EXPERIMENTAL TEST OF THE GENERAL THEORY OF TRANSFORMATION KINETICS:
Homogeneous nucleation in a $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass

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Experiments were carried out to test the validity of the Johnson–Mehl–Avrami theory of transformation kinetics. The isothermal crystallization of a nearly stoichiometric $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass was studied at $627°C$ and $629°C$ by optical microscopy, density measurements and X-ray diffraction. Both nucleation and growth rates were measured by single and double stage heat treatments up to very high volume fractions transformed and the experimental data for crystallinity were compared with the calculated values at the two temperatures. The early crystallization stages were well described by theory for the limiting case of homogeneous nucleation and interface controlled growth. For higher degrees of crystallinity, both growth and overall crystallization rate decreased due to compositional changes of the glassy matrix and the experimental kinetics could be described by theory if diffusion controlled growth was assumed. It was also demonstrated that the sole use of numerical fittings to analyze phase transformation kinetics, as very often reported in the literature, can give misleading interpretations. It was concluded that if proper precautions are taken the general theory predicts the glass–crystal transformation well.

1. Introduction

An important class of phase transformation takes place by nucleation and growth of secondary phases. The kinetics of such processes is usually described by a theory derived in the period 1937–1939 by Kolmogorov [1], Johnson and Mehl [2] and Avrami [3–5], best known as the Kolmogorov–Avrami or Johnson–Mehl–Avrami (JMA) theory. Since that time this theory has been intensively used by materials scientists to study the various mechanisms of phase transformations in metals. More recently, the JMA theory has been employed by polymer and glass scientists. Examples of technological importance include the study of stability of glassy metals, curing of odontological plasters, devitrification time of radwast glasses, glass ceramics and kinetics calculations of glass formation [6].

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2. Theory

Avrami [3–5] has assumed that: (i) nucleation is random, i.e. the probability of forming a nucleus in unit time is the same for all infinitesimal volume elements of the assembly; (ii) nucleation occurs from a certain number of embryos ($\overline{N}$) which are gradually exhausted. The number of embryos decreases in two ways; by growing to critical sizes (becoming critical nuclei) with rate ν per embryo *and* by absorption by the growing phase; (iii) the growth rate (U) is constant, until the growing regions impinge on each other and growth ceases at the common interface, although it continues normally elsewhere.

Under these conditions Avrami has shown that the transformed fraction volume, α, is given by

$$\alpha = 1 - \exp\left[\frac{-6g\overline{N}U^3}{\nu^3}\left(\exp(-\nu t) - 1 + \nu t - \frac{(\nu t)^2}{2} + \frac{(\nu t)^3}{6} \right)\right], \quad (1)$$

where g is a shape factor, equal to $4\pi/3$ for spherical grains, and t is the time period.

There are two limiting forms of this equation, corresponding to very small or very large values of νt. Small values imply that the nucleation rate, $I = \overline{N}\nu \exp(-\nu t)$, is constant. Expanding $\exp(-\nu t)$ in eq. (1) and dropping fifth and higher order terms gives

$$\alpha = 1 - \exp\left(-gU^3 I t^4/4\right). \tag{2}$$

This is the special case treated by Johnson and Mehl [2] and is valid for $\overline{N}$ very large when the number of embryos is not exhausted until the end of the transformation (homogeneous nucleation). Large values of νt, in contrast, means that all nucleation centers are exhausted at an early stage in the reaction. The limiting value of eq. (1) is then

$$\alpha = 1 - \exp\left(-g\overline{N}U^3 t^4\right) \tag{3}$$

Eq. (3) applies for small $\overline{N}$, when there is a rapid exhaustion of embryos at the beginning of the reaction (instantaneous heterogeneous nucleation). Avrami has proposed that for a three-dimensional nucleation and growth process, the following general relation should be used

$$\alpha = 1 - \exp\left(-Kt^m\right), \tag{4}$$

where $3 \le m \le 4$. This expression covers all cases where I is some decreasing function of time, up to the limit when I is constant. Eq. (4) also covers the case of heterogeneous nucleation from a constant number of sites, which are activated at a constant rate till becoming depleted at some intermediate stage of the transformation. In the more general case, where I and U are time dependent

$$\alpha = 1 - \exp\left(-\frac{4\pi}{3}\int_0^t I(\tau)\left[\int_\tau^t U(t')\,dt'\right]^3 d\tau\right), \tag{5}$$

where τ is the time of birth of particles of the new phase. Table 1 shows values of m for different transformation mechanisms. Thus, if spherical particles grow in the internal volume of the sample then m should vary from 1.5 to 4. If growth proceeds from the external surfaces towards the center (collumnar shape) then m will be different.

Table 1
Avrami parameter for several mechanisms (spherical growth)

	Interface controlled growth	Diffusion controlled growth
Constant I	4	2.5
Decreasing I	3–4	1.5–2.5
Constant number of sites	3	1.5

The above treatment, whilst including the effects of impingement neglects the effect of the free surfaces. Thus if transformation occurs in a thin sheet solid material, it may happen that the average dimension of a transformed region is greater than the thickness of the sheet. Growth in this direction must soon cease, and thereafter growth is essentially two-dimensional. This problem was recently treated by Weinberg [7].

Eq. (4) is usually written as

$$\ln \ln(1 - \alpha)^{-1} = \ln K + m \ln t. \tag{6}$$

This expression is intensively employed by materials scientists *to infer* the mechanisms of several classes of phase transformation from the values of m, that is the slope of $\ln \ln(1 - \alpha)^{-1}$ versus $\ln t$ plots. The linearity of such plots is taken as an indication of the validity of the JMA equation. It should be emphasized, however, that the ln–ln plots are insensitive to variations of α and t and that the value of the intercept K is seldom compared to the theoretical value. This is mainly due to the great difficulty in measuring the high nucleation and growth rates in metallic and ceramic (low viscosity) systems.

3. Literature review – application to glass crystallization

In an extensive number of studies the JMA theory has been employed to analyze experimental data for crystallinity versus time in both isothermal and non-isothermal heat treatments of glass systems. Emphasis was usually given to values of m obtained from the slopes of experimental $\ln \ln(1 - \alpha)^{-1}$ versus $\ln t$ plots. In [8–12] for instance, m ranged from 1 for surface nucleation to

Table 2
Isothermal crystallization studies

Glass	T ($^{\circ}$C)	m	Comments
$Li_2O \cdot 2SiO_2$	600	2.3	XRD, mixed surface
	575	1.4	and internal nucleation [8]
	549	1.4	
$MgO-Al_2O_3-SiO_2$	950	3.2	XRD, internal nuclea-
$-ZrO_2-TiO_2$	900	2.7	tion of two phases [9]
	850	1.1	
$2CaO \cdot MgO \cdot 2SiO_2$	946	1	XRD, surface nucleation
	929	1	[10]
	895	1	
$Li_2O \cdot 2SiO_2$	600	2.9	Positron annihilation,
	635	2.9	internal nucleation
	600*	1.2*	(*surface nucleation) [11]
$Li_2O \cdot 2SiO_2$	580	3	DSC, internal nucleation
	542	3	[12]
	500	3	

3 for internal nucleation. Table 2 summarizes the results of [8–12] for isothermal crystallization of several glasses from a fixed number of nucleation sites. In no case has the intercept been compared with the theoretical value.

In 1982, Zanotto and James [13] tried to compare the experimental values of crystallinity for a $BaO \cdot 2SiO_2$ glass with those predicted by eq. (2). The attempt was not successful due to the complex crystallization behavior of this system (spherulitic growth with large induction time). In the period 1983–1984 two independent studies of the type described in [13] were performed with a $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass [14] and with a $2Na_2O \cdot 1CaO \cdot 3SiO_2$ glass [15] at one temperature.

In this article the crystal nucleation and growth rates of a $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass were measured up to high volume fractions transformed. The experimental values for crystallinity were determined by several techniques as a function of time at two temperatures and compared with the theoretical values.

4. Experimental methods

For the present study the $Na_2O \cdot 2CaO \cdot 3SiO_2$ (NC_2S_3) glass composition was chosen because it presents a measurable rate of internal (homogeneous) nucleation of spherical grains (single crystals) which apparently grow with constant velocity [16]. Therefore, complicating features such as transient nucleation and growth, metastable phase formation, large compositional changes upon crystallization, non-spherical or spherulitic growth and combined bulk and surface crystallization were absent (the surface layers were polished off).

The glass was prepared from washed Brazilian sand (99.95% SiO_2), Na_2CO_3 (Merck) and $CaCO_3$ (Ecibra) A.R. grade. A 150 g batch was melted in a Pt crucible at 1480°C and homogenized by crushing and melting six times. The melt was finally cast and pressed between steel plates. Clear samples 2–3 mm in thickness were obtained.

The chemical analysis shown in table 3 indicates some departure from the target (stoichiometric) composition.

The heat treatments were carried out in tubular furnaces maintained within $\pm 1^{\circ}$C with a proportional controller. The furnace usually attained the equilibrium temperature about 10 min after insertion of the cool specimens, with a maximum variation of $\pm 10^{\circ}$C in the first minutes. Three different series of treatments were employed. In the first series, specimens were treated at 629°C for 3.5–4.0–4.5–6.0–7.0 and 8.0 h (single stage). In the second series, specimens were heated at 629°C for 0.0–0.5–1.0–1.5–2.0–2.5 and 3.0 h, quenched and reheated, all together, to $(690 \pm 10)^{\circ}$C for 10 min (double stage). In the final series, the specimens were subjected to a single stage at 627°C for longer periods (3.5–4.0–5.0–7.0–9.0–14.3–17.3 and 18.0 h) to achieve a higher degree of crystallinity.

The treated specimens were mounted on glass plates with Canada balsam, ground with SiC 400 and polished with a mixture of rare earth oxides.

Table 3
Chemical analysis (mol%)

	SiO_2	CaO	Na_2O	Fe_2O_3
Theoretical	50.0	33.3	16.7	0.00
NC_2S_3 glass	51.2	32.4	16.4	0.02

An etching of 15 s in a 0.05% HF e 0.1% HCl solution was sufficient to reveal the microstructure.

Photographs were taken in an optical microscope with 40 × objective lenses. About 500 crystalline particles were counted and measured in each specimen. The average number of crystals per unit volume ($\overline{N}_v$) was obtained by the equation of De Hoff and Rhines [17]. The radius R_m of the largest particle was measured in each specimen since it should represent the crystal which first nucleated and would give an accurate measure of the growth rate. The volume fraction of crystals was obtained by the technique of Hilliard and Cahn [18].

The weight fraction crystallized was also determined by the X-ray diffraction technique of Wakelin et al. [19]. This was transformed to volume fraction through a simple calculation which takes into account the specific weight of a glassy sample (ρ_0) and that of a 100% crystalline sample (ρ_{100}).

Density measurements also allowed crystallinity determinations through the following equation:

$$\alpha = \rho_X - \rho_0/\rho_{100} - \rho_0, \tag{7}$$

where ρ_X is the specific weight of the partially crystallized sample. For X-ray and density measurements, glass samples of $15 \times 10 \times 3$ mm^3 were slightly ground to remove the crystalline surface layer.

A semiquantitative EDS analysis was carried out in one sample heated for 14.3 h at 627°C.

5. Results

Optical micrographs of the NC$_2$S$_3$ glass treated for different periods at various temperatures were shown by Gonzalez-Oliver and James [16]. The crystals are quasi-spherical.

Fig. 1 shows the largest crystal radius (R_{max}) as a function of heat treatment time at 627°C (single stage) and at 629°C (double and single stage). The development treatment at 690°C for the double stage specimens adds a constant increment in radius ($\Delta R = 3.28$ μm) to all particles which was subtracted from the measured radii to give R_{max} at 629°C. This procedure allows for the de-
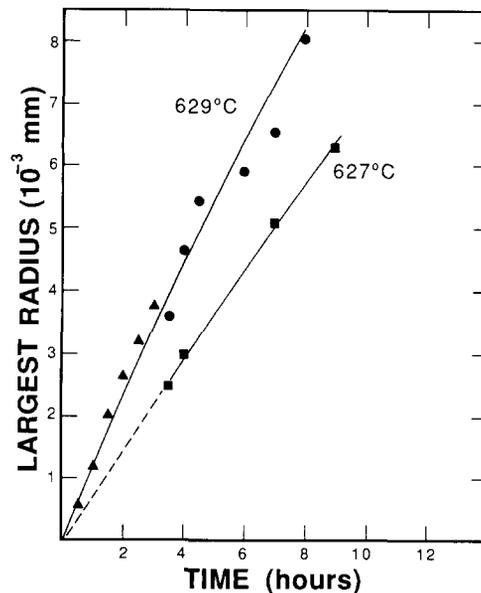

Fig. 1. Largest crystal radius versus time. Samples heat treated at: (●) 629°C, single stage; (▲) 629°C, double stage; (■) 627°C, single stage.

termination of the growth rate at short times when transformation is at an early stage ($\alpha < 2.5\%$).

At 629°C, the linear least squares fit to the first 6 experimental points ($\alpha < 0.03$) shows a significantly higher slope (growth rate) than the 6 last points ($0.05 < \alpha < 0.55$) i.e. 3.55 μm/s and 2.39 μm/s, respectively. The average over the whole range being 2.62 μm/s, with a small positive intercept. At 627°C no data were available for short times. The growth rate from 3.5 to 9.0 h ($0.03 < \alpha < 0.40$) is 1.91 μm/s, or 1.96 μm/s if the point (0, 0) is included in the calculation. Again, a small positive intercept is observed in the R_{max} axis.

The continuous curves shown in fig. 1 were obtained through log R_{max} versus log (time) fits and have slopes of 0.90 and 0.97, respectively. Therefore, they are less than 1.0, the value expected for a constant growth rate. Taken in total, these results indicate the possibility that growth slows down with time, although the observed decrease is within the limits of experimental error and cannot be assured at this stage. Later, other evidence will be provided to reinforce this suggestion.
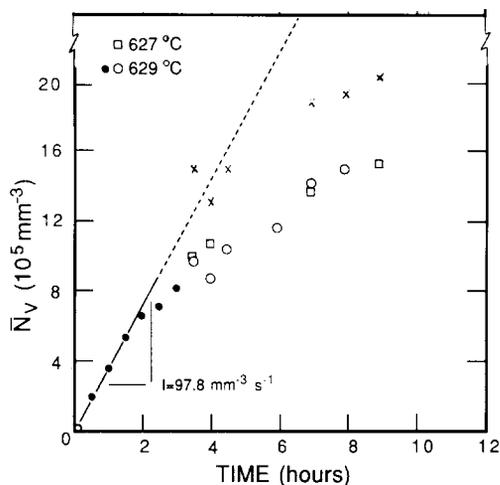
Fig. 2. Crystal nucleation density versus time. The crosses are the corrected values due to stereological errors: (○) 629°C, single stage; (●) 629°C, double stage; (□) 627°C, single stage.

Fig. 2 shows the average crystal nucleation density ($\bar{N}_v$) for both single and double treatments at 629°C and for a single treatment at 627°C. The stereological errors due to the limited resolution of the optical microscope (taken as 1.0 μm in the present case) were allowed for by correcting the experimental $\bar{N}_v$ values through the equations of Zanotto and James [13,20]. The crosses in fig. 2 represent the corrected values of $\bar{N}_v$. The nucleation rate, which is initially 97.8 nuclei mm^{-3} s^{-1}, decreases for increasingly longer

times ($t < 3$ h) or higher crystallinities. This will be explained later.

Table 4 shows the volume fractions transformed obtained by optical microscopy for samples heat treated at 629°C, as well as the values determined by three different techniques at 627°C. The agreement between the xrd and o.m. determinations is very good throughout the full range of crystallinities. The values obtained by density measurements are slightly higher than the first two up to $\alpha \approx 0.40$. For higher crystallinities, the three techniques are in excellent agreement. This result is expected since the uncertainty in the measurements is greater for low crystallinities. It should also be emphasized that densification of heat treated glasses tend to overestimate the density values and that both xrd and o.m. tend to underestimate the fraction crystallized. Taking into account these experimental difficulties, it is reasonable to say that the overall agreement is good and that the combined set of results can be used to test the theory.

6. Discussion

The large majority of crystalline phases growing in viscous liquids are spherulitic (only partially crystalline) and in such cases the "crystallinity" values depend on the experimental technique

Table 4
Experimental and calculated values of crystallinity at 629°C and 627°C

Time (h)	629°C		627°C			
	o.m. [a]	Theoretical	o.m. [a]	xrd [b]	Density	Theoretical
3.5	0.054	0.048	0.028	–	0.032	0.019
4.0	0.103	0.080	0.046	0.039	0.062	0.033
4.5	0.143	0.125	–	–	–	0.052
5.0	–	0.184	0.071	0.075	0.087	0.078
6.0	0.299	0.345	–	–	–	0.156
7.0	0.410	0.543	0.205	0.195	0.224	0.269
8.0	0.549	0.737	–	–	–	0.414
9.0	–	0.882	0.394	0.385	0.451	0.575
14.3	–	0.962	–	0.814	0.817	0.996
17.3	–	0.99	0.921	0.963	0.949	0.999
18.0	–	0.999	0.945	0.985	0.970	0.999

[a] o.m. = optical microscopy.
[b] xrd = X-ray diffraction.

employed [13]. The good agreement in the measurements by the three techniques (xrd, density and o.m.) used here indicates that the NC_2S_3 particles are *single crystals*, in agreement with [16]. This will be a key issue in the discussion to follow.

The main objective of the present work is to compare the experimentally determined values of crystallinity with the theoretical values calculated by the general JMA equation. For spherical growth several cases may be analyzed: (i) homogeneous nucleation with interface controlled growth, i.e. constant nucleation and growth rates ($m = 4$ in eq. (2)); (ii) instantaneous heterogeneous nucleation from a fixed number of sites with constant growth rate ($m = 3$ in eq. (3)); and (iii) intermediate cases where I or U are time dependent ($1.5 \leq m < 4$). In order to test the theory it is necessary to study a given system which behaves in one of the ways described above. An intrinsic difficulty, however, is to know "a priori" the material's behavior. In the present study independent measurements of nucleation and growth behavior allowed the transformation mechanism to be inferred, as will be discussed below.

To analyze the overall transformation kinetics it is necessary to understand the observed decrease in both nucleation and growth rates. Here, it should be pointed out that very few, if any, authors have reported nucleation and growth measurements from negligible to high volume fractions transformed. In this paper, both $\overline{N}_v$ and R_{max} were measured up to 55% crystallinity and thus new effects, unobserved in previous studies, could be detected.

Physical effects, such as impingement, could reduce the apparent growth velocity; and ingestion of embryos by the growing phase could reduce the homogeneous nucleation rate, as recently demonstrated by Zanotto and Weinberg [21].

The lowering of the nucleation rate at 629°C is detected from 4 to 8 h ($0.05 < \alpha < 0.55$). This can be shown, quantitatively, to be mostly due to ingestion of embryos (decreased volume available for nucleation), at least in the time period considered, although other additional effects cannot be ruled out. The decrease in growth rate, as indicated by the two different slopes at 629°C (at early and advanced crystallization stages) are

detected early in transformation and cannot be attributed solely to impingement, since this would be appreciable only in more advanced stages.

The decrease in nucleation and growth rates could also be related to *chemical* effects, i.e. rejection of impurities at the growth fronts. It should be stressed that this effect, in principle, would affect growth at an early transformation stage due to the single crystal nature of the NC_2S_3 particles. The nucleation frequency would be affected only when diffusion fields at the crystal fronts reach the dimensions of the interparticle spacings at more advanced stages.

Indeed, a semiquantitative EDS analysis (fig. 4) indicated an increase in Si and decrease in Na and Ca in the glassy matrix when compared with crystalline particles. Furthermore, the chemical analysis of table 3 shows that the parent glass was richer in Si and poorer in Ca and Na than the stoichiometric composition. Therefore, it is reasonable to expect that enrichment of Si and lowering of Ca and Na at the growth fronts would increase the viscosity thus decreasing both growth and nucleation rates and consequently the overall crystallization rate.

Fig. 3 compares the experimental crystallinities as a function of time at 629°C and 627°C. The theoretical curves were obtained by means of eq. (2) with the independently measured values of I and U and $m = 4$. In this case the *average* growth rates obtained from the single stage treatments, between 0–8 h at 629°C and 0–9 h at 627°C, were used along with the initial nucleation rate. The experimental points for both temperatures initially coincide (in detail, lie slightly above) with the theoretical curves and drop for higher crystallinities.

For the present purposes only the extra "chemical" effects are important since the other "physical" effects are (supposedly) taken into account by the JMA theory. Therefore, if the decrease in nucleation rate, at least up to the limit of the N_v determinations ($\alpha = 0.55$), is caused by ingestion, and this is assumed by the theory, the initial rate, I_0, can be used in eq. (2). However, the use of a constant (initial or average) growth rate, as assumed by Avrami, leads to a discrepancy between predicted and experimental crystallinities when
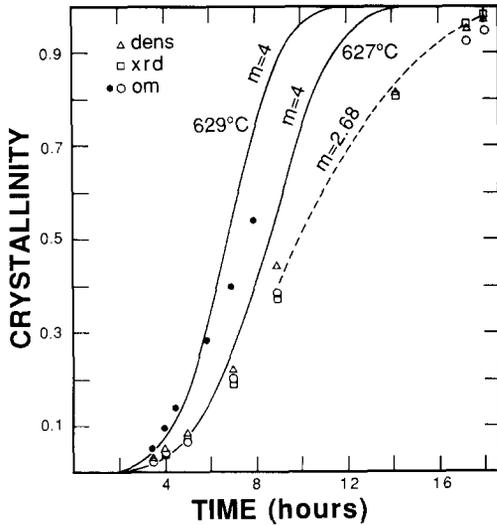
Fig. 3. Crystallized fraction versus time, samples heat treated at (●) 629°C, measured by optical microscopy; (○) 627°C, measured by optical microscopy; (□) 627°C, measured by X-ray diffraction; (△) 627°C, measured by density.

the volume fractions transformed are significant. Therefore, in the following section the sensitivity of the theoretical curves to time dependent growth will be tested.

It is possible to use eq. (2) and the experimental values of α and I to calculate the growth rate for the different times (crystallinities). A plot of U_{calc} versus time at 627°C and 629°C shows that an exponential, almost linear, decreasing growth rate

Fig. 4. EDS scan of both glassy and crystalline phase in a sample heat treated for 14.3 h at 627°C.

would restore agreement with theory. It should be stressed, however, that this procedure has no adequate theoretical sanction since in Avrami's derivation (eq. (2)) U is assumed to be constant. On the other hand, it furnishes an approximate alternative possibility to explain the discrepancy in fig. 3.

At this point, two important observations can be made: first, it is very easy to confuse slowly decreasing with constant growth rates. The time dependent U was only observed because R_{max} was measured up to high crystallinity. Second, it is obvious but seldom realized that the JMA equation is extremely sensitive to variations in growth rate and here a slowly decreasing growth rate would explain the considerable differences in fig. 3.

Another possibility is to analyze the transformation kinetics by numerical fittings with the experimental values of α as often reported in the literature. The results of a linear least squares fit (through eq. (6)) as well as of an exponential least squares fit (through eq. (4)) are shown in table 5.

The values of m are 3.50–3.08 at 629°C where crystallinities up to 55% have been measured, and 2.87–2.86 at 627°C, where crystallinities up to 98% have been measured. It must be stressed that eq. (4) can be satisfied for time dependent nucleation and growth rates, with an apparent value of $1.5 \leq m < 4$, depending on the mechanism, as demonstrated by Christian [22].

If only the more advanced stages are studied (9 to 18 h at 627°C) the experimental (fitted) value for m is 2.68, i.e. approaches the case of diffusion controlled growth discussed by Christian ($m = 2.5$). This result is expected since the compositional changes at the growth fronts are likely to become very significant for high fractions transformed, although no measurements of R_{max} could be performed in that region to confirm the R_{max}
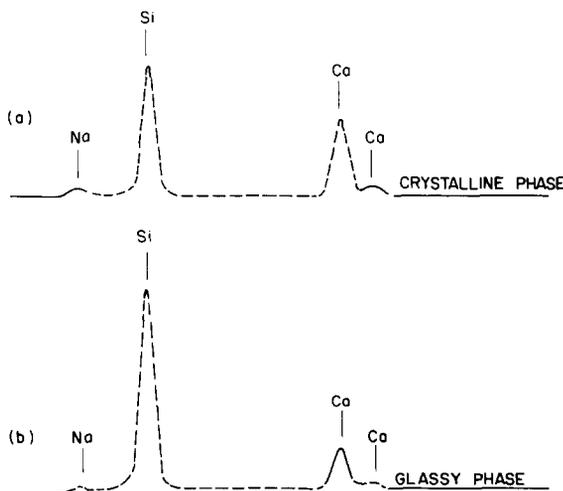
Table 5
Kinetic parameters obtained by numerical fittings

	629°C		627°C	
	Linear	Exponential	Linear	Exponential
m	3.08	3.50	2.86	2.87
r	0.995	0.996	0.997	0.999

versus $\sqrt{t}$ dependence. Summarizing, the apparent value of m decrease during transformation; the early stages ($\alpha < 0.15$) are well described by simultaneous homogeneous nucleation and interface controlled (constant) growth with $m = 4$ in eq. (2). The latter stages are better described by diffusion controlled growth ($m = 2.5$ in eq. (4)).

From the previous discussion it is clear that the *sole* use of linear or more sophisticated numerical fittings to analyze phase transformations kinetics through the experimental values of m, as very often reported in the literature, can give misleading interpretations for the transformation mechanism.

7. Conclusions

At early stages, the transformation kinetics of the $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass is well described by the JMA theory with $m = 4$ in eq. (2), i.e. homogeneous nucleation and interface controlled growth.

The determination of number density (N_v) and largest radius up to high crystallinities demonstrated that in more advanced stages both nucleation and growth rates decrease. The diminished nucleation is mostly due to ingestion of embryos by the growing particles, but this is taken into account by the JMA theory. The suggested decrease in growth rate is likely due to compositional variations at the growth fronts. Due to the reduced growth, discrepancy develops between theory and experiment unless a diffusion controlled growth is assumed ($m = 2.5$) and indeed, the experimental value of m is 2.68 for the latter stages.

Therefore, it has been demonstrated that if extra, detailed knowledge on the transformation mechanism is available the JMA theory describes well the transformation kinetics on most of the transformation range. In order to test the theory in the intermediate transformation range one would have to develop a growth model which incorporates both diffusional and interfacial effects. Since most model and commercial materials are not perfectly stoichiometric and in general, there are compositional differences between parent and new phase, the Avrami parameter m, obtained from the sole use of numerical fits, represents an average and can give misleading interpretations for the phase transformation mechanism.

Finally, it is suggested that computer simulations for different transformation mechanisms and further work involving a rigorously stoichiometric glass could provide a definitive test of the theory.

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