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A Review of Glass and Crystallizations of Glass-Ceramics

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Abstract

The fundamental science behind glass and glass-ceramics in relation to research including syntheses, processing, characterization and applications are critically reviewed in this paper. The crystalline structure of the crystalline phases/s investigated in the literature is also discussed. Throughout this paper, the scene is set toward the overall picture of the rationale behind the choice of a glass system. Additionally, earlier reviews do not include the most recent literature in this fast-moving field. The main methods of synthesizing glasses and glass-ceramics are explained and described in relation to their applications. The paper concludes with recommendations for future research.

Keywords

Glass Formation Theories, Crystallization, Glass-Ceramics, Processing of Powder and Bulk Glasses

1. Introduction

1.1. Glassy State

There are common characteristics, which define a glass, such as the absence of the long-range order of a crystal and its random three-dimensional network with no defined periodicity (**Figure 1**). The atomic distributions of glass structure resemble liquid matter in a solid state, but not crystalline solids [1].

Different definitions of glass have been put forward, but the most common one is that introduced by the American society for testing and materials (ASTM), "glass is an inorganic product of fusion which has cooled to a rigid condition without crystallising" [2]. However, some organic substances would not be included in this definition, such as glucose or glycerol which can be supercooled to a rigid condition without crystallising and would have many of the
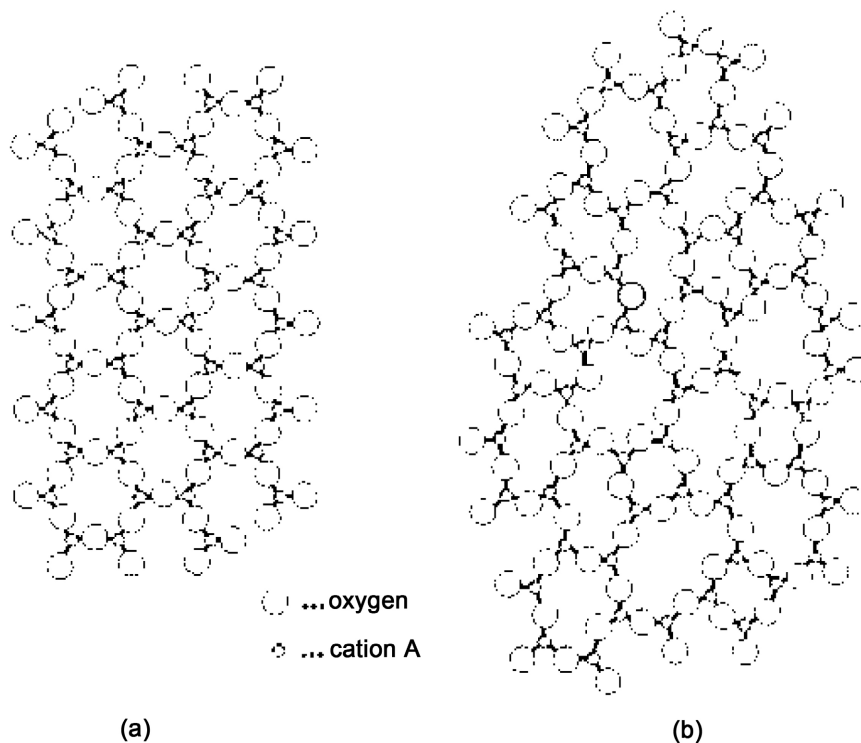
Figure 1. Illustration comparing structural differences between (a) ordered crystalline phase and (b) a continuous random glass network [1].

characteristics of glasses [3]. Any other amorphous substances prepared by methods other than melt cooling, such as vacuum evaporation, would also not be included in the ASTM definition [4].

1.2. Glass Formation Theories

Early theories explained why some materials form a glass while others do not [5]. Those are still relevant to the current understanding of the behaviour of silicate melts and the structure of silicate crystals. Some special structural features of a melt were found to allow production of a glass on rapid cooling; while the lack of certain features interrupts the formation of glass [1]. Therefore, different fundamental theories were introduced for glass formation in oxides, which have had the most impact on current scientific thinking toward glass [6]. Only important fundamental theories are discussed in this review.

1.2.1. Goldschmidt's Radius Ratio Criterion

Goldschmidt (1926) is said to be one of the first who identified the common characteristics of a glass forming oxides, on the basis of the radius ratio criterion [7]. Goldschmidt pointed out that, if the ratio of the cation (M^{n+}) radius to oxygen ion radius, R_m/R_o, lies between 0.225 and 0.414, the coordination number for M^{n+} cations introduced as an oxide M_xO_y will be four. If so, the oxygens are arranged at the corners of a tetrahedron with the cation taking a central position. Thus, a tetrahedral shape occurs in the crystalline state and the glass state in a

number of glass forming oxides, such as SiO_2, GeO_2, B_2O_5 and P_2O_5. Therefore, Goldschmidt and others suggested that this might be the basis of glass formation [8] [9]. He also explained that the ability of an oxide to form a glass can be related to the way the oxygen atoms are arranged around the cation, producing a structural unit similar to a unit cell of the crystal lattice.

1.2.2. Zachariasen's Random Network Theory

Zachariasen (1932) [1] discussed that if an oxide has the ability to form a tetrahedral configuration that this does not mean this oxide is able to form a glass. Zachariasen's example for this assumption was that of BeO which cannot be obtained in a glassy state, but still can form tetrahedral groups with four oxygen atoms around the beryllium ion. In that period, Silverman suggested that, extensive sources of minerals are available, in particular, the group with magnesium, calcium and barium, whose compounds had been used to prepare silicate glasses, and perhaps, such oxides reveal unique properties when in use to form glass [9]. Hence, the developments of the random network theories evolved and research work is ongoing which contribute in the understanding of the characteristic of glass forming oxides [10].

The interatomic forces in the glass and crystal must be similar and the atoms in both glasses and crystals oscillate about similar equilibrium positions. This means that the structural units in the glass and in the crystal, will be identical. However, these structural units are built up to give a regular repeated network in the crystalline state and a random network in the glassy state. He also pointed out that the atoms should form a three-dimensional network in the glass similar to the crystal but are random [1]. While the energy content of the substance in the glassy state should be different from that of the corresponding crystal structure. In brief, Zachariasen [1] summed up his findings as four rules and emphasizes how the structure of SiO_2 glass differs from the crystalline form, in relation to the energy content of the substance. These four rules for oxide glass formation are:

1) An oxygen atom must not be linked to more than two glass forming atoms.

2) The coordination number of the glass forming atoms must be small, (usually 4).

3) The oxygen polyhedral should share corners with each other only, but not edges or faces.

4) The polyhedral must be linked in three-dimensional networks.

1.2.3. Glass Network Formation

Oxides, which form glasses when melted and fast cooled, are known as glass forming oxides or network forming oxides, because of their ability to build up a continuous three-dimensional random network. The number of anions in a stable crystal structure, directly surrounding a cation is known as the coordination number [1]. The literature offers different approaches to the understanding of how glass is formed. However, key researchers suggest an oxide can form a glass

if the coordination numbers of the cation in the glass and in the crystal, are closely similar [3] [11]. Early works suggested that, cations having ability to form bonds with oxygen with a fractional ionic character near 50% should act as glass network forming cations [12]. Examples of cations which can form glass are: B^{3+}, Si^{4+}, P^{3+}, P^{5+}, As^{3+}, As^{5+} and Ge^{4+}.

Sun (1947) [13] argued that oxides which form glass have the ability to rearrange their bonds during crystallisation process. Sun also calculated the single bond strength of the M – O in the oxide $MO_{x/y}$ and concluded that the single bond strength and the energy required to dissociate the molecule is dependent on the coordination number.

To give an illustration to this, oxides which have a single bond strength above or near 80 kcal/mol (334 kJ·mol^{-1}), are considered as a glass forming oxides. For instance, Si^{4+} has a single bond strength of 106 kcal/mol. Whereas, oxides has bond strength below 60 kcal/mol such as the alkaline earth group, Na^+ (20 kcal/mol) behave as glass modifiers. While oxides showing single bond strength between 60 and 80 kcal/mol act as glass intermediates, for example the calculated bond strength for Al^{3+} is around 67 kcal/mol (Sun, 1947). Therefore, cations forming a network have a high field strength (1.3 to 2), for example field strength Si^{4+} is 1.57, while cations functioning as modifiers have a lower field strength (0.1 to 0.4). For instance, Na^+ is reported to be 0.19 and for intermediate cations (0.5 to 1.1) such as in Al^{3+} 0.84 [11].

1.2.4. Network Modifiers

The role of a modifying oxide is that when such an oxide, for instance sodium oxide, is introduced into a silica glass to produce a sodium silicate glass system, the structure of glass will change. Instead of the bridging oxygens which form the link between two SiO_4 tetrahedra, the sodium oxide introduced to the silicate network makes a gap in the continuous network structure. As a result, sodium ions are accommodated in such "gap" forming ionic bonds with non-bridging oxygen as illustrated in **Figure 2** [3].
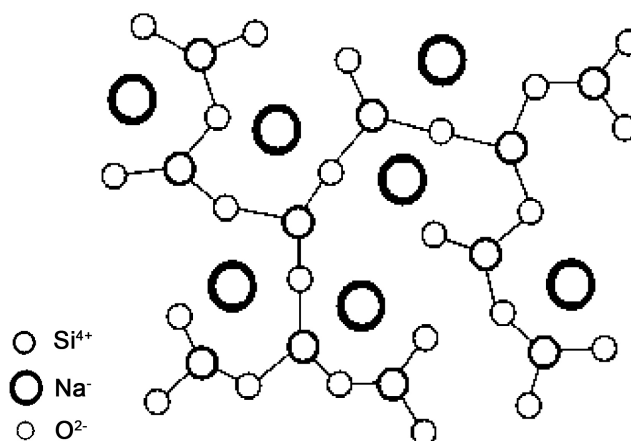

Figure 2. Illustration showing the effect of bond breaking between Si-Si groups, due to introducing modifying oxide, sodium, to silicate network [3].

Furthermore, introducing different amount of Na_2O into a glass forming system result in significant modification in the end glass properties. These modifications are commonly observed on the viscosity of the glass, which influences the properties such as thermal expansion coefficient and/or chemical durability [14] [15].

Other alkali and alkali earth metal oxides, such as lithium, potassium or calcium oxides, can take part in the glass structure in a similar manner to fulfil the role of glass modifiers [16]. However, multicomponent glass systems containing mixed alkalis, as a structural modifying oxides, have far more complex changes in many properties, and such effects are discussed in depth elsewhere [17] [18].

1.2.5. Intermediate Oxides

An intermediate oxide does not form a glass on its own, due to the lack of their glass forming characteristics as discussed in Section 1.2.3. However, such oxides are reported to take part in the glass network only in the presence of a glass forming oxide [17]. Examples of such oxides are aluminium oxide, titanium oxide, and magnesium oxide. Alumino-silicate, alumino-borate and alumino-phosphate glasses are good examples where aluminium behaves as an intermediate oxide [19].

The role of the modifier oxides differ in the crystal compared to glass structures. For instance, the aluminium ion is found to be octahedrally (AlO_6) or tetrahedrally (AlO_4) coordinated with oxygen in crystalline structures. While in glassy state the aluminium found in its tetrahedral coordination AlO_4 only, which gives it the charactistic of a "glass forming oxide" [20].

In alumino-silicate glasses, when Al^{3+} takes part in the glass network formed with silicagroup, the aluminium is required to be charge-balanced by a cation such as Na^+ in order to form tetrahedral AlO_4 [21]. Thus, the amount of aluminium oxide in the glass composition is commonly associated with at least an equal amount of an alkali oxide in the glass network with ratio of 1:1 [22]. This will be discussed further in the next Section (1.2.6) describing the network connectivity changes due to addition of different oxides.

1.2.6. Network Connectivity

Glass network connectivity is commonly discussed on the basis of their Q^x structure. The Q^x structure in an alkali silicate glass network, is a notation used to describe the number of bridging oxygens "x" in a tetrahedron, and generally divided into four main Q^x structural groups [23]. The silica structure itself, referred to as Q^4 glass structure, is characterised by four bridging oxygens per a silicon tetrahedron with no non-bridging oxygens (NBO) (pure SiO_2 made of $SiO_{4/2}$ units) and has a highly cross linked network (see **Figure 3**). The Q^3 tetrahedra contain three bridging oxygens (BO) and one NBO per silicon, as a result of introducing network modifying oxide ($Na_2O + 2SiO_2$ made of $NaOSiO_{3/2}$ units). While, Q^2 refers to two BO and two NBO per silicon ($Na_2O + SiO_2$ is made of $(NaO)_2SiO_{2/2}$ units), and Q^1 refers to one BO with three NBO ($3Na_2O + 2SiO_2$ made of $(NaO)_3SiO_{1/2}$ units). Q^0 glass has four NBO only ($2Na_2O + SiO_2$
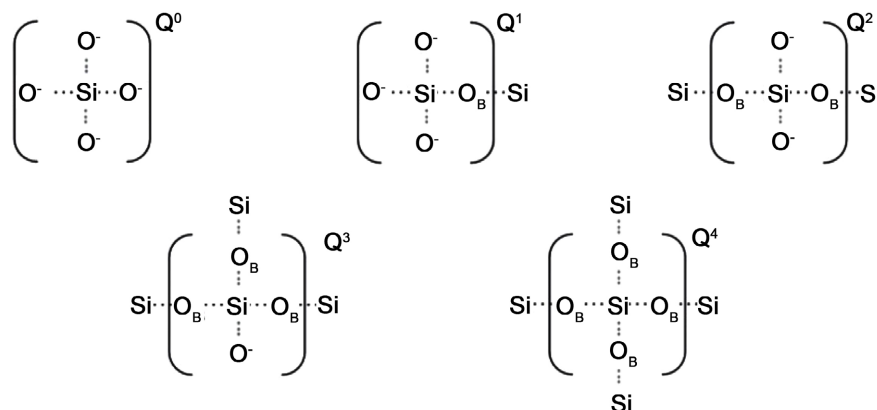
Figure 3. Illustration of network connectivity in silicate glasses showing different Q^x structures as a results of number of bridging (O_B) and non-bridging oxygens (O^-)[25] [24].

made of $(NaO)_4Si$ units) [23]. Thus, the glass properties can be assumed on the basis of their network Q^x distribution [24]. For instance, practically, increasing the network connectivity (numbers of bridging oxygens), decreases the flow properties, leading to increase in viscosity, and the reverse is true [25].

Introducing an intermediate oxide to an alkali silicate glass network system (for instance Al_2O_3) changes the network connectivity of the glass structure. Such glass systems are referred to as, alkali alumino-silicate glasses [26]. Here, the network connectivity of the glass Q^x depends on the ratio between the network modifiers and intermediate oxides to the glass forming $(Al_2O_3/Na_2O):SiO_2$. For instance, introducing aluminium to a Q^3 alkali silicate glass network (Na_2O + $2SiO_2$ made of $NaOSiO_{3/2}$ units) + Al_2O_3, drives the network to cross-link further and re-arrange to Q^4 structure.

The Al^{3+} ion enters the glass network as a forming oxides, having a tetrahedral coordination, charge balanced by the alkali ion (Na^+) leading to the removal of one NBO. Thus, AlO_4 forms on the basis of $(Al_2O_3/M_2O) = 1$. While, Q^3 and Q^2 alkali alumina silicate glass structure are formed when this ratio is controlled to <1. However, when introducing further Al^{3+} to the alkali silicate glass network, where $(Al_2O_3/M_2O) > 1$, the Al^{3+} ion role in the glass network changes from network forming to a modifier having an octahedral coordination (AlO_6). Such octahedral groups are known to interfere with the electrical conductivity and the diffusion coefficients of alkali ions in alkali alumina-silicate glasses. Nevertheless, a multicomponent alkali alumina-silicate glass system has a rather complex structure, and perhaps, different Q^x structures can be present in multicomponent glass systems [20].

Distinguishing between oxides and their roles in any given glass system, is of significant importance to the field of glass and glass-ceramics. Adding different oxides to the starting glass composition can have a huge influence on the thermal, chemical and mechanical properties of the prepared glass, as well as the kind of crystalline phase/s formed upon crystallising such glasses [27]. To that end, it should be possible to design novel compositions leading to successful

glass synthesis, while tailoring the materials overall behaviour, based on composition-structure-properties relationships, in order to prepare glass or glass-ceramics which serve for the intended application.

2. Glass Formation from Melt

Glass is conventionally made by melting high purity raw materials, consisting of a mixture of glass forming, modifier and/or intermediate oxides, at a high temperature. During glass formation from the melt, atoms are believed to rearrange continuously as the temperature decreases and the viscosity increases [28]. Therefore, when a glass forming liquid is fast cooled, structural arrangement into a defined order (*i.e.* crystallisation) is hindered, due to rapid increase in viscosity [4]. Hence, the random network structure of a liquid occurs in the solid state, where atoms are frozen due to the high viscosity and can no longer rearrange to the equilibrium crystalline structure [29] [30].

Cooling a liquid containing glass forming oxides to any temperature lower than the melting temperature of the crystal or higher than the glass transition temperature (T_m or T_g), would usually drive the system to nucleate and can lead the material to form an uncontrolled arrangement of a long-range periodic crystal [3] [31]. The glass transition region (T_g) is believed to be affected by the cooling rate, therefore, it is common to relate T_g to a fictive time-temperature (T_f) dependent parameter, that is a result of cooling rate from melt (see **Figure 4**). For example, when the same glass is melted and fast cooled at different cooling rates, T_g of each melt can be different [29] [32].
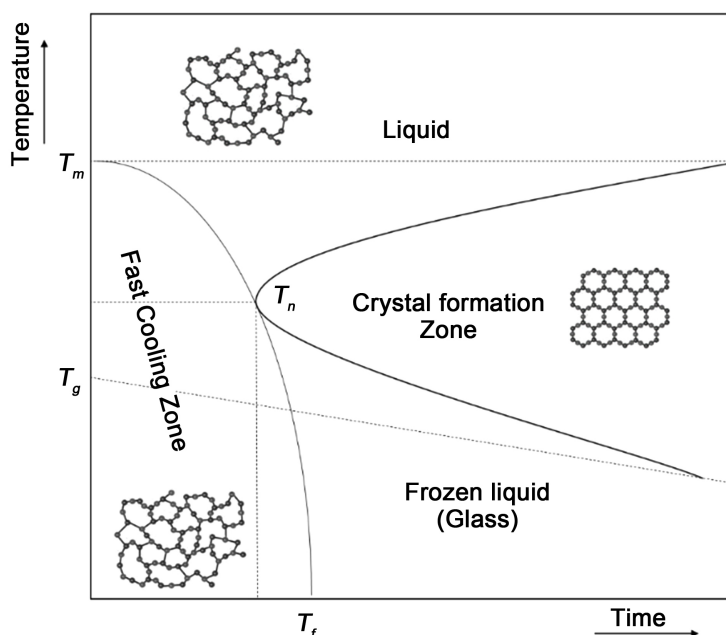

Figure 4. Time-Temperature-Transformation diagram, illustrate the importance of fast cooling the melt from T_m to below T_g without passing the critical nucleation zone (T_n), whereby not enough time is giving to the system to arrange its structure.

2.1. Glass Viscosity

Glass structure is best approached as a frozen liquid (amorphous solid), and on this basis, properties of glass are better understood through the changes in viscosity [14]. The term viscosity (η) describes and measures the resistance of a liquid to shear deformation and flow over a wide range of temperatures [33]. The relation between changes in viscosity and glass properties, are usually expressed as a function of temperature changes, for example, glass viscosity, can be discussed through-out cooling from melt (T_m) to the freezing point (T_g), or the reverse from heating up a frozen glass structure to the melting point [34] [35]. Thus, glass structure changes as well as its behaviors, during a typical viscosity scale from $\log_{10}$ viscosity 1 Pa·s being low viscosity (flowing liquid-melting point) to about 13.5 Pa·s (frozen liquid – solid) (see **Figure 5**) [36] [37] [38].

2.2. Viscosity Scale and Glass Properties

A number of glass viscosity points have been identified within the intermediate range between melting point (T_m) and the glass transition (T_g). These are used as reference points, due to their importance in glass processing and melt forming science. In general, glasses homogeneously melt at $\log_{10}$ viscosity point ≤2 Pa·s (T_m), while pressed and/or shaped at about 3 to 4, referred to as working and
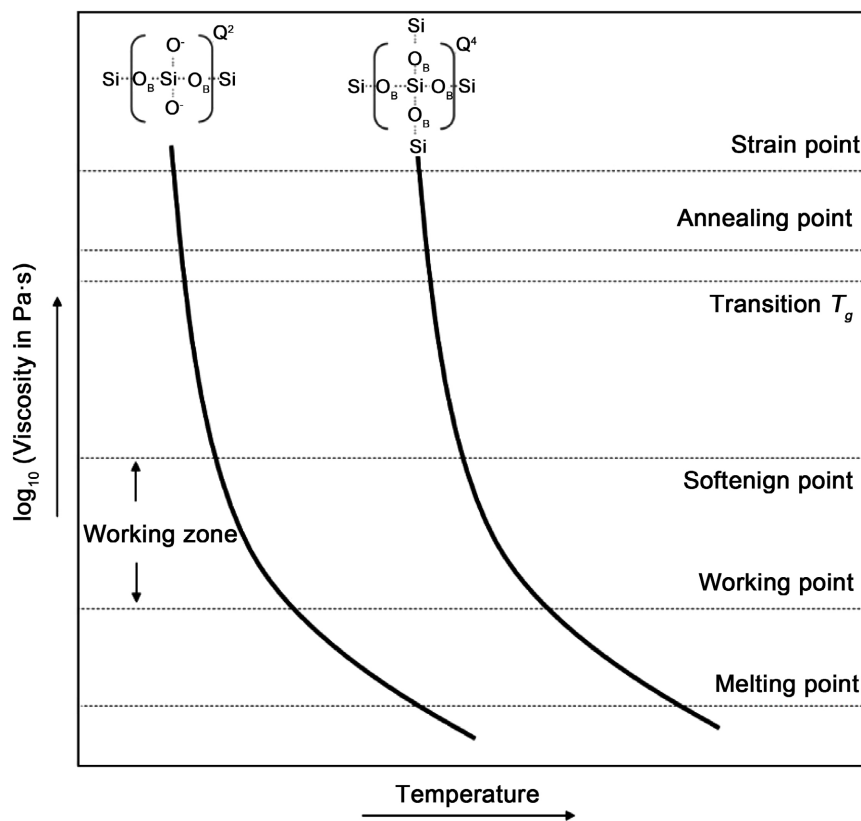

Figure 5. Illustration of a typical viscosity graph for common silicate glasses with different Q^x structure, showing changes in the viscosity points as a function of temperature – glass network connectivity.

flow points. Glass has been found to deform under its own weight at $\log_{10}$ viscosity point about 6 Pa·s, and soften when loaded at about $\log_{10}$ viscosities from 8 to 10 Pa·s, depending on the load applied. At higher $\log_{10}$ viscosities, 11 to 12, the glass network structure start to translate its behavior to a rigid like material, and this region is known as a glass transition point (T_g) [30]. Below T_g, at a range of $\log_{10}$ viscosities from 12 to 13, glass undergoes stress relaxation and relieves stresses caused by rapid changes in temperatures, especially during fast cooling from melt. Therefore, stresses can be relieved and or generated at two important points on the glass viscosities scale, namely the annealing and strain points [33] [37].

2.3. Composition-Temperature-Viscosity Relationships

Chemical composition of the starting glass plays a key role on the end system viscosity [39]. It is important to note that, at a given $\log_{10}$ viscosity point, temperature varies from one glass system to another and depends on the starting composition, which reflects on the Q^x structure of the glass as discussed in the network connectivity Section (1.2.3). For instance, in two different glass systems, one of which is a Q^4 glass and the other is Q^2, the working points for both will be at $\log_{10}$ viscosity of about 3 to 4 Pa·s but at different temperatures. The number of bridging oxygens in a Q^4 glass is higher, therefore, it requires higher energy to reach such viscosity, and the opposite is true for a Q^2 glass (**Figure 5**).

Further to this, the working temperature at exact $\log_{10}$ viscosity of 3 to 4 Pa·s for the same glass, can be significantly different [36]. This is dependent on whether the system is heated up from its solid state to the working point, or, cooled from melt. Nevertheless, glass is expected to behave in a similar manner once at a specific viscosity [34]. Therefore, a wide range of temperatures are used to process and crystallize glasses developed through-out the literature, while, viscosities are within the discussed scale.

2.4. Viscosity Models

A viscosity model should closely describe the activation process of a new glass system as a result of introducing energy to it, in order to predict the atomic motions of the body at a microscopic level. However, this remains a challenging goal to reach in glass science [40] [41] [42]. Nevertheless, different viscosity models have been proposed in the past decades throughout mathematical equations based on statistical analyses of large experimental works [43]. This is to aid in closely predicting the viscosity behaviors of a given glass system compositions before syntheses.

One of the earliest viscosity models was based on the assumption that fluid viscosity η is a thermally activated phenomenon, using constant activation energy for viscous flow (ΔH_η) in a basic equation to describe his approach:

$$\log_{10}\eta = A\exp\left(\Delta H_\eta \big/ RT\right) \qquad (1)$$

where T is temperature in Kelvin, A is a constant and R is the molar gas con-

stant. However, this work was criticized, because it cannot be expressed as an Arrhenius type behavior at intermediate temperatures, where the activation energy of viscosity (ΔH_η) differs from temperature [44]. Thus, different viscosity models were proposed since Frenkel-Andrade [39] [45]. The most common and systematic studies which led to relatively useful modeling equations for glass viscosity prediction over a range of different compositions and temperatures are those proposed by Vogel, Tamman and Fulcher, termed as VTF [33]. The VTF global equation of modeling glass viscosity adds a temperature fitting variable (T_0) to account for the activation energy change at an intermediate range, and is expressed as follows:

$$\log_{10} \eta = A + B/(T - T_0) \tag{2}$$

Here T and T_0 refer to temperature Kelvin, while A and B replaces (ΔH_η) from Equation (1). T and T_0 are constant characteristic of a specific glass composition/s vary regularly with compositional changes, and determined by fitting the expression to experimental data available in the literature [43]. This model has limitations and is not intended to provide an accurate viscosity prediction of newly developed glass systems, especially in the case of multicomponent glass compositions [46]. The limitations and details of the fundamental science behind the global VTF viscosity approach, is best found elsewhere [47] [48] [49] [50]. An appropriate use of such models can aid in narrowing the experimental work in the case of novel glass syntheses, providing an estimation of; glass melting points, working points, glass transitions and annealing points.

3. Glass Crystallisation

Crystallisation in glass is the process of arranging the amorphous atomic structural state of a glass system from randomly ordered network lacking long range order to a well-ordered periodic crystalline structure. Crystallization involves two key processes known as nucleation and crystal growth, which can occur via two phenomena namely; surface and/or volume crystallization. These are totally dependent on the melt viscosity that is selectively determined by the starting glass composition [51].

In general, crystallization phenomena in glass occur by different complex mechanisms which represent the way the structure is arranged from the amorphous to crystalline state. These mechanisms are mainly governed by the heat gradients throughout the system during heat treatment. The starting glass composition has a direct influence on the viscosity of the system, which is a key parameter in crystal nucleation and growth [52].

Crystallization is commonly observed to begin from the surface of the material toward its bulk. This mechanism is the case in most silicate based glasses, which possibly results in an undesired microstructure reflecting on the end properties of the glass-ceramic [53]. Nucleating agents are often added to the starting glass composition to bring such systems to volume crystallization before processing via melt casting and monolithic crystallization [54]. Only few glass

systems are known to rearrange their amorphous structure homogeneously throughout the volume of a monolithic body upon heating [55]. It is important to understand glass crystallization mechanisms in order to control the crystallization process of a specific glass system that is intended for successful glass-ceramic materials development. Therefore, the following sections in this review paper are focused on glass crystallization mechanisms, and a review of the classical crystal nucleation and growth theories, as well as the influence of the starting glass composition on glass-ceramics processing methods.

3.1. Surface Crystallisation

Surface crystallized glasses transport heat differently compared to those that crystallize thought-out their volume [56]. Hence, the structural arrangement process is initiated from the hot surface gradually to the interior of the monolith. Generally when a monolithic glass of a surface crystallized system is reduced to fine powders, the effect of heat gradients is low such that the heat transfer through the glass particles become faster and approaches equilibrium. This is due to the increase in the surface area; hence, nucleation sites exposed to the heat are greater compared to those available in a large bulk of monolithic body [57].

The crystal growth rate in surface crystallized glasses is comparable to those crystallized via volume mechanisms and this is discussed further on the growth rate section (see Section 3.3). In certain applications, surface crystallized monolithic glasses are used to prepare "glass-ceramics" having a thin surface layer of crystalline phase, while the interior remains as glass. The objective behind developing such materials is mainly to change the chemistry of the surface as compared to the interior body while maintaining the optical transparency of the end product [53]. Such methods of preparing glass-ceramics are reported to improve its mechanical strength due to the development of surface layer in compression as a result of controlled thermal expansion differences between the interior and surface of the end material [58] [59].

3.2. Volume Crystallisation

Glass systems, which crystallize throughout their volume, exhibit a chemical composition that allow for equilibrium heat to flow gradually during heat treatment process [60] [61]. By which the crystalline microstructure is possible to control, for instance, crystallite size, morphology and volume fraction. The end glass-ceramics properties of volume crystallized glass systems (e.g. thermal, chemical, mechanical and optical properties) are greatly influenced by the crystallization process (time, temperature and heating rates) [3].

Homogenously crystallized glasses which require no use of a nucleation agent are rarer to find and are usually based on narrowly defined stoichiometric compositions, such as the limited range in lithium silicate, barium silicate and sodium calcium silicate systems [51]. However, heterogeneously crystallized

glasses are in general based on surface crystallization mechanisms, and are brought to volume nucleation via the use of nucleating agents and strict heat treatment process. Theories behind these two mechanism and the role of nucleating agents are discussed further individually in Sections 3.2.1 and 3.2.2, respectively.

3.2.1. Homogenous Crystallisation

In homogeneous nucleation, the composition of the crystallising phase is the same composition as the parent glass. In contrast with heterogeneous nucleation, the residual glassy phase composition differs compared to the crystallised phase and requires the addition of nucleating agents to initiate nucleation, within the volume [55]. In both cases of volume crystallised glasses, the rate of nucleation is usually specified, in order to produce a nucleus of a critical size which will grow, rather than dissolving back into the melt [62] [63].

The nucleation rate can be determined by dividing the concentration of nuclei by the total time of the isothermal heat treatment at the nucleation temperature [64]. Two barriers will occur during the formation of a nucleus, these are the kinetic (ΔG) and thermodynamic (W^*) free energy barriers [19]. The kinetic barrier is the required energy to activate an atom to cross the liquid-nucleus interface. This should allow for bond breaking, which then results in reorganising the network structure from random into more ordered structure. Whereas, the thermodynamic barrier is the change of the net free energy of the system after the nucleus formation [64] [65]. As illustrated in **Figure 6**, the homogeneous nucleation rate (I) increases with the temperature, and can be expressed by the following equation, which was proposed by Becker in 1940 [64]:

$$I = A\exp\left[-\left(W^* + \Delta G_D\right)/kT\right] \tag{3}$$

where: (k) represents the Boltzmann constant, (T) is the absolute temperature, (A) is a constant and (D) refers to diffusion, where the constant A is expressed as follows:

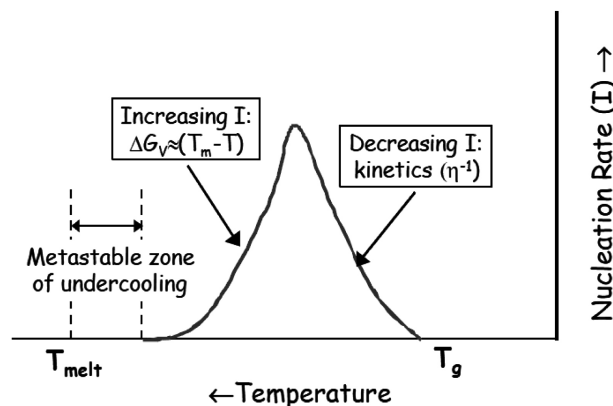$$A = n_v\left(kT/h\right) \tag{4}$$

Figure 6. Rate of homogeneous nucleation in a viscous liquid [19].

n_v is referred to the number of the atoms forming the crystalline phase per unit volume of the liquid, and h is Planck's constant.

The kinetic barrier free energy (ΔG) measurements are not commonly available even for a basic glass system made of one component [51]. However, ΔG can be estimated using the following expression:

$$\Delta G = \Delta H_f \left(T_L - T \right)/T_L \tag{5}$$

ΔH_f represents the heat of fusion the system requires for crystallisation, and T_L is the liquids temperature that can be estimated by means of viscosity measurement or modelling.

The changes in the atomic arrangement within the embryo create strain energy. Hence, the free energy barrier increases due to the change in the kinetic barrier (ΔG_D) which represent the liquid to crystal transformation. This change in the thermodynamic free energy (W), for radius of spherical embryo (r), is expressed by the following equation [64]:

$$W^* = \left(4/3 \right) \pi r^3 \Delta G_v + 4\pi r^2 \gamma \tag{6}$$

The term (ΔG_v) represent the change in kinetic barrier per unit volume and the term ($4\pi r^2 \gamma$) represents the change in surface energy (the difference between the free energy per molecule of the bulk and that of the surface is referred to as surface energy) as illustrated in **Figure 7**. (γ) is used to express the interfacial energy between the crystal and liquid phase.

The surface energy governs the small radius of the spherical embryo, unless the radius increases in size to allow the fraction of the total surface energy change to become relatively smaller [64]. The surface energy term remains predominant if the embryo does not reach its critical size [3]. When the spherical embryo reaches its critical radius the volume free energy will start dominating which then leads to more growth along with a decrease of free energy until the embryo reaches its stability [63]. The critical radius (r^*) is the value of critical sized nucleus (r) as shown in **Figure 7**, and is given by the following equation:

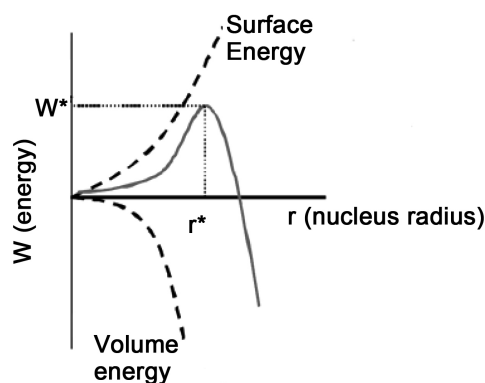$$r^* = 2\gamma/\Delta G_v \tag{7}$$

Figure 7. Illustration of the critical radius (r^*) leading to thermodynamically stable particles when ($r \geq r^*$) [19].

The validity of the nucleation theories discussed above is questionable, and were based on several assumptions made during the time period of the development of these classical theories, and most of the parameters cannot be directly measured [66]. For example the investigated maximum nucleation rate theoretically and experimentally was found to "differ by more than 20 orders of magnitude" [67].

3.2.2. Heterogeneous Crystallisation

In heterogeneous nucleation, the free energy is different to that of the homogenous nucleation, and it requires lower energy due to the occurrence of pre-existing surfaces such as impurities, crucible walls or nucleating agents [12] [55] (see **Figure 8(a)**). Therefore, the control of the catalysing surface is specified by the contact angle (θ) at the substrate-liquid junction (see **Figure 8(b)**).
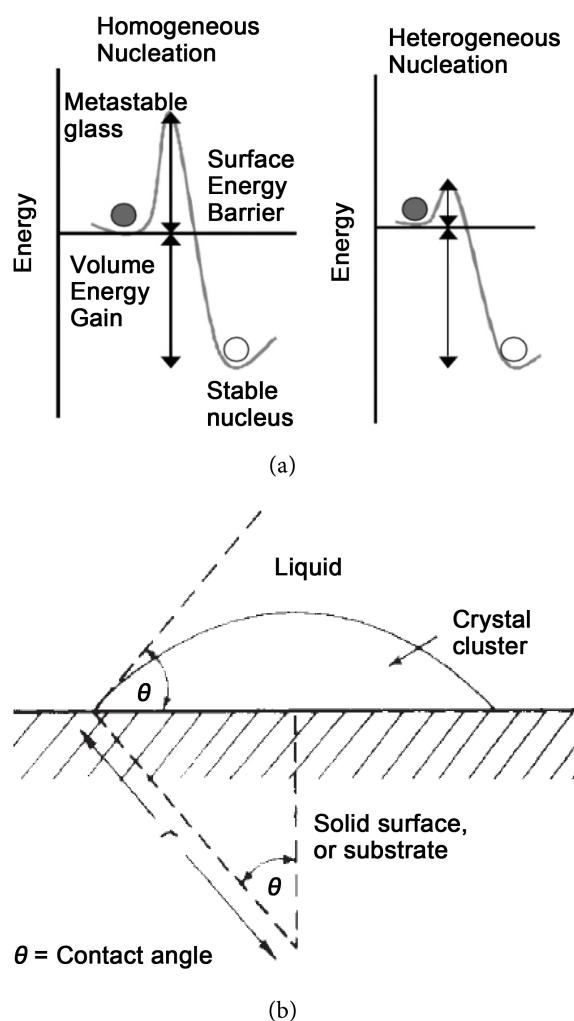

(a)

(b)

Figure 8. (a) Illustration showing a comparison of free energy barrier between homogeneous and heterogeneous nucleation [19]. (b) Schematic diagram showing the contact angle (θ) at the substrate-liquid junction of heterogeneous nucleation on a solid surface [66].

However, as a result of the lower surface energy there will be a reduction on both the thermodynamic barrier and the kinetic barrier causing a pre-dominance of surface nucleation. The heterogeneous nucleation rate (I_{het}) is given by:

$$I_{het} = n_s \left(kT/h \right) \exp \left[- \left(W_{het}^* + \Delta G_D \right) \middle/ kT \right] \tag{8}$$

"Het" is written to distinguish heterogeneous nucleation rate from homogenous rate, and (n_s) represents the number of atoms forming the nucleus unit, $W_{het}^* = f\left(\theta\right)W^*$, here $f(\theta)$ is the contact angle function between the crystal nucleus and the pre-existing surfaces (substrate). This equation is used to predict the shape of the heterogeneous nucleation rate per unit volume [68].

Previous studies pointed out that, pre-existing surfaces may prevent the nucleation process as the nucleation site may dissolve during heat treatment [69]. The presence of such nucleation sites can have a negative impact on controlling the surface crystallisation process, for instance, different crystal phases may occur each time due to the different kinds of nucleation sites.

1) Nucleating Agents and the role of TiO$_2$

Since surface crystallisation is the case for most silicate glasses, the composition of the parent glass is designed to contain nucleating agents to enhance volume crystallisation [67]. Nucleating agents can be metallic such as Au, Ag, Pt and Pd or non-metallic including TiO_2, ZrO_2, and P_2O_5 and different fluorides [70]. It is requisite of nucleating agents to have the ability to exist in the form of a dispersion of particles in the glass to minimize the effect of temperature gradients through-out the system during heat-treatment, which lead to uncontrolled crystallisation [71]. Nucleating agents are also known to act as nuclei for heterogeneouscrystal growth, as well as increasing the crystallisation rate with a very uniform distribution of small crystals [3]. Furthermore, the addition of nucleating agents is often found to decrease the overall system viscosity and the activation energy which eases the processing of monolithic glasses into glass-ceramic [72] [73].

The use of TiO_2 as a nucleating agent has been proven to be effective in a range of alkaline derivative alumino-silicate glass systems, such as those based on lithium, sodium, calcium and magnesium [74]. TiO_2 is commonly added to the starting glass composition with a maximum of 15% by weight as a nucleating agent [75].

Amorphous phase separation was reported to influence the nucleation mechanism when adding large amounts of titanium dioxide [76] [77]. The amount of nucleating agents added to the glass composition could have a critical limit for phase separation to occur and lower the total free energy of the system. As a result of such additives in the original glass composition, the phase with higher modifier content can crystallise easier than the phase richer in silica, whereby the monolithic glass maintains its shape during processing without deformation [3].

Adjusting the concentration of nucleating agents has a high influence on the final glass-ceramic product including mechanical and chemical properties. In-

vestigating the effect of a compounds ability to act as a nucleation agent, requires systematic research work to determine the optimum amount of nucleating agent/s needed [78].

3.3. Crystal Growth Rate

Crystal growth is the step of the crystallisation process of a monolithic glass which comes once a stable nucleus has been formed [54]. The nucleus usually grows by introducing the nucleated glass to a higher temperature and allowing further energy to flow to the system. The nucleated glass is then held at the growth temperature for a specific period of time that is a key factor influence the growth rate [3].

Crystal growth involves molecules movement from the glassy phase across the glass/crystal interface into the crystal. Such atomic movements are driven by the differences in ΔG between the glassy and crystalline phases, which is a thermally activated process known as activation energy [79]. The crystal growth rate (U) is similar to the nucleation rate, as shown in **Figure 9**. While different expressions can be found in the literature to describe (U), in general, (U) can be expressed by the following equation:

$$U = \left(kT/3\pi a_o^2 \eta\right)\left[1 - \exp\left(\Delta G/kT\right)\right] \tag{9}$$

The crystal growth rate is controlled by the thermodynamic barrier which is represented as $[1 - \exp(\Delta G/kT)]$, while ($kT/3\pi a_o^2 \eta$) represents the kinetic barrier, which is for example related to the movement or motion of groups of atoms in the glass. Where (a_o) represents atomic jump distance, (ΔG) is the difference
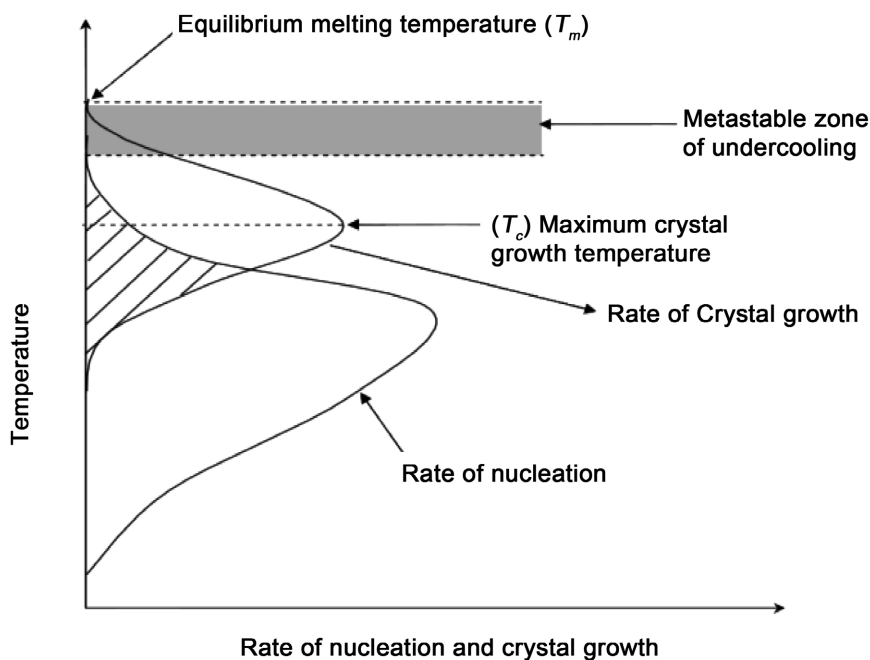

Figure 9. The effect of temperature on the nucleation rate and crystal growth in a viscous liquid [79].

in thermodynamic energy between the solid (crystalline) and liquid phase (glassy) [68].

At temperatures (T) higher than the melting point (T_m), the free energy change (ΔG) is positive. As a result of this, crystals will start to dissolve at temperatures at or higher than their melting point. The expression [1 − exp($\Delta G/kT$)], should be a negative number resulting in a negative value of crystal growth rate (U), where $T = T_m$, $\Delta G = 0$, which results in $U = 0$. Crystal growth rate must be controlled, as a rapid growth may not allow equal heat gradients across the melt, which can lead to uncontrolled crystallisation [3].

The thermodynamic barrier factor [1 − exp($\Delta G/kT$)] has a high impact on the crystal growth rate at a region where the temperature (T) is decreased below the melting point (T_m), due to low viscosity and negativity of the higher driving force (ΔG). However, at the equilibrium temperature where $T \leq T_m$, the kinetic factor mostly governs the crystal growth rate [65]. Here, the changes occur in the crystal growth rate due to the changes of the thermodynamic and kinetics factors. Hence, the curve of the nucleation rate (I) and crystal growth rate (U) are plotted together against temperature as shown in Figure 9.

4. Glass-Ceramics

Partially crystallised glasses, often referred to as glass-ceramics, are a multiphase material containing amorphous and crystalline phase/s with various ratios (normally from 20% to 95%) [80]. The aim behind preparing glass-ceramics is that the end material should have superior properties, which cannot be achieved from the original glass, such as thermal shock resistance, control of thermal expansions, mechanical strength, optical properties etc [60].

Glass-ceramics are produced using different routes for a wide range of applications through controlling the crystallisation mechanisms of specially designed bulk glasses using two step or single step heat treatments in general known as crystallisation process (involve nucleation and crystal growth) [64]. Alternatively, the parent glass is made into fine powders then processed into monolithic glass-ceramics body using a combined sintering and crystallisation processing route, which depends on the crystallisation mechanisms of the chosen glass system [80] (Figure 10).

4.1. Crystallisation of Bulk Glasses

In general, for bulk glass crystallisation, initially, an amorphous glass is prepared through melt casting into a monolithic body. That is then introduced to a careful heat treatment schedule (time, temperature, heating rate) to bring the monolith to a viscosity level (usually 30°C to 50°C above T_g) such that the atomic motions are evident to partially arrange the glass structure while not deforming the starting monolithic body [3]. Therefore, slow heating and cooling rates (5°C up to 20°C per minute) are commonly applied during the heat treatment process for different purposes; namely, to avoid thermal shocking the monolithic body,
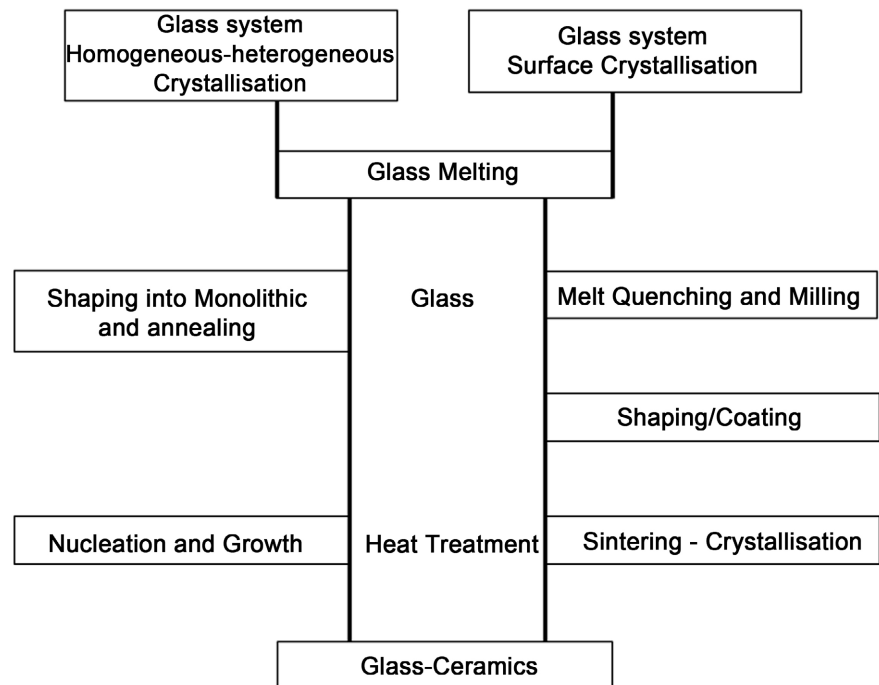
Figure 10. Illustration diagram common processing routes for glass crystallisation to produced monolithic glass-ceramics, showing the influence of crystallisation mechanisms on the process methods, where volume crystallised glasses are processed as pre-shaped monolith glass compared to surface crystallised glass families.

and allow heat gradient through the bulk, which prevents early nucleated areas of the monolith to undergo crystal growth. The heating rate has been found to decrease the glass viscosity. Nevertheless, once the system starts to crystallise the viscosity increases, hence, deformation of the body is avoided [81].

Crystal nucleation and growth in bulk glasses may occur separately or overlap, which is dependent on the starting glass composition and the system viscosity **Figure 11**. Common glasses, intended for preparing glass-ceramics, are heat treated above their T_g for nucleation, for about 30 minutes to 2 hours depending on the size of the monolith [82].

Glass composition and the heat treatment (crystallisation process) which the monolithic glass is subjected to, influences the type of crystalline phase developed in the final glass-ceramic. Ideally, for mechanical strength purposes, the end glass-ceramics should consist of a large number of interlocked small grain sized crystals (<5 μm) [59].

The volume crystallization mechanism is a complex process involving the previously discussed two key mechanisms, *i.e.* homogenously and/or heterogeneously arraignments of the glass structure into crystalline phase with the aid of nucleation agents. Whereas, glass melt-casting itself is a simple process for large scale production. The scale-up of large monolithic bodies with absence of porosity are simple and reliable for glass-ceramics production, which is difficult to produce by other means (*i.e.* powders route). Those monolithic bodies might be sheets, plates or shallow rings made through shaping the melt into a pre made
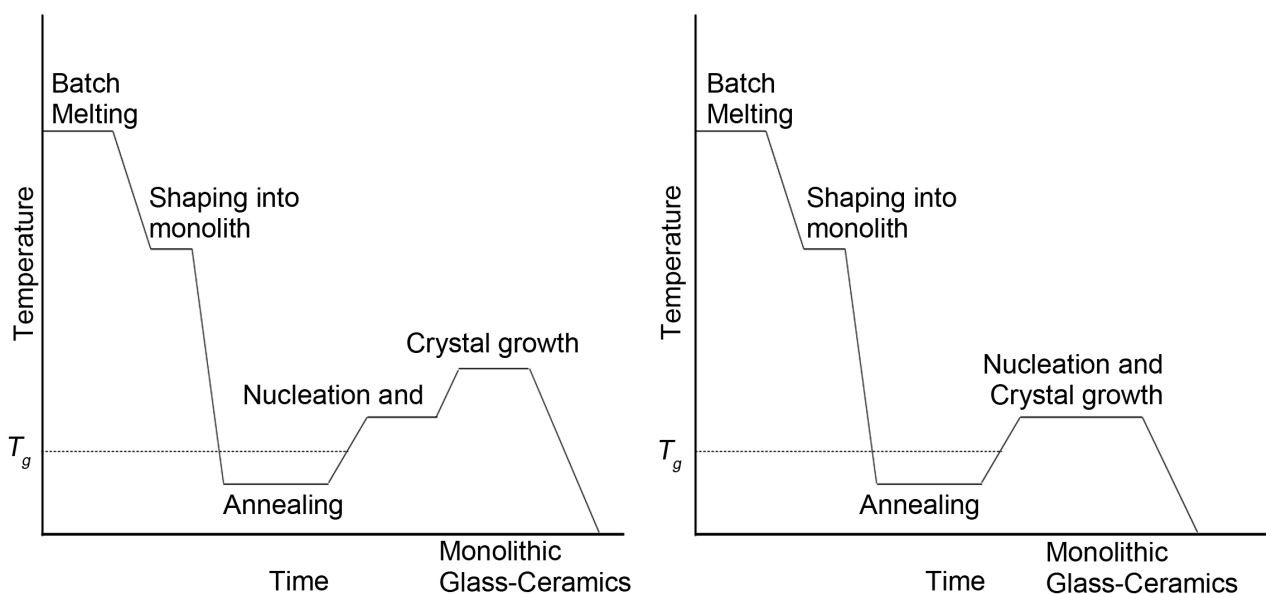
Figure 11. Illustration of conventional processing steps for glass melting and shaping at high temperature. Crystallization process here is used for monolithic glass systems which crystallizes via volume mechanisms, where nucleation and growth are processed above the glass transition T_g, individually (left) or overlapped (right).

mold [60]. However, melt casting and crystallization of the monolith may not be as simple for other applications such as in medical glass-ceramics, where small objects having fine and detailed complex geometries are the intended end glass-ceramics.

4.2. Crystallisation of Powder Glasses

Preparing monolithic glass-ceramics using a powder route also requires conventional glass melting. However, here, the glass is not cast as a monolithic body, but rather quenched in air or water to prepare a glass frit that is then dried and ground to fine powders, which usually results in a range of particle sizes and morphology (an hour of dry ball milling for common glass systems should provide fine powders with average particle size of less than 125 μm) [83], see **Figure 12**.

Objects are then made here through a range of routes, such as, dry pressing into blanks, or mixing with liquid binders to form a slurry that is then shaped into the desired form known as a green body. These are then introduced to a careful sinter-crystallisation heat treatment schedule, in order to bring the glass particles together via viscous flow sintering and avoid premature crystallisation that might prevent viscous flow. The crystallisation activation energy and viscous flow of the glass at the sintering temperature is such that the crystallisations process is activated during or after the sintering step. Sinter-crystallisation temperatures are found to be optimal at $\log_{10}$ viscosity points between 3 to 4 Pa·s, where the pressing and/or shaping of bulk glasses is made [84]. However, if the crystallisation occurs before the densification process, the viscosity of the system increases and therefore viscous flow decreases, leading to a mechanically weak
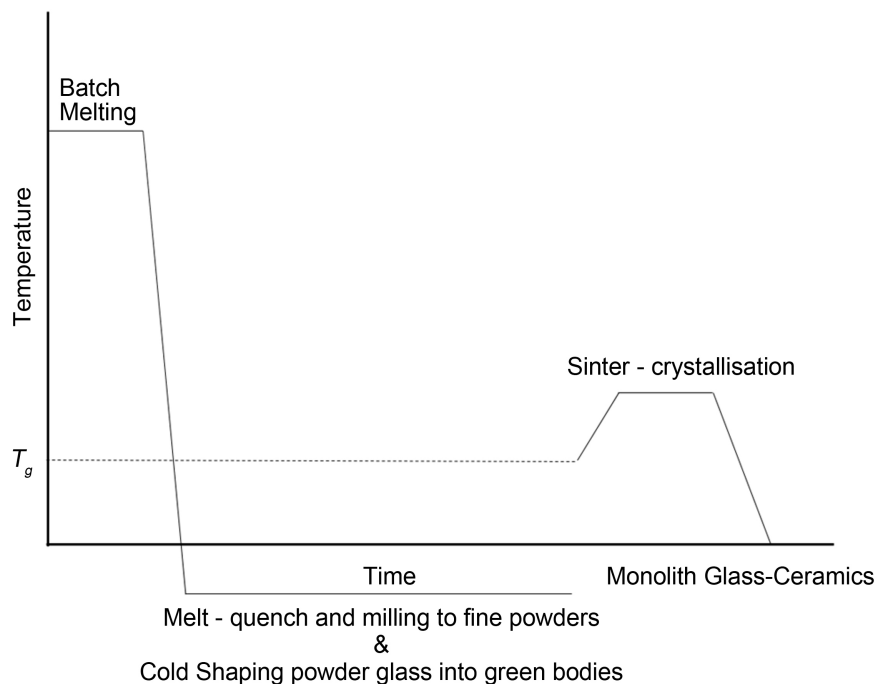
Figure 12. Illustration of conventional processing steps for glass melt-quenching (air/water) that is then mechanically reduced to fine powders. Here shaping done at room temperature. While the sinter-crystallization process starts from T_g and above, (no risk of monolithic thermal shock), such process is common for glass systems which crystalizes via surface mechanism, where densification, is combined with crystallization.

and optically poor glass-ceramics [83]. Only a narrow range of alkali alumino-silicate glass systems are compatible for glass-ceramic preparation using a sinter-crystallization route.

A successful sinter crystallization heat treatment should provide monolithic glass-ceramic materials that are comparable in properties to those made using a monolithic glass route [84]. However, such crystallization mechanism may not be practical for certain glass compositions or applications (such as those derived from the lithium silicate systems). In particular, glasses which resemble crystallization mechanism obeying the volume nucleation rules, which believed not to be attractive for powder processing route and may lead to a porous and mechanically week material [85]. This is mainly due to the high crystallization tendency of such glasses once in fine particles form, rather than monolithic body [86]. On the other hand, certain surface crystallized glasses (such as those based on leucite, cordierite and diopside chemistry, potassium or magnesium alumino-silicate, or magnesium calcium silicate systems) display a relatively high viscosity, which require long and uneconomical crystallization schedules to form the desired crystalline phase [87] [88]. Such systems are best partially crystallized in a powder form then mechanically milled to reduce the crystallite size before sintering. The prepared glass-ceramics powders are then shaped into green body and sintered into dense monolithic glass-ceramics [89]. Sintering of such glass-ceramics systems is required to be done at a temperature that is typically from

0.5% to 0.9% below the crystalline phase melting point in order to density the green body [90].

Sintering and Crystallisation of Glass Powders

Sintering is usually referred to as the process of heat treating (time/temperature) a powder compact with closely packed particles. The particles start to densify via viscous flow diffusion to their neighbouring particles, eliminating the gaps (porosity) between the particles [91]. Glass systems obey surface crystallization mechanisms intended for preparing monolithic glass-ceramics via a sinter-crystallization route, preferably exhibit a moderate activation energies for crystallization to allow partial crystallization of the glass structure into the desired crystalline phase while maintaining the viscous flow step during the densification process [92].

The densification mechanisms of viscous flow sintering were looked at experimentally by Mackenzie and Shuttleworth (1949) [93]. Thereafter, Murray *et al.*, (1954) [94] developed an extended model for calculating the densification rate (the time required for optimum densification at a giving viscosity) that is $(\mathrm{d}D/\mathrm{d}t)$, and expressed as follow:

$$\mathrm{d}D/\mathrm{d}t = 3/4\eta\left(2\gamma/r\right)\left(1-D\right) \tag{10}$$

where the relative density $D = p/p_c$, p here the starting compact density before sintering in general assumed to be 0.25% dense or less (for random packing of rigid spheres), while the (p_c) represents the relative density after densification. Where γ represents the surface energy, and η is viscosity at viscous flow (which is assumed to be in the range between $\log_{10}$ viscosity points 3 to 4 Pa·s); however, this assumption is only the case before any crystallization process begin. The value for $(1 - D)$ is time dependent which require different dwelling time at the densification temperature; hence, the following expression is used:

$$\ln\left(1-D\right) = -3/\eta t + \ln\left(1-p\right) \tag{11}$$

where t is the required time for densification (sintering) to reach p_c density, and is a viscosity dependent variable, where:

$$t = 7.5\eta \tag{12}$$

Decreasing the viscosity, by increasing the temperature or modifying the starting composition, influences the densification time. For instance, densification time at $\log_{10}$ viscosity 2 Pa·s should be less compared to 4 Pa·s., when crystallization process starts during or before viscous flow. All the above mentioned assumptions are not practical and the densification process has far more complex mechanisms due to the dramatic change in the glass viscosity during crystallization [95].

One of earliest studies related to viscous flow sintering showed that particles bond occur via viscous flow, and suggest no difference between sintering both amorphous and crystalline materials [96]. The developed viscosity models do not necessarily apply for sintering crystalline materials, whilst sintering can oc-

cur via solid-state bonding between particles [93]. The discussed equations above show the importance of viscosity in the densification process, as well as the crystallization process once monolithic glass-ceramics are intended to be made via sinter-crystallization process. Nevertheless, it is not an objective of this review to validate these equations.

5. Conclusion

This paper has presented a critical review of glasses and their crystallizations methods with reference to their main components and applications. The structure and chemistry of common glasses are introduced, and the main methods for compositional designing, glass synthesis and crystallizations of different glass systems, are described in detail. The main applications of glasses and glass-ceramics are explained, and some commercially available glass-ceramics, along with their processing methods in relation to the end application, are mentioned. Glass and glass-ceramics materials offer unique characteristics of a wildly used material in our daily life. The future for glass sciences remains very bright, even in a time when knowledge continues to expand. Future research in glass and glass-ceramics sciences should explore the potential of combining several crystalline phases in one glass-ceramics system and introduce this class of material into wider applications.

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Conflicts of Interest

The author declares no conflict of interest.

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