

Crystallisation in oxide glasses – a tutorial review

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Glasses and glass-ceramics have had a tremendous impact upon society and continue to have profound industrial, commercial and domestic importance. A remarkable number of materials, with exceptional optical and mechanical properties, have been developed and enhanced using the glass-ceramic method over many years. In order to develop glass-ceramics, glass is initially prepared *via* high temperature synthesis and subsequently heat treated, following a carefully designed and controlled process. A glass-ceramic system comprises crystalline and non-crystalline phases; in multicomponent systems these phases are significantly different from the initial glass composition. The properties of glass-ceramics are defined by microstructure, crystal morphology as well as the final chemical composition and physical properties of the residual glass. Knowing the mechanism of glass crystallisation, it is possible to predict and design a glass-ceramic system with near-ideal properties that exactly fulfil the requirements for a particular application. This tutorial review is a basic introduction to the crystallisation in glasses and mainly focuses on silicate and closely related oxide glasses. The review describes and discusses key learning points in five different sections, which facilitate the understanding of glass crystallisation and development of glass-ceramics.

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Key learning points

- (1) Nucleation and crystal growth are two fundamental stages of crystallisation in glass.
- (2) The structure and unique properties of glass-ceramics can be controlled and specifically tailored for an application through the manipulation of the initial glass composition.
- (3) At the pre-nucleation stage the processes occurring in a glass dictate the subsequent mechanism of crystallisation.
- (4) Nanocrystallisation can be achieved in the glass if certain glass design rules are followed.
- (5) A combination of the structural techniques available in modern science rather than a single method is more likely to characterise accurately the mechanism of glass crystallisation.

Introduction

The process of crystallisation is widely applicable to many materials that can crystallise from the amorphous state or the melt; this includes materials as diverse as oxide glasses, organic polymers, metals, chalcogenides and molecular systems *e.g.* water. In glass-ceramic (GC) systems, major advances in understanding the process of crystallisation, in particular the role of nucleating agents, have significantly extended the nano-level control of crystallisation for a vast variety of inorganic materials.

Glasses are amorphous solids that exhibit characteristic glass transition temperature (T_g) and are typically obtained

upon rapid cooling or quenching the melt to the temperatures below the glass transition to prevent crystallisation. Fig. 1 schematically demonstrates the path difference for a specific physical property change, *e.g.* molar volume, enthalpy or density *etc.*, when the liquid state is supercooled and the glass transition range is achieved compared to slow cooling followed by crystallisation. Thus, the quenching stops the melt from following the thermodynamically favoured path towards crystalline matter and traps the system in a metastable amorphous state.

The nature of the glass transition still remains one of the most problematic issues within the field of amorphous solids. It has been described variously as a quasi-thermodynamic transition or a kinetic process. It is the process in which a fundamental change takes place in the physical properties of the materials *e.g.* specific heat capacity, volume, enthalpy, *etc.* The truth is that both thermodynamics and kinetics play an important part in this transition and its exact nature lies beyond the scope of this review.^{1–4}

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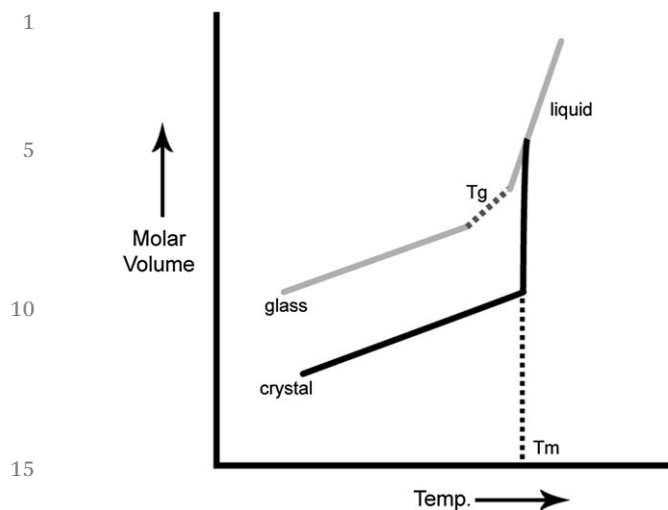


Fig. 1 Glass formation via supercooling and glass transition behaviour of a melt cooled down with the temperature schematically demonstrated via the molar volume change as a function of temperature. Here two alternative pathways are clearly shown which are contingent upon the cooling rate. Rapid cooling (top pathway) allows the formation of a glass going through a T_g region. Slower cooling (bottom pathway) allows crystallisation at the melting temperature, T_m , to form a crystal.

Although some materials readily form a glass and others do not do this so easily, it is now understood that nearly all materials can be forced into the amorphous state provided a high enough quenching rate is achieved. Thus, it is the quenching technology that may be a limitation for the glass formation, the latter is also termed vitrification. Currently the quenching rate up to 10^4 – 10^6 K s^{-1} is possible to achieve for silicate (SiO_2 -based) glasses using the laser melting and hammer- or roller-quenching.^{5–7}

A critical cooling rate, *i.e.* the minimum quenching rate needed for a successful vitrification of material, was introduced to quantify the glass forming ability. If the critical cooling rate is not achieved upon quenching the obtained glass would contain a fraction of crystals, *i.e.* glass would crystallise or “devitrify”. The presence of crystals in the glass can fundamentally alter the properties and structure of the glass and therefore is not desired when it occurs in an uncontrolled manner upon quenching.

Another way of assessing how readily a glass of a given composition forms is to look at glass stability (GS) against crystallisation when it undergoes heat treatment. Most of the introduced GS parameters can be calculated from the relationships between T_g , T_m and crystallisation temperature T_c ,⁸ the latter will be defined in the text below. Over decades a number of theories have been put in place to establish the relationship between the composition of glasses and the crystallisation mechanism, in particular for silicate glasses. This resulted in significant progress in glass science and also enabled development of GC materials with desired microstructure and properties.⁹

Heat treatment of inorganic oxide glasses¹⁰ produces GCs. The term “ceramic”, however, has had a poorly defined meaning in the scientific literature. Here, we define ceramics to mean the ordered or crystalline component present within the glassy or amorphous matrix. Hence GCs would contain both

crystalline and non-crystalline phases. The nature of crystalline regions in GCs can vary significantly from the poorly crystalline species with the high number of defects and/or imperfections up to well developed and defined crystals. This has a fundamental influence on the physical and chemical properties of the GC material. It is advantageous to induce crystallisation in glass in a carefully controlled manner. The rate, extent and degree of crystal formation in glass are therefore of great interest.

The inorganic oxide glasses and GCs, *e.g.* silicates, phosphates, borates, aluminosilicates *etc.*, have tremendous industrial, commercial and domestic importance. They have an immense number of applications from optical and electrical materials to bioactive and machinable GCs.⁹ The crystallisation processes within these systems have been extensively studied in the literature.^{9,11} In particular, two classic examples of the studied mechanism of crystal nucleation in glass, the lithium disilicate and calcium sodium silicate systems, have received substantial attention over a number of decades.^{12,13} The lithium disilicate has had considerable commercial application especially in the area of optical and dental GCs.

This review serves as an introduction to the crystallisation in glasses and formation of GCs. Here, we will focus on glass forming melt-derived silicates and aluminosilicates and their closely associated derivatives and will discuss the basics of the effects of heat treatment upon these glasses.

1 Nucleation and crystal growth are two fundamental stages of crystallisation in glass

Thermodynamically metastable glasses can undergo crystallisation upon heat treatment when the amorphous component partially converts into crystalline material. Glass crystallisation is an exothermic event and can be investigated by thermal analysis, such as differential scanning calorimetry (DSC) or the closely related differential thermal analysis (DTA) (*cf.* Section 5). On a typical DSC trace for a given glass composition the crystallisation will be displayed as an exothermic event following the glass transition as demonstrated in Fig. 2. The glass crystallisation temperature, T_c , corresponds to the exothermic peak temperature on a DSC trace.

The solid obtained after heat treatment (if complete re-melting into a glass melt has not been attained) contains both the crystalline and residual amorphous phases and the final material is frequently referred to as a GC. The physical and chemical properties of the GCs are radically altered compared to the properties of the glass before devitrification including the physical appearance as seen from Fig. 3.

In glasses crystallisation occurs in two steps, the first, nucleation, is the formation of small nuclei often on a nano-scale and the second is growth of the nuclei into well-formed crystals. The nucleus is defined as a submicroscopic cluster of the new crystalline phase that would evolve from it. Knowing the temperature dependence for the both steps it is possible to

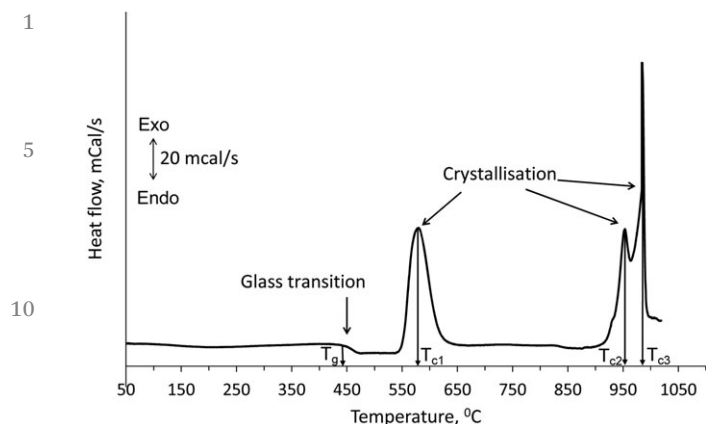


Fig. 2 Experimental DSC trace of glass. As glass is heated the glass transition is observed first followed by the crystallisation exotherm with the peak temperature defined as crystallisation temperature (T_{c1}). Glass transition temperature is defined here as the onset of glass transition. Two more crystallisation exotherms are observed at higher temperatures for this composition (T_{c2} and T_{c3}). Note that the T_g is endothermic and reversible.

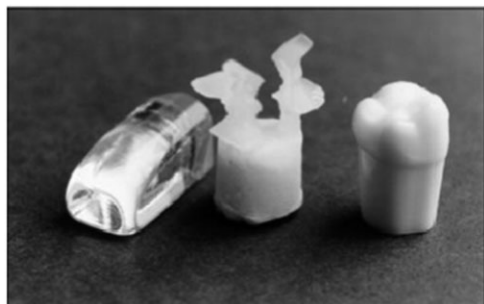


Fig. 3 This shows that GC is used for fabrication of dental restorations. The original glass (left) is heat treated to form the final GC (middle and right). The lost wax casting was used to form the desired shape.

control glass crystallisation and obtain GC with desired properties. A schematic diagram (Fig. 4i–iv) demonstrates that nucleation typically occurs at temperatures at or just above T_g , whereas the optimal crystal growth rate is usually shifted to higher temperatures.

The temperature range where the crystal growth approaches the melting temperature (Fig. 4i) is the metastable supercooling or the Ostwald–Miers range. In this region no new nuclei form and only those formed at the lower temperature would grow. A glass quenched directly from the melt down to this temperature range and heat treated here would not crystallise due to the absence of nucleation.

Nucleation as the initial stage of crystallisation plays the ultimate role in determining the microstructure and properties of the final GC and, therefore, has been the focus of extensive research for decades. A number of experimental approaches for the investigation of nucleation in glasses have been developed over the years and will be discussed below (Section 5). However, to study the nucleation experimentally still remains fundamentally challenging. In parallel with the experimental approach, several theoretical approaches were developed to describe

kinetics and thermodynamics of nucleation including the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory and Classical Nucleation Theory adopted for glass crystallisation by Weinberg, Zanotto, and Fokin.^{14–16}

There are two mechanisms of nucleation, homogeneous and heterogeneous. In homogeneous nucleation, the nucleus forms in the absence of any phase inhomogeneity, surface borders or interfacial boundaries. Whereas heterogeneous nucleation starts at the interface boundaries and surfaces and is catalysed by the presence of foreign impurities and nucleating agents.

The general expression of the nucleation rate is an exponential function of the thermodynamic and kinetic barriers that are needed to overcome to form a crystal nucleus in glass. The rate of the steady-state or time-independent nucleation I (eqn (1)) can be expressed as^{15,17}

$$I = I_0 \exp\left(-\frac{W^* + \Delta G_D}{k_B T}\right) \quad (1)$$

where I_0 is the pre-exponential term, k_B is the Boltzmann constant, and T is the absolute temperature. The ΔG_D is the activation energy for transfer of a species through the melt/nucleus interface and is the kinetic contribution to the nucleation rate. The W^* , which is a thermodynamic barrier for nucleus formation, is the free energy change due to the formation of a new nucleus of critical size r^* . Below the critical size r^* the small atomic clusters or embryos are not stable and can dissolve in the original glass without producing a nucleus.

The work of homogeneous nucleation W_{hom}^* (2) needed for the formation of the critical size nucleus is

$$W_{\text{hom}}^* = \frac{16\pi\sigma^3}{3\Delta G_V^2} \quad (2)$$

where σ is the interfacial energy required for formation of a new surface of the nucleus and ΔG_V^2 is the free energy change per volume that is produced upon formation of a new nucleus.¹⁷

For the heterogeneous nucleation the work for nucleation W_{heter}^* (3) will be

$$W_{\text{heter}}^* = W_{\text{hom}}^* \left[\frac{(1 - \cos \theta)^2 (2 + \cos \theta)}{4} \right] \quad (3)$$

where θ is the contact or wetting angle of liquid at the surface of the cluster on a solid substrate.¹⁷

Regardless of the θ value the work for heterogeneous nucleation cannot exceed the work for homogeneous nucleation. Except for $\theta = 180^\circ$ (under no wetting conditions, $W_{\text{heter}}^* = W_{\text{hom}}^*$), the relationship $W_{\text{heter}}^* < W_{\text{hom}}^*$ is always true and $W_{\text{heter}}^* = 0$ at $\theta = 0^\circ$ (absolute wetting). Thus, the thermodynamic barrier for heterogeneous nucleation is significantly decreased due to the presence of a catalytic surface, e.g. walls of a crucible, impurity particles or nucleating agents.

Most of the glasses crystallise *via* the heterogeneous nucleation, whereas homogeneous nucleation is rare because of the higher activation energy barrier for this process. There are few oxide glasses that nucleate homogeneously,¹⁵ e.g. lithium disilicate glass $\text{Li}_2\text{O}-2\text{SiO}_2$ and sodium calcium silicate glass of

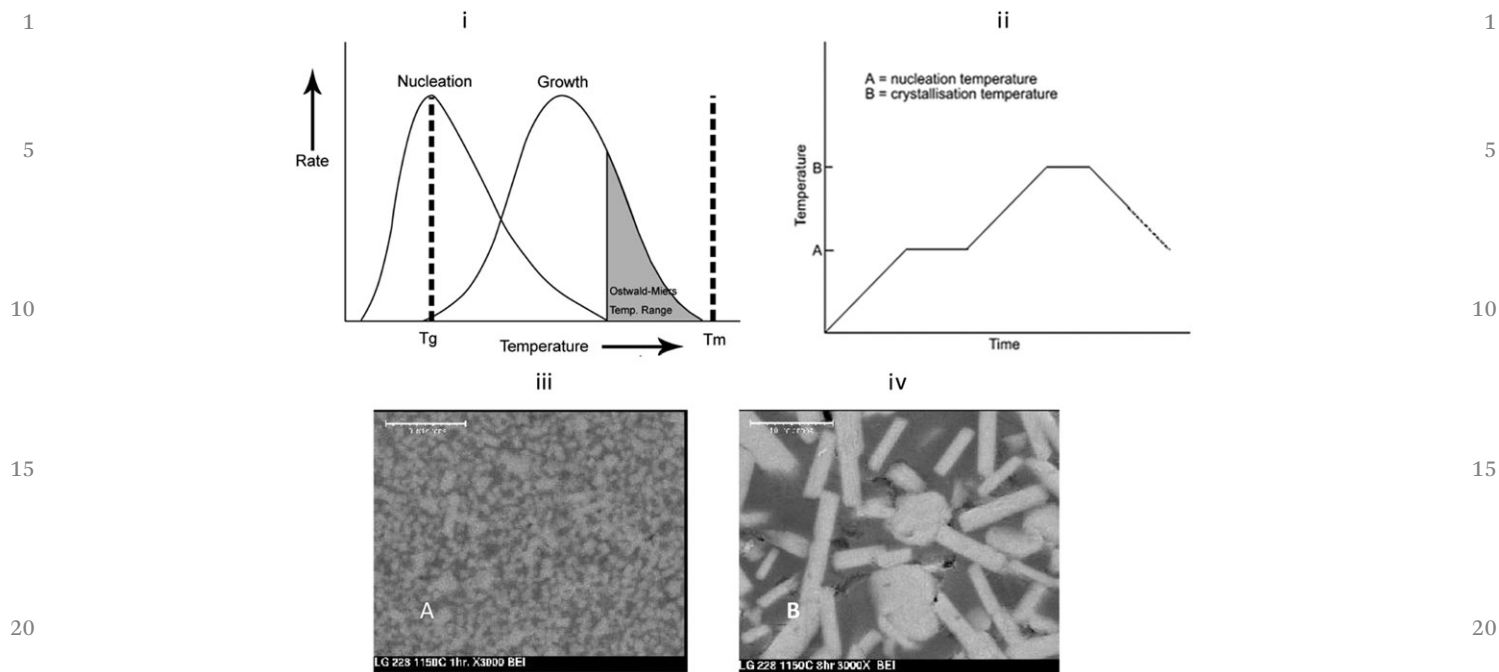


Fig. 4 (i) This schematically shows the rates of nucleation and crystal growth as a function of temperature. The width and temperature range of the curves are different for each individual composition. (ii) Two-step heat treatment is used for development of a GC. During the first hold at the nucleation temperature A the nuclei form in glass as shown in the SEM photomicrograph (iii) During the second hold at the crystal growth temperature (B – crystallisation temperature) nuclei grow into crystals as seen in the SEM photomicrograph (iv).

composition $\text{Na}_2\text{O}-2\text{CaO}-3\text{SiO}_2$, and it remains unclear why these compositions are able to crystallise *via* the homogeneous nucleation. The glass composition $\text{Li}_2\text{O}-2\text{SiO}_2$ is stoichiometric to the crystalline lithium disilicate $\text{Li}_2\text{Si}_2\text{O}_5$ and the glass composition $\text{Na}_2\text{O}-2\text{CaO}-3\text{SiO}_2$ corresponds to the crystalline phase of combeite or $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$. It is believed that the atomic arrangement in the homogeneously nucleating glasses resembles the structure of the corresponding stoichiometric crystalline phases. This would minimise free energy of formation of a nucleus. Some experimental evidence of the structural similarity in the intermediate range between the crystal and glass of homogeneously nucleating compositions has been obtained.^{18–20}

Another classification of the nucleation mechanism, which is, perhaps, more important for practical applications is whether glass starts nucleating crystals from the bulk, which is termed bulk or volume nucleation, or from the surface *i.e.* surface nucleation. The lithium disilicate glass $\text{Li}_2\text{O}-2\text{SiO}_2$ typically bulk nucleates, whereas glass composition stoichiometric to diopside $\text{CaO}-\text{MgO}-2\text{SiO}_2$ nucleates at the surface. These two mechanisms can generally be distinguished from the DSC traces run for different particle sizes of glass powder or frit (*cf.* Section 5). The crystallisation effect and peak temperature would not be affected in the case of bulk nucleation but would shift to the lower temperature for the smaller particle size of glass powder if the glass nucleates from the surface (Fig. 5).

Additionally, the bulk nucleating glass typically exhibits a sharp crystallisation exotherm over the narrow temperature interval unlike the broad exotherm of the surface nucleating glass frequently dispersed over the wide temperature range.

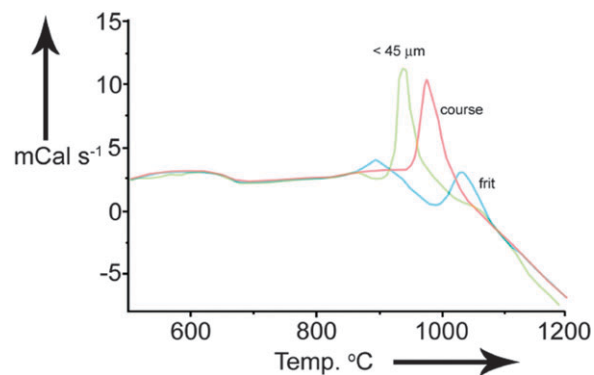


Fig. 5 DSC traces of three different glass particle sizes demonstrating surface nucleation. The smallest particle size crystallises at the lowest temperature, followed by coarser sized particles crystallising at a higher temperature, finally the largest particle size (frit) crystallises at the highest temperature. The finer are the particles the lower is the crystallisation temperature.

However, in multicomponent glass-ceramics the nucleation mechanism is likely to be a mixed bulk-surface.

The bulk rather than surface nucleation is preferred for development of practical GCs since it is easier to control. This is where the action of nucleating agents takes place. Metal oxides such as ZrO_2 , TiO_2 , CeO_2 , Cr_2O_3 , Sb_2O_3 , and Nb_2O_5 are typically used as nucleating agents in silicate glasses. These species added in small quantity to a glass batch are not completely miscible with the silicate melt and form submicroscopic clusters, evenly dispersed in the bulk of the quenched glass. On heat

1 treatment these species serve as an inhomogeneity for the for-
 2 mation of nuclei around these clusters that subsequently grow into
 3 crystals.²¹

4 Addition of large quantity of nucleating agent may increase
 5 the ability of glass to crystallise but would not necessarily
 6 improve the properties of the glass-ceramics crystallised from
 7 the glass. Moreover, various nucleating agents may promote
 8 crystallisation of different crystalline phases in the same base
 9 glass composition. Therefore, the amount and type of the
 10 nucleating oxide should be optimised for a particular glass
 11 composition to obtain the desirable effect on the microstructure
 12 and properties of the final GCs.

13 Other non-metal oxides, e.g. P₂O₅, have been used as nucle-
 14 ating agents in certain compositions of silicate glasses for
 15 instance for promoting lithium disilicate crystallisation. Simi-
 16 lar to metal oxides phosphorus pentoxide does not mix well
 17 with the silicate matrix and forms an amorphous orthophos-
 18 phate phase extracting cations from the silicate network. This
 19 orthophosphate phase promotes the crystallisation of many
 20 silicate glasses.

21 Colloidal metallic species represent another type of nucleat-
 22 ing agent for silicate glasses. Incorporated as oxides, e.g. Ag₂O,
 23 Cu₂O, Ag⁺ or Cu⁺, cations reduce to metallic Ag and Cu upon
 24 photoirradiation of glass. To ensure that the redox process
 25 occurs upon irradiation a glass composition typically contains
 26 cations of f-elements that oxidise upon irradiation, e.g. cerium
 27 oxide. These submicron metallic species precipitate in the glass
 28 matrix providing surfaces for formation of the nuclei and thus
 29 promote glass nucleation.²²

30 Upon surface nucleation the nuclei start forming at the
 31 surface, around and at the edges of the cracks and crystal-
 32 lisation then propagates inside the bulk of the glass. This type
 33 of nucleation is more difficult to control as the nature of the
 34 nucleation sites is not understood,²³ though there are a number
 35 of commercial GCs known to surface nucleate such as apatite-
 36 wollastonite.⁹ The way to control the surface nucleation is by
 37 regulating the surface area of glass powder for example by
 38 optimisation of the milling procedure and obtaining the desired
 39 particle size of glass before heat treatment. The current powder
 40 processing technology allows milling of glass powder down to
 41 0.1 μm, which significantly increases the surface area and the
 42 number of nucleation sites.

43 The second stage of glass crystallisation, the crystal growth,
 44 starts once the nuclei of critical (*r*^{*}) and supercritical sizes are
 45 formed. The general expression for the crystal growth rate *u* eqn
 (4) proposed by Turnbull is

$$u = \frac{fk_{\text{B}}T}{3\pi a_0^2 \eta} \left[1 - \exp\left(\frac{\Delta G}{k_{\text{B}}T}\right) \right] \quad (4)$$

46 where *f* is the interface area for crystal deposition, *a*₀ is the
 47 diffusion jump distance, *η* is the melt viscosity, Δ*G* is the free
 48 enthalpy of motion, *k*_B is the Boltzmann constant and *T* is the
 49 absolute temperature.¹⁰

50 Several different mechanisms of crystal growth can be dis-
 51 tinguished, depending on the direction of growth and the
 52 available surface as well as the local chemistry of the glass

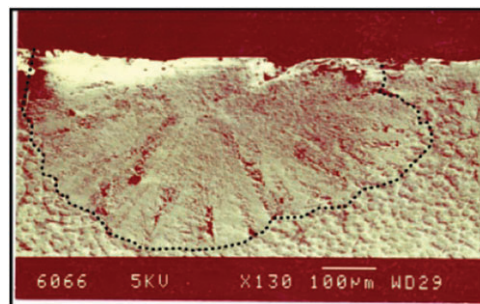


Fig. 6 SEM photomicrograph of a glass surface that has undergone heat treatment to form a GC. The demarcated region (dotted line) indicates a fluorapatite crystal nucleated at the glass surface and growing from the surface towards the glassy matrix.

53 phase around the nuclei.⁹ In the case of *normal* or *primary*
 54 *growth* the crystals deposit on the nuclei surface up to micro-
 55 scopic size with a linear increase in surface area until these
 56 start impinging on each other. *Secondary grain growth* may be
 57 observed after complete growth when the crystal surface area
 58 no longer increases but decreases. It is thought that *surface*
 59 *crystal growth* (Fig. 6) is closely related to the surface nucleation.
 60 After nuclei form on the surface the growth of crystals often
 61 proceeds vertically towards the bulk and the final microstructure
 62 of GCs can be controlled only by increasing nucleation sites on
 63 the surface.

64 *Anisotropic growth* occurs when crystals grow with the specific
 65 preferred orientation.^{24,25} If this is under control it can yield the
 66 GCs with the superior properties such as toughness, strength and
 67 machinability. However, the exact reason and the complex
 68 mechanism of anisotropic growth are poorly understood. It has
 69 been frequently observed that the nature of the crystalline phase
 70 that grows anisotropically is different from the crystalline phase
 71 nucleated initially.⁹ Thus, a decomposition of the primary crystal-
 72 line phase occurs alongside the growth of the anisotropic crystals.
 73 At certain compositions local chemistry and the nature of crystals
 74 are such that growth occurs more rapidly in a particular lattice
 75 direction leading to particular crystal morphologies. In other
 76 cases the characteristic *dendritic* or *spherulitic* morphology of
 77 the crystalline phase is formed generally in diffusion limited
 78 cases as a way of preventing material excluded from the crystal
 79 reducing growth rates.

2 The structure and unique properties of glass-ceramics can be controlled and specifically tailored for an application through the manipulation of the initial glass composition

80 A GC is the route of choice for development of materials in
 81 numerous application fields due to the superior properties of
 82 the final solid that can be achieved; Fig. 7 demonstrates the
 83 products for some applications. This route often enables the
 84 formation of crystalline phases that otherwise would be too

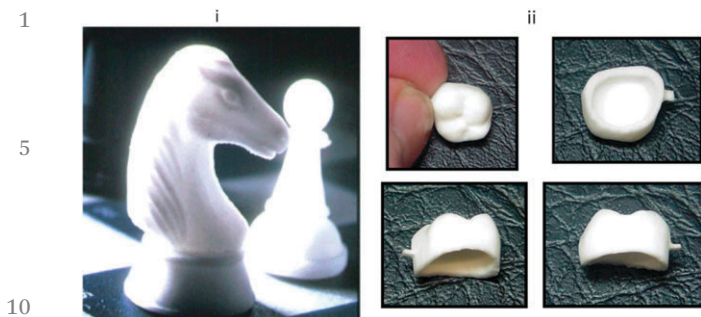


Fig. 7 (i) A GC cast chess piece; (ii) GC teeth crowns.

reactive or not possible to synthesise directly. By tailoring for instance the thermal expansion coefficient and the refractive index between the crystalline phase and the residual glass phase it is possible to make superior GCs *via* adjusting the initial glass composition.^{9,26} Working with a systematic series of glasses varying one compositional factor at a time, *e.g.* the amount of one of the components, rather than formulating a single glass is typically the way to produce a glass-ceramics with the unique properties required for a specific application. Investigations in compositional series allow identification of key components of the glass which deliver the required properties. This results in commercial formulations of the viable range of glass compositions producing optimal glass-ceramics.

The nature of the crystals that may form on heat treatment of an individual glass composition can be approximately predicted from the phase diagram. However, it should be noted that phase diagrams represent thermodynamic equilibrium. Whereas glasses are in a metastable state and often phases obtained upon devitrification at a particular heat treatment temperature are not thermodynamically favoured according to the phase diagram but are kinetically determined products. A number of high temperature crystalline forms can be stabilised at room temperature *via* the GC route. For some of the glass systems studied extensively over the years pseudo phase diagrams have been reconstructed that outline the fields of main phases crystallising at particular temperatures with variations in composition. The conventional way of representing the type of phases crystallising from a glass composition at various temperatures is *via* the TTT-diagrams shown schematically in Fig. 8; TTT stands for time–temperature–transformation.^{9,17}

Simple glass with composition near the stoichiometry of a crystalline phase appearing on heat treatment usually crystallise copiously with the high volume fraction of the crystalline phase up to 90%. This is also observed in compositions near the stoichiometry of the eutectic point on phase diagrams. Such an ample crystallisation is difficult to control. On the other hand, there are examples of simple glass systems that are difficult to crystallise, *i.e.* those requiring high temperature and extended duration of heat treatment. These are fully polymerised glasses with an interconnected three-dimensional network and a low fraction of non-bridging oxygen, *e.g.* $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ glass. Crystallisation is suppressed with increase in the number of components in glass composition. In silicate glasses it is known

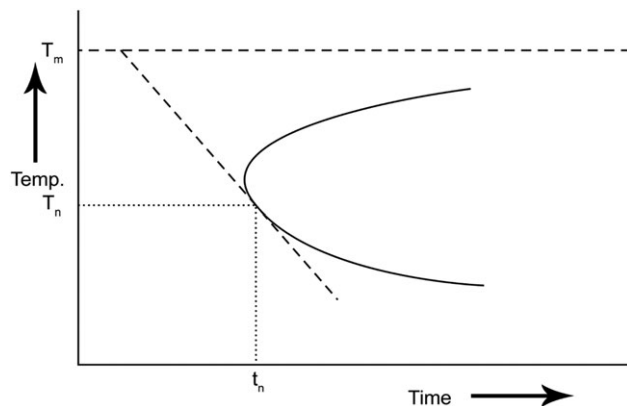


Fig. 8 The schematic of the TTT-diagram that used to outline the conditions of heat treatment, *i.e.* the temperature and duration, corresponding to a given crystalline phase formed from a glass.

that addition of MgO or ZnO to the batch would inhibit crystallisation of glass. Unlike transition metal oxides that serve as nucleating agents as described above, magnesium and zinc oxides are miscible in silicate glasses and magnesium and zinc cations can form MgO_4 or ZnO_4 tetrahedra that do not disrupt significantly the silicate tetrahedra network.^{27,28}

The volume fraction in the broad range of 5–60% as well as the morphology and the size of the crystals in multicomponent GC can be controlled *via* manipulation of the parent glass composition and adjusting the concentration of nucleating agent. Careful design of the glass from which the crystal phase is grown and the role of different nucleating agents have a direct impact on these factors and significantly influence the final material properties.

Optimisation of the heat treatment procedure is another tool for controlling the microstructure and properties of GCs. The heat treatment procedure usually involves two-step heat treatment (Fig. 4). The temperature of the first step, nucleation, is normally selected from the range T_g and $T_g + 50$ °C. The second hold temperature for growing the crystals can be taken at which the crystallisation event is observed from the thermal analysis, *e.g.* DSC exotherm peak temperature. However, in order to maximise the number of nuclei appearing on nucleation hold it is often required to finely optimise the nucleation temperature. The easiest way to do this is to use the thermal analysis. This is usually done during the DSC runs by performing holds at different nucleation temperatures within the T_g and $T_g + 50$ °C range and finding the minimal crystallisation peak temperature. The plot in Fig. 9 demonstrates that the hold temperatures correspond to the maxima of the experimental curves where the minimum crystallisation temperature observed should be selected as the optimal nucleation temperature.

To optimise the crystal growth step treatment is more laborious as it requires the evaluation of the microstructure for different temperatures and the durations of heat treatment. Anisotropic crystal growth observed for the apatite GCs as well as other oxyfluoride GCs such as fluorrichterite, fluorcanasite, and fluorphlogopite can be evaluated using the scanning electron microscopy (SEM), the examples are given in Fig. 10.

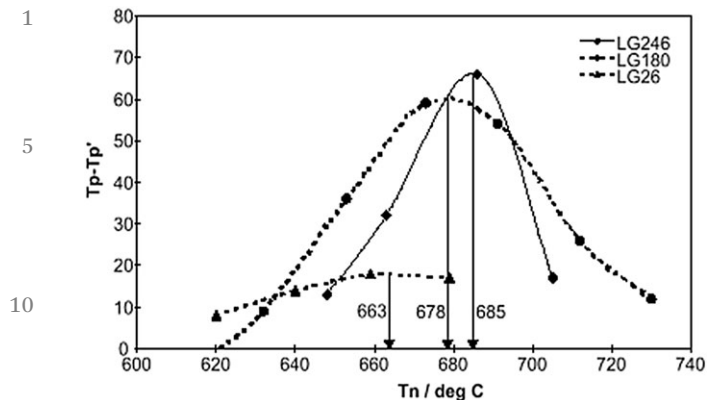


Fig. 9 Example of optimisation of the nucleation temperature for three phosphoaluminosilicate glass compositions. The difference in crystallisation temperatures with (T_p') and without (T_p) holds during the DSC run is plotted against the hold temperatures (T_n). The maximum of each individual curve is indicated with the arrow and the temperature value corresponds to the optimal nucleation temperature.

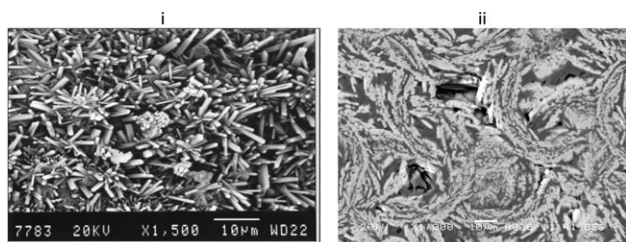


Fig. 10 Examples of SEM photomicrographs showing different morphologies of the growing crystals: (i) fluorapatite needles in fluorapatite GC and (ii) barium fluormica GC.

Fig. 10i shows the SEM images of the apatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ crystals with the size and morphology that have been optimised. The morphology of the long thin needle-like fluorapatite crystals formed in glass on holding at the apatite crystallisation temperature has been optimised to maximise the high length to diameter aspect ratio.^{25,29} This apatite crystal morphology is similar to the natural morphology of the biomineral apatite found in dentine and enamel.

A classic GC that has enabled the careful control of the crystal structure is that based on “stuffed” β -quartz (SiO_2): “stuffed” here indicates a solid substitution of a typical AlO_4^- tetrahedron with an associated Li^+ ion for a SiO_4 tetrahedron. β -quartz exhibits a negative thermal expansion at high temperature above 500 °C. The substitutions in the quartz structure give rise to a stuffed β -quartz structure at room temperature, which when combined with a residual glass phase with a positive thermal expansion can be used to give a zero expansion coefficient. The volume fractions of the two phases are carefully adjusted to engineer a zero coefficient of expansion material. In addition, having a high nucleation rate and a low crystal growth rate result in the stuffed β -quartz crystals having dimensions <100 nm that are much shorter than the wavelength of light resulting in optical transparency. This makes the material suitable for mirrors in optical telescopes, digital projectors and domestic cooker hobs.

Another classic glass-ceramic system is the machinable fluormica GCs (Fig. 10ii). The microstructure is based on a “house of cards” microstructure consisting of plates of mica typically 10–20 μm across and 1–2 μm in thickness that impinge on one another. This imparts machinability when cracks propagating in the material follow the easy cleavage planes in the mica and are deflected by the stronger impinging microstructure. Upon carefully controlled heat treatment the initially small mica crystals undergo coarsening until they grow to the desired dimensions and interlock. This allows the GCs to be easily machined to any shape without using diamond tooling. Commercially this process is used in the production of Macor[®] ceramics.

3 At the pre-nucleation stage the processes occurring in a glass dictate the subsequent mechanism of crystallisation

Here we define the conditions that often pre-exist in the glass prior to the beginning of crystal nucleation, which we termed pre-nucleation. These can be a specific interaction between the glass components leading to a phase separation or specific structural arrangements facilitating or catalysing glass crystallisation.

There has been considerable debate over the extent of ordering that occurs in amorphous, glassy material. However, it is widely recognised that most amorphous materials have some sort of order⁴ and this order has been described by three different regimes: short range order (SRO), medium range order (MRO) and long range order (LRO). Though there is some dispute as to the exact demarcation between the distance scales, they can typically be of 2–5 Å for SRO, 5–20 Å for MRO and for LRO distances exceeding 20 Å.³⁰

The SRO is described by structural units of the glass network with corresponding distribution of the bond distances and angles. Although positions of the atoms in crystals are absolutely defined, glasses and crystalline counterparts are built with the same chemical bonds between atoms, have similar structural units that form a three-dimensional network. Therefore, the nature of phases crystallising from the glass can give some information about the local environment (SRO) of atoms in the original glass, though the interpretation varies significantly for different glass components (*cf.* Section 4). Furthermore, most of the spectroscopy methods including solid-state nuclear magnetic resonance, Fourier transform infrared and Raman spectroscopy extensively employed for glass structure characterisation are essentially based on this similarity between the glass and the crystal at SRO and use information obtained on crystalline solids for interpretation of spectra of glasses.

The MRO includes fragments of the interconnected structural units and network topology. The presence of rings and clusters in the glasses can pre-exist emerging of certain

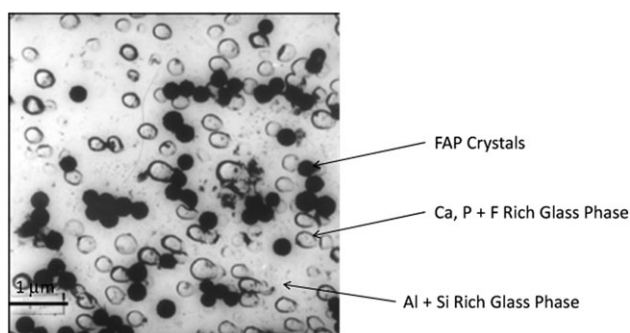
1 crystalline phases that cannot be obtained otherwise in GCs, *e.g.* high-temperature modifications of crystals. Unlike crystals, glasses lack periodicity, symmetry and LRO. However, there are a number of bigger scale heterogeneities in glass, such as fluctuations in density, microsegregation and phase separation that belong to the LRO phenomena.

5 The amorphous phase separation (APS) or liquid-liquid immiscibility is one of the key pre-nucleating phenomena in glass and this phenomenon belongs to the scale of the LRO in glasses. The presence of two liquid phases not completely miscible with each other can appear in the glass-forming melt at high temperature or more frequently occurs as two not completely miscible glass phases upon quenching the melt.

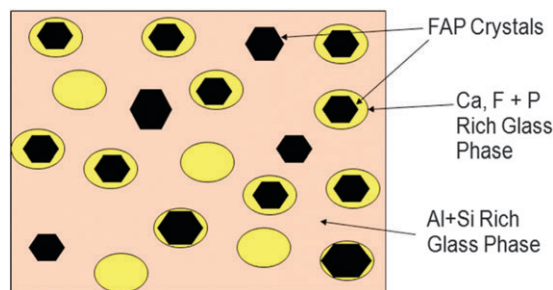
10 It results in regions that are rich in one phase and poor in another and if the domains of both phases are large enough they can be observed experimentally. The morphology of the APS can be droplets of one phase embedded in a matrix of the second phase (Fig. 11).³¹ Alternatively, both phases can co-exist as domains of one phase alternating with another. The morphology depends on glass composition and can change from one to another as the amount of the component in one of the phases gradually changes. There are plenty of studied examples of APS in glasses, *e.g.* sodium borosilicate glasses and lithium silicate glasses.

15 It is likely that APS exists in majority of the multicomponent glasses, though the domains of the separating phases might not be large enough for detection. The droplet-matrix morphology of the APS favours the beginning of crystallisation by aiding the formation of nuclei within the droplet on heat treatment. However, due to the compositional difference between the droplet and the matrix phase, crystal growth of the nuclei is restricted within the size of the droplet, as shown schematically in Fig. 12. This can be used for development of GCs with the small crystal size.

20 A special case of the APS observed for some glass composition is spinodal decomposition. In most of the glass compositions in order to start nucleation within the droplets of the phase separated glass the energy barrier has to be overcome corresponding to the activation energy for crystallisation.



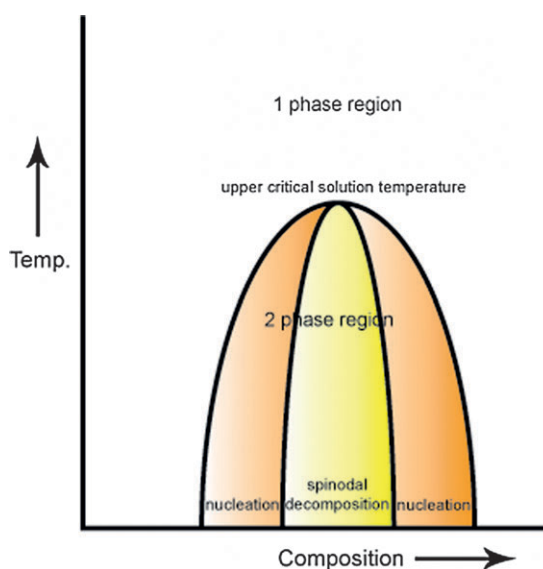
25 **Fig. 11** In this GC the careful design of the composition controls the crystallite size via APS as a pre-nucleation phenomenon. Initially the glass undergoes APS; a droplet phase forms in a continuous phase. From the droplet phase fluorapatite starts to crystallise upon heat treatment, the crystal size is determined by the boundaries of the droplet phase.



30 **Fig. 12** A phase separated glass showing droplets in a glass matrix. Some of the droplets (yellow) nucleated the crystals (black). However, the crystals cannot grow outside the droplet phase due to difference in composition of the droplet and the glassy matrix (beige). The initial droplet is determined by the structure present in the melt.

35 However, few glass compositions fall into the region where spinodal decomposition occurs. This is shown schematically in Fig. 13 where the centre of the bimodal dome is the region of the spinodal decomposition (yellow region Fig. 13). In contrast to the nucleation regions, the spinodal decomposition is a thermodynamically driven process where spontaneous separation of a homogeneous solution or melt into two distinct phases occurs and there is no activation energy barrier.

40 Spinodal decomposition can occur on a wide variety of length scales but starts as a sinusoidal composition fluctuation in three dimensional space and gives rise to a highly periodic



45 **Fig. 13** This is a composition-temperature diagram which shows one and two phase regions. The x-axis indicated the composition of the system, as a certain composition will exhibit two phase behaviour. The spinodal region is in yellow and the nucleation region is in orange. Above a certain temperature there is only one phase and the system is homogeneous, this is demarcated by a single point, at the top of the two phase region, the upper critical solution temperature. Below the upper critical solution temperature two phase formation is possible. Depending upon the composition the formation of two phases can take place by two distinct processes: nucleation or spinodal decomposition. Nucleation and growth have been discussed previously. Spinodal decomposition happens spontaneously and is driven by thermodynamics.

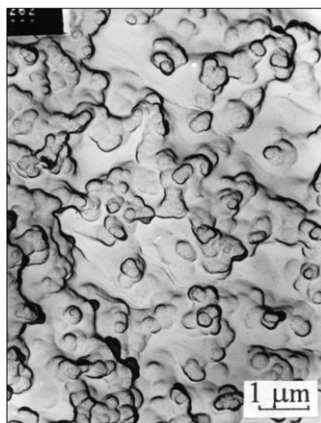


Fig. 14 The example of the SEM photomicrograph showing the APS but with a clear interconnected morphology between the two liquid phases. A spinodal decomposition is supposed from this micrograph.

structure. The length scale and extent depend markedly upon the temperature and composition of each phase. When nano-scale separation on the scale of a few nm occurs this can directly lead to crystallisation on a similar length scale. Fig. 14 shows the micrograph of the system with an interconnected structure indicative of spinodal decomposition.

4 Nanocrystallisation can be achieved in the glass if certain glass design rules are followed

It is possible to achieve crystallisation in the glass at the nano-level producing crystals of ≤ 100 nm size. The glass with the embedded crystals of this size (e.g. Fig. 15) can be termed nanocrystalline GCs. Nanocrystalline GCs have certain advantages over the micro-crystalline GC, e.g. nanocrystalline GCs are transparent to visible light, which is particularly useful for optical applications and up-conversion lasers.³²

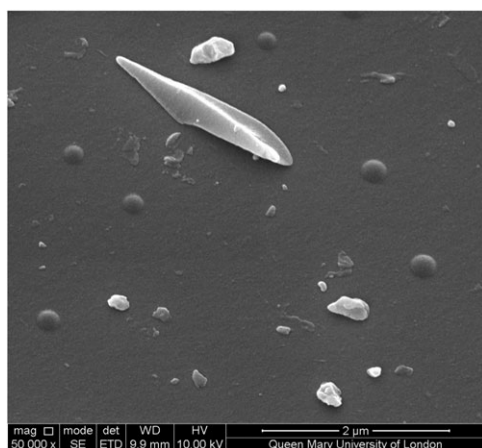


Fig. 15 The SEM photomicrograph shows formation of small crystals or nuclei on the surface of glass. The small droplets of the APS are also seen in the glass. The photomicrograph is kindly provided by Dr Xiaohui Chen (Queen Mary University of London).

Nanocrystallisation occurs upon heat treatment when a crystal phase is nucleated in the glass matrix but the crystals do not grow significantly. Thus, the nucleation rate should be much higher than the crystal growth rate, which can be achieved for example by selecting an appropriate heat treatment regime (cf. Fig. 4ii). Furthermore, some glasses inherently exhibit high nucleation rates and low crystal growth rates, which promote nanocrystallisation.

Over the years the crystallisation in oxyfluoride silicate glasses ($\text{SiO}_2\text{-M}_x\text{O}_y\text{-MF}_z$, where M stands for Group I-III metal or transition element cation) proved to be one of the prominent examples of nanocrystallisation in glass.³³⁻³⁶ The fluoride component has a limited solubility in silicate glasses that can be enhanced by the presence of certain cations that preferentially bind with fluoride.³⁷ In silica-rich glasses, due to the cation deficiency, the fluoride solubility in silicate glass is low and significant fluoride losses/volatilisation during the synthesis can be observed. Typically the fluoride containing crystalline phases are well dispersed in a silicate glass matrix with the crystal size in the submicroscopic or nano-range.³⁸ The DSC traces of the fluoride containing glasses often show crystallisation exotherm at a much lower temperature and hence glass needs only to be heat treated at relatively low temperature, slightly above T_g of the original glass, to obtain nanocrystalline GCs.

The direct relationship between the fluoride speciation in silicate glass and the nature of crystal phase is the key to the ability of oxyfluoride silicate glasses to crystallise at the nano-scale.³⁹ In modifier- or cation-rich silicate glass the fluoride is associated with the cation of the largest charge-to-size ratio (the cation field), which results in crystallisation of the fluoride phase with the very same cation upon heating.⁴⁰ In multicomponent calcium aluminosilicate glasses the F-Ca(*n*) species crystallise upon heat treatment as the CaF_2 phase or as the fluorapatite $\text{Ca}_3(\text{PO}_4)_2\text{F}$ in phosphoaluminosilicate glass.⁴¹ Fig. 16 demonstrates ^{19}F nuclear magnetic resonance (NMR) spectra of the

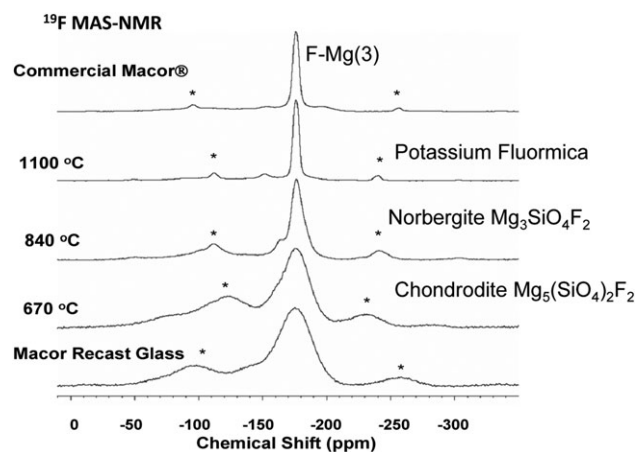


Fig. 16 ^{19}F NMR spectra of the commercial GCs (top), original glass (bottom) and intermediate forms prepared upon heat treatment of the original glass at temperatures indicated. The crystals formed are indicated. The main signal at -176 ppm is assigned to fluorine atoms surrounded with three magnesium atoms F-Mg(3). This structural arrangement is seen in all spectra starting from the glass and up to the final GCs.

commercial GCs Macor[®]. The main signal at the position of -176 ppm in the final GC is also seen in the initial glass and in the intermediate crystalline forms and is assigned to the fluorine surrounded by the three magnesium atoms (F-Mg(3)).

Thus, although this may depend on each composition, the chemical environment of fluoride in glass provides a precursor for the phase crystallisation upon heat treatment. A structural re-arrangement which is required to convert glass into crystal is minimised due to the similarities observed in chemical speciation of the fluoride in glass and crystalline phases. This ultimately aids the nucleation of the fluoride crystal phase.

The efficiency of fluoride in reducing viscosity and T_g of silicate glass is well known and documented. Upon nucleation and formation of the fluoride containing crystals the composition of the residual glass around the crystals changes, it becomes fluoride poor. As a result both the T_g and viscosity of the residual glass matrix increases leading to a decrease in the crystal growth rate according to eqn (4). In addition, the volume fraction of the fluoride containing the nanocrystalline phase is usually low, about 5%. This additionally restricts the crystal growth rate *via* increasing the diffusion jump distance a_0 , *cf.* eqn (4), over which diffusion has to take place for ripening the crystals.

The alternative to suppress crystal growth in order to achieve nanocrystallisation in glass could be to move glass composition away from the stoichiometry of the crystal phase nucleating. Addition of some components in silicate glasses is known to inhibit crystal growth and/or crystallisation, *e.g.* MgO. The amorphous phase separation discussed above generally favours nucleation but disfavors crystal growth beyond the boundaries of the phase, which is advantageous for the nanocrystallisation.

5 A combination of the structural techniques available in modern science rather than a single method is more likely to characterise accurately the mechanism of glass crystallisation

Amorphous glasses and GCs can be intractable materials and problematic to characterise. However, advances in many methods have provided valuable insights into their structure. It is far more challenging to study the mechanism of glass crystallisation as the structural changes are temperature dependent and information obtained from room temperature experiments can be misleading to recover the structural transformations occurring at the elevated temperatures. High-temperature *in situ* characterisation methods deliver perhaps the most revealing information,⁴² however, they are often costly and not readily accessible. In trying to determine the structure of glasses or GCs a combination of different methods is best as each method has its own individual strengths and weaknesses.

As seen in Section 1, the DSC or other thermal analysis methods are the classical techniques used for investigation of crystallisation in glass.⁴³ Relationships between the characteristic temperatures that can be obtained from these methods can be

used to characterise the glass forming ability or GS against crystallisation. A number of isothermal (JMAK) and non-isothermal methods for characterisation of crystallisation kinetics of glass have been developed. The Kissinger method based on variation of the crystallisation peak temperature at different heating rates can estimate the activation energy for crystallisation E_a using the Kissinger eqn (5):

$$\ln\left(\frac{\beta}{T_c^2}\right) = -\frac{E_a}{RT_c} + \text{const} \quad (5)$$

where β is the heating rate and T_c is the crystallisation peak temperature. Other non-isothermal methods, *e.g.* the Ozawa or Matusita and Sakka methods, can deliver information regarding the extent of surface or bulk mechanism of nucleation.⁴⁴

For glasses and GCs a simple optical inspection can be very revealing and misleading at the same time. Optically non-transparent glass either has APS or is partially crystallised. From an optically clear glass a statement can be made about the presence of crystallinity in the glass *viz.* that there are either no crystals or that any crystals present are below the wavelength of light (~ 380 – 740 nm). Furthermore, with the presence of a polarising filter, it is possible to determine whether or not the crystals are birefringent. This can also be combined with the use of oils of different refractive index to identify different crystalline phases provided that the crystal size is large enough and to measure the refractive index of the glass phase.

The presence of crystalline regions within GCs enables the identification of phases by X-ray diffraction (XRD).⁴⁵ X-ray scattering is the interaction of X-ray radiation with the electron density of the material. The coherent scattering from the X-ray diffraction allows the reconstruction of the lattice parameter that makes up the crystalline unit cell. However for GCs it is not always possible to grow a single crystal for XRD and therefore powder XRD is often used instead. XRD has had great success in establishing and quantifying the different crystalline phases present in GCs. The Rietveld refinement is often used for relative quantification of the crystalline phases identified in the XRD pattern. However, where there is a substantial background from the amorphous fraction still present in the GC it can be problematic to accurately quantify the amount of different crystalline phase present.

The conventional XRD cannot be used to quantify accurately the amount of amorphous fraction. Neutron scattering is an alternative to X-ray scattering as these have excellent penetrating power through the dense glass or GCs. In particular for glasses this technique is being developed for characterisation of the SRO and MRO.⁴⁶ The penetrating power of neutrons has been useful for studying crystallisation in monolithic bulk samples that are insensitive to surface nucleation whereas with X-rays only relatively thin samples can be used. However the restricted number of neutron sources compared to that of X-ray limits the availability of this technique.

XRD can be used for studying the nucleation or nanocrystallisation in glass. Crystals of small size produce an additional broadening of the diffraction peaks of the XRD patterns, given by the Scherrer broadening eqn (6)

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (6)$$

where D is the crystal size, K is a numerical factor referred to as the shape factor, λ is the wavelength of the incident X-rays, β is the line broadening at full width half height, and θ is the Bragg angle of the scattered radiation.

By measuring the full width half height of the diffraction lines it is possible to quantify the size of the nuclei emerging and growing from the glass. The XRD measurements can be performed at room temperature on quenched samples as well as *in situ* at high temperature. There are several limitations to this method. There could be other contribution to line broadening of the diffraction lines, *e.g.* defects and disorder within the crystallite structure. To be quantified the nuclei (about ≥ 10 nm) have to be large enough to be detectable by XRD. The very early stages of nucleation and pre-nucleation are therefore problematic to study by XRD.

The SEM is a useful technique for studying the crystallisation processes, microstructure in GCs and morphology of the growing crystals.^{43,47} It is often combined with electron probe micro analysis (EPMA) or SEM energy dispersive X-ray (SEM-EDS) spectroscopy that enables elemental analysis to be performed using the microscope, which is useful for phase identification. The SEM can be used in two principal modes: secondary electron imaging that images in terms of surface topography and the back scattered mode which images in terms of electron density or atomic number contrast.

Sample preparation with SEM is relatively straight forward unlike transmission electron microscopy (TEM) that requires the preparation of ultrathin ($\ll 1$ μm thick) samples that are thin enough to image. The transmission electron microscopy (TEM) studies are shown to be essential for looking at the MRO and SRO in glasses and especially recently the early nucleation stages.⁴⁸ The advantages of TEM is the higher resolution compared to SEM and the ability to perform electron diffraction.

Direct quantification of the SEM images is one of the grossly utilised methods for investigating the nucleation. The number of nuclei is simply counted from the crystals in the SEM photomicrographs. This simple, though extremely laborious, technique proved to be effective for optimisation of nucleation and crystal growth in GCs. However, the number of crystals grown in the glass matrix counted from the SEM images is not identical to the number of nuclei emerged in the nucleation step. This is the main limitation for using this directly for nucleation quantification.

Spectroscopy is the interrogation of matter with electromagnetic radiation; here electromagnetic radiation of different wavelengths is used to interact with the glass or GCs. This has given rise to optical, infrared, Raman, and NMR spectroscopies amongst many others that enable the structural determination of these materials.

The method of choice for determination of the structure of glass is solid-state nuclear magnetic resonance spectroscopy (NMR).⁴⁹ For the structural determination of amorphous materials this technique is unparalleled and for GCs this method is also extremely useful, especially in combination with XRD. In this, the sample is placed in a strong magnetic field (>4.7 T) and nuclei are interrogated directly with radiofrequency

radiation. For glasses and GCs the typical nuclei examined are ^{29}Si , ^{27}Al , ^{19}F , ^{31}P , ^{11}B , and ^{23}Na , and with isotopic labelling ^{17}O and ^{43}Ca amongst many others.

In the solid-state, compared to the solution state however, there are additional line broadening interactions that have to be overcome. The three major line broadening interactions are (a) nuclear dipole-dipole (b) nuclear-electron dipole or chemical shift anisotropy (CSA) and (c) quadrupolar. The last is only applicable to certain nuclei that have an asymmetric distribution of electron charge with their nuclei *e.g.* ^{27}Al and ^{17}O . Investigating these line broadening interactions is often useful and many NMR experiments are often carried out in a static mode.

More commonly solid-state NMR is employed with Magic Angle Spinning (MAS). Here the sample is often powdered and packed into an air-bearing ceramic rotor and spun at the magic angle ($\theta = 54.74^\circ$ with respect to the magnetic field). Here it is found that many of the line broadening or anisotropic interactions are removed, partially or totally, if the spinning speed (3–80 kHz) is at least equal to that of the magnitude of the interaction (dipolar, CSA or quadrupolar) in the magnetic field. This allows direct investigation of the isotropic chemical shift value for the nuclei involved. An example of the MAS-NMR spectra can be seen in (Fig. 17).

The solid-state NMR has been most useful for structural characterisation at the SRO and MRO (*cf.* Section 3). Simple MAS type experiments are sensitive to SRO and are indicative of the chemical bonds around the nuclei under examination in the glass. It is being increasingly recognised that MRO is important in glass structure, and this extends beyond the immediate next nearest neighbour. The advent of distance determination in NMR by sophisticated two dimensional NMR methodologies has been increasingly employed to investigate the MRO in glass.

Infrared and Raman spectroscopies⁵⁰ are complementary to each other and both give useful information on the different

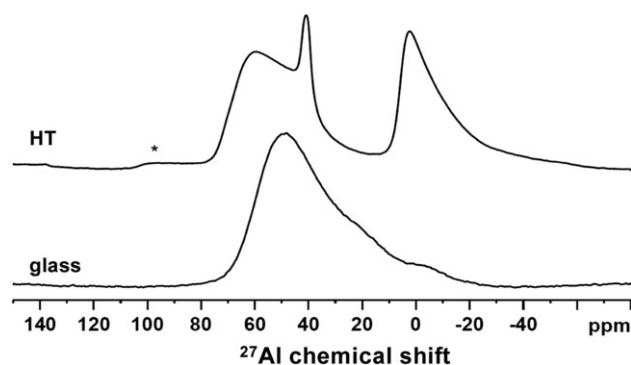


Fig. 17 ^{27}Al MAS-NMR spectra of a phosphoaluminosilicate. The glass (bottom) and heat-treated (HT) GC (top) show the change in structure upon heat treatment and formation of GCs. The peaks represent ^{27}Al nuclei in different chemical environments *e.g.* in the glass (bottom) the broad peak at ca. 50 ppm is characteristic of a tetrahedral environment that changes upon HT (top). The peak at ca. 0 ppm in HT GC (top) shows the formation of an octahedral site in the GCs.

1 type of structural bonds present within the glass. For strong
absorption infrared spectroscopy requires a permanent electro-
nic dipole in contrast to Raman spectroscopy which is sensitive
to transient dipoles. The chemical bonds present within the
5 glass or GCs e.g. Si–O–Si or Al–O–Si have a characteristic
absorption which is traditionally measured in wavenumbers
(cm^{-1}). Furthermore advances in these techniques have
enabled the generation of microbeam radiation (μm) which
can give spatial resolution across a sample.

Conclusions

The key for the development of glass-ceramics is an under-
standing of the mechanism of crystallisation in glasses.
15 Although studied for many decades, crystallisation in glasses
remains a fascinating area of science with a number of funda-
mental questions yet to be answered. Understanding the com-
position–structure–property relationship for glasses and GCs is
still the essence of research methods in glass crystallisation.
20 The complexity, diversity and amorphous nature of glasses are
the main challenges for experimental detection and evaluation
in the early nucleation stages, which continue to be the most
interesting area of research. The recent advancement in several
physicochemical techniques for the interrogation of amor-
phous and poorly crystalline solid matter, e.g. neutron scatter-
ing, NMR, and TEM, should be able to deliver crucial
information on nucleation and pre-nucleation processes in
glasses in the nearest future.

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