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The initiation of crystal growth in glasses

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SUMMARY. The application of classical nucleation theory to the initiation of crystal growth in glasses is discussed. Its application to experimental results obtained for the rate of nucleation in three types of glass, one showing nucleation separately from crystal growth, another showing simultaneous nucleation and growth, and the third showing crystal growth after metastable liquid/liquid phase separation, is then described. Recent work on the kinetics of unmixing in glasses is outlined. The influence of so-called 'nucleating agents' in the glasses described appears to be exerted through changes in the anionic structure.

FOR many purposes it is convenient to think of glasses as liquids that have been cooled below their freezing points without crystallization. The atoms in the glassy structure are thus arranged in a similar way to those in the liquid; but as the temperature is lowered, and the viscosity increases, so the translational motion of the atoms becomes more and more restricted. The physical properties become observable functions of time as the viscosity increases, and relaxation times become very long at temperatures below the transformation range (viscosity, $10^{13.5}$ poises), so that the properties are similar to those of crystalline solids within the time limits set for experimental observations.

Thus a glass exists in a state of metastable equilibrium, and this metastable condition has a free energy higher than that of the corresponding mixture of crystalline phases of the same composition. In order to transform itself from the metastable to the stable state, it must undergo two types of reaction: nucleation, and crystal growth. Tammann pointed out in 1925 that these two processes have different rate-controlling mechanisms, so that the rate of maximum nucleation often occurs at a temperature lower than the temperatures at which the growth rate is significant.

In most glasses of commercial importance, the kinetics of nucleation and growth

of crystals are such that devitrification takes place at a negligible rate. Glass objects many thousands of years old with no signs of crystal formation are known to archaeologists, and natural glasses, such as obsidian, have existed for millions of years without devitrification. However, in more recent times, the controlled crystallization of certain types of glass to produce opal glasses, which contain large numbers of particles of a dispersed second phase in a glassy matrix, and glass-ceramics, which are a micro-crystalline mass of interlocking crystals sometimes with a small percentage of residual glass between the crystals, has stimulated an interest in the basic physical chemistry of the mechanisms of nucleation and growth of crystals. The present paper is confined to a discussion of the nucleation phenomena. It deals with current theories of nucleation as applied to glasses, and illustrates the application of theory to three sets of experimental work carried out at Imperial College. Since the interest of the author and his colleagues has a metallurgical bias, these glasses are related to slags and hence have higher melting points than are common in glass technology.

Theory of homogeneous nucleation in condensed phases

The classical theory of nucleation is based on the treatment of phase stability by Willard Gibbs, nearly a hundred years ago, who considered small fluctuations whose properties differed appreciably from the parent phase. The theory was first developed for the condensation of gases (Volmer and Weber, 1926; Becker and Döring, 1935; Becker, 1938) and was extended to describe homogeneous nucleation in condensed phases by Turnbull and Fisher (1949).

The work required to form a spherical embryo of the new phase is

$$w = 4\pi r^2 \sigma + 4\pi r^3 \Delta g_v / 3,$$

where σ is the specific interfacial tension between the matrix and the new phase, r is the radius of the embryo, and Δg_v is the difference in free energy between the matrix and the new phase, per unit volume. This function passes through a maximum value at a particular value of r, the critical radius r^*, which can be obtained by differentiation: $r^* = -2\sigma/\Delta g_v$. Particles beyond this radius will grow spontaneously, because any increase in size is accompanied by a decrease in energy. The corresponding value of w is equal to ΔG^*, the free energy of formation of a nucleus of critical size,

$$\Delta G^* = 16\pi\sigma^3 / 3(\Delta g_v)^2.$$

If a Boltzmann distribution is assumed and the number of embryos is much smaller than the total number of molecules, then the rate of nucleation is given by

$$I = A \exp(-\Delta G^*/kT).$$

The exponential term in ΔG^* describes the thermodynamic barrier to nucleation. The pre-exponential factor A represents the kinetic probability of a molecule crossing the interface from the matrix to the particle, $A = nv \exp(-\Delta G_a/kT)$, where ΔG_a is the free energy of activation for motion of molecules across the matrix–embryo interface, n is the number of molecules of the nucleating species per unit volume and v is the molecular jump frequency, equal to kT/h.

The above treatment has been criticized because it involves a mixture of thermo-

dynamic and statistical arguments, and so the problem of condensation in gases has been treated using the methods of statistical mechanics to calculate the steady state concentrations of clusters of molecules (Lothe and Pound, 1962; Andres, 1965). Evaluation of the integrals obtained is only possible for small clusters of a few molecules, because only next nearest neighbour interactions are included, and consequently there are large errors in the calculations for the bigger clusters (Stogryn and Hirschfelder, 1959). The contributions of rotational and translational motion to the partition functions has been the subject of much recent discussion in the literature (Reiss *et al.*, 1967, 1968; Lothe and Pound, 1968) and different approaches can result in nucleation rates differing by many factors of ten. A rigorous statistical-mechanical approach to nucleation in glasses involves many more difficulties than those arising in a treatment of condensation, and the classical approach, which gives surprisingly good agreement with experimental results for nucleation from the melt (see, for example, the review of Jackson, 1965), will be applied here.

We thus have the following equation for the nucleation rate I per unit volume in a glass at temperature T: $I = (nkT/h)\exp\{-(\Delta G_a + \Delta G^*)/kT\}$. This gives the bell-shaped curve predicted by Tammann (1925) for the temperature dependence of nucleation, since ΔG^* rapidly approaches zero at a particular value of T below the melting point, but the kinetic barrier to nucleation becomes higher as the temperature becomes less (and the diffusivities of the components decrease). The rapid approach of ΔG^* to zero at a particular temperature ΔT below the melting point T_m can be illustrated for a single-component system by substituting $\Delta h . \Delta T/T_m$ for Δg_v in the equation for ΔG^*, where Δh is the heat of fusion per unit volume. Then $\Delta G^* = 16\sigma\pi^3 T_m^2/3(\Delta h)^2(\Delta T)^2$, and ΔG^* is inversely proportional to the square of ΔT. When the nucleus has a composition different from that of the matrix, then its chemical potential when dissolved in the matrix may be used to determine Δg_v.

The application of the classical theory of nucleation to glasses has several important disadvantages. The most serious of these is that it is unsafe to assume that the interfacial energy for a flat interface can be applied to particles of very small radius, that is, to particles containing only small numbers of molecules. As the radius of the cluster becomes of the same order as the range of the intermolecular forces, then σ, the interfacial tension, becomes a function of size (Buff, 1955). The use of macroscopic values for σ is said to be valid only down to cluster sizes of about 50 molecules (Benson and Shuttleworth, 1951). However, in silicate glasses the nature of the molecular species that should be considered for the purposes of nucleation theory is, at best, uncertain. Furthermore, for small clusters of molecules, the concept of a surface breaks down, particularly in glasses, with their network, ring, or chain structures. There are no experimental data available for the macroscopic crystal/glass interfacial tension anyway, and values must be estimated, for example, by use of Antonov's rule (Bondi, 1953) connecting the interfacial energies between solid, liquid, and gas and the contact angle θ: $\sigma_{L/S} = \sigma_{S/G} - \sigma_{L/G}\cos\theta$.

When we consider the application of the classical equations for nucleation to particular real systems, for example those used for the manufacture of glass-ceramic materials, we find that we have an additional disadvantage in that the equilibrium

thermodynamic data for temperatures well below the liquidus are not known. In fact, for many of the systems with more than three components, the liquidus temperature itself has not been determined for the whole composition range. Furthermore, the phase that crystallizes first is often not that which would be expected purely from thermodynamic considerations. The appropriate value for the change in free energy on forming a nucleus is therefore hard to estimate.

### Nucleation in glasses containing iron oxides

Glasses containing iron oxide additions are of particular interest to metallurgists because of their bearing on the use of slags for manufacture of glass-ceramics, such as 'Slag-ceram' (Klemantaski and Kerrison, 1966). Iron oxides, added in small percentages as so-called 'nucleating agents' in such systems, can affect both the rate of nucleation and the rate of crystal growth. Rogers and Williamson (1969) have investigated the kinetics of both these stages in devitrification; Williamson (1970) describes some of the growth rate measurements.

Homogeneous glasses were prepared in which iron oxides were added to a variety of compositions in the $CaO-MgO-Al_2O_3-SiO_2$ quaternary system. The oxidation state of the iron in these glasses was controlled by the melting time and the nature of the iron oxide addition. Samples of the quenched glass were then heat treated, and thin sections of the heat treated samples were examined under the microscope. The number of crystals growing in the glass per unit volume was determined from the number of crystals visible in a given area and the thickness of the thin section.

It was found that only glasses containing added ferric oxide showed any tendency to nucleate and grow crystals internally; the nucleation rates, determined from two-stage heat treatments, were appreciable only for a fairly small range of compositions. It is convenient to think of the two stages in the heat treatment as a 'nucleation stage' and a 'crystal-growth stage'. This can be justified by the fact that the number of crystals that grew in the glass was largely dependent upon the treatment in the 'nucleation stage', and that samples quenched after this stage showed no signs of crystallization either optically under the electron microscope or by X-ray diffraction. There was also no evidence of liquid/liquid phase separation (see later).

At low nucleation rates, the heat-treated glasses developed large dendrites of diopside during the second part of the heat treatment (fig. 1). At higher nucleation rates, suitable two-stage treatments could produce a mass of small dendritic crystals, as shown in fig. 2. In some of these crystals, it was possible to detect a different phase at the centre of the crystal, which exhibited little or no birefringence under crossed polars. However, these were very small (less than 2 μm) and precise optical observation was not possible.

A number of glass samples were heated for a fixed time at a series of nucleating temperatures ranging from 690 to 790 °C. The samples were cooled and then returned to a furnace at a higher temperature, so that the whole batch was given an identical crystal-growth treatment. Fig. 3 shows the variation in the numbers of crystals observed as a function of temperature for two glass compositions and different heat
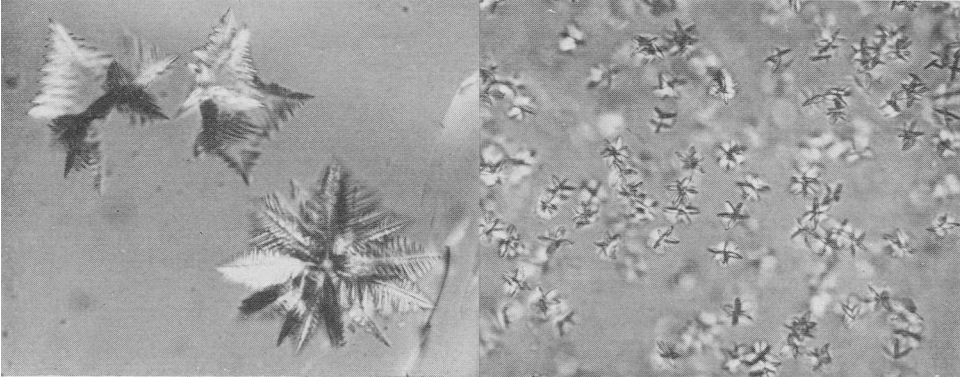
FIGS. 1 and 2: Fig. 1 (left). Diopside dendrites grown in a glass of composition 30% CaO, 2 MgO, 15 Al_2O_3, 53 SiO_2 with 10 g added Fe_2O_3 per 100 g base glass. Heat treatment, 720 °C/24 h, 810 °C/20 h, 940 °C/2¼ h. Transmitted light, ×125. Fig. 2 (right). Spinel-nucleated diopside crystals in a glass of composition 28% CaO, 10 MgO, 20 Al_2O_3, 42 SiO_2 with 13 g added Fe_2O_3 per 100 g base glass. Heat treatment, 728 °C/1½ h, 923 °C/¼ h. Transmitted light, ×250.
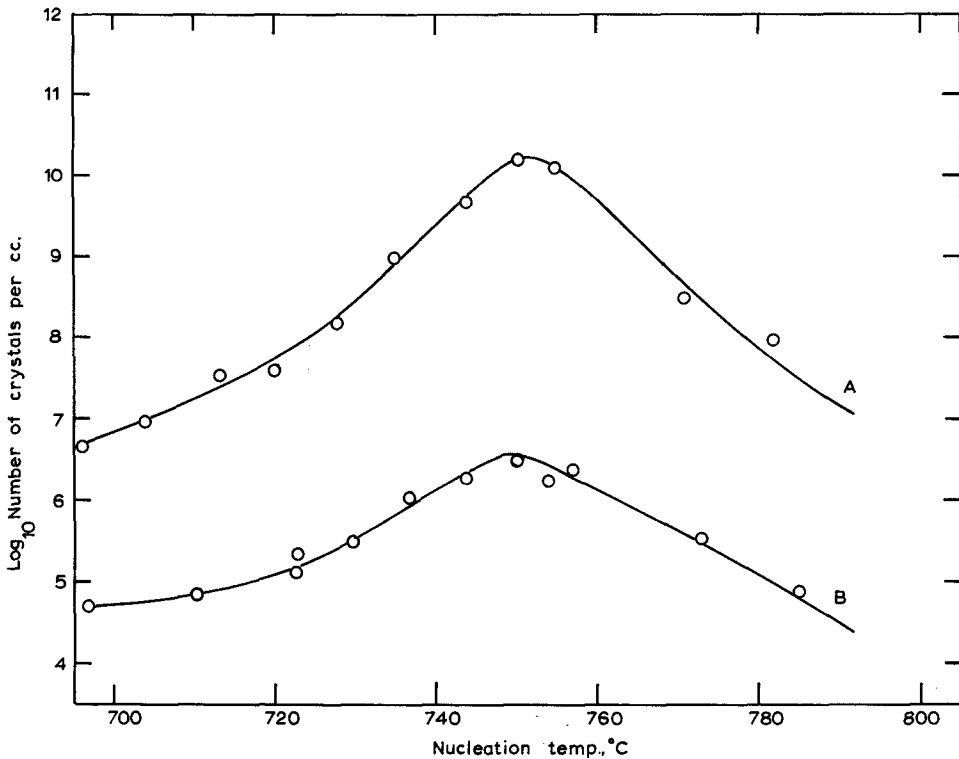

FIG. 3. Variation in number of crystals per cm^3 with nucleation temperature. Curve A. Glass as in fig. 2 (13 g Fe_2O_3 per 100 g base glass). Nucleated for 2 h, crystallized, 925 °C/25 min. Curve B. Same base glass, but with 10 g Fe_2O_3 added per 100 g. Nucleated for 17 h, crystallized, 910 °C/2 h.

treatment schedules. These curves are qualitatively as predicted by the classical nucleation theory. It can be seen that the glass containing the smaller amount of Fe_2O_3 required longer periods for both nucleation and crystal growth, but that the maximum occurred at approximately 750 °C in both cases.

Now, according to the Turnbull and Fisher equation, on the low-temperature side of the bell-shaped curve the nucleation rate is controlled by the kinetics of movement of molecules across the newly formed interface. If we determine an activation energy from an Arrhenius plot of the appropriate data, then we obtain values of 120 kcal/mole and 100 kcal/mole ($\pm$10 kcal) respectively for the two curves. These high values for the activation energy are greater than those to be expected for cation diffusion (Doremus, 1962), and are more akin to the activation energies for viscous flow determined for similar glass compositions (Williamson, Tipple, and Rogers, 1968). It would seem therefore that the ΔG_a term in the above equation for nucleation rate is not a simple diffusivity relationship, but involves some major form of reconstruction.

The X-ray patterns for glasses in the earlier stages of devitrification showed diopside and spinel. Now, although the X-ray patterns included only traces of spinel, it was possible from the four strongest reflections to determine the parameters of the cubic unit cell. The two spinels $MgAl_2O_4$ and $MgFe_2O_4$ exhibit complete solid solution with each other, and cell dimensions increase linearly with composition as Al is replaced by Fe (Rait, 1950). The composition of the spinel phase as determined from the measured lattice parameters indicated that it had a mole ratio Al_2O_3:Fe_2O_3 of 12:1 while in the original glass the ratio was closer to 3:1. The effect of the heat treatments therefore was to produce spinel nuclei in which the Al_2O_3:Fe_2O_3 ratio was four times higher than in the glass in which they were being formed. So, although Fe_2O_3 is incorporated to a small extent in the nucleating species, its main role seems to be to enhance the ability of spinel nuclei to form.

The state of coordination of aluminium ions in glasses has been the subject of considerable debate. Douglas (1961) has reviewed the evidence from physical property measurements, and concluded that the ions exist in both four- and six-fold coordination in alkali silicate glasses. Density and infra-red spectrum studies by Day and Rindone (1962) indicate that this is true in Na_2O–Al_2O_3–SiO_2 glasses if the Al:Na ratio is greater than one. The thermodynamic activity determinations of Rein and Chipman (1965) in melts of the quaternary system CaO–MgO–Al_2O_3–SiO_2 indicate that the effect of Al_2O_3 additions on the activities of CaO and SiO_2 is that of a diluent. This suggests that aluminium can occur in both network-forming and modifying positions and would therefore be present in both four- and six-fold coordination.

Recent spectroscopic work (Steele and Douglas, 1965; Kurkjian and Sigety, 1968) has shown that ferric iron is present in glasses in tetrahedral coordination, and so additions of ferric ions to tetrahedral sites in CaO–MgO–Al_2O_3–SiO_2 glasses may well upset the balance of four- and six-fold coordinated Al ions in favour of the six-fold state. Now, in the normal spinel structure, all the Al ions are in six-fold coordination, and the displacement of Al ions in the glass would put them in more favourable positions for the production of spinel nuclei by interaction with the relatively mobile Mg^{2+} cations.

A further interesting aspect of this piece of work is that the nucleation rates at constant temperature were not constant with respect to time, but increased by a factor of about 4:1 over the rate at zero time (fig. 4). The time taken to reach an apparently steady rate decreased from about an hour for the lowest curve to less than half an hour for the highest. Turnbull (1956) has pointed out that the nature of the embryos present in the glass, and hence the rate of nucleus formation, will depend upon its thermal
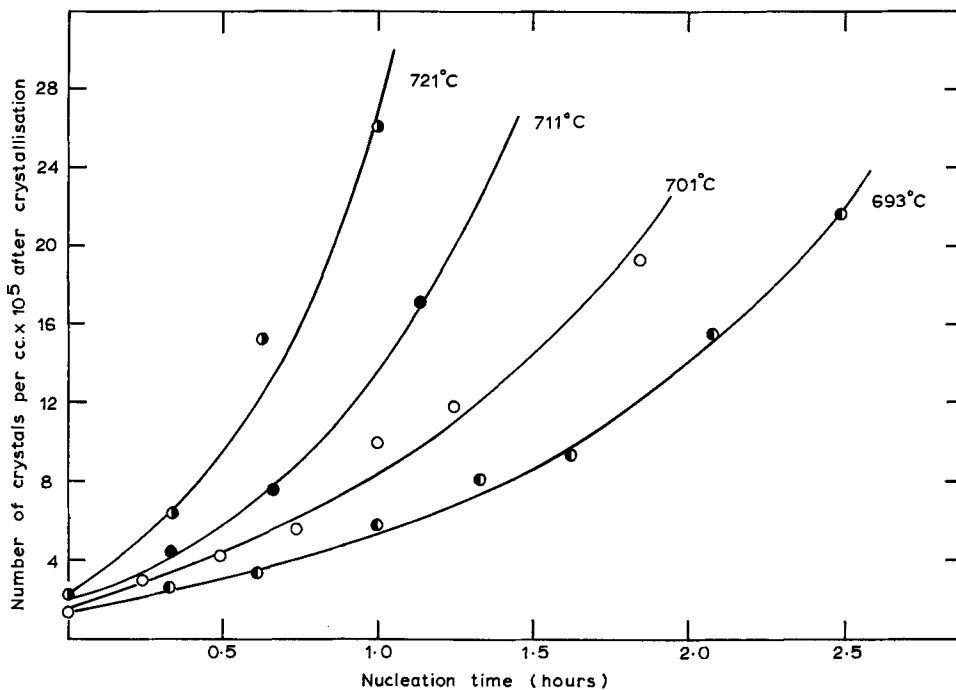

FIG. 4. Variation in the rate of nucleation of spinel crystals with time for temperatures shown, with crystal growth at 980 °C/15 min. Same glass as in fig. 2.

history. At high viscosities, incubation times will exist during which embryos grow to critical size before a steady state nucleation rate is reached. These times will become very short as the viscosity decreases. Hillig (1962) has calculated a value of one hour for this incubation time at a viscosity of 10^{10} poise, assuming infinite quenching rate and three-dimensional random walk, with diffusivities calculated from the Stokes–Einstein relationship. This calculated incubation time is much longer than the experimental observations quoted here, due to the assumptions that have to be made in Hillig's treatment. However, care must be taken in the interpretation of nucleation data obtained at high viscosities.

Another reason for time-dependence of the apparent nucleation rate is that as we have seen (p. 743) the size of the critical nucleus increases with increasing temperature. Thus, if nucleation rates are measured by subjecting samples to two-stage heat

treatments for nucleation and crystal growth, then it is possible that nuclei produced at the lower temperature may disappear when the temperature is raised. However, during the nucleation treatment nuclei that reach the critical size will continue to grow, so that their size will be beyond the critical diameter and render them stable at the higher temperature. Again, this will only be true if the quantity of crystalline material in the nuclei is much less than the potential quantity of that phase in solution in the matrix.

It is worth mentioning that the curves do not show zero nuclei for zero length of nucleation heat treatment. This is because a small number of crystals originate during the crystallization stage of the heat treatment, due to overlap of the crystallization curves. This effect is of great importance in the next example to be discussed, in which small additions of chromium oxide to similar glasses in the $CaO–MgO–Al_2O_3–SiO_2$ system have been investigated (Keyworth and Rogers, 1970).

Nucleation in glasses containing chromium oxides

Chromium oxide only has a very small solubility (1 wt % or less) in melts of compositions similar to those studied with iron oxide additions. Glasses containing suffi-
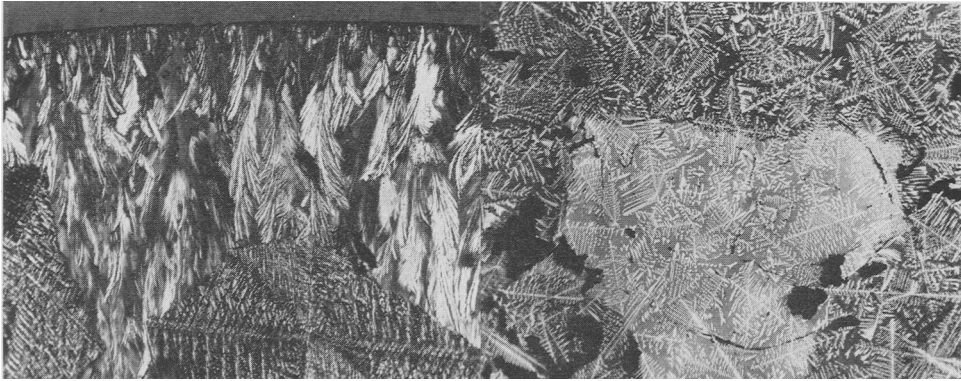
FIGS. 5 and 6: Fig. 5 (left). Surface nucleated anorthite branches impinging on internal dendrites of diopside. 26 CaO, 6 MgO, 15 Al_2O_3, 53 wt % SiO_2 with 0·6 wt % added Cr_2O_3. Transmitted light, ×75. Fig. 6 (right). Interior of partially crystallized glass specimen, showing anorthite (grey), glass (pale grey), and diopside dendrites (white). Composition as for figs. 5 and 7. Reflected light, ×50.

cient chromium oxide (greater than 0·3 wt %) and magnesia (6 wt % or more) crystallized on heat treatment both by surface (heterogeneous) nucleation and by internal nucleation, so that eventually the crystals produced by the two nucleation mechanisms impinged upon each other; this is shown in fig. 5. The surface growth was a hitherto unreported phase, nucleated on tiny surface dendrites of diopside. This phase was metastable, and transformed to anorthite $CaO.Al_2O_3.2SiO_2$ when the specimen was held for a sufficiently long period at the crystallization temperature. The length of time required became shorter with increasing temperature.

The internal devitrification proceeded in two stages, first the crystallization of clinopyroxene (diopside) and then the crystallization of anorthite, which occupied the

spaces between the dendrites. This two-stage process was followed by plotting the volume fraction crystallized X, against time. Fig. 7 shows a typical set of curves. It is interesting to note that the anorthite begins to form, by secondary nucleation, on the diopside dendrites after the metastable phase in the surface growth begins to transform to the stable anorthite phase. This would suggest that the glassy structure is time-dependent, and steady-state conditions for nucleation and growth are not immediately achieved. It was not possible to separate the two processes of nucleation and growth by using a two-stage heat treatment procedure for all temperatures at which devitrification took place, as it was found that the two steps were concurrent.
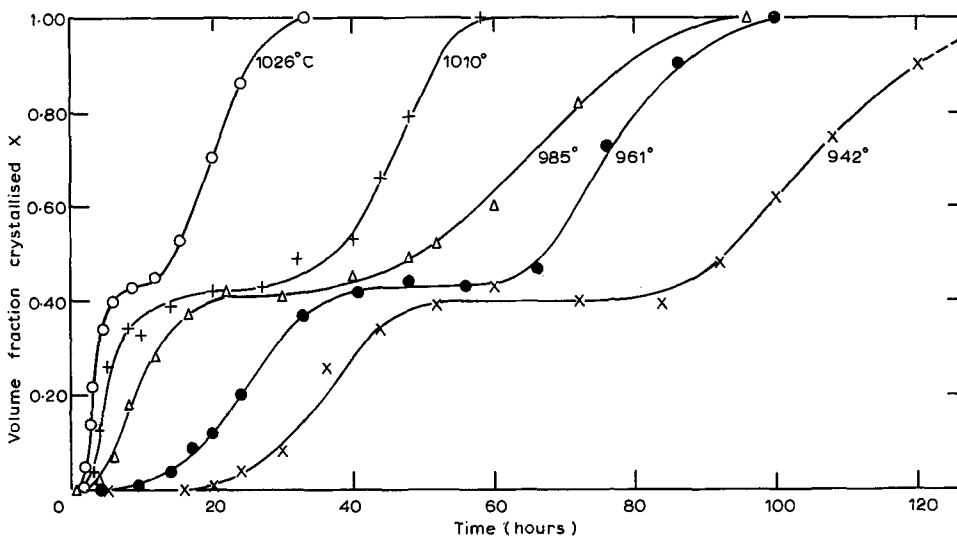

FIG. 7. Volume fraction crystallized as a function of time. Glass composition as for fig. 5.

It is possible to attempt an analysis of the nucleation rates for the diopside (single crystal) dendrites in two ways. The one that ought to be the most rigorous is the Johnson–Mehl–Avrami treatment (Johnson and Mehl, 1939; Avrami, 1941; Evans, 1945). Different assumptions about the time dependence of nucleation and growth lead to different integrated forms of the J.M.A. equation, and these have been reviewed by Mandelkern (1964) and Sharples (1966). In general, if the initial linear growth rate is u and the nucleation rate is I, then the volume fraction X crystallized at time t is given by: $-\ln(1-X) = Zt^m$ where Z is equal to $\pi \rho_c u^3 I / 3\rho_g$, ρ_c and ρ_g are the densities of crystal and glass, and m is the Avrami exponent which takes various values according to the time dependence of the nucleation and growth rates, as shown in Table I. So, by taking logs, and plotting values of $\ln\{-\ln(1-X)\}$ against $\ln t$, it is, theoretically, possible to determine both m and Z from the slope of the straight line and the intercept on the ordinate axis.

Fig. 8 shows a typical set of plots from the experimental results. The plots are fairly linear over the range in which between 5 and 20 % of the material is crystalline.

Values of m calculated from these curves were 3·3, 3·0, 2·8, and 3·4 for four glass compositions, and because of the insensitivity of the plots the mean value can be taken

TABLE I. *Values of m for various kinds of nucleation and growth processes*
(Mandelkern, 1964)

Growth habit	First order nucleation		Instantaneous nucleation	
	Linear growth	Diffusion controlled growth	Linear growth	Diffusion controlled growth
3 dimensional (spheres)	$3+1 = 4$	$3/2+1 = 5/2$	$3+0 = 3$	$3/2+0 = 3/2$
2 dimensional (plates)	$2+1 = 3$	$1+1 = 2$	$2+0 = 2$	$1+0 = 1$
1 dimensional (needles)	$1+1 = 2$	$\frac{1}{2}+1 = 3/2$	$1+0 = 1$	$\frac{1}{2}+0 = \frac{1}{2}$

as about 3. This would suggest that the growth process is a mixture of linear (when m would have a value of 4) and diffusion-controlled (when m would have a value of 5/2).
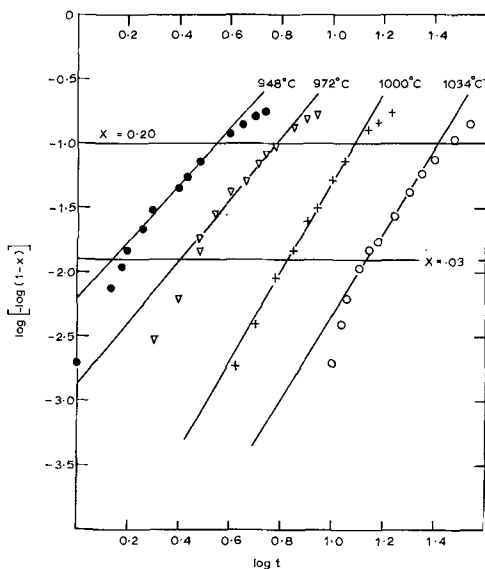

FIG. 8. J.M.A. plots for glass as in figs. 5, 6, and 7, but containing 1 wt % added Cr_2O_3.

In the case of linear growth, which is usually observed in single component glasses (that is, when the crystalline phase and the glass have the same composition) the rate controlling steps occur at the interface (Jackson, Uhlmann, and Hunt, 1967), and are dependent upon the same factors as viscous flow (that is, the movement and reorientation of anionic group). Since the dendritic phase has a different composition from the matrix glass, the progressive build-up of a boundary layer through which the precipitating phase must diffuse is to be expected.

In order to calculate the nucleation rate from the J.M.A. plots in the present case, the value of Z in the equation must be modified to take account of the different growth rates along the x, y, and z axes of the dendrites, which are in the ratio 2:1:1. We then have $Z = \rho_c u^3 I/24\rho_g$. The calculation of the nucleation rate then becomes possible by substitution of crystal growth rates, measured on the advancing layer of surface crystallization. This derivation gave values for I that were inconsistent, varying between values of about one and a thousand per cubic centimetre per sec for similar samples, and generally decreasing with increasing temperature.

However, nucleation rates determined by counting dendrites on polished sections under the microscope increased with increasing temperature, and gave linear Arrhenius plots. The unreliability of the nucleation rates derived from the J.M.A. equation is demonstrated by the fact that no extra nuclei can be produced by a preliminary heat treatment at a temperature a hundred or so degrees below the crystallization temperature, although the trend of the J.M.A. results would lead us to expect this.

The failure of the J.M.A. equation in this case is not altogether surprising, since it was originally derived for a crystallizing system of constant composition, and in most glasses the composition of the matrix must change as crystallization proceeds. It is also probable that, as in the case of the glasses containing added iron oxide, the number of nuclei is not a linear function of time, and the J.M.A. equation requires this.

The values of the nucleation rate determined by counting must of course be lower than the true value. However, the linearity of the Arrhenius plots gives some confidence in them. Activation energies derived from these for added Cr_2O_3 of o·6, o·8, and 1·0 wt % were 110, 130, and 100 kcal/mole ($\pm$ 10 kcal). These values are close to the activation energies determined by Keyworth for crystal growth in the same glasses and for viscous flow in similar glasses (Williamson, Tipple, and Rogers, 1968), and indicate that the same rate-controlling mechanisms are involved in all three processes.

The calculated activation energies given above were determined for glasses melted in air. These glasses contained a mixture of chromium ions of two oxidation states, Cr^{6+} and Cr^{3+}, with 17 % of the chromium in the higher oxidation state. Glasses melted in oxygen contained 32 % of their chromium in the Cr^{6+} state, i.e. about twice the quantity. The observed rate of nucleation was increased by two orders of magnitude. For example, at 1000 °C, the nucleation rate was increased from 40 cm^{-3} sec^{-1} to 3000 cm^{-3} sec^{-1}. Electron-probe microanalysis of the dendrites (Scholes, 1969) showed an increase in chromium concentration of about 20 % over a distance of about 4 μm at the centres. It therefore seems likely that the nuclei are formed of a chromium-rich phase, and the necessity for a substantial amount of magnesia in the composition suggests that this nucleating species, as in the earlier iron-oxide-containing glasses, is a spinel, in this case, $MgO . Cr_2O_3$. The Cr^{6+} ion would probably be surface-active on large silicate anions in the glassy structure, since two non-bridging oxygens are necessary in order to satisfy the six positive charges. The presence of chromium ions in these positions would thus make the precipitation of chromium spinel nuclei possible, with the transference of charge to a Cr^{3+} ion.

Liquid/liquid phase-separation by nucleation and spinodal decomposition

Metastable unmixing below the liquidus so that the glass separates into two glassy phases often precedes the nucleation of crystalline material. Crystal nucleation can then proceed either by homogeneous nucleation within one of the separated phases, or by heterogeneous nucleation on the freshly formed interfaces between the two glassy phases. Unmixing of this kind can take place either in systems where there is a region of stable immiscibility in the liquid, or where there is a very flat region on the liquidus curve, indicating incipient unmixing (Roy, 1960). Metastable immiscibility gaps of

these kinds exist in many systems used in the manufacture of commercial glass-ceramics, particularly those containing TiO_2 or P_2O_5 (see, for example, the monograph by McMillan, 1964).

The separation of the glass into two phases can take place either by classical nucleation and growth of droplets (Ohlberg et al., 1965; Haller, 1965) or by spinodal decomposition (Cahn and Charles, 1965). Each of these mechanisms can produce a two-phase system with intersecting growth in the later stages of development (Haller and Macedo, 1968), but they are very different in kind during their early stages. Experimental evidence (Moriya, Warrington, and Douglas, 1967; McCurrie and Douglas, 1967; Zarzycki and Naudin, 1967) obtained from electron microscopy and small-angle X-ray scattering has shown that nucleated droplets grow by 'Ostwald ripening', that is by the dissolution of the smaller particles, and an associated increase in size of the larger ones, as a means of lowering the over-all interfacial free energy. The mean particle radius $\bar{r}$ increases with the cube root of time, according to the equation $\bar{r}^3 - \bar{r}_0^3 = 8\sigma D C_0 V_m^2 t/9RT$, where $\bar{r}_0$ is the initial mean radius, D is the diffusion coefficient of the solute in the matrix, C_0 is the equilibrium solubility of a particle of infinite radius, and V_m is the molar volume of the particle. The number of particles per unit volume is thus inversely proportional to t (Wagner, 1961; Lifshitz and Slyozov, 1961).

In the case of spinodal decomposition, the unmixing takes place by continuous variations in composition over a longer range than in classical nucleation, and the separation takes place without the need to overcome an interfacial energy barrier. The gradient of these compositional variations increases with time, and the distinction between the phases becomes more clear. The interconnecting phases produced in the early stages of decomposition thus become separated into droplets after long heat treatments. The kinetics of the separation process have been discussed by Cahn and Charles (1965). The difference between spinodal decomposition and nucleation of droplets is shown by the two diagrams (fig. 9). Inside the spinodal region, $\partial^2 G/\partial C^2$ is negative, so that small fluctuations in composition always result in an over-all decrease in energy, and phase separation can take place without nucleation. Diffusion is thus rate-controlling. Outside the spinodal region, but inside the region of immiscibility, the formation of a second glassy phase can only take place by nucleation and growth of droplets. As the spinodal is approached, however, the critical nucleus no longer has a sharp boundary, but begins to have a diffuse interface (Haller, 1965), and nucleation is more like a process of continuous composition change. Just inside the spinodal region, compositional fluctuations of short wavelength are unstable, but further inside the spinodal the glass is unstable even to short-wavelength fluctuations.

Experimental evidence of separation by a spinodal decomposition mechanism has been obtained by Zarzycki and Naudin (1967) from small-angle X-ray scattering studies with the system B_2O_3–PbO–Al_2O_3 and by Neilson (1969) and Tomozawa, Herman, and MacCrone (1969) for the system Na_2O–SiO_2. The kinetics of the separation in the latter case show that the controlling diffusion coefficient is close to that for oxygen self-diffusion, indicating that the motion of anions is the rate-controlling step.

Nucleation in glasses containing fluoride or phosphate

In the third example from experimental work, metastable liquid/liquid phase separation is the first step in the devitrification process. Mukherjee and Rogers (1967) studied the rate of nucleation in a Na_2O–CaO–Al_2O_3–SiO_2 glass in which some of the oxygen ions had been replaced by an equivalent molecular proportion of fluoride ions. Fluorine contents were in the range 2–4 wt % F, with a base glass composition of 5 Na_2O, 32 CaO, 7 Al_2O_3, 56 wt % SiO_2.

It was found that, by using appropriate two-stage heat treatments, the nucleation and crystal-growth steps in devitrification could be separated. Under these conditions, the number of nuclei in the glass after the first stage (550–750 °C) of the heat treatment could be determined by counting the number of spherulites of wollastonite produced in the higher (crystal-growth) stage at 850 °C. The nucleation rate showed a sharp maximum at 662±3 °C, which was independent of the fluorine content, but the maximum had a lower absolute value as the fluorine content was reduced.

Electron micrographs of replicas taken from specimens after the nucleation treatment, but before the crystal growth stage, showed that the glass had undergone a separation into two glassy phases. It was notable, however, that the number of spherulites that could be grown in a subsequent higher temperature heat treatment was two or more orders of magnitude less than the scale of the phase separation would have suggested, if this had been responsible for nucleation of crystals. It may be thought that metastable liquid/liquid separation should make the conditions for nucleation of crystals more favourable, but the experimental evidence of Mukherjee and Rogers shows that the connection between the two processes is not an obvious one. The low interfacial energy to be expected
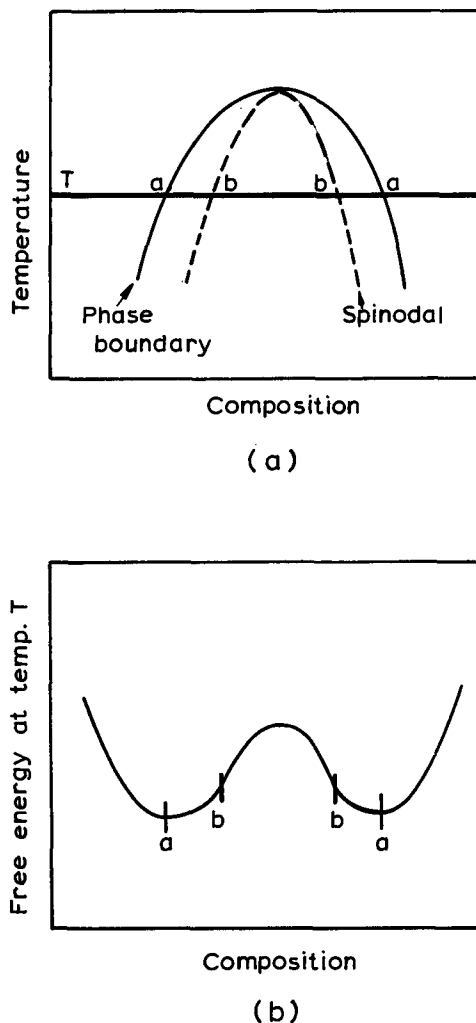

FIG. 9. (a) Hypothetical phase diagram showing two-liquid and spinodal regions. (b) Free energy of mixing corresponding to temperature T on fig. 9 (a).

between two glassy phases would not easily induce nucleation of crystals, and this would be especially so if the separation had taken place by a spinodal mechanism. Liquid/liquid separation would therefore only be expected to increase the probability of crystal nucleus formation if one of the separated phases had more favourable parameters for substitution in the classical nucleation equation, i.e. a higher thermo-dynamic driving force or a more favourable diffusion parameter.

The relationship between spherulitic growth and liquid/liquid phase-separation is shown in the optical micrograph in fig. 10. The heat-treated specimen in this case was a similar glass to that of Mukherjee and Rogers, but contained phosphate ions instead
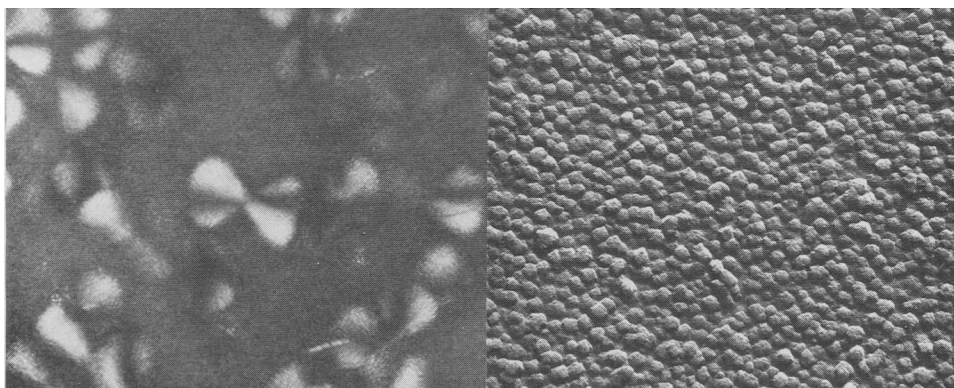
FIGS. 10 and 11: Fig. 10 (left). Spherulites growing in a phase separated glass, of composition 5 Na_2O, 31 CaO, 7 Al_2O_3, 51 SiO_2, 6 wt % P_2O_5. Heat treatment, 825 °C/2 h, 950 °C/¼ h. Transmitted light, ×200. Fig. 11 (right). Electron micrograph (carbon replica) showing crystallites formed in a phase separated glass; composition as for fig. 10. Heat treatment, 660 °C/7 h, 850 °C/24 h, ×32 000.

of fluoride ions, in the same range of ionic percentage (Rogers, Coomber, and Arnold, 1969). Because of the opacity induced in the specimen by phase separation and the small droplet size of the glassy phases (about 1 μm), the resolution is poor. However, the spherulites can be seen to be growing through the two-phase glass, so that complete crystallization would result in a body with grain-size much larger than the scale of the phase separation.

Fig. 11 shows an electron micrograph of a similar specimen of glass containing phosphate ions, but subjected to a heat treatment at lower temperatures. In this case, the resulting crystalline material has a grain structure corresponding to the phase separation that preceded devitrification, since growth of each crystallite has stopped at the droplet boundary.

The spherulitic growth, both in the case of the glasses containing fluoride and of those containing phosphate, consisted of crystalline phases with long chain structures, which were members of solid solution series, thus favouring spherulitic growth. In the case of the fluoride additions the crystalline phases were fluor-pectolite and β-wolla-stonite; in the phosphate case, the crystalline phase was a complex solid solution with a structure similar to fluor-apatite, but so far unidentified. The nucleation behaviour of

the two types of glass on heat treatment was similar, as shown by the temperature dependence curves in fig. 12; the differences in absolute rate and the position of the maximum would arise from differences in liquidus temperature and viscosity for the
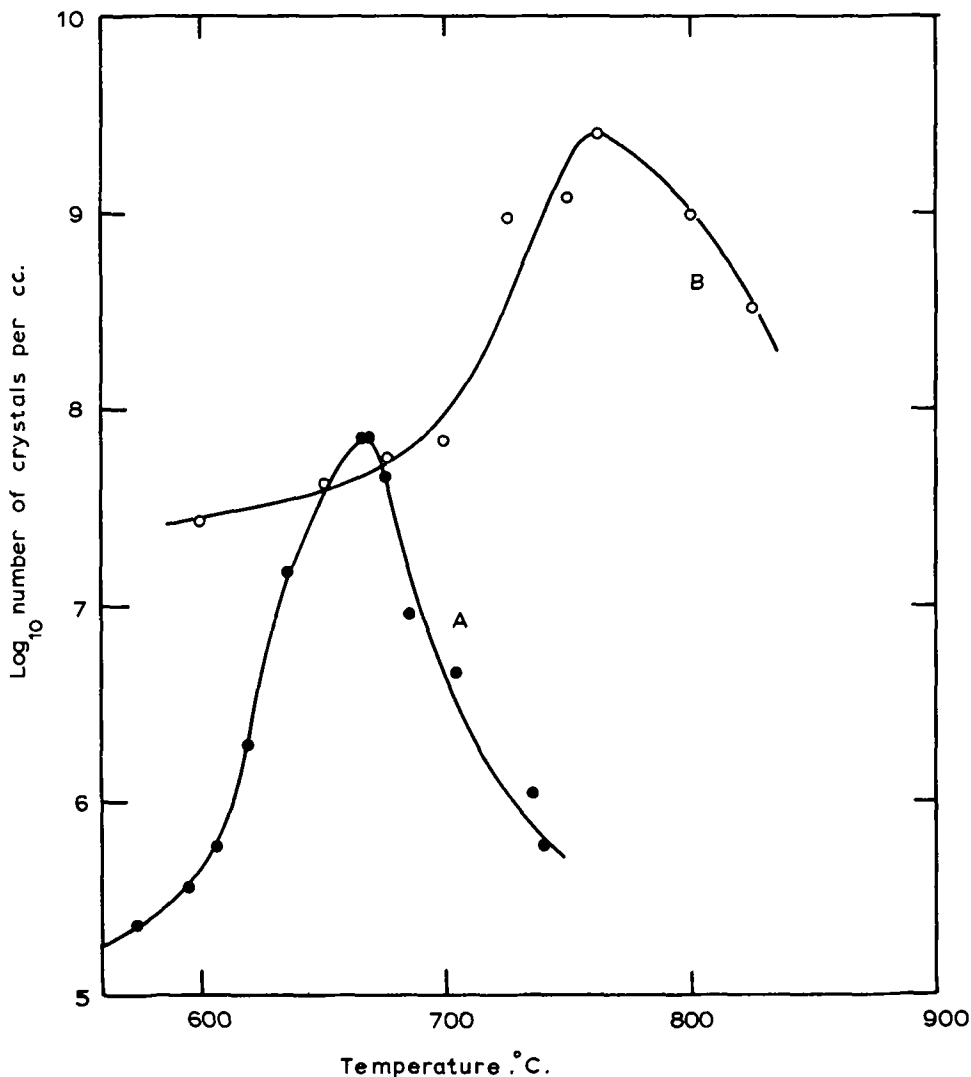

FIG. 12. Temperature dependence of nucleation rates for similar base glasses. Curve A, additions of fluoride (3·4 wt % F); nucleated for ¼ h, crystallized, 850 °C/¼ h. Curve B, additions of phosphate (6 wt % P_2O_5), as for figs. 10 and 11; nucleated for 2 h, crystallized, 950 °C/¼ h.

two compositions. Both fluoride and phosphate ions would act as network breakers in the glassy anionic structure because they remove bridging oxygens, and their influence on devitrification probably depends on this property.

The experimental work on the influence of fluoride and phosphate ions shows that, if metastable liquid/liquid separation takes place before crystallization, then the crystal nucleation kinetics are complex. In the earlier examples, of glasses containing iron oxides or chromium oxides, which did not show metastable immiscibility, the experimental results could be explained remarkably well by the classical nucleation theory. When glassy-phase separation takes place before crystallization, as in this case, the rate-controlling process may no longer be one of classical nucleation. The two phenomena of metastable liquid/liquid phase-separation and the initiation of crystal growth may be linked together, so that neither can be sensibly described as the rate-controlling step. When experimental results are available for more systems, and particularly for those systems whose equilibrium phase diagrams are well established, then a chemical interpretation in terms of the micro-structure of the glass may be possible.

Concluding remarks

Rawson (1967), in his monograph on glass-forming systems, has pointed out that no *simple* structural theory of glass formation can be expected to apply to *all* glasses. He therefore suggested that an interpretation of glass formation in terms of chemical kinetics and thermodynamics is more fruitful. It has been shown in the present paper that experimental data on nucleation rates can be explained in those terms, in spite of the simplifications that have to be made in the derivation of the rate equations. The ultimate test of the applicability of the theoretical treatment would be its use to predict the behaviour of specific cases, which could then be tested by experiment. Any suitable systems that suggest themselves are severely handicapped by the lack of basic values for the parameters appearing in the rate equations; this is particularly so for the multi-component systems of interest to geologists or materials technologists. More information, for example from ionic diffusivity measurements and calorimetry, will be of great help when it becomes available. The field in which the most rapid progress is being made is the exploration of the composition regions in multi-component systems where metastable liquid/liquid unmixing can occur; this information will also prove useful in the prediction of nucleus formation for specific compositions, such as those used commercially for the manufacture of glass-ceramics.

Because of this lack of basic physico-chemical data, it is often necessary to adopt a mixed approach in which thermodynamic factors are considered in terms of molecular structures and bond character, and the changes in these that take place during nucleation. In silicate glasses at high viscosities, the disordered structure is made up either of an anionic framework or of large silicate anions; in each case a large amount of energy is needed to re-orientate these anionic groupings so that they form an ordered structure. Additions to the glass composition of constituents that can encourage such a reconstruction at high viscosities will therefore help to initiate the crystal-growth process. This effect is illustrated by the examples given earlier in the paper, where additions of iron or chromium oxides, fluoride, or phosphate all achieved an increase in the nucleation rate by modifying the anionic structure, although the mechanism by which this took place was different for each case.

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