from Refs 35-37	131859	1047	-1.94	1036	707	193.6	-346.2	-

(*) Experimental ΔG data from Ref. 26

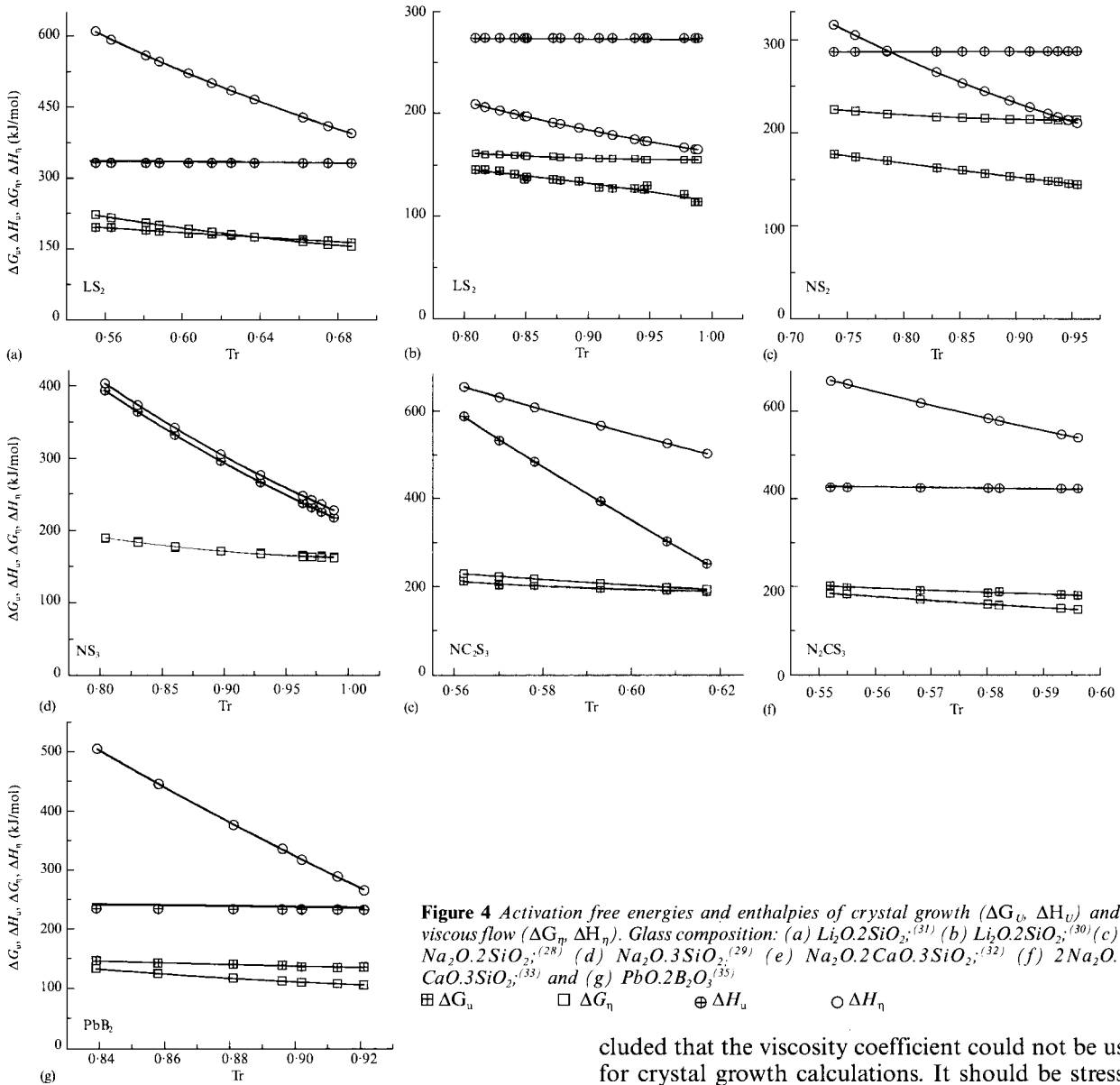


Figure 4 Activation free energies and enthalpies of crystal growth (ΔG_U , ΔH_U) and viscous flow (ΔG_η , ΔH_η). Glass composition: (a) $Li_2O \cdot 2SiO_2$;⁽³¹⁾ (b) $Li_2O \cdot 2SiO_2$;⁽³⁰⁾ (c) $Na_2O \cdot 2SiO_2$;⁽²⁸⁾ (d) $Na_2O \cdot 3SiO_2$;⁽²⁹⁾ (e) $Na_2O \cdot 2CaO \cdot 3SiO_2$;⁽³²⁾ (f) $2Na_2O \cdot CaO \cdot 3SiO_2$;⁽³³⁾ and (g) $PbO \cdot 2B_2O_3$.⁽³⁵⁾ \blacksquare ΔG_U \square ΔG_η \oplus ΔH_U \circ ΔH_η

In contrast to the activation free energies, activation enthalpies for crystal growth, $\Delta H_U = \Delta G_U - T\partial\Delta G_U/\partial T$, and viscous flow, $\Delta H_\eta = \Delta G_\eta - T\partial\Delta G_\eta/\partial T$, exhibit considerable differences (Figure 1) which result from the different temperature dependencies of ΔG_U and ΔG_η : $-\Delta S_U = \partial\Delta G_U/\partial T \neq \partial\Delta G_\eta/\partial T = -\Delta S_\eta$ (see Table 2). Slight differences in ΔS_U and ΔS_η cause appreciable differences in $T\Delta S_U$ and $T\Delta S_\eta$, Equations (3) and (6), and in the corresponding activation enthalpies.

When replacing the effective diffusion coefficient by the viscosity coefficient in the equation for crystal growth, one assumes that activation free energies of the two processes are comparable. Indeed, the results of Figure 3 and Table 2 demonstrate the similarity of these two quantities. The parallelism of ΔG_U and ΔG_η indicates that molecular reorientation or bond-breaking required for crystallisation is similar to the processes involved in viscous flow,⁽⁴¹⁾ however, $\Delta H_U \neq \Delta H_\eta$.

The fact that $\Delta H_U \neq \Delta H_\eta$ is an important finding which explains why several authors (erroneously) con-

cluded that the viscosity coefficient could not be used for crystal growth calculations. It should be stressed that, according to Eyring's theory⁽⁴²⁾ the activation free energy, not the activation enthalpy, determines the rate processes. Despite the small values of activation entropy, ΔS , the term $T\Delta S$ compensate the large values of ΔH . Therefore, if the inaccuracy in the various parameters used in the calculations and the limitations of the models are taken into account, one concludes that the observed differences of 2–34 times between the calculated and experimental growth rates of cordierite phases are not very high.

Other glasses

Figure 4 presents the activation energies ΔG_U , ΔG_η and enthalpies ΔH_U , ΔH_η as a function of reduced temperature for six other glasses. The activation enthalpies for crystal growth, ΔH_U , do not vary much, within the limits of experimental error, in the temperature interval under study, except for glasses $Na_2O \cdot 2CaO \cdot 3SiO_2$ and $Na_2O \cdot 3SiO_2$. The values of activation free energies are close for the six glasses, as observed for the cordierite glass. The growth kinetics of $Na_2O \cdot 2SiO_2$ crystals are not

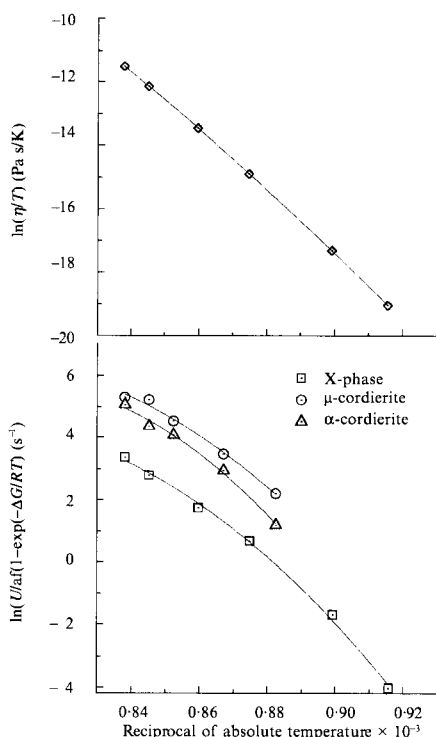


Figure 2. $\ln(\eta/T)$ and $\ln[U/af(1-\exp(-\Delta G/RT))]$ as a function of reverse temperature for a cordierite glass

mental results obtained for that glass could be generalised, literature data on the growth rate, viscosity and thermodynamic parameters for other six stoichiometric glasses were selected from the literature. Table 3 shows several parameters used to obtain ΔG and η for the analysed glasses.

For all compositions, with the exception of the $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glass, crystal growth and viscosity data were obtained from the same melt conferring a great reliability to the calculations contrary to the common practice of comparing data from distinct references. The thermodynamic driving force, ΔG was also calculated for these glasses. Similarly to the analysis carried out for the cordierite glass, the activation parameters for viscous flow and crystal growth, ΔG_η , ΔH_η , ΔS_η and ΔG_U , ΔH_U and ΔS_U were estimated. Figure 4 shows ΔG_η , ΔH_η and ΔG_U , ΔH_U as a function of reduced temperature $T_r \equiv T/T_m$ (T and T_m are given in K) for all compositions studied.

Discussion

Cordierite glass

The screw dislocation growth mechanism has been suggested for μ -cordierite by Hübner *et al.*⁽³⁸⁾ Yuritsin

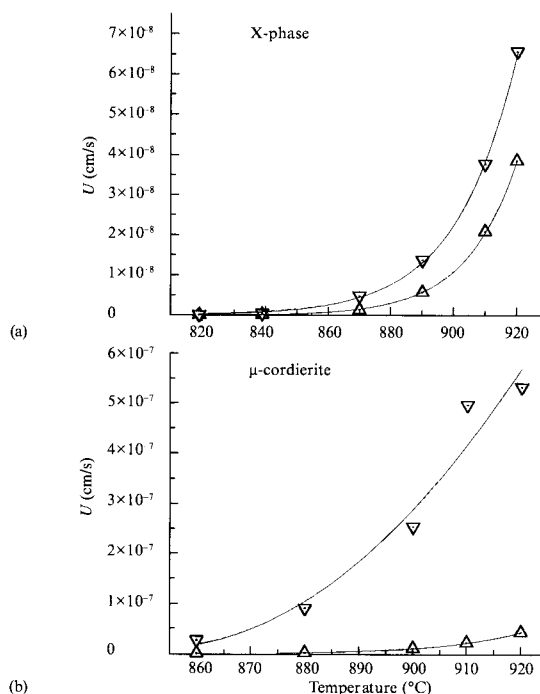


Figure 3. Experimental and calculated, Equation (13), growth rate: (a) X-phase and (b) μ -cordierite as a function of temperature Δ theory ∇ experiment

et al.⁽¹⁵⁾ have measured the growth rates of the X-phase in cordierite; however, they did not propose a growth model. No information was found about the growth kinetics of the spherical crystals of α -cordierite. Hence, based on Jackson's criteria and on the observed (faceted) interface morphologies, we assumed the screw dislocation as the most probable governing mechanism of crystal growth for these three phases of cordierite.

It is interesting to note that $U_\alpha \approx U_\mu$ (Table 1), while in the case of crystals grown in the specimen volume (nucleation catalysed by TiO_2) $U_\alpha \ll U_\mu$.⁽³⁹⁾ Thus, the transition of μ -cordierite to α -cordierite (as in the present case) proceeds more easily than the transformation of glass to α -cordierite. Müller also made similar observations for α -cordierite crystals grown within a compact surface layer of μ -cordierite perpendicular to the sample surfaces.⁽⁴⁰⁾

The values of the activation free-energies [$\Delta G_U(T)$ and $\Delta G_\eta(T)$] listed in Table 2 and plotted in Figure 1 are quite similar. It should be stressed that the uncertainty in the values of v_o , τ_o and l , in Equations (1) and (6), may introduce errors of up to 10% in the activation free energies. However, these errors do not affect the temperature dependence of these free energies.

Table 3. Literature data for thermodynamic parameters and viscosity for six stoichiometric glass forming compositions: (i) $\log_{10}\eta$, (ii) ΔC_p

Glass	ΔH_m (J/mol)	T_m (K)	(i) $\log \eta = A + B/(T - T_o)$ (Pa s)			(ii) $\Delta C_p = a + bt + ct^2$		
			A	B	T_o (K)	a	$b \times 10^3$	$c \times 10^{-5}$
NS ₂ : $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$. Data from Refs 27 & 28	35 581	1147	-2.55	3889	437	48.01	-68.9	-37.8
NS ₃ : $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$. Data from Refs 27 & 29	36 050	1084	-1.20	2712	563	32.23	-73.3	-15.24
LS ₂ : $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. Data from Refs 26, 27 & 30	57 300	1307	-1.44	3370	460	(*)	(*)	(*)
LS2 ^F : $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. Data from Refs 26, 27 & 31			-7.52	6259	406	(*)	(*)	(*)
NC ₂ S ₃ : $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$. Data from Refs 27 & 32	87 900	1564	-4.86	4893	547	71.41	-103.3	-56.97
N ₂ CS ₃ : $2\text{Na}_2\text{O}\cdot \text{CaO}\cdot 3\text{SiO}_2$. Data from Refs 27, 33 & 34	64 883	1448	-8.94	5376	485	71.41	-103.3	-56.55
PbB ₂ : $\text{PbO}\cdot 2\text{B}_2\text{O}_3$. Data from Refs 35-37	131 859	1047	-1.94	1036	707	193.6	-346.2	-

(*) Experimental ΔG data from Ref. 26

well described by any standard model.⁽¹⁾ In a simulated calculation, assuming normal growth of Na₂O.2SiO₂ crystals, the values of ΔG_{η} approximate to those of ΔG_{η} , i.e. $\Delta G_{\eta}/\Delta G_U \approx 1$. Close agreement between all activation parameters is exhibited by the Na₂O.3SiO₂ glass.

Therefore, our calculations based on our own experiments with cordierite as well as on literature data for six other glasses, indicate that the magnitudes of the activation free energies of crystal growth and viscous flow are fairly close: $\Delta G_{\eta} = \Delta H_{\eta} - T\Delta S_{\eta} \approx \Delta G_U = \Delta H_U - T\Delta S_U$. On the other hand, in general, the activation enthalpies and entropies of crystal growth and of viscous flow show distinct temperature dependencies. Hence, the high values of activation enthalpies are compensated by the term $T\Delta S$ so that $\Delta G_U \approx \Delta G_{\eta}$.

A similar conclusion was reached⁽⁷⁾ for ΔG_{η} and the free energy of activation of molecular displacement from a glass to a nucleus of critical size, ΔG_a , calculated from the time lag of nucleation. However, it should be kept in mind that the interfaces of small crystals of critical size are probably more diffuse than those of micron size crystals dealt with in crystal growth determinations.⁽⁴³⁾

Conclusions

Based on our data for a cordierite glass and on literature data for six other glasses, we demonstrated that the values of the activation free energies for crystal growth are close to those for viscous flow. However, in general, the values of the activation enthalpies and entropies for these processes are different. The similarity of ΔG_U and ΔG_{η} , suggests that the molecular reorientation or bond breaking required for crystallisation is not identical but is similar to the mass transport mechanisms involved in viscous flow. Thus, in a first approximation, viscosity data may be used to estimate crystal growth rates in silicate glasses.

Acknowledgements

The authors acknowledge the financial assistance provided by CNPq (Grant No. 359847/94-0), CNPq/RHAE (Grant No. 36.0062/90-0), PADCT/CNPq (Grant No. 62.0058/91-9) and CNPq/RHAE (Grant No. 360246/96-6). We also thank the critical comments of Professor I. Gutzow, Dr E. C. Ziemath and Dr R. Müller of the TC7 Committee of the ICG.

References

- Uhlmann, D. R. Crystal growth in glass forming systems: a ten year perspective. In *Advances in ceramics. Volume 4. Nucleation and crystallization in glasses*. 1982. Edited by J. H. Simmons, D. R. Uhlmann & G. H. Beall. American Ceramic Society, Columbus, Ohio. Pp 80–124.
- Kirkpatrick, J. R. Kinetics of crystal growth in the system CaMgSi₂O₆-CaAl₂SiO₆. *Am. J. Sci.*, 1974, **274**, 215.
- Eagan, R. J., De Luca, J. P. & Bergeron, C. G. Crystal growth in the system PbO-B₂O₃. *J. Am. Ceram. Soc.*, 1970, **53** (4), 214.
- Christian, J. W. *The theory of transformation in metals and alloys*. Part 1. *Equilibrium and general kinetic theory*. 1981. Pergamon Press, Oxford, New York.
- Cahn, J. W., Hillig, W. B. & Sears, G. W. The molecular mechanism of solidification. *Acta metall.*, 1964, **12**, 1421.
- Leko, V. K. Relation between viscosity and crystallization in quartz glasses. *Izv. Akad. Nauk. S.S.S.R., Neorg. Mater.*, 1976, **12**, 99.
- Fokin, V. M., Kalinina, A. M. & Filipovich, V. N. Nucleation in silicate glasses and effect of preliminary heat treatment on it. *J. Crystallogr. Growth*, 1981, **52**, 115.
- Henderson, D. W. & Ast, D. G. Viscosity and crystallization kinetics of As₂Se₃. *J. Non-Cryst. Solids*, 1984, **64**, 43.
- Avramov, I., Gutzow, I. & Grantscharova, E. Crystallization kinetics and

reology of undercooled melts. *J. Crystallogr. Growth*, 1988, **87**, 305.

- Jackson, K. A. Mechanism of growth. In *Liquid metals and solidification*. 1958. American Society for Metals, Cleveland Ohio.
- Jackson, K. A. *The nature of solid liquid interfaces*. 1958. Dover Publications, Inc., New York.
- Filipovich, V. N. The viscosity of SiO₂ and GeO₂ glasses added R₂O. *Glass Phys. Chem.*, 1975, **1** (5), 426.
- Frenkel, J. Kinetic theory of liquids. In *Liquid metals and solidification*. 1958. American Society for Metals, Cleveland Ohio.
- Ziemath, E. C., Diaz-Mora, N. & Zanotto, E. D. Crystal morphologies at the surface of a cordierite glass. *Phys. Chem. Glasses*, 1997, **38** (1), 1–5.
- Yuritsin, N. S., Fokin, V. M., Kalinina, A. M. & Filipovich, V. N. Kinetics of crystal nucleation on the surface of cordierite glass. *Proc. 16th Int. Congr. on Glass., Madrid: S. E. de Cerámica y Vidrio*, 1992, **5**, 21.
- Heide, K., Volksch, G. & Hanay, C. H. R. Characterization of crystallization in cordierite glass by means of optical and electron microscopy. *Proc. 16th Int. Congr. on Glass., Madrid: S. E. de Cerámica y Vidrio*, 1992, **5**, 111.
- Schreyer, W. & Schairer, J. F. Composition and structural states of anhydrous Mg-cordierites: a re-investigation of the central part of the system MgO-Al₂O₃-SiO₂. *J. Petrol.*, 1961, **2** (Pt 3), 324.
- Karkhanavala, M. D. & Hummel, F. A. The polymorphism of cordierite. *J. Am. Ceram. Soc.*, 1953, **36** (2), 389.
- Miyashiro, A., Toshimichi, H., Yamosaki, M. & Miyashiro, T. The polymorphism of cordierite and indialite. *Am. J. Sci.*, 1955, **253**, 185.
- Miyashiro, A. Cordierite-indialite relation. *Am. J. Sci.*, 1957, **255**, 43.
- Müller, R. Untersuchungen zum Einfluss der Korngröße auf die Kristallisation von Glaspulvern der Zusammensetzung 2MgO.2Al₂O₃.5SiO₂.xTiO₂ (x<0.7). *PhD Thesis*. Zentralinstitut für Organische Chemie, Berlin. 1989.
- Robie, R. A., Hemingway, B. S. & Fischer, J. R. Thermodynamic properties of mineral and related substances at 298.15K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. *US Geol. Survey Bull.*, 1978, 1452.
- Sesták, J. *Private communication*. 1994.
- Yuritsin, N. S., Fokin, V. M., Kalinina, A. M. & Filipovich, V. N. Crystal nucleation on the surface of cordierite glass. In *Ceramic Transactions*. Volume 30. 1993. Edited by M. C. Weinberg. The American Ceramic Society, Westerville. (*Proc. Fourth Int. Symp. on Nucleation in Liquids and Glasses*, Stone Mountain (GA, USA). 1992. Pp 379–82.
- Richet, P. & Bottinga, Y. Anorthite, andesine, wollastonite, diopside, cordierite and pyrope: thermodynamics of melting, glass transitions, and properties of the amorphous phases. *Earth Planetary Sci. Lett.*, 1985, **67**, 415.
- Takahashi, K. & Yoshio, T. Thermodynamic quantities of alkali silicates in the temperature range from 25°C to the melting point. *Yogyo-Kyokai-Shi*, 1973, **81** (12), 524.
- Babushkin, V. I., Matveyev, G. M., Mchedlov-Petrosyan, O. P. *Thermodynamics of silicates*. 1985. Springer-Verlag, Berlin. Translation of *Thermodynamika Silikatov* by B. N. Frenkel & V. A. Terentyev.
- Meiling, G. S. & Uhlmann, D. R. Crystallization and melting kinetics of sodium disilicates. *Phys. Chem. Glasses*, 1967, **8** (2), 62–8.
- Scherer, G. W. & Uhlmann, D. R. Crystallization kinetics of Na₂O.3SiO₂. *J. Crystallogr. Growth*, 1975, **29**, 12.
- Matusita, K. & Tashiro, M. Rate of crystal growth in Li₂O.2SiO₂ glass. *Yogyo-Kyokai-Shi*, 1973, **81** (11), 60.
- Fokin, V. M. *SciGlass*, 1996.
- González-Oliver, C. J. R. Crystal nucleation and growth in soda-lime-silica glasses. *PhD Thesis*, University of Sheffield, England. 1979.
- Fokin, V. M. Investigation of stationary and non-stationary crystal nucleation rate in quality glasses of stoichiometric composition Li₂O.2SiO₂ and 2Na₂O.CaO.3SiO₂. *PhD Thesis*, Institut of Silicate Chemistry of Russian Academy Sciences. 1980.
- Mazurin, O. V., Streltsina, M. V. & Shvaiko-Shvaikovskaya, T. P. *Handbook of Glass Data*. 1987. Physical Science Data **15**, Elsevier, Amsterdam. Part C: 92-318.
- De Luca, J. P., Eagan, R. J. & Bergeron, C. G. Crystallization of PbO.2B₂O₃ from its supercooled melt. *J. Am. Ceram. Soc.*, 1969, **52** (6), 322.
- Ricker, J. M., Bergeron, C. G. & Eagan, R. J. Enthalpy of fusion of PbO.2B₂O₃. *J. Am. Ceram. Soc.*, 1968, **5** (7), 410.
- Stewart, D. R. & Rindone, G. E. High temperature energy relations in borate: alkaline-earth and lead borate compounds and their glasses. *J. Am. Ceram. Soc.*, 1963, **46** (12), 593.
- Hübert, T., Müller, R. & Kirsch, M. Untersuchungen zur Oberflächenkristallisation von Glas mit der Zusammensetzung des Cordierite <2MgO.2Al₂O₃.5SiO₂>. *Silikatechnik*, 1988, **39** (6), 183.
- Fokin, V. M., Kalinina, A. M., Filipovich, V. N., Polyakova, I. G. Catalyzed crystal nucleation rate of μ and α -cordierite in cordierite glass doped with TiO₂. *Glass Phys. Chem.*, 1986, **12** (4), 651.
- Müller, R. *Private communication*. 1996.
- Uhlmann, D. R. & Uhlmann, E. V. Crystal growth and melting in glass forming systems. A view from 1992. *Ceram. Trans.*, 1993, **30**, 109.
- Glasstone, S., Laidler, H. J., Eyring, H. *The theory of rate processes*. 1941. Princeton University, New York, London.
- Kelton, K. F. & Weinberg, M. C. Calculation of microscopic rates from nucleation data. *J. Non-Cryst. Solids*, 1994, **180**, 17.