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Examining the role of nucleating agents within glass-ceramic systems

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ABSTRACT

Nucleation is one of the primary contributions to the microstructure of glass-ceramics. However, the nucleation process within glass-ceramics is not understood across all glass systems, nor is the specific role of nucleating agents. The present article proposes a comprehensive definition of a nucleating agent: "**a nucleating agent is a minority component of the glass composition that leads to increased internal nucleation rates or precipitation and control of desired crystal phases, either by lowering the thermodynamic or the kinetic barrier for nucleation, or some combination thereof**". We also examine the role that five important nucleating agents (TiO_2, ZrO_2, MoO_3, P_2O_5, and OH^-) play in different systems, particularly in their effect on the thermodynamics and kinetics of the nucleation process. We argue that nucleating agents help control the nucleation process either by decreasing the thermodynamic or kinetic barrier or some combination of the two and provide a method to distinguish their effect.

1. Background

Any scientist who studies glass knows the famous story of S. Donald Stookey's accidental discovery of glass-ceramics in 1953 [1–3]. A less famous part of the tale includes the deliberate steps Stookey took shortly after his discovery to ensure his lithium-disilicate glass-ceramics could be reliably and consistently produced, leading to valuable industrial products. His first samples were not meant to crystallize and, therefore, did not have all the necessary components that a standard glass-ceramic has today. He studied the precipitation of silver nanoparticles in the glass to investigate its effect on photosensitivity. However, Stookey found that silver did not work efficiently as a nucleating agent for aluminosilicate crystals. Using a combination of his own intuition and knowledge of the literature, he added titania to his composition, which proved to be an effective nucleating agent for his system. This led to the production of rocket nose cones and CorningWare® [1–3]. The importance of this compositional change should not be overlooked.

It has been demonstrated that glass-ceramics containing multiple phases may have unique combinations of properties [2–5]. Therefore, it would be beneficial to have a better understanding of how to properly control the nucleation of each phase. Glass-ceramics could potentially be designed to nucleate multiple phases from a single nucleating agent, or multiple nucleating agents could be incorporated into the composition if two or more target phases could not be effectively nucleated by a single agent. Note that work has been done on compositions containing more than one nucleating agent [5–9], but it is difficult to determine the exact effects of each agent on nucleation in this situation; therefore the impact of multiple nucleating agents will not be examined in the current study. The timing of this article is propitious as there has been a recent push to define imprecise terms often used in our community [10]. Recently, glass-ceramics have been redefined for the purpose of increased clarity by Deubener et al. [11]. This new definition clarifies that controlled crystallization is a key step for producing glass-ceramics. The paper also discusses the idea that control is often achieved through nucleating agents, which is a concept that remains ill-defined.

There are a few imprecise terms used by the glass-ceramic community that should be addressed. The terms "nucleating agent" and "nucleation agent" are often used interchangeably; here we will adopt "nucleating agent" for our discussion. Within the literature, the term nucleating agent is sometimes used to describe the starting batch material, but it may also describe the structural unit within the glass network; at other times it describes the functional phase. In the present work, the term "nucleating agent" will be used to describe the compound that is introduced in the batch when there is no metallic functional phase involved, but it will also describe the starting batch material used to introduce the component in the system when the functional

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phase is metallic. The term metallic nucleating agent refers to nucleating agents that affect nucleation via a functional phase that is metallic in nature. Additionally, the definition of a nucleating agent varies depending on the source and is not well documented in general. The proposed definition that will be used henceforth is the following: *a nucleating agent is a minority component of the glass composition that leads to increased internal nucleation rates or precipitation and control of desired crystal phases, either by lowering the thermodynamic or the kinetic barrier for nucleation, or some combination thereof.*

Let us break down each part of this definition. The definition specifically states that the nucleation agents generally increase the rate of nucleation and also, in certain cases, might lead to better control of the nucleation process (i.e., induce the precipitation of desired crystal phases). The word "control" is necessary since thermodynamics are involved, and an increase in the nucleation rate only implies that kinetics is affected by the addition of a nucleating agent. Some components, which can be called nucleation "inhibitors" or "suppressors," have the opposite effect; they slow down nucleation kinetics, as a result of lower nucleation rates and longer nucleation induction times, improving the glass forming ability [12]. Structurally, a nucleating agent can be directly involved in the nucleation mechanism or indirectly involved via an intermediate crystal phase, or by enhancing liquid-liquid phase separation (LLPS) [13]. Moreover, a nucleating agent generally makes up a small concentration of the overall system because it can only be present up to the solubility limit of the system, where the final parent glass shows no spontaneous crystallization after the glass forming process [14].

Increased nucleation rates are quite common in most cases; however, the cause for increased control of nucleation of a desired phase in a multicomponent glass has not been well studied for many systems. The structural effects of TiO_2 and ZrO_2 have been considered in select systems [15–21], but the structural role of a nucleating agent within a glass network and the resulting glass-ceramic is not well-known for many systems. There is a wide range of knowledge among the many systems. Therefore, we have chosen several examples that are more well studied to thoroughly examine, as well as one relatively novel nucleating agent.

Table 1
The following table is a summary of the common nonmetallic nucleating agents and their roles within various glass-ceramic systems. Empty cells did not have conclusive data at the time of writing the current manuscript.

Nucleating Agent	Base Glass	Mechanism	Nucleating site / Functional phase	Nucleated Crystal
P_2O_5	SiO_2-Li_2O-Al_2O_3-K_2O-B_2O_3	Epitaxy	Li_3PO_4 surface	Li_2SiO_3, $Li_2Si_2O_5$, SiO_2(cristobalite) [31]
	SiO_2-Li_2O-Al_2O_3-K_2O	Promote phase separation	Interface: residual glass ↔ amorphous/(disordered)nano-crystalline Li_3PO_4 phase separation	Li_2SiO_3, $Li_2Si_2O_5$ [3]
	SiO_2-Li_2O-K_2O-MgO-CaO-Al_2O_3	Consumption of Li-ions → enrich residual glass in silica → Promote phase separation → consume (bond) Li-ions	SiO_2-Li_2O-K_2O-MgO-CaO-Al_2O_3-P_2O_5	Li_2SiO_3, $Li_2Si_2O_5$, Li_3PO_4, quartz, cristobalite [33]
	SiO_2-Al_2O_3-MgO-CaO-Na_2O-K_2O-F	Promoting phase separation → Homogenous nucleation in phase separation	Phase separation	Apatite (mica-apatite glass-ceramics) [34]
	SiO_2–Al_2O_3–MgO–ZnO			β-quartz-spinel [3,35]
	SiO_2-P_2O_5-Na_2O-CaO-F	Nanoimmiscibility of the phosphor-silicate base-glass		Rhenanite [36]
CaF	SiO_2-CaO-R_2O	High interfacial energy	Interface: residual glass ↔ CaF crystal	Canasite [37]
TiO_2	MgO-Al_2O_3-SiO_2		$MgTi_2O_5$ crystals	Cordierite; enstatite, forsterite, β-quartz-solid-solution; α-quartz-solid-solution [3,38]
	MgO-Al_2O_3-SiO_2	Phase separation	Al_2TiO_5	Cordierite [39]
	SiO_2–Al_2O_3–Na_2O			Nepheline [3,40]
	SiO_2–Al_2O_3–MgO–ZnO	Glass-in-glass phase separation		Spinel, gahnite, β-quartz-solid-solution; α-quartz-solid-solution [41–43]
	SiO_2-Al_2O_3-Na_2O-BaO			$BaAl_2Si_2O_8$; nepheline, $NaAlSiO_4$, anatase (TiO_2) [3,44]
ZrO_2	P_2O_5-Al_2O_3-CaO-Na_2O-F	High interfacial energy	Interface Na-Zr-Phosphate ↔ residual glass	Apatite, Berlinite [3,45]
	MgO-Al_2O_3-SiO_2		ZrO_2 crystals	β quartz-solid-solution; α quartz-solid-solution; cordierite, enstatite; forsterite [37,46]
	SiO_2–Al_2O_3 - Li_2O	Al-rich growth barrier that surrounds the ZrO_2	Nanoscaled ZrO_2 crystals	β quartz-solid-solution, β-spodumene solid-solution [47,48]
	SiO_2–Al_2O_3–Cs_2O	Phase separation	ZrO_2 crystals	Pollucite [49]
	SiO_2–Al_2O_3–ZnO			Zn-stuffed β-quartz, willemite-zincite [3,35,50]
	SiO_2–Al_2O_3–MgO–ZnO		ZrO_2 crystals	Spinel, gahnite, β-quartz-solid-solution; α quartz-solid-solution [51]
	SiO_2-Al_2O_3-MgO-CaO-F		ZrO_2 crystals	Spinel [52]
TiO_2; ZrO_2	MgO-Al_2O_3-SiO_2		$ZrTiO_4$ crystals	β-quartz-solid-solution; α-quartz-solid-solution [53]
	SiO_2–Al_2O_3 - Li_2O		$ZrTiO_4$ crystals	β-quartz-solid-solution, β-spodumene solid-solution [54]
	SiO_2–Al_2O_3–MgO–ZnO		$ZrTiO_4$ crystals	Spinel, gahnite, β-quartz-solid-solution; α quartz-solid-solution [51]
Ta_2O_5	SiO_2–Al_2O_3 - Li_2O			β-quartz-solid-solution, β-spodumene solid-solution [55]
Nb_2O_5	MgO - Al_2O_3 - SiO_2			Quartz, Spinel [56]
	Na_2O–Al_2O_3–SiO_2			$NaAlSiO_4$,$NaNbO_3$ [57]
	Li_2O–SiO_2			$LiAlSi_3O_8$, Li_2SiO_3 [58]
OH^-	Li_2O–SiO_2			$Li_2Si_2O_5$ [59,60]
	Na_2O–CaO–SiO_2			$Na_2Ca_2Si_3O_9$ [59,61]

In addition, we made sure to choose at least one representative nucleating agent for each mode of functionality (thermodynamics, kinetics, or a combination). A summary of nucleation mechanisms, nucleating agents, and functionalities is included in Table 1. Among these are the systems we chose to examine, which are highlighted.

According to Höland and Beall [3], nucleation is influenced by two factors: an appropriate selection of the chemical composition of the base glass (including one or more nucleating agents) and a controlled thermal history. The thermal history includes a heat treatment with time and temperature as process variables. As the proposed definition suggests, the three options for a nucleating agent are to decrease the thermodynamic barrier of forming crystals, the kinetics of nucleating crystals are better controlled by the agent, or by some combination of these two mechanisms. It is also likely that the structural mechanism by which the nucleating agent aids in accelerating nucleation of the desired crystal phase is highly system specific. Although the exact mechanisms are unknown for various systems, several trends exist with respect to nucleating agents.

Although most glass-ceramics of technological interest only present internal crystallization by adding a nucleating agent, there are some self-nucleated systems that undergo volume nucleation if submitted to proper heat treatment. Owing to the race between the diffusion and thermodynamics controlling crystal nucleation, only silicate glasses with a reduced glass transition temperature (T_g/T_l, in which T_l is the liquidus or melting temperature in Kelvin) below ~0.6 undergo internal homogeneous nucleation detectable in a laboratory time scale [22]. The predominance of homogeneous nucleation rather than surface nucleation is related to the similarity of the structures of the parent glass and precipitated crystal [23,24].

Most of the self-nucleated systems are stoichiometric and present isochemical crystallization, where the chemical composition of the crystalline phase is the same as the parent glass, e.g., $Li_2O{\cdot}2SiO_2$, $Na_2O{\cdot}2CaO{\cdot}3SiO_2$, $2Na_2O{\cdot}CaO{\cdot}3SiO_2$, $BaO{\cdot}2SiO_2$, $5BaO{\cdot}8SiO_2$ and $2BaO{\cdot}TiO_2{\cdot}2SiO_2$. However, non-isochemical crystallization in the volume without adding any nucleating agent is also possible, as in the case of Li_2O-CaO-SiO_2 [25], ZnO-Al_2O_3-SiO_2 [26], and Na_2O-CaO-SiO_2 systems [27].

It should be stressed that, to the best of our knowledge, no single component has been reported to effectively behave as an effective nucleating agent for all systems, except "water" (OH^-). However, a small group of compounds is commonly used in various systems. The following oxides have been reported to behave as nucleating agents for at least one base glass system: TiO_2, ZrO_2, P_2O_5, Ta_2O_5, MoO_3, WO_3, Fe_2O_3, Nb_2O_5, Cr_2O_3, and F [28]. However, this list is not fully inclusive; a more comprehensive list can be seen in Table 1. Note that this table excludes metallic nucleating agents; noble metals can also be used as effective nucleating agents [29], but we will not be focusing on them in the current study.

The discovery of novel nucleating agents is a current topic of interest. For instance, a fairly recent study by Maeda and Yasumori [30] examined the role of MoO_3 and WO_3 (separately) on the nucleation of enstatite crystals in the MgO-Al_2O_3-SiO_2 (MAS) system. An additional area of active research is multifold nucleation, where one nucleating agent is used to produce two or more crystalline phases [3]. This mechanism can be used to combine the properties of two phases, such as high toughness and translucency from a lithium disilicate phase, and a high CTE from cristobalite [31] or a cesium aluminosilicate phase [32], as well as machinability and bioactivity via the combination of mica and apatite [3]. However, this type of research is outside the scope of this perspective article, as we are largely examining the relationships between a nucleating agent and a single target phase.

There are a few points to note from these examples. First, as stated previously, no single nucleating agent is reported to boost nucleation rates in every system, except "water". Second, a couple of compounds were tested in multiple systems and were reported to behave as a nucleating agent in one system but act differently in another [28]. There was often very little discussion detailing how each nucleating agent was chosen for each particular crystal system [28,30]. These observations led to several questions, the most obvious being why each agent was chosen for each system, how it is known that the compounds are in fact acting as nucleating agents, and most importantly why these components are behaving as nucleating agents. However, before any of these questions is addressed, the topics of the nucleus and nucleation need to be addressed.

Each crystal in a glass-ceramic originates from one specific nucleus. Unlike what is known for nucleating agents, the chemical components of a nucleus must originate from the non-crystalline structure of the parent glass and must represent all chemical components of the evolving crystalline phase [23]. However, the close and long-range order of these components, as well as the nucleus stoichiometry, may deviate considerably from the macroscopic properties (composition, structure, density) of the nucleated crystalline phase [62]. Except for the mechanism of epitaxy, where similar lattice parameters are assumed to be the prerequisite for successful nucleation, in general, there is no chemical or structural correlation assumed between the nucleating agent and the nucleus. There is consensus that a nucleus must have a critical size R^* to overcome the thermodynamic barrier for being able to grow to what is, at a certain point, called a crystal. Whether this is a continuous process of growth of a nucleus up to the critical size (classical nucleation theory, CNT) or whether there are discrete compositional and structural changes (stages) to generate a nucleus of critical size is a subject of recent discussion [62,63]. Furthermore, it was reported that the heterogeneous nucleation mechanism shows evidence of the stochastic nature of nucleus formation [64].

Glass-ceramics are produced either through controlled surface nucleation or controlled internal nucleation of a parent glass [3,65], but the current study will focus only on internal nucleation. Crystallization occurs in two steps: nucleation and crystal growth. Before they can grow, crystals must be nucleated at some temperature (T_n), which typically occurs in between the glass transition onset temperature (T_g) and the crystallization peak temperature (T_c) of the primary crystal phase in a DSC or DTA experiment. As many standards with glass-ceramics, this temperature range should be used as a guideline or initial starting point to determine the appropriate temperature. Note that T_g is defined as the intersection point (on a thermal analysis curve) between the tangent line to the curve at the maximum of the first derivative in the transition and the tangent line to the curve chosen at a point just before the transition begins. After the crystals have been nucleated in the sample, they must be grown by heat treating the sample near to or above the T_c for a given crystal phase. This chosen temperature is known as the crystal growth temperature (T_{gr}) [3,65]. However, for systems that show extremely high nucleation rates, ceramization can be performed by a single heat-treatment [3].

Kinetics plays a large role in these processes because the rate of nucleation (I) and the rate of crystal growth (U) vary as a function of the temperatures chosen for heat treatments [3,65]. This is illustrated in Fig. 1. The processes related to nucleation are complex, but the nucleation of crystals within a glass-ceramic is known to be largely influenced by two main elements: first, the chemical composition of the parent glass (including the addition of a nucleating agent) and second, the controlled heat treatment of the parent glass utilizing both temperature and holding time as independent variables [3,65]. Most heat treatments are carried out in two steps, but one-step heat treatments have also been explored [3].

The nucleation and growth rates are governed by both thermodynamics and mass transport. This means that any nucleating agent added to these systems must either change the kinetics of these processes or the thermodynamics. In CNT, the prevalent theory among the many theories proposed to understand the origin of nucleation [65–71], the nucleation rate of a system with no barrier is simply given by $I = n\nu$, where n is the density of possible nucleation sites and ν is the vibrational frequency. However, this is an overly simplified solution to this problem as it does

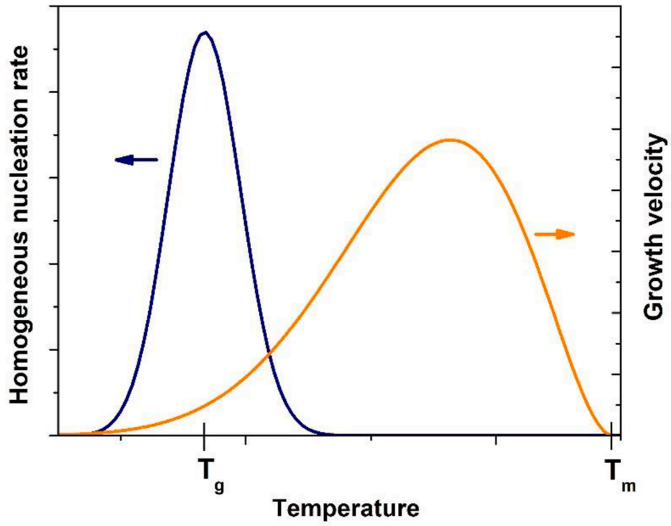

Fig. 1. Schematic nucleation and crystal growth rates as a function of temperature (linear scale).

not account for any energy barriers. Instead, the commonly used experimental nucleation rate is written as [63,66,72]

$$I(T)=\sqrt{\frac{\sigma}{kT}}\left(\frac{D(T)}{d_0}\right)\exp\left[-\left(\frac{16\pi\sigma^3}{3kT}\right)\left(\frac{1}{\Delta G_\nu}\right)^2\right]. \tag{1}$$

In this equation, σ is the nucleus/liquid interfacial free energy, T is the temperature, k is Boltzmann's constant, D is the diffusivity, d_0 is the jump distance, and ΔG_ν is the thermodynamic driving force per unit volume of the crystal. Eq. (1) is only valid for homogeneous nucleation of spherical nuclei in the absence of any internal stress, therefore the equation would be modified in cases where the nucleating agent promotes heterogeneous nucleation [65]. The diffusion coefficient is often approximated by the inverse of viscosity using the Stokes-Einstein (SE) relation since the diffusivity cannot be easily measured [68]. The validity of the SE expression is often questioned for predicting nucleation. Recently, experimental evidence showed that the crystal growth velocity can be a better proxy for the effective diffusivity controlling crystal nucleation in glass-forming substances [73]. However, at least the high-temperature side of the nucleation curve can be reasonably described by viscosity. Therefore, we use the SE relationship because it easily encompasses the kinetics for the purpose of discussions. The SE relation states[68]

$$D(T)=\frac{kT}{6\pi a\eta}. \tag{2}$$

Here a is a parameter related to the size of the diffusing particle (which is often related to d_0 of Eq. (1)), and η is the equilibrium shear viscosity, as given by the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation of viscosity (given below) [74],

$$\log_{10}\eta(T)=\log_{10}\eta_\infty + (12-\log_{10}\eta_\infty)\left(\frac{T_g}{T}\right)\exp\left[\left(\frac{m}{12-\log_{10}\eta_\infty}-1\right)\left(\frac{T_g}{T}-1\right)\right]. \tag{3}$$

In the MYEGA expression, there are only three unknowns: the T_g, the fragility (m), and the infinite temperature limit of viscosity ($\log_{10}\eta_\infty$), which is generally considered a constant equal to about −3 in log(Pa·s) units [75]. Since diffusion represents the kinetics of the system and viscosity is being substituted, the two variables related to kinetics are the fragility and the glass transition temperature. In other words, if a nucleating agent modifies the T_g or the m, it modifies the kinetics. However, if the nucleation curve is altered while the T_g and the m remain unchanged, then the change in the curve is thermodynamic in nature. Note that the fragility and the glass transition temperature (for practical purposes T_g is defined as the temperature where the viscosity reaches a certain value $\eta(T_g)\sim 10^{12} Pa{\cdot}s$). This temperature is easily detected in DTA or DSC experiments performed at 5–10 K/min. It can, in principle, be explicitly predicted as a function of composition and structure by using the topological constraint theory (TCT) [76,77]. In the future, this technique may allow for a parameterization of nucleation without extensive experimental work.

A major challenge is to characterize and easily parameterize the thermodynamics and kinetics of a system and separate their influence on nucleation. Thermal analysis of the parent glass via differential scanning calorimetry (DSC) can be used to understand the influence of nucleating agents on the kinetics and thermodynamics of the system [78–83]. Despite being more appropriate to use small monolithic pieces, instead of powders, to study internal nucleation by DSC, the effect of a given nucleating agent can still be evaluated if similar particle sizes are used (in any given study). It is relevant to stress that one widespread method to infer whether a nucleating agent is efficient is to compare DSC or DTA traces of powders and monolithic pieces of the studied glass. If the traces coincide (more or less), it is clear that internal nucleation induced by the catalyzer predominates over surface nucleation.

As previously stated, the variables associated with kinetics are the T_g and the m, while the variables associated with thermodynamics are the Gibbs free energy of nucleus formation and the interfacial surface energies. The glass transition temperature can easily be determined via DSC, but the fragility is more difficult to observe. It has been widely suggested that the width of the glass transition (ΔT_g) is a function of the glass transition temperature and the fragility [78–80]. A change in the width could be a strong indication of a change in the fragility [78–80], or alternate methods based on many DSC scans of a single composition are available to explicitly calculate fragility [81,82]. Another marker of a change in the fragility is a change in the heat capacity (C_p) jump at the glass transition, which is due to the changing configurational contributions, as shown by Smedskjaer et al. [83]. However, when adding small amounts of nucleating agents, these weak C_p changes are very hard to detect.

The thermodynamic quantities are harder to consider, but there have been some attempts at predicting the driving force from DSC. The methods to calculate driving forces were compared in an article by Cassar [84]. Note that there is a driving force for each crystalline phase that will form but calculating individual driving forces for each phase remains a challenge. The simplest form of the driving force, which gives an upper bound, can be estimated by [68]

$$\Delta G_\nu=\frac{\Delta H_f(T-T_l)}{T_l}. \tag{4}$$

In this equation, T is temperature, T_l is the liquidus temperature, and ΔH_f is the heat of fusion. Both the liquidus temperature and the heat of fusion can be found through DSC, as explained in a review article by Zheng et al. [85]. There is an individual ΔH_f for each possible crystalline phase, so the ΔH_f for the primary phase will not affect the nucleation of secondary phases. Eq. (4) shows that the difference between the liquidus temperature and the temperature of nucleation is a metric proportional to the driving force for nucleation; thus a larger difference results in a higher thermodynamic driving force compared to a sample with a similar heat of fusion and smaller difference between the liquidus and nucleation temperatures. The last component to calculate the effects of nucleating agents from DSC is the liquid/nucleus interfacial energy. Unfortunately, this parameter cannot be directly measured and is most commonly fit to nucleation rate data [65]. For some substances it has been determined by Molecular Dynamics Simulations by a method called seeded nucleation [86–88] and by an energy landscape approach [89].

This manuscript proposes a clear, updated definition for nucleating agents and a method to distinguish their effect, supported by a critical literature review on the most crucial nucleation catalyzers. We will go through the available literature describing the roles that several nucleating agents take on in their respective systems. Then, we will discuss the effect of each nucleating agent on the thermodynamics and dynamics of nucleation. This will have an **emphasis on the nucleating agent's role on the variables discussed in Eqs. (1)–(4).** We will also explain how each nucleating agent adheres to the proposed rules mentioned above.

2. TiO_2

2.1. TiO_2 introduction

TiO_2 is one of the most common nucleating agents, partially because it was extensively studied after it was used by Stookey on early lithium disilicates, but also because it appears to promote enhanced nucleation rates for multiple systems. Most glass-ceramics are produced in one of the various silicate systems, including silicates, borosilicates, aluminosilicates, and their various subfamilies. Among all these potential systems, TiO_2 has mostly been added to various aluminosilicate systems, especially in more recent work. However, in pioneering glass-ceramic work, Stookey experimented with it in lithium disilicate compositions [3], and Schultz followed his lead by incorporating TiO_2 into ultra-low expansion (ULE) silica-rich glasses [90].

Schultz [90] focused on a simple binary ULE SiO_2-TiO_2 composition. Note that this composition was not a glass-ceramic, and the main goal of the project was to study the relationship between the addition of TiO_2 to the network and thermal expansion properties. The study did not directly look at the role of TiO_2 as a nucleating agent for the system, but it provided one of the first examples of TiO_2 promoting nucleation. No formal definition of a nucleating agent was provided, but Schultz pushed the limits of the glass forming ability of the system and, therefore, found where the system crystallized. The amount of TiO_2 greatly affected the optical properties. Compositions containing 16.8, 18.5, and 19.4 wt% TiO_2 became transparent, translucent, and opaque after annealing at 960 °C [90]. Schultz believed phase separation played a role in the nucleation process but acknowledged that there was not enough kinetics data to definitively conclude that mechanism as the source [90].

2.2. TiO_2 in non-magnesium aluminosilicate systems

More recently TiO_2 was added to various aluminosilicate systems as a nucleating agent to help produce numerous phases such as leucite, Sr-feldspar-tielite, celsian, apatite, cordierite, and mullite. The aluminosilicate networks were modified by alkali or alkaline-earths like potassium, strontium, barium, and calcium. Cattell et al. [91]. included a small amount (0.4 wt%) of TiO_2 in an aluminosilicate K_2O-Al_2O_3-SiO_2 system and observed a phase separation mechanism for the nucleation of leucite crystals. The authors suspected this was due to the high coordination of TiO_2, which caused separation from the aluminosilicate network.

Beall reported needing very high TiO_2 content ranging from 8 to 18 wt% to promote internal volume nucleation for a couple of alkaline-earth-modified aluminosilicate systems [29]. For a SrO-Al_2O_3-SiO_2 system, 8–15 wt% was used to produce a Sr-feldspar-tielite phase (Al_2TiO_5), while 7.5–11 wt% was used to nucleate a celsian phase for a BaO-Al_2O_3-SiO_2 system [29]. In both cases, the reported mechanism for nucleation was TiO_2 substitution for Al_2O_3 tetrahedra, leading to phase separation [29]. However, no formal definition of a nucleating agent was provided in this reference. As previously stated, many studies report what nucleating agent was used but rarely provide a definition of a nucleating agent or a specific, in-depth discussion of how the nucleating agent led to increased nucleation rates or control over nucleation of the target phases. However, several studies do provide a definition.

Fathi and Johnson [92] defined a nucleating agent as a catalyst of the internal crystallization by promoting nucleation of nano-phases that act as sites for the heterogeneous nucleation of other desired phases. This is a rather limited definition, which is only valid only for this particular mechanism. They studied the effect of increasing TiO_2 content in a SiO_2-Al_2O_3-P_2O_5-CaF_2-TiO_2 system to produce apatite-mullite glass-ceramics. Thermal data showed that the addition of TiO_2 decreased the T_g and both of the T_c's, corresponding to apatite and mullite, respectively [92]. Also, the exotherms became sharper. XRD results showed the main phases were fluoroapatite and mullite, with a minor content of cristobalite. The peak intensities for the major phases were altered as a function of TiO_2 content, and no minor phases consisting of titania were produced [92]. While the phase evolution was not greatly affected, the morphology of the crystals was. The microstructure became more pronounced with large crystals as TiO_2 content increased, and there was also an increase in the number of crystals [92]. Note that the same nucleation and growth temperatures were used for all compositions, so the only variable being altered was the TiO_2 content. The authors found a correlation between the sharpness of the exothermic peaks via DTA analysis and grain refinement seen under SEM, as well as a higher likelihood of promoting bulk crystallization as opposed to surface crystallization [92]. A TiO_2 concentration of 2 wt% led to the best results, as a lower concentration did not promote bulk crystallization, but higher concentrations led to less grain refinement (and less sharp exothermic DTA peaks) [92]. The authors argued that TiO_2 is an effective nucleating agent for this system due to its ability to promote phase separation.

2.3. TiO_2 in magnesium aluminosilicate systems

TiO_2 has been incorporated into magnesium aluminosilicate (MAS) systems more so than any other system. This is due to both the proven track record of TiO_2 leading to favorable nucleation results, as well as the promising properties acquired through cordierite, the target phase. Zdaniewski [93] reported a liquid-liquid (also referred to as glass-in-glass) phase separation mechanism for the volume crystallization of μ-cordierite (from 850 to 1100 °C) and α-cordierite (above 1100 °C) within a MAS system. The composition contained over 7.4 wt% TiO_2, and the work discussed the structural role of TiO_2 within the glass network. TiO_2 caused phase separation upon cooling of the melt due to its high coordination number of 6, as opposed to a coordination number of 4 that is typically allowed for a network former. Additionally, phase separation was increased by heat treatment of the specimens [93].

Barry et al. [94] examined the effects of TiO_2 on a MAS system with the goal of forming cordierite as the main crystalline phase. The paper included a discussion on the amount of nucleating agent needed to promote internal bulk nucleation as opposed to crystal growth from free surfaces. The authors reported needing 11.5 wt% TiO_2 to effectively promote crystallization of cordierite. The paper defined a nucleating agent's role as helping to control the resulting microstructure [94]. It backed this claim up through a discussion of the varying phases that occurred when changing nucleating agent content in the composition. Thermal analysis showed the T_g, the T_c, and the melting point all decreased as a function of increased TiO_2. Cordierite and other minor phases became more prevalent with increasing TiO_2 content.

Following the trend, Hutton and Thorp [95] determined that the addition of TiO_2 to a MAS system causes phase separation of the silica network. Unlike many other studies, they used Raman spectroscopy to determine this. The effect became more apparent as more TiO_2 was added to the composition, and a maximum of 10 wt% TiO_2 was added [95].

Fokin and Zanotto [39] studied TiO_2's role on cordierite glass-ceramics produced from a MAS system. The study incrementally increased TiO_2 content and found a threshold value (a minimum of $>$6.2 wt%) was needed to promote volume nucleation. Both surface and volume crystallization proceeded through heterogeneous nucleation. The study determined that an increase in TiO_2 content did not lower the thermodynamic barrier. Instead, they proposed that the increase in nucleation rate (*I*) was due to an increase in the number of active nucleation sites [39]. Their evidence for the claim was that only surface nucleation occurred when less than 8 wt% TiO_2 was present in the composition. Above that threshold value, LLPS occurred, and Al_2TiO_5 sites acted as catalysts for volume nucleation [39].

Muller et al. [96] reviewed the kinetics of surface and volume nucleation rates in cordierite, anorthite, and diopside glass-ceramics within the MAS system. The authors found that surface nucleation rates reach a maximum at a much higher temperature than volume nucleation. They also reported that TiO_2 only promoted volume nucleation after high concentrations (>8 wt%) of TiO_2 were included in the composition [96].

Wange et al. [97] studied microstructure-property relationships of cordierite, aluminum titanate, and cristobalite glass-ceramics from a MAS system. XRD results showed that cordierite (and aluminum titanate) only formed after a heat treatment with a growth temperature of 1200 °C or above. Note that a nucleation temperature of 800 °C was used for all heat treatments. Lower growth temperatures resulted in α- and β-quartz. There was no discussion of why TiO_2 was chosen as a nucleating agent or even that it was acting as a nucleating agent. The discussion focused on the microstructure's dependence on thermal history, as opposed to controlling the nucleating agent content. Therefore, there was also no definition of what a nucleating agent is.

Al-Harbi tested multiple nucleating agents on a Li_2O-ZnO-MAS system, including TiO_2, Cr_2O_3, and ZrO_2 [98]. Thermal analysis of the glasses showed that TiO_2 decreased the exothermic onset temperature of the main peak in the original glass. It also added an extra, weak exothermic peak at a lower temperature range, and it did not influence the T_g onset temperature. XRD results showed that TiO_2 allowed for the nucleation of virgilite at low temperatures and Li-aluminum silicate at high temperatures, Cr_2O_3 led to the nucleation of gahnite at low temperatures and virgilite at high temperatures, and ZrO_2 led to virgilite at high temperatures. When comparing the XRD results of the sample without any nucleating agent to the one with TiO_2, it is important to note that the compositions behaved similarly, but the peaks became more intense in the TiO_2 sample [98]. The authors reported the addition of nucleating agents aided in the control of nucleation of different phases. The mechanism behind nucleation was believed to be phase separation.

Cormier et al. [19] varied TiO_2 content from 2 to 10 mol% in a MAS system. The coordination of the Ti polyhedra within the glassy and crystalline phases was extensively studied. Ti coordination did not vary as a function of TiO_2 content, but it did change during heat treatments in the following manner. The majority of Ti polyhedra were $^{[5]}$Ti in the glassy phase originally [19]. Upon heat treatments, there was a change of coordination to $^{[6]}$Ti in the nanocrystals of a $MgTi_2O_5$-Al_2TiO_5 phase that acted as precursor sites for the nucleation of further phases, while the remaining Ti became 4-coordinated in the glassy phase [19]. The T_g and the first T_c (corresponding to β-quartz) temperatures decreased as a function of increasing TiO_2 content, and the exothermic peak sharpened with increasing TiO_2 content. The nucleating agent also affected secondary exothermic peaks, as a peak corresponding to indialite decomposed while a peak for cordierite formed at high TiO_2 contents. The authors reported a threshold value of approximately 7 mol% TiO_2 to be an effective nucleating agent but admitted they could not explain the reason for this threshold [19]. They included a discussion of their previous work on an increase in the fraction of higher coordinated Al species around 7 mol% TiO_2 but again explained they do not know why there is an increase at 7 mol%. The authors did not provide a strict definition for a nucleating agent, but all their arguments were thermodynamic in nature.

Guignard et al. [20] examined the structural role of TiO_2 in a MAS system. The study defined a nucleating agent as a component of the composition that can aid in nucleation either by speeding up the kinetics of phase separation or by decreasing the thermodynamic barrier associated with nucleation [20]. TiO_2 content was varied from 0 to 15 mol%. Using solid state nuclear magnetic resonance (NMR), the study determined that as TiO_2 content was increased in the glass network, the amount of higher coordinated Al atoms increased. In other words, in a glass with no TiO_2, most Al atoms were 4-coordinated, but as TiO_2 was introduced, 5-coordinated and 6-coordinated groups appeared in the structure. This was the main structural change that occurred in the parent glass [20]. The glass transition temperature decreased as TiO_2 was increased, and TiO_2 did not cause inhomogeneity or phase separation in the glass as it had been reported to do in the previously discussed systems [20]. Therefore, if phase separation was the mechanism for nucleation, it would have to be induced via a post-synthesis heat treatment. The study concluded, however, that TiO_2 increased the speed of nucleation through an edge-sharing mechanism between the titanium atoms and highly coordinated aluminum atoms in the glass. These more highly ordered sites acted as seeds for nucleation during a heat treatment, and the authors believed they were reducing the height of the thermodynamic barrier for nucleation of the magnesium aluminotitanate crystals [20]. The nanocrystalline sites then acted as seeds for the nucleation of the target phase, cordierite.

Maeda et al. [14] synthesized cordierite and enstatite phases in a MAS system using both TiO_2 and MoO_3 as nucleating agents. The goal was to compare the results of the two agents, but this discussion will focus on the TiO_2 results. Concentrations included 5, 7.5, and 10 wt% (up to 7.2 mol%) TiO_2 provided nucleating sites for the main crystalline phases, but additionally precipitated itself into minor phases [14]. This is consistent with other reports that made structural arguments about the local coordination of TiO_2 and the network formers around it. Thermal analysis showed trends of decreasing the T_g and the T_c with increasing TiO_2 content, and the sharpest exothermic peak occurred for the highest TiO_2 content [14]. Enstatite was grown at temperatures of 1000 and 1100 °C. Cordierite became the main phase at 1200 °C, but enstatite was still present in the microstructure. Secondary phases of rutile, magnesium aluminum titanate (MAT), and magnesium titanate (MT) were also nucleated [14]. The highest amount (10 wt%) of TiO_2 was needed to promote effective internal nucleation and a fine microstructure. The authors suspected that TiO_2 remains stable and dissolves in MAS glasses up to the threshold value and only acts as a nucleating agent once its wt% exceeds the solubility limit [14].

3. ZrO_2

3.1. ZrO_2 in lithium aluminosilicate systems

Besides TiO_2, another often used nucleating agent is ZrO_2, which can be added either individually or combined with other oxides to enhance nucleation kinetics. One of the most important glass-forming systems of technological interest is the Li_2O-Al_2O_3-SiO_2 (LAS), that originates low CTE glass-ceramics. Dressler et al. [99] evaluated the crystallization of LAS glasses with different additions of ZrO_2 and SnO_2, keeping the total content of nucleating agents ($ZrO_2 + SnO_2$) to 2.1 mol% (SnO_2 content varying from 0 to 1.0 mol%). The crystallization of the glass without SnO_2 started from the initial precipitation of tetragonal ZrO_2 (*t*-ZrO_2), suggesting that the role of ZrO_2 as a nucleating agent in LAS glasses is related to homogeneous nucleation of this phase, which triggers heterogeneous nucleation of β-quartz solid solution (ss). The temperature of maximum nucleation rate was well above T_g (~100 K), likely due to the presence of preferential nucleation sites, *t*-ZrO_2 or orthorhombic srilankite ss ($(Zr_{0.5}Ti_{0.5-y}Sn_y)O_2$ with $y = 0.5$), depending on the content of each nucleating agent.

Kleebusch et al. [100] added ZrO_2 (3 mol%) as a nucleating agent in a LAS glass-ceramics with compositions similar to Robax™, a commercial glass-ceramic from Schott AG. The crystallization behavior was evaluated by XRD and (S)TEM, using treatment temperatures from 680 to 750 °C and an annealing time of 24 h. In the XRD pattern corresponding to samples treated at 720 °C or above, a broad peak was observed, which can be assigned to either cubic or tetragonal ZrO_2 nanocrystals. This result indicates that the nucleation and growth of the final predominant crystal phases (LAS and α-/β-quartz ss) was preceded by the precipitation of nanocrystals of the nucleating agent. Besides that, the STEM analyses showed a region enriched in Al surrounding ZrO_2 nanocrystals, forming a core-shell structure. The authors argued that such a structure arises from initial LLPS, favored by the nucleating agent. It is supposed that spontaneous crystallization of ZrO_2 occurs within the droplets and Al is expelled from the crystal, remaining in a shell circumjacent to them, which acts as a diffusion barrier and prevents a significant increase in the ZrO_2 nanocrystals' size, which remains in the range of 5–15 nm even for a longer annealing time.

Complementing their previous work [100], using a LAS glass with 3 mol% ZrO_2 as a nucleating agent, Kleebusch et al. [48] proposed a study upon the formation and development of nanocrystalline ZrO_2 in the early nucleation stages. To follow the development of ZrO_2 crystals as a function of heat treatment time at 725 °C, they combined analyses by XRD, TEM, and X-ray absorption near-edge spectroscopy (XANES). From TEM micrographs, the authors confirmed that annealing initially leads to LLPS with the formation of liquid droplets enriched in Zr, favoring further precipitation of ZrO_2 nanocrystals within them. According to the XRD patterns, ZrO_2 nanocrystals appear only in samples treated for more than 1.75 h. These conclusions were backed by XANES analyses, which showed that for 1.75 h of annealing, approximately half of Zr remained in the glassy phase, sixfold coordinated, whilst the other half was crystallized, being eightfold coordinated. In the final stages of crystallization (24 h), the growth of the LAS crystalline phase starts on the ZrO_2 nanocrystals, probably facilitated by the differences between the chemical composition of the precursor glass and the Al-rich barrier around the ZrO_2 nuclei. Therefore, the study of Kleebusch et al. [48] confirmed that the initial precipitation of ZrO_2 explains the role of this oxide in improving nucleation kinetics in LAS glasses, even though the authors did not propose any definition for a nucleating agent.

3.2. *ZrO_2 in magnesium aluminosilicate systems*

ZrO_2 is also widely added to MAS glasses to accelerate internal nucleation kinetics. One of the oldest studies regarding the influence of some additives in the internal nucleation kinetics of MAS glasses was carried out by Zdaniewsk [101]. He compared the crystallization kinetics of a MAS glass with 7 wt% of either ZrO_2 or TiO_2. Furthermore, to evaluate the possibility of controlling crystallization of glasses through lanthanides oxides, he studied compositions with 5 or 10 wt% CeO_2, which has an opposite effect to ZrO_2 or TiO_2, acting as a nucleation inhibitor. Similar to the results observed for LAS glasses, during crystallization of the ZrO_2-bearing MAS glass, firstly the precipitation of *t*-ZrO_2 nanocrystals occurs, followed by the development of the final predominant crystal phases, β-quartz ss, and high-cordierite. The occurrence of LLPS during the first steps of heat treatment is suggested due to the presence of micrometric spherical aggregates dispersed in the glass matrix, which was called "macrophase separation". According to the author, the effect of TiO_2 and ZrO_2 in enhancing nucleating of the main phase is by "lowering the activation energy for nucleation". Hence, these additives affect the thermodynamics of nucleation.

Structural information may provide the key to explaining why some components act as a nucleating agent within a given glass-ceramic system. In this regard, Dargaud et al. [15] used XANES to investigate the evolution of nucleation in a MAS glass with 4.03 mol% ZrO_2. They verified that the coordination number of Zr^{4+} in this particular glass is higher than 6 (the value commonly observed in most glasses). This relatively high coordination number along with the absence of efficient local charge compensation can promote structural instability of Zr^{4+}, favoring precipitation of nanocrystalline ZrO_2, in which Zr^{4+} is eightfold coordinated ($^{[8]}Zr^{4+}$). Therefore, the initial precipitation of ZrO_2 during annealing can be attributed to the high coordination of Zr^{4+} in the precursor glass, raising the hypothesis that atomic-scale processes are responsible for the transition glass-crystal, besides giving clues for the structural effect of nucleating agents. On the other hand, in glasses that present Zr^{4+} in octahedral coordination ($^{[6]}Zr^{4+}$), it is expected that ZrO_2 will not act in nucleation catalysis.

In another study to evaluate the correlation between structural aspects of the precursor glass and nucleation behavior in MAS based glass-ceramics, Dargaud et al. [16] used X-ray Absorption Spectroscopy (XAS) to evaluate the Zr^{4+} environment in the early crystallization steps, comparing the behavior of glasses with 0 and 4 mol% ZrO_2. Both glasses presented similar T_g (~830 °C), however in the glass with ZrO_2, a new exothermic peak appeared at around 945 °C, corresponding to ZrO_2 precipitation. Moreover, the other two crystallization peaks and T_l shifted approximately 20 °C to lower temperatures. These changes in the thermal events when ZrO_2 is added indicate that this compound has a minor influence on the kinetic barrier and its role as a nucleating agent is related to the thermodynamic barrier. Concerning structural information, XAS analyses show that the Zr-Zr distance in the parent glass is 3.40 Å, which is much lower than the theoretical value of 11 Å, estimated by considering a random distribution of Zr^{4+} in the glass. In addition, they verified that the coordination number of Zr^{4+} in the precursor glass is 7, and these ions are mostly linked to Si(Al,Mg) tetrahedra by edge sharing with other Zr^{4+} in a structure responsible for lowering the activation energy for ZrO_2 nanocrystals formation. The initially precipitated ZrO_2 nanocrystallites, confirmed by HRTEM, acted as nuclei for crystallization of the desired phases that become predominant in the advanced stages of crystallization.

Dittmer et al. [46] studied the crystallization in a MAS glass with 5.7 mol% of ZrO_2 in the temperature range of 950–1200 °C. The XRD pattern of the glass-ceramics showed that the main crystal phase was quartz ss (in some glass-ceramics β-quartz ss is stabilized at room temperature by Mg and Al in its crystal lattice), besides ZrO_2 (cubic or tetragonal) and spinel. Even though this work does not focus on the role of ZrO_2 as a nucleating agent, the initial precipitation of nanocrystals of ZrO_2 was confirmed. In addition, the authors proposed that, unlike the presence of an Al-rich layer surrounding the crystals in LAS glasses [100], as crystallization progresses, the residual glass in glass-ceramics from MAS system becomes enriched in SiO_2 and the crystals become surrounded by a Si-rich viscous layer, which has the same effect as the Al diffusion barrier, preventing crystal growth.

Dargaud et al. [17] used high-angle annular dark field scanning transmission microscopy (HAADF-STEM) to evaluate the mesoscale ordering in a MAS glass with 4.1 mol% ZrO_2. Using the HAADF-STEM, intrinsic nanoscale heterogeneities could be detected in the parent glass, with some regions enriched in Zr, with a size smaller than 10 nm. Since this mesoscopic ordering resembles the nucleating crystal (ZrO_2), in those domains enriched in Zr less energy is required for precipitation of ZrO_2. This hypothesis is corroborated by TEM images showing spherical crystals of 3–5 nm evenly dispersed in the matrix and a Zr-rich region around them. Hence, these experimental results suggest that in a MAS glass having only ZrO_2 as a nucleating agent, the energetic barrier is reduced due to the intrinsic heterogeneous structure of the parent glass in the mesoscopic scale, i.e., the effect is of ZrO_2 in boosting nucleation is of thermodynamic nature.

Dittmer et al. [102] performed a study of crystallization in MAS glasses with different contents of ZrO_2 (4.0–6.3 mol%). In contrast to the previously cited works, in some compositions the authors used yttria-stabilized *t*-ZrO_2 as a nucleating agent. According to XRD analyses, the glass-ceramics prepared from glasses with 4 mol% *t*-ZrO_2 the predominant crystal phase was only β-quartz ss, whereas in glass-ceramics from glasses with monoclinic ZrO_2 or yttria-stabilized *t*-ZrO_2 in content higher than 4 mol%, β-quartz ss and spinel are formed. Therefore, the nucleating agent crystal structure and content, as well as proper heat treatment, are essential to control the crystalline phases of the glass-ceramics, which may improve mechanical properties. The difference in the phases developed when varying zirconia content indicating that 4 mol% is too low to accelerate nucleation kinetics of the

Al- and Mg-bearing crystal phases.

Patzig et al. [103] evaluated the phase evolution with time using an annealing temperature of 950 °C in a glass of the MAS system with 5.7 mol% ZrO_2. Based on XRD and TEM analysis, they proposed that crystallization starts with the precipitation of star shaped ZrO_2 crystals, forming a region depleted in Zr around them. Then, the change in chemical composition in the region near ZrO_2 crystals favors crystallization of β-quartz ss upon the crystals or in the region depleted in Zr. Therefore, this study also shows that ZrO_2 behaves as a nucleating agent in the MAS system by providing preferential nucleation sites.

Aiming to evaluate the possible correlation between the intermediate range order and the role of ZrO_2 as a nucleating agent in glasses of the MAS system, Dargaud et al. [18] used STEM-HAADF. They prepared two glasses with the same chemical composition, in which MgO was partially replaced by ZnO and 4.03 mol% ZrO_2, but submitted to different cooling rates, by quenching in air or water. Regardless of the cooling procedure, they observed chemical fluctuations in the glasses. In the air-quenched glass, which was opalescent, LLPS with regions enriched in Zr/Zn with sharp boundaries and length scale of approximately 50 nm appeared. On the other hand, the water-quenched glass presented domains with different Zr/Zn content, but with a smaller length scale, and smoother boundaries. Those regions in the glass subjected to a higher cooling rate may be associated with early LLPS or mesoscopic heterogeneities intrinsic to its structure, which can promote ZrO_2 nucleation. Therefore, is suggested that the role of ZrO_2 in aiding nucleation is related to its effect on the structure of aluminosilicate glasses. Furthermore, the authors proposed that nucleation, even occurring apparently with the same probability in the glass volume, could not be simply treated as a process in a fully homogeneous matrix, due to the presence of static fluctuations induced by the addition of ZrO_2.

Dittmer and Rüssel [104] studied the crystallization of glasses of the MAS system with 4 to 7 mol% of ZrO_2, and one composition with partial replacement of MgO by ZnO; and in one glass they also added P_2O_5 as nucleating agent. A variation in the ZrO_2 content did not affect T_g, considering the error limits, indicating that this additive did not affect the kinetic barrier for nucleation. In the glass-ceramics prepared at lower temperatures and in the composition with 4 mol% of ZrO_2, even heat treated at higher temperatures, only β-quartz and ZrO_2 were present, whereas in the compositions with $ZrO_2 > 4$ mol% treated at $T > 950°C$, α-quartz and spinel are formed. Although in MAS glasses with ZrO_2 the stability of β-quartz decreases with increasing time/temperature due to the formation of spinel, only 4 mol% ZrO_2 seems to be not enough to nucleate spinel, resulting in the reported difference in the phases developed. Therefore, these outcomes reinforce the role of ZrO_2 in improving nucleation kinetics of the target phases–quartz and spinel–in MAS glasses.

Microstructure and properties of MAS glass-ceramics with ZrO_2 as nucleating agent and Y_2O_3 addition were studied by Gawronski et al. [105]. Different heat treatments were performed in MAS glasses with 5.7 mol% ZrO_2, 5.5 mol% ZrO_2 and 2.5 mol% Y_2O_3. This study complements the conclusion of similar work where quartz was not a crystalline phase [106]. In glass-ceramics from the glass without yttria, β-quartz ss grows from star-shaped ZrO_2 crystals. However, if yttria is added to the precursor glass, the glassy matrix is stabilized, precluding the nucleation and growth of quartz. Thus, in yttria doped glass-ceramics the main phase is ZrO_2 in needle-shaped and dendritic morphology, and in an advanced stage of crystallization, spinel is formed from ZrO_2 dendrites. The authors stated that the presence of star-shaped crystals in yttria-free glass-ceramics owes to the hindering of ZrO_2 growth in the preferential dendritic morphology by the nucleation of β-quartz in its surrounding. These results corroborate to the crystallization mechanism of MAS glasses proposed by Patzig et al. [103] and again show evidence that the role of ZrO_2 as a nucleating agent is attributed to the initial precipitation of ZrO_2.

The crystallization behavior of a MAS glass with 4 mol% ZrO_2 was studied by Patzig et al. [107] using XRD and STEM techniques. The heat treatments were performed at 950 °C during 0–100 h. LLPS in a droplet-like structure was observed using STEM micrographs, which was followed by the formation of β-quartz ss with ZrO_2 nanocrystals therein. There is no development of secondary phases (spinel or indialite) even for a longer soaking time, and the transformation of β- to α-quartz was absent, probably due to the low ZrO_2 content that leads to slow nucleation kinetics of phases rich in Mg and Al, since in the previous study [102], glass-ceramics obtained from MAS glasses with ZrO_2 content higher than 4 mol% presented other phases besides β-quartz and ZrO_2. As the micrographs do not allow us to verify the transition from phase-separated droplets to β-quartz and ZrO_2, the authors proposed three crystallization mechanisms. Supposedly, there are chemical fluctuations in the glassy matrix during annealing, which may provide good conditions for precipitation of β-quartz ss within those local domains with different compositions. The first mechanism suggests that those regions in which β-quartz ss grows are near the nanocrystalline ZrO_2 nuclei. The other possibility is the growth of β-quartz ss in the vicinity of larger ZrO_2 dendrites. Finally, the growth of β-quartz ss can occur near Si-rich droplets. Thus, some proposed mechanisms consider that the effect of ZrO_2 as a nucleating agent is not assigned to the direct nucleation and growth of other crystalline phases upon ZrO_2 nanocrystals. Nevertheless, in all crystallization mechanisms, the thermodynamic barrier for nucleation is reduced, by a change in the surface energy or in the chemical composition in some regions of the glassy phase.

Aiming to assess the structural effect of ZrO_2 added as a nucleating agent in MAS glasses, Patzig et al. [108] used XANES and STEM to analyze glass-ceramics from a MAS precursor glass with 5.7 mol% t-ZrO_2 (stabilized by 0.17 mol% Y_2O_3) heat treated at 950 °C for times up to 16 h. According to XANES results, Zr^{4+} has a coordination number of 6 in the parent glass, suggesting a homogeneous distribution in the mesoscopic scale. This outcome contrasts with the verified inhomogeneous distribution of Zr^{4+} in the glass by Dargaud et al. [16]. When crystallization is completed, the coordination number of Zr^{4+} increases to 8, due to the precipitation of nanocrystals of t-ZrO_2. The STEM micrographs indicate that crystallization of those glass-ceramics begins with the nucleation of star-shaped ZrO_2 nanocrystals, which presents a local depleted region around it. The chemical gradient in that region likely supplies the driving force for the isotropic growth of β-quartz ss in the volume, which expulses spherical ZrO_2 nanocrystallites, that appears embedded in quartz ss. Hence, it can be inferred that the nucleating agent acts in the thermodynamic barrier of nucleation.

Seidel et al. [109] evaluated crystallization of MAS glasses with stoichiometric cordierite composition varying the nucleating agent content from 6 to 9 mol% ZrO_2. As observed in the already mentioned works, in the glass-ceramics, ZrO_2, β-/α-quartz ss and spinel were detected in the volume, along with surface crystallization of indialite. The fraction of the surface crystal layer of indialite decreases with increasing ZrO_2 content, which also improves the translucence due to smaller crystals in the volume. This is a strong indication of the effect of ZrO_2 in aiding the internal nucleation kinetics of MAS glasses. According to the thermal behavior of the glass, the effect of the nucleating agent is on the thermodynamic barrier, since T_c corresponding to quartz crystallization decreases with the increase in the ZrO_2 content, while T_g is slightly affected by the nucleating agent content.

3.3. ZrO_2 in other systems

Besides aluminosilicates, many glass-ceramic systems have their internal nucleation kinetics enhanced when ZrO_2 is added. Feng et al. [110] prepared sintered glass-ceramics from the MgO–CaO–SiO_2 system using monoclinic ZrO_2 (m-ZrO_2) as a nucleating agent in different contents (up to 11 wt%). According to XRD and TEM, crystallization in that system initiates through the precipitation of t-ZrO_2 and proceeds with nucleation and growth of $CaMgSi_2O_6$ upon t-ZrO_2 crystals. Although an in-depth study regarding the role of m-ZrO_2 was not made, the experimental results support the role of this oxide in aiding nucleation of the target crystal phase through a mechanism similar to heterogeneous nucleation, in which *t*-ZrO_2 nuclei acts as preferential sites, as can be observed in the crystallization of LAS and MAS glass-ceramics.

Kruger et al. [111] evaluated the nucleation kinetics of lithium metasilicate crystals as a function of ZrO_2 content, added up to 12 wt% in a lithium disilicate (LS_2) based glass used for dental glass-ceramics production. In contrast to most studies in the aluminosilicate systems that reported a decrease in T_c with the nucleating agent addition, the DSC curves of the LS_2 based glass showed a trend in increasing T_g and T_c with increasing ZrO_2 content. However, T_l decreased approximately 49 K when comparing to the reference glass, without ZrO_2, and the glass with 12 wt% ZrO_2. Although it was shown that ZrO_2 promotes the increase in glass viscosity, the temperature of maximum nucleation rate (T_{max}) in all compositions occurs at the temperature in which viscosity is $\sim 10^{9.7}$ Pa·s. Additionally, a comparison between nucleation rates of the reference glass and the glass with the higher content of ZrO_2 showed that the maximum nucleation rate (I_{max}) increased up to 2 orders of magnitude, resulting in the decrease in lithium metasilicate crystals' size with increasing ZrO_2 content. Thus, if it is considered that diffusivity is defined by Eq. (2), the role of ZrO_2 as a nucleating agent in this system could not be associated with the kinetic barrier. The authors stated that this oxide accelerates the nucleation of lithium metasilicate due to changes in the thermodynamic barrier. The thermodynamic effect was ascribed to an initial LLPS allowed by the additive, leading to the formation of amorphous interfaces that behave as sites for heterogeneous nucleation of lithium metasilicate crystals. Since precipitation of ZrO_2 nanocrystals was not detected in these glass-ceramics [111], the hypothesis that precipitation of ZrO_2 nanocrystals is a prerequisite for the role of this oxide in nucleation catalysis of lithium metasilicate crystals is excluded, as commonly assumed in other glass systems.

In another study to evaluate the effect of ZrO_2 as a nucleating agent in sintered glass-ceramics, Hsiang et al. [112] added 0 to 8 wt% ZrO_2 to CaO–MgO–Al_2O_3–SiO_2 (CMAS) glass, which was sintered at different temperatures in the range of 850–1000 °C for 1 h. The addition of ZrO_2 affected the thermal events, as both T_g and the temperature for the onset of crystallization increases with ZrO_2 content. In the reference composition, there are two exothermic broad peaks at ~800–1000 °C, whereas in the DTA curve of the glass with 8 wt% ZrO_2, two more defined peaks are presented at 850 and 900 °C, where the first peak corresponds to surface crystallization of phyllosiloxide. Therefore, ZrO_2 shows thermodynamic and kinetic contributions in the crystallization of these glasses.

Liu et al. [113] evaluated the effect of ZrO_2 (0–3.0 mol%) in the crystallization in a glass of the SrO-BaO-Nb_2O_5-Al_2O_3-SiO_2 (SBN-AS) system. All glass-ceramics were obtained from heat treatment at 1150 °C for 3 h. The crystallized fraction, considering the two phases developed, $Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$ and $BaAl_2Si_2O_8$, increases when ZrO_2 is added up 0.5 mol% and then decreases for higher contents. The authors assumed that adding up to 0.5 mol%, ZrO_2 acts as a nucleating agent in this system; however, in higher contents (1–3 mol%), ZrO_2 increases the glass stability and no longer has a positive effect on nucleation kinetics.

Chakrabarti and Molla [114] studied the effect of adding different amounts (0–5 mol%) of ZrO_2 to the crystallization and dielectric properties of $BaBi_2Ta_2O_9$ (BBT) based ferroelectric glass-ceramics. When adding ZrO_2 up to 3 mol% the T_g decreases, whereas for the glass with 5 mol% ZrO_2, T_g is higher than that verified for the reference glass. These glasses presented two crystallization peaks: the first T_c is slightly affected by increasing zirconia content, despite its intensity decreases and the peak becomes broader; and the second T_c tends to decrease and becomes more defined for addition of 5 mol% ZrO_2. Besides that, crystallization enthalpy in the first T_c decreases with the increase of ZrO_2 and in the second T_c, the enthalpy decreases for 1 and 3 mol% of ZrO_2 and increases again for 5 mol% of ZrO_2, suggesting a higher crystallized fraction for the composition with 5 mol% ZrO_2. Thus, the thermal analysis indicates that ZrO_2 favors crystallization of the phase corresponding to the second T_c. The authors ascribed this behavior to the change in the glass network owing to ZrO_2 presence and the consequent increase in nuclei available for internal nucleation. Another piece of evidence showing that ZrO_2 is beneficial for nucleation kinetics is the more uniform microstructure and higher crystallized fraction in the glass-ceramics with 5 mol% ZrO_2, which allows a glass-ceramic with a higher dielectric constant.

According to the study of Chakrabarti and Molla [115], ZrO_2 can also act as a nucleating agent in ferroelectric $BaBi_2Nb_2O_9$ (BBN) glass-ceramics. It was observed that the addition of zirconia allows volume crystallization, and the transparent BBN glass-ceramics could be prepared due to the presence of nanosized crystals of BBN (main phase) and $BaNbO_3$. Since the reduced T_g is below 0.58 for all compositions, homogenous volume nucleation is expected. The role of ZrO_2 as a nucleating agent in this glass system can be inferred from the thermal behavior, as the first T_c tends to decrease with increasing ZrO_2 content and, compared to the reference glass, by adding the nucleating agent, a second peak is evident, and its temperature increases with additions of up to 4 mol% ZrO_2 and decreases with 5 mol%. On the other hand, the softening temperature increases with increasing ZrO_2 content, indicating an increase in the kinetic barrier, considering that Eq. (2) is valid. Thus, ZrO_2 affects both thermodynamic and kinetic barriers, but its positive effect in crystallization suggests that the thermodynamic governs its role as a nucleating agent. In contrast to the previous work in another ferroelectric glass-ceramic (BBT) [114], the development of ZrO_2 during heat treatment could not be detected by the XRD pattern.

4. MoO_3

Molybdenum oxide has received less attention than some other popular nucleating agents. However, it shows promise as an effective nucleating agent for several systems, often requiring less content than its counterparts to achieve a nucleating agent effect [14,116]. Early work by Bahat focused on various alkaline earth aluminosilicate systems, namely barium, strontium, and calcium aluminosilicate [116]. Hexacelsian glass-ceramics were produced through the introduction of various concentrations (1.5 to 2 wt%) of MoO_3 to BaAS, while Sr-feldspar and Ca-feldspar were produced from the addition of 2 wt% MoO_3 to SrAS and CaAS, respectively. Molybdenum oxide and tungsten oxide (WO_3) were sometimes used in tandem in the study, and in other compositions only molybdenum oxide or only tungsten oxide was used. Much less MoO_3 was required than WO_3 to produce hexacelsian from the BaAS system, as >9 wt% WO_3 was needed [116]. Bahat did not provide a strict definition of a nucleating agent but did mention that many nucleating agents were effective at aiding in the nucleation of hexacelsian regardless of their crystal structure [116].

Drummond studied the effect of MoO_3 on the crystallization of a hexacelsian phase within a BAS system [117]. It was reported that hexacelsian was the dominant phase after the addition of 1 wt% MoO_3 [117]. This occurred regardless of the growth temperature used in heat treatments, and the main secondary phase crystallized was mullite. However, the agent was not effective at nucleating celsian in the same composition, regardless of the thermal history [117].

Alizadeh and Marghussian [118]. studied the effect of several combinations of nucleating agents on a SiO_2-CaO-MgO system, where the target phases were wollastonite and diopside. MoO_3 was added to the composition in conjunction with V_2O_5 in one series of glasses and with CaF_2 in another series. The total nucleating agent content was 8 wt% of the composition, with half of it being MoO_3. Regardless of the nucleating agent used, compositions with high CaO content formed wollastonite, while diopside was nucleated in samples with high MgO content [118]. Thermal analysis showed that MoO_3 plus V_2O_5 led to a lower T_c. However, the combination of MoO_3 plus CaF_2 led to higher intensities of the peaks for both thermal analysis and XRD [118]. Note that a third series of glasses using Fe_2O_3 and WO_3 was also studied but did not effectively lead to internal nucleation.

Maeda and Yasumori [30] investigated several combinations of

MoO_3 and WO_3 in reducing or oxidizing environments on a MAS system. They found that both a nucleating agent and carbon powder, as well as a reducing environment (while melting the glass) was needed to induce bulk crystallization. The reducing environment was needed to form metallic particles that behaved as active sites for crystallization. Without the introduction of a nucleating agent, cordierite was grown on the surface of the samples, but when 0.5 wt% MoO_3 was present in the composition, enstatite was the main phase and was nucleated in the bulk [30]. The addition of a nucleating agent had very little effect on the glass transition temperature and crystallization temperature of the glass.

As previously discussed in the TiO_2 section, Maeda et al. [14] synthesized both cordierite and enstatite phases in a MAS system using TiO_2 and MoO_3 separately as nucleating agents. Similar to their previous work on MoO_3 and WO_3 [20], very little MoO_3 content was needed (0.1–0.5 wt%) to control nucleation of the desired phases, but the process required a reducing environment and carbon powder when melting to form metallic particles in the glass [14]. Increasing MoO_3 content had no impact on the T_g of the glass but increased T_c, and the sharpest exothermic peak occurred for the lowest MoO_3 content, which was 0.1 wt% [14]. Unlike the samples containing TiO_2, the MoO_3 samples did not produce secondary phases since the nucleating agent content was so low.

In addition to their work on MAS systems, Maeda and Yasumori [119] studied the effect of MoO_3 on a calcium aluminosilicate (CAS) system. Similar to the MAS system, very little nucleating agent content was needed to achieve a heterogeneous nucleating effect. The composition included 0.05 wt% MoO_3 and 0.4 wt% graphite powder to produce a reducing environment that resulted in metallic molybdenum particles in the melt [119]. Heat treatments resulted in the formation of dmisteinbergite (this phase has the same chemical composition as anorthite, $CaAl_2Si_2O_8$) for the compositions that included the nucleating agent. A control composition that only contained the graphite powder was also heat treated but did not precipitate any crystals within the glass matrix. To build off this work, the same group conducted additional studies on the same system to verify that the particles were in fact metallic molybdenum particles using transmission electron microscopy [120], and to confirm the crystal structure of the dmisteinbergite phase using scanning transmission electron microscopy (STEM), XRD, and Raman spectroscopy [121].

5. P_2O_5

5.1. P_2O_5 in non-lithium silicate systems

Similar to TiO_2 and ZrO_2, P_2O_5 is a common nucleating agent. Bao et al. [122] analyzed the effect of B_2O_3 and P_2O_5 on the crystallization of Li_2O-MgO-Al_2O_3-SiO_2 (LMAS) glass-ceramics. They did not specify that P_2O_5 was acting as a nucleating agent and did not provide a rigid definition of a nucleating agent, but they did include a discussion of P_2O_5 leading to phase separation. The addition of 5 wt% P_2O_5 to the system led to a small decrease in the T_c and a larger decrease in the melting point. There was no change to the glass transition, and the exothermic peak became sharper [122]. XRD data showed the base composition produced the same phases as the composition that included P_2O_5, with the main phase being $Li_2Al_2Si_3O_{10}$ [122]. The phases were produced by heat treating the samples at the temperatures of their respective exothermic peaks.

Developing a base glass in the SiO_2-P_2O_5-Na_2O-CaO-F^- system, Höland et al. [123] succeeded in producing bioactive rhenanite-type glass-ceramics. Nucleation was not studied in detail and no phase separation phenomenon was detected. However, nano-immiscibility of the phosphor-silicate base-glass was assumed to be the driving force for nucleation [123].

Sandu et al. [124] added 1 wt% P_2O_5 to study magnetic properties of a borosilicate system. A magnetite phase was observed in XRD, but no thermal data was collected. They did not provide a formal definition of a nucleating agent but mentioned that P_2O_5 was promoting phase separation within the glass network, leading to crystallization [124].

Thieme et al. [125] added up to 4 mol% P_2O_5 to a BaO-SrO-ZnO-SiO_2 system. They made the argument that P_2O_5 did not act as a nucleating agent for this system. Thermal data showed that there was little effect on the T_g as P_2O_5 content was increased, but T_c increased, and the exothermic peaks became less sharp [125]. Melting points were not shown in the data. A $Ba_{0.6}Sr_{0.4}Zn_2Si_2O_7$ phase was the major phase, while Zn_2SiO_4 was the minor phase [125]. They also did not observe phase separation under SEM.

5.2. P_2O_5 in lithium silicate systems

von Clausbruch et al. [126] studied the nucleation of lithium disilicate within a silicate system. They found that at least 1 mol% of nucleating agent was needed in order to produce the desired lath-like microstructure, and the nucleation was reported to be heterogeneous. In addition to the primary lithium disilicate phase, lithium metasilicate formed as a precursor phase, and cristobalite and lithium phosphate (Li_3PO_4) formed as secondary phases. Thermal analysis data did not include glass transition information, but it showed a decrease in the T_c as a function of increasing P_2O_5 content, and the shape of the peaks became less sharp [126]. There was no shift in the T_m, and lastly second and third exothermic peaks were present in compositions containing at least 1.5 mol% P_2O_5 [126].

Höland et al. [127] studied the impact of adding P_2O_5 to a silicate system. They found that P_2O_5 was an effective nucleating agent for the system, increasing control of nucleation by means of heterogeneous nucleation via a lithium phosphate precursor phase [127], but no rigid definition of a nucleating agent was provided. The composition included 3.3 wt% P_2O_5 and SEM micrographs showed a typical interlocking microstructure. Building off their previous work, Holand et al. [128] examined the nucleation of lithium metasilicate and lithium disilicate as a function of increasing P_2O_5 content up to 3.2 wt%. They found that maximizing the growth rate of lithium metasilicate led to a maximum in lithium disilicate as well, and that lithium phosphate acted as a precursor phase for the heterogeneous nucleation of later phases [128]. Thermal analysis showed an increase in the T_g and a decrease in the T_c as a function of increasing P_2O_5 content. There was a very small shift in the melting temperature peaks, and the shape of the exothermic peaks became sharper as nucleating agent concentration increased [128]. A second exothermic peak appeared for the sample with the highest P_2O_5 content. Not that based on the results of NMR and HR-SEM analyses Höland and Beall suggested considering the high energy interface between an amorphous or nanocrystalline lithium phosphate precursor phase and the glass-matrix as the nucleation site for lithium silicates [3].

Fernandes et al. [129] studied the nucleation of lithium metasilicate and lithium disilicate glass-ceramics using several different nucleating agents, one of which was P_2O_5. Several compositions were made with varying amounts of P_2O_5, anywhere from 1 to 3 mol%, but the quality of the glasses with 2 and 3 mol% nucleating agent was determined to be unsatisfactory, so only the composition with the least nucleating agent content was studied. They found that the formation of Li_3PO_4 led to the heterogeneous nucleation of the target phases [129]. Thermal analysis showed an increase in the T_g, but it was unclear if the height or width of the transition varied from the control sample to the sample with P_2O_5. The T_c decreased and became sharper, a second exothermic peak was present, and the data ended before the T_m was shown, so it was unknown if the melting point shifted [129].

Soares et al. [130] studied the effect of the molar ratio of SiO_2 to Li_2O on the crystallization of lithium disilicate. They included a formal definition of a nucleating agent, stating that it should help control the types of phases that form, as well as the amount of crystallization and the features of the crystal such as size and aspect ratio [130]. The study held the amount of P_2O_5 constant between the two compositions at 0.72 mol%. Therefore, for the purposes of the current work there was no control sample to compare thermal data to, but the data showed two exothermic peaks that corresponded to the nucleation of lithium metasilicate and lithium disilicate, respectively. They reported that the microstructure resembled standard lithium metasilicate and lithium disilicate [130].

Ghaebi Panah et al. [131] studied the nucleation of lithium disilicate while examining the effect of adding TiO_2 or P_2O_5 to a photosensitive silicate system. They did not provide an exact definition of a nucleating agent but mentioned that the addition of TiO_2 or P_2O_5 could lead to the production of a fine-grained microstructure after an appropriate heat treatment [131]. A control sample was synthesized, along with the samples containing the two different nucleating agents, specifically 4 wt% TiO_2 and 2 wt% P_2O_5. XRD results showed that lithium disilicate was produced only in the composition containing P_2O_5, but all samples contained lithium metasilicate. The P_2O_5 sample produced the most intense lithium metasilicate peaks [131]. Thermal analysis showed that the addition of P_2O_5 had no effect on the glass transition, but it decreased both the T_c and the exothermic peak's sharpness. The melting point also decreased with the addition of the nucleating agent [131]. The authors suspected the mechanism behind the increased nucleation rates and control of nucleation to be heterogeneous nucleation associated with the formation of lithium phosphate as a precursor phase.

Huang et al. [132] studied crystallization kinetics of lithium disilicate via synchrotron XRD. They did not define a nucleating agent but did show that a composition including 1.7 mol% P_2O_5 could effectively form a lithium disilicate phase [132]. The study did not include thermal analysis and focused on high-temperature XRD to determine the weight fraction of the phases present in the material via Rietveld phase refinement.

Bai et al. [133] added 2 mol% P_2O_5 to a silicate system while studying the effect of heat treatments on the microstructure of a lithium disilicate glass-ceramic. They acquired thermal data but did not have a control sample to compare the data against, so trends could not be determined. They did not include a strict definition of a nucleating agent or an explanation for the increased control of nucleation. XRD data clearly showed a progression from lithium metasilicate to lithium disilicate phases as the growth temperature was increased [133].

Shan et al. [134] studied a silicate system doped with different alkali modifiers. While it was not specified, P_2O_5 was used as a nucleating agent and it was held constant at 1.1 mol% over all compositions in the study. The authors stated that it was incorporated to promote phase separation and lower the crystallization temperature [134]. Since the P_2O_5 content was held constant, no conclusions could be drawn from the thermal data. XRD showed lithium metasilicate and lithium disilicate as the main phases, with secondary phases of quartz and cristobalite [134].

Glatz et al. [135] studied the role of P_2O_5 within a LAS system. They included a discussion of the role of P_2O_5 within the network, stating that it can affect the viscosity of the system or promote phase separation to affect crystallization; they also mentioned that Li_3PO_4 crystals promote heterogeneous nucleation [135]. Many different compositions with varying amounts of Al_2O_3 were synthesized. For each amount of Al_2O_3, there were two compositions, one with low (~0.01 mol%) P_2O_5 content and one with high (~0.8–1.1 mol%) P_2O_5 content. The thermal data showed that the glass transition temperature was altered from low to high nucleating agent content, but sometimes it increased and other times it decreased with no clear trend [135]. All changes to the T_g were minor. For the compositions with less than 10 mol% Al_2O_3, the crystallization temperature decreased as P_2O_5 content increased. However, in compositions with at least 10 mol% Al_2O_3, the crystallization temperature increased as P_2O_5 content increased. The exothermic peaks always became sharper as nucleating agent content increased [135]. The data did not include melting points. XRD data showed that lithium disilicate and lithium metasilicate were the main phases, with secondary phases on Li_3PO_4, petalite, and β-quartz [135].

Gaddam et al. [136] simultaneously studied the influence of P_2O_5 and the influence of the SiO_2-Li_2O ratio on the crystallization of lithium disilicate within a silicate system. Their thermal data showed that samples containing 1 mol% P_2O_5 had a very small shift in the T_g and a much larger shift in the T_c [136]. The crystallization peak temperature decreased significantly, the primary exothermic peak became much sharper, and a second exothermic peak appeared as P_2O_5 was added to the composition; the data did not show melting points [136]. The authors did not define what a nucleating agent is in general but mentioned that P_2O_5 leads to higher nucleation rates, and it also decreased activation energies for nucleation by adding more nucleation sites, which lead to crystallization occurring at lower temperatures [136]. The study argued that P_2O_5 was not promoting heterogeneous nucleation through a preliminary Li_3PO_4 phase but rather was controlling the thermodynamics of the liquid phase, affecting homogeneous nucleation rates.

Copéret et al. [137] examined nucleation in a lithium disilicate-apatite system. They did not define a nucleating agent, but extensively discussed the role of P_2O_5 in the nucleation and crystallization of lithium disilicate and other phases. XRD data showed that lithium metasilicate and lithium disilicate precipitated before a Li_3PO_4 phase did, so they do not believe Li_3PO_4 leads to the heterogeneous nucleation of the other phases. On top of that, the nucleation of silicate phases was found to be independent of the nucleation of phases containing phosphorus [137]. No thermal data were included in the study.

Rampf et al. [31] studied the impact of P_2O_5 on a silicate system containing a high SiO_2 to Li_2O ratio. The nucleating agent content was varied from 0.5 to 2.5 mol%. For all compositions containing more than 0.5 mol% P_2O_5, a lithium orthophosphate phase was detected after a heat treatment of only the nucleation temperature [31]. The authors stated that this phase helped promote heterogeneous nucleation from the preliminary phase to the main phases. At high growth temperatures, quartz was the dominant phase over $Li_2Si_2O_5$, which was likely due to the high amount of SiO_2 in the parent glass [31]. Their thermal data exhibited complex trends because as the glass transition temperature increased, the height of the transition appeared to decrease with additional P_2O_5 content. Also, the main exothermic peak temperature decreased from the control composition to the first composition containing greater than 0.5 mol%, but then the T_c increased as more P_2O_5 was added [31]. The sharpness of the peak greatly increased from the control to the composition containing 1.2 mol% P_2O_5, but then the sharpness decreased for all subsequent compositions. A second exothermic peak appeared for all compositions other than the control composition. Lastly, the melting point decreased as P_2O_5 content increased [31]. Rampf et al. [138] also studied the effect of adding CaO and MgO to a silicate system to produce a lithium disilicate glass-ceramic with a minor phase of $CaMgSi_2O_6$. Nucleating agent content was held constant at 2.1 mol%, so there was no control sample to measure against when examining thermal data trends. XRD diffractograms showed that P_2O_5 led to the effective nucleation of lithium metasilicate and lithium disilicate depending on the heat treatment [138].

Zheng et al. [139] examined the effect of adding P_2O_5 to a silicate system, and they also looked at the effect of heat treatments on the phase assemblage and microstructure of lithium disilicate glass-ceramics. They stated that P_2O_5 aided in heterogeneous internal nucleation by a phase separation mechanism [139]. Nucleating agent content was varied from 0 to 4 mol% over four compositions. DSC data showed that P_2O_5 had no impact on the glass transition. However, there was a decrease in the T_c for the compositions containing 1 and 2 mol% P_2O_5, but then there was a slight increase in the peak temperature for the composition containing 4 mol% relative to the two preceding compositions [139]. Similarly, the exothermic peaks became sharper and the melting point increased until the trend reversed slightly for the composition containing 4 mol% P_2O_5 [139]. Note that the 4 mol% P_2O_5 composition broke all trends compared to the compositions containing less nucleating agent, but it still followed the general trends relative to the control composition.

6. OH^-

Although the effect of water (OH^-) in nucleation kinetics was less cited than the previously discussed nucleating agents, OH^- is an important compound that even in a small amount (<1 wt%) behave as a nucleating agent in several glass-ceramic systems. One of the first studies that tested the influence on OH^- on the glass crystallization kinetics was carried out 45 years ago by Abe et al. [140], in which they compared the crystallization kinetics in two magnesium metaphosphate glasses with different water contents. In that glass system, the growth velocity of magnesium tetra metaphosphate spherulites was barely affected by the OH^- content. However, the Avrami parameter tended to increase with higher OH^-, which the authors assumed to be an effect of water on the crystallization mechanism.

A few years later, Gonzalez-Oliver et al. [59] evaluated the effect of different water contents in the nucleation and growth kinetics in $Li_2O{\cdot}2SiO_2$ and $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ glasses, which present internal nucleation even without any nucleating agent addition. Experimental data showed that small amounts of water, 0.053 to 0.377 mol% in the lithium silicate and 0.023 to 0.133 mol% in the soda-lime-silica, were able to significantly affect the nucleation kinetics. Regardless of the glass system, higher water content led to higher nucleation rates and growth velocity, shifting T_{max} to lower values, and reducing viscosity. In $Li_2O{\cdot}2SiO_2$, the increase in the nucleation rate scaled with the decrease in viscosity, thus, it is only a minor effect in the thermodynamic barrier. On the other hand, in the $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ glass, both kinetic and thermodynamic barriers of nucleation were lowered by increasing the water content. It is worth mentioning that was also changed the contents of the component oxides in the base glasses of Na_2O-CaO-SiO_2 system. However, even with increasing SiO_2 content from 50.7 to 53.6 mol% in the soda-lime-silica glass, which tends to increase the kinetic barrier and decrease the thermodynamic driving force, the maximum nucleation rate (I_{max}) increased about one order of magnitude for higher water content, showing that the water effect overcompensates the effect of chemical composition in the viscosity. Therefore, water clearly plays the role of a nucleating agent in both studied systems and their effect in nucleation mainly arises from a decreased kinetic barrier. As nucleation and growth rates are likely controlled by oxygen and the silica ions diffusion coefficient, which increase in water-bearing glasses due to the rupture of the silicate network by OH^-, the crystallization rate increases.

Further analysis of nucleation kinetics in lithium disilicate glass as a function of water content was performed by Davis et al. [60]. They evaluated crystal nucleation in glasses with 130 ppm of water up to 975 ppm. The experimental data obtained for those glasses showed that the nucleation rate (I) and induction time for nucleation (t_{ind}) have an exponential dependence on water content, and such an effect of water in accelerating crystal nucleation kinetics is not merely assigned to the lower glass viscosity promoted by higher water contents. The positive correlation between water content and $\log(I{\cdot}t_{ind})$, a parameter that is viscosity independent, suggests that water addition also affects some thermodynamic property related to nucleation kinetics. The authors estimated that the thermodynamic barrier for nucleation decreases approximately 8% when the water content is raised from 130 to 975 ppm. This conclusion is against the arguments of Gonzalez-Oliver et al. [59], who stated that the role of water in lithium disilicate is only of kinetic nature.

Potapov et al. [61] carried out another study that indicates the role of water as a nucleating agent by evaluating the influence of water in nucleation and growth kinetics in soda-lime-silica glasses with compositions close to the stoichiometric $Na_2O{\cdot}2CaO{\cdot}3SiO_2$. Corroborating previous works, they observed that increasing water content has a remarkable influence, as it increases both nucleation and growth rates, as well as reduces t_{ind} and T_{max}. Nucleation in a glass with water content about eight times higher presents t_{ind} by approximately 2 orders of magnitude lower, whereas I_{max} becomes one order of magnitude higher. In this work [61], it was assumed that the kinetic barrier for nucleation is defined by t_{ind}, rather than viscosity (Eq. (2)). Since the calculated (fitted) temperature dependence of the interfacial energy was not influenced by the water content, they conclude that is a negligible effect of water in the thermodynamics of nucleation. Therefore, this work strengthens the hypothesis that the role of water as a nucleating agent is mostly related to the decrease in the kinetic barrier and, consequently, the lower activation energy for the diffusion of structural units through the crystal-liquid interface.

7. Discussion

Although it is not the aim of this paper to discuss the combined effect of nucleating agents, it is worth mentioning that the simultaneous use of TiO_2 and ZrO_2 is common, as in the study of Kleebusch et al. [9], where TiO_2 and ZrO_2 were added to LAS glasses, varying the total fraction of nucleating agents but keeping the TiO_2/ZrO_2 ratio constant (2.1/0.9 mol % and 4.2/1.8 mol%). The nucleating agents trigger the initial formation of $ZrTiO_4$ nanocrystals embedded in a shell enriched in Al. Only for longer soaking times was it possible to observe LAS crystals that were bigger than the $ZrTiO_4$ crystals. Therefore, this outcome indicates that these latter crystals grow on top of the $ZrTiO_4$ nanocrystallites. The results of Kleebusch et al. [9] suggest that simultaneously adding TiO_2 and ZrO_2 favors internal nucleation in LAS based glasses by a nucleation mechanism such as the one observed when ZrO_2 is the unique nucleating agent, in which nanocrystals of ZrO_2 are preferential sites for nucleation of the target phases (as α-/β-quartz and spinel) [48,100]. Even when individually added, ZrO_2 and TiO_2 may affect the nucleation process through the decrease of the activation energy for nucleation [101,104].

Most systems in which TiO_2 behaves as a nucleating agent also have their nucleation kinetics accelerated by adding ZrO_2, where aluminosilicate glass-ceramics comprises the majority of systems that use these nucleating agents. The advantage of total replacement of TiO_2 by ZrO_2 is that the latter provides colorless glass-ceramics without changing the predominant crystalline phases [109], a characteristic of paramount importance for some applications. Generally, the ZrO_2 addition does not change the T_g [102,104], whereas the T_c and T_l tend to be shifted to lower temperatures with increasing zirconia content [16,21]. Therefore, considering the current definition of nucleating agents proposed, ZrO_2 can be defined as a nucleating agent because it acts on the thermodynamic barrier of nucleation. Moreover, as observed in systems with nucleation kinetics allowed by only TiO_2 addition, there is experimental evidence that the nucleation mechanism in LAS and MAS glass with only ZrO_2 as nucleating agent starts from LLPS [18,48,100,101,107], where a droplet like structure is formed. As the droplets are enriched in Zr, their chemical composition favors the precipitation of ZrO_2 nanocrystals in the early nucleation stages.

To gather information concerning the structural role of ZrO_2 as nucleating agents in aluminosilicate glasses, Cormier et al. [21] performed a study aiming to define the structural correlation between the Zr environment in each glass system (Li-, Mg-, Ca-, Zn- Na- aluminosilicates, named as LAS, MAS, CAS, ZAS, and NAS) and nucleation. For the sake of comparison, the authors prepared a reference glass composition without ZrO_2 and a Zr-glass with 4.03 mol% ZrO_2. According to DSC curves, the added ZrO_2 is not effective for enabling internal nucleation only in NAS glass. The effect of ZrO_2 in the thermal behavior is similar for some analyzed systems, decreasing T_c in MAS, ZAS, and CAS glasses, besides yielding the presence of a crystallization peak in the LAS glass, which does not show any exothermic peak in the composition without ZrO_2. Regarding the structural features, in LAS and NAS glasses Zr is six-fold coordinated, whereas in MAS, CAS, and ZAS glasses the coordination number of Zr is seven. Thus, there is no clear influence of the coordination state of Zr and its role as a nucleating agent, as octahedral sites ($^{[6]}$Zr) are presented both in LAS and NAS glasses.

Hence, considering the experimental data of Cormier et al. [21], the authors argue that the key factor for the effect of Zr in nucleation kinetics enhancement is the medium range order of Zr distribution within the parent glass, as only NAS glass does not show Zr-Zr linkages, whereas in other systems–ZAS, MAS, and CAS–EXAFS results indicate the presence of Zr clusters. These clusters can favor the initial precipitation of ZrO_2 nanocrystals during heat treatment as less rearrangements and atomic displacement to form crystallites are required. Indeed, a previous study [16] focusing on the MAS system had already proposed the presence of Zr-Zr linkages in the parent glass, in a structure schematically shown in Fig. 2, where Zr^{4+} is surrounded by Si(Mg,Al) and Zr sites are linked by edge sharing. This structural arrangement reduces the activation energy required for precipitation of ZrO_2 nanocrystals, whose presence was verified by many authors dealing with glass-ceramics with only ZrO_2 as the nucleating agent [48,99–103,141]. Therefore, the structural arrangement of Zr seems to be responsible for the thermodynamic effect of this compound in nucleation kinetics.

By evaluating the crystallization behavior of MAS glass-ceramics with ZrO_2 as a nucleating agent, it can also be noted that the content of ZrO_2 directly affects the crystalline phases. Although none of the cited authors defined a threshold for ZrO_2 to be able to promote internal nucleation in the MAS system, the minimum content reported in the compositions nucleated with ZrO_2 was 4.0 mol%. However, having a small quantity of zirconia, the nucleation kinetics of Al-/Mg-bearing crystal phases seem to be too slow to promote the transition of metastable $MgAl_2O_4/SiO_2$ (quartz solid solution) to spinel and pure quartz, even though this reaction is thermodynamically favored [104]. On the other hand, higher zirconia amounts (e.g., 5.7 mol% ZrO_2) allow the crystallization of spinel in the advanced stages of nucleation, and β-quartz ss become depleted in Al and Mg, transforming to α-quartz in the cooling path. Therefore, if the ZrO_2 content is high enough and the proper heat treatment is performed, the final glass-ceramics can present α-quartz, spinel, and ZrO_2 [105], while for lower ZrO_2 contents or low temperature/time of annealing only ZrO_2 and β-quartz ss (stabilized at room temperature by the presence of Mg and Al in its lattice) should be present.

Upon examination of the literature focused on using TiO_2 as a nucleating agent, we found that the results were very dependent on the target crystalline phases. Cordierite was the target phase in roughly half of the studies examined, but the other half included phases such as leucite, feldspar, celsian, apatite, virgilite, and β-quartz. According to the thermal analyses of several studies, TiO_2 affected the thermodynamic driving force when it was used to promote control over nucleation of phases other than cordierite, evidenced by changes to the shape and position of the exotherms [29,92,98]. This is in good agreement with the experimental observation that phase separation occurred more prevalently as TiO_2 content was increased. Additionally, recall from Eq. (1) that changes in the T_g, the width of the glass transition, and the height of the glass transition indicate an effect on the kinetics of the system, specifically the diffusivity. Changes in T_{liq} indicate changes in the thermodynamics, whereas changes in T_c could be linked to changes in the kinetics, thermodynamics or both.

For the rest of this discussion, when referencing TiO_2, we will largely be focusing on the studies where cordierite was the target phase, where TiO_2 affected the kinetics of the system, as evidenced by changes to the glass transition temperature [14,94,20]. However, it should be kept in mind that when a relatively large amount of any nucleating agent is added to a glass composition, it also changes the T_g, even if its main effect is on the thermodynamics.

Throughout the studies examined involving the combination of TiO_2 as a nucleating agent and cordierite as a target phase, there are some clear trends in the factors that lead to control of nucleation. Oxide glasses are known to lack long-range structure and consist of a network of corner-shared cation polyhedra [65]. The addition of highly coordinated TiO_2 groups to the system leads to network polyhedra experiencing higher and abnormal coordination within the network that will shift to edge-share, rather than only experiencing corner-sharing. In this case, the highly ordered, edge-sharing sites locally phase separate, which decreases the kinetic barrier for nucleation due to a decrease in rigid constraints [76]. These sites are able to form precursor crystal phases at low temperatures and then act as seeds for the nucleation of further phases.

Analysis of thermal data largely showed the addition of TiO_2 to aluminosilicate glass systems decreased the glass transition temperature. It also typically decreased the first crystallization temperature and melting temperature by similar amounts in most cases, so the difference between the two was unaltered. If heat of fusion is not altered, then the driving force remains similar. These trends are shown in Fig. 3 when TiO_2 is being compared to MoO_3 on the same system. An examination of available XRD data showed that the concentration of TiO_2 content influenced the phases that could be crystallized from the glass. The intensity of the peaks was increased as TiO_2 was incorporated into the parent glass. Also, in the studies that tested multiple nucleating agents, it

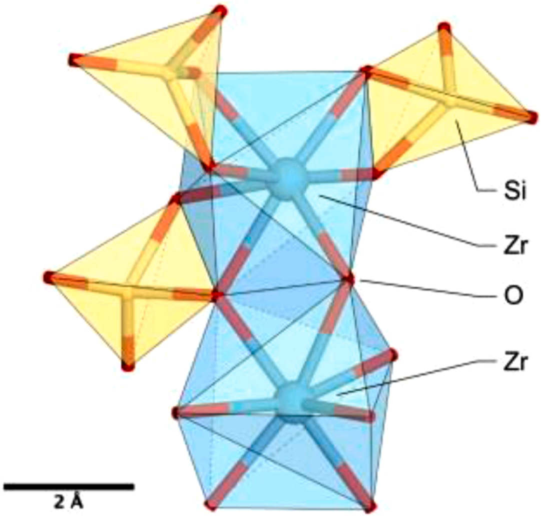

Fig. 2. Structural model of Zr in a MAS glass proposed by Dargaud et al. [16]. Zr atoms are in blue, yellow polyhedral refers to Si (Al,Mg) and oxygen atoms are in red.

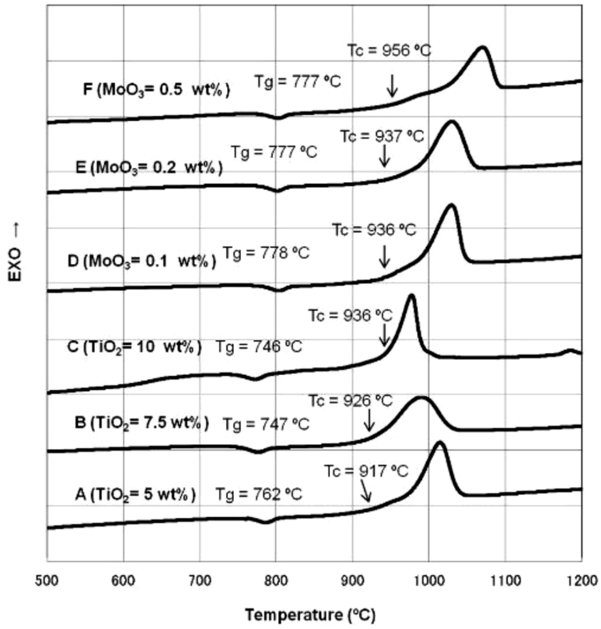

Fig. 3. Overlaid thermal data. The bottom three scans belong to glasses containing TiO_2 as a nucleating agent, while the top three contain MoO_3. The graph is reproduced from Maeda et al. [14].

was clear that the choice of nucleating agent affected the crystallization rates and phases present. For example, Al-Harbi showed that TiO_2 promoted crystallization in a MAS system, while Cr_2O_3 and ZrO_2 did not [98]. SEM micrographs were often collected to reinforce the change in the intensity of the XRD peaks. The main change seen in the microstructure was the decreased size of the crystallites and refinement of the microstructure as the TiO_2 content was increased. This indicates that TiO_2 aided in nucleation, as suspected.

Guignard et al. [20] made several key observations in their data. First, as more Ti was added to the network, the T_g was decreased as well as the viscosity of the melt. Controlling the viscosity provides additional evidence for a kinetic argument when discussing control of nucleation. A second observation was that the number of highly coordinated Al atoms greatly increased once Ti content was above 7 mol%. Although they could not provide a concrete explanation for why seven mol% was the threshold for the structural change, Maeda et al. [14] provided a possible explanation. They proposed that TiO_2 remains stable and dissolves in MAS glasses up to a certain solubility limit. Once this limit is reached, which appears to be around 7 mol% in this case, TiO_2 begins to alter the structure of the glass and lower the number of constraints in the system as higher order is promoted. This in turn decreases the kinetic barrier for nucleation [14]. Needing to reach a threshold concentration of nucleating agent content was constant among the majority of the studies examined, especially for the MAS system [14,19,29,90,93–96]. The best available explanation for this phenomenon is the solubility limit argument.

The literature provided many valuable insights into the structural role of TiO_2 in the aluminosilicate systems [14,20,93], but the studies often lacked formal definitions of what a nucleating agent is or reasons for why a particular agent was chosen. The definitions that were provided varied from each other, so a more universal definition would be valuable to the community. TiO_2 follows all the rules proposed in the new definition of a nucleating agent. First, generally it was reported that roughly 7 wt% was required to effectively promote nucleation, which falls under the requirement of being a relatively small concentration within the network [14–19,90,93–96]. Also, the agent repeatedly provides control of nucleation, either through thermodynamics or kinetics depending on the target phase. It proved to be especially effective for aiding in the nucleation of cordierite by decreasing the kinetic barrier. This is much different from the method of nucleation control promoted by MoO_3.

MoO_3 has been used as a nucleating agent for phases like hexacelsian, wollastonite, diopside, cordierite, and enstatite. Often only a couple of wt% or less of it is required to achieve a nucleating effect, but it is also sometimes paired with another component, such as V_2O_5, CaF_2, or carbon [14,30,118–121]. Alizadeh and Marghussian [118] tested several potential nucleating agents and observed that the choice of a nucleating agent had a clear impact on the phases that were nucleated in their system. The nucleating agent also affected the morphology of the microstructure. Moreover, additional compounds that were paired with MoO_3 had an impact on the number of crystallites nucleated.

Maeda and Yasumori [30] did not specifically include a definition of a nucleating agent, but they stated that metals with high melting points are generally good for nucleation because they easily precipitate in the glass and create heterogeneous nucleation sites. They also argued that choosing a metal that is easily reducible is beneficial, as the metallic ions need to be reduced to precipitate into the glass [30]. These guidelines do not generally apply to all nucleating agents since they do not all precipitate into the glass as metallic particles. However, this knowledge is valuable when the desired mechanism for increasing nucleation rates is producing free surfaces for heterogeneous nucleation sites.

An analysis of the available experimental data shows that MoO_3 enhances control over nucleation by affecting the interfacial free energy of the nucleus to liquid interfaces within the system as well as the thermodynamic driving force. The changing thermodynamic driving force could be due to a surface formation producing a heterogeneous nucleation. Once again, the evidence lies in the thermal analysis data, shown below in Fig. 3. The addition of MoO_3 to the system had little to no effect on the T_g, its height, or its width, all of which are kinetic effects. Additionally, the addition of MoO_3 was shown to increase the crystallization temperature, as well as the shape of the exothermic peak [14]. This points towards a change in the thermodynamic driving force.

MoO_3 follows all the rules proposed in the new definition of a nucleating agent. First, often it was reported that only a few wt% or less was required to effectively promote nucleation [14,30,116–119]. MoO_3 consistently increased control of nucleation by decreasing the interfacial energy by precipitating out as metallic particles, creating free surfaces. This is shown in Fig. 4 below. It was especially effective at aiding in the nucleation of enstatite and dmisteinbergite [14,30].

Compared to MoO_3, P_2O_5 is one of the more common nucleating agents and is non-metallic like TiO_2 and ZrO_2. It has primarily been studied in lithium silicate systems [126–139], but it has also been examined in other systems [122–125]. There were some fairly clear trends in the thermal data for the studies where lithium disilicate was not the main target phase. The driving force was being altered across all these systems. However, a change in the driving force does not always lead to enhanced nucleation. For the two non-lithium silicate studies that included thermal data, the crystallization temperature and the shape of the exothermic peak changed, both thermodynamic factors [122,125]. However, P_2O_5 was used to increase the nucleation rates of lithium disilicate most often, so the rest of the discussion will focus on that system.

The thermal data is very consistent across all the studies where P_2O_5 is incorporated into lithium silicate systems. The glass transition temperature increased (often slightly), but the studies did not report on the height or width of the transition. In almost every study, the crystallization temperature decreased, and the exothermic peak became sharper. Some studies did not include data for the melting point, but most of the ones that did include it reported that it decreased [126–139]. In other words, P_2O_5 aids in the control of nucleation by affecting both the kinetics and thermodynamics of the system. It is difficult to quantitatively determine which plays a larger role, but qualitatively it appears that thermodynamics is the dominant force as the exothermic peaks are altered more dramatically than the glass transition is by the addition of P_2O_5.

As was stated previously, there may be an ideal amount of nucleating agent content in the case of P_2O_5. In several studies, there was a trend of the thermal data being altered as a function of nucleating agent content, but if too much P_2O_5 was in the composition, then the trends began to be reversed [31,139]. This is depicted below in Fig. 5 and implies that there is a maximum concentration where P_2O_5 can act as a nucleating agent, which appears to be approximately **2.5 mol%** from the examined literature [126–139]. Beyond that concentration, P_2O_5 is likely taking on a different structural role within the glass network. Many of the studies reported that the mechanism for nucleation was the preliminary growth of a Li_3PO_4-type crystalline or non-crystalline phase, whose interface acted as heterogeneous sites that lithium metasilicate and eventually lithium disilicate could nucleate on [31,126–129,131,135,139]. When P_2O_5 has too high of a concentration, it may inhibit the initial nucleation of the lithiophosphate phase or phase separation.

P_2O_5 acts as a nucleating agent according to the new definition of a nucleating agent. It promoted control of nucleation, and the maximum concentration reported from the examined literature was **4 mol%** [125,139]. P_2O_5 increased the nucleation rates primarily for lithium silicate systems but also for some additional systems. Unlike the other nucleating agents that have been examined, P_2O_5 affects both the kinetics and thermodynamics associated with nucleation. This makes for an interesting comparison to TiO_2 and MoO_3.

Maeda et al. [14] provided an insightful comparison of TiO_2 and MoO_3. MoO_3 only needed to make up 0.1 to **0.5 wt%** of the composition to effectively act as a nucleating agent in the same MAS system that required approximately 10 wt% TiO_2 to promote internal nucleation

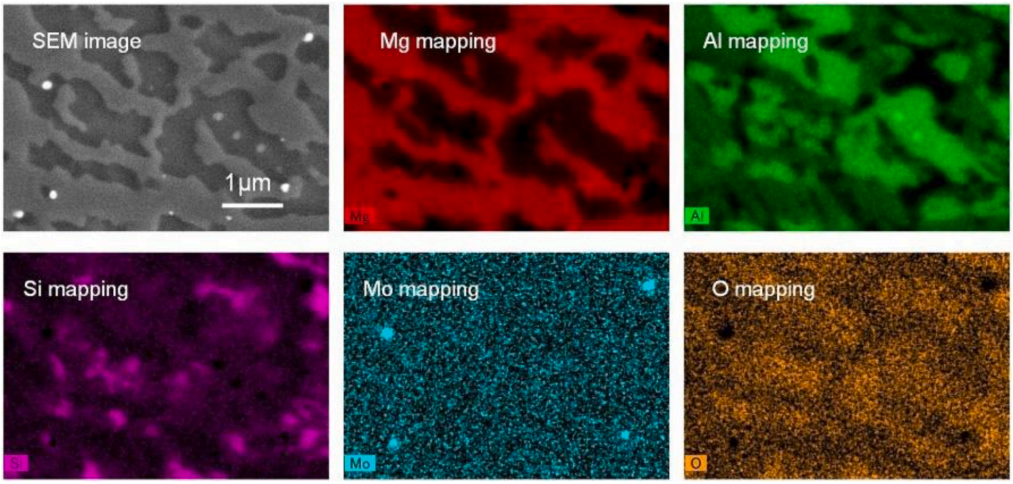

Fig. 4. SEM micrograph accompanied by an energy dispersive X-ray (EDX) map of the elements present. The metallic molybdenum particles appear bright white. The graph is reproduced from Maeda et al. [14].

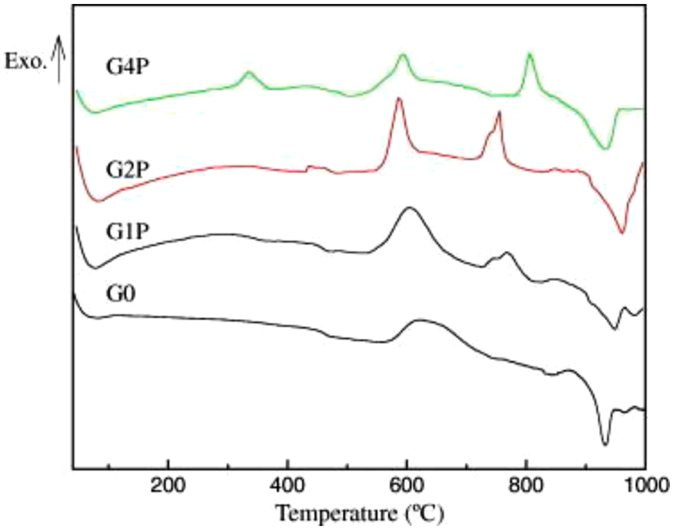

Fig. 5. Thermal data for four different lithium disilicate compositions via Zheng et al. [139]. Label G0 corresponds to a control composition with no nucleating agent, while G1P, G2P, and G4P contain 1, 2, and 4 mol% P_2O_5 respectively.

[14], and this behavior was confirmed by Benitez et al. [56]. The authors reported that metallic Mo particles of varying sizes (dependent on heat treatment) provided heterogeneous sites for nucleation. This would indicate that MoO_3 provided a catalytic effect on nucleation by lowering the thermodynamic barrier for nucleation since heterogeneous nucleation has a lower energy barrier than homogeneous nucleation. It is clear that TiO_2 and MoO_3 are acting as nucleating agents in different ways since such widely different concentrations are needed from each to act as a nucleating agent in their respective systems. The different concentrations are likely needed because any inorganic nonmetallic nucleating agent incorporated in a base glass is present in ionic form (its nucleating effect can be activated or initiated upon forming a crystalline phase, e.g., via thermal treatment, though). However, metallic nucleating agents can develop their nucleating activity after their ions are reduced in and by the components of the base glass and can be present in the base glass as (crystalline/colloidal) metals. In addition to their varying concentrations, TiO_2 and MoO_3 had varying impacts on thermal properties.

As previously discussed, TiO_2 affects the kinetics of the system while MoO_3 affects the interfacial free energy and thermodynamic driving force. The TiO_2 and MoO_3 glasses behaved rather differently during thermal analysis (see Fig. 3), as TiO_2 systematically decreases the T_g and the T_c while MoO_3 had no effect on the T_g and actually increased the T_c [14]. Once again, this supports the idea that the two nucleating agents are implementing enhancement of nucleation kinetics by decreasing different energy barriers. The XRD data for the two compositions is fairly similar, as both promoted the growth of enstatite at 1000 and 1100 °C and also cordierite at 1200 °C in addition to enstatite [14]. However, TiO_2 also produced secondary phases while MoO_3 did not [14]. Lastly, the enstatite peaks were sharper for the MoO_3 sample while the cordierite peaks were sharper for the TiO_2 sample. Note that the two samples used for XRD both contained the largest amount of respective nucleating agent and experienced the most dramatic nucleating effects [14].

TiO_2 and MoO_3 promote enhanced nucleation through separate mechanisms. TiO_2 controls nucleation by breaking Zachariasen's rule of cation polyhedra only sharing corners. It provides regions of higher order in the network, allowing for TiO_2 and Al_2O_3 polyhedra to edge-share rather than only corner-share. These sites speed up the kinetics associated with homogeneous internal nucleation. We believe this mechanism requires a large amount of highly coordinated sites to effectively control nucleation, as each site only slightly lowers the energy barrier. On the other hand, MoO_3 assists in nucleation by creating interfaces between metallic molybdenum particles and the glassy matrix. These interfaces act as free surfaces for heterogeneous nucleation, which greatly lowers the energy barrier for nucleation [3,65]. Therefore, much less nucleating agent amount is required to increase nucleation rates.

Finally, we discuss the effect of water (OH^-) in accelerating nucleation kinetics. In contrast to the previously cited nucleating agents, where the increase in internal nucleation rate is due to a lowering of the thermodynamic barrier or in both thermodynamic and kinetic barriers, the role of water as a nucleating agent seems to be predominantly kinetic. Gonzalez-Oliver et al. [59] stated that with increasing water content, the effective diffusion coefficient for nucleation increases due to easier oxygen ion diffusion.

Even though Davis et al. [60] proposed that the thermodynamic barrier for nucleation is also lowered with OH^- presence in the lithium disilicate glass, the higher nucleation rate provided by water is predominantly assigned to the reduction in the kinetic barrier. These conclusions are corroborated by the study of Potapov et al. [61] in a soda-lime-silica glass, in which experimental data support that OH^- affects the kinetic barrier for nucleation, leading to higher I_{max} and shifting T_{max} to lower temperatures. According to Heslin and Shelby

[142], water can also increase the nucleation rates of a lithium diborate glass along with decreasing viscosity. Thus, OH^- can be considered a nucleating agent in distinct glass systems, as it is able to increase nucleation rates with very small contents (ppm) in the precursor glass.

Although the reported studies about the behavior of water as a nucleating agent are based on glasses with polymorphic or isochemical crystallization, all the conclusions can likely be expanded to multi-component glass systems of commercial relevance. An advantage of accelerating nucleation kinetics by water addition is the absence of distinct crystal phases, beyond those formed by the main components of the base glass.

7.1. Method to infer the role of nucleating agents

A strategy to infer the role of nucleating agents–purely kinetic ($D(T)$), thermodynamic (σ or ΔGv), or a combination of both–is to analyze their simultaneous effect on crystal nucleation (I) and growth rates (U). Eq. (5), which is a modified form of Eq. (1) to take heterogeneous nucleation into account, shows the specific importance of each of the main parameters on the nucleation rates.

$$I(T) \sim K_1 N D_I \exp\left[-K_2 \frac{\sigma^3}{T \Delta G_v^2}\right], \tag{5}$$

where K_1 and K_2 are constants and $\boldsymbol{N}$ is the number of nucleation sites. For homogeneous nucleation $N = N_{ho}$ = number of all structural units per unit volume of the supercooled liquid ($\sim 10^{28}/\mathrm{m}^3$), whereas for heterogeneous nucleation $N = N_{he}$ = number of active sites. Please note that in most cases $N_{he} << N_{ho}$.

The Screw Dislocation (SD) growth equation, which describes crystal growth velocities for most oxide glasses [143–145], can be written as:

$$U_{SD}(T) \sim K_3 D_U \left(1 - \exp\left[-\frac{|\Delta G|}{RT}\right]\right). \tag{6}$$

Whereas the two-dimensional or Secondary Nucleation growth model (2D) is given by

$$U_{2D}(T) \sim K_4 D_U \exp\left[-K_5 \frac{\sigma^2}{T|\Delta G|}\right], \tag{7}$$

where K_n = constants, D_U = diffusivity controlling crystal growth and ΔG is the molar crystallization driving force.

Considering that $\boldsymbol{D_I \sim D_U = D}$ (there is growing evidence [73, 146–148] that this is indeed a very good assumption), and realizing that the term $1 - \exp[-|\Delta G|/RT] \sim 1$ at deep supercooling, where nucleation is most significant, then the crystal nucleation rates are controlled by 4 parameters, whereas crystal growth is controlled by only one (D_U) in the case of the SD growth model, or 3 parameters (D_U, ΔG and σ) in the case of the 2D growth model. However, the effect of σ in I ($I \propto \sigma^3$) is stronger than in U_{2D} ($U_{2D} \propto \sigma^2$). Please note that when using the $\boldsymbol{D_I \sim D_U = D}$ assumption to analyze crystal nucleation kinetics, *experimental* values of $D_U(T)$, measured in the same temperature range where nucleation rates are detectable, must be used; not the values calculated from the SD or any other crystal growth model. Therefore, with these arguments, the effects of nucleating agents on the maximum temperatures and crystallization rates can be summarized in Table 2.

Therefore, by checking their combined effects on T_{max}, I_{max}, and U_{max}, one can distinguish the role of nucleating agents in glass-ceramics. Combinations, such as a simultaneous decrease of σ and D could, perhaps, be possible. However, the effect of σ on the nucleation rates is always predominant.

Components that have an opposite effect in any of these parameters (decrease D without decreasing σ, or increase σ), are called nucleation *inhibitors* or *suppressors*. Finally, there is a possible effect on ΔG. In this case, in general, the closer the composition of the parent glass to the nucleating crystal phase, the more efficient [23] (it is easier to understand this concept when only one phase nucleates).

Table 2
Possible effects of nucleating agents on D, σ, N, and ΔG and, consequently, on measurable parameters: $T_{max\text{-}I}$, $T_{max\text{-}U}$, I_{max}, and U_{max}, which refer to the temperatures and magnitudes of maximum nucleation and growth rates.

Effect of nucleator	$T_{I\text{-}max}$	I_{max}	$T_{U\text{-}max}$	U_{max}
Increases *D*	unchanged	increases	unchanged	increases
Decreases s	increases	increases	SD - unchanged 2D - increases less than $T_{I\text{-}max}$	SD - unchanged 2D- increases less than I_{max}
Increases N_{he} (e. g., metal particles)	unchanged	increases	unchanged	unchanged
Increases *DG*	increases	increases	SD - unchanged 2D - increases less than $T_{I\text{-}max}$	SD -unchanged 2D - increases less than I_{max}

8. Conclusion

A plethora of previous studies on nucleating agents largely report on which nucleating agent was chosen for a given system, but they do not provide much discussion beyond that. In most cases, the ability of certain components in boosting crystal nucleation rates or controlling the precipitation of certain crystal phases in glasses has been assigned to either: (i) precipitation of ceramic or metallic nanocrystals that work as heterogeneous sites for nucleation of the desired crystal phases; (ii) the induction of liquid-liquid phase separation; one of the glassy regions that is compositionally close to a crystal phase behaves as preferential loci for nucleation and growth of a target crystal phase; or (iii) precipitation of crystals of an insoluble inorganic phase that act as nuclei for the major phases. Thus, the nucleating agents favor nucleation by lowering the overall activation energy of the process.

To further understand the effect of nucleating agents, we propose that changes in the T_g, the width and the height of the glass transition inflection indicate their effect on the system diffusivity. A more powerful strategy to discover their role on nucleation is to check for effects on some measurable parameters, such as: $\boldsymbol{T_{I\text{-}max}}$, $\boldsymbol{T_{U\text{-}max}}$, $\boldsymbol{I_{max}}$ and $\boldsymbol{U_{max}}$, which are a consequence of changes in D, σ, N, and ΔG.

Some studies have begun to examine the structural roles of a few compounds within the glassy network (e.g., TiO_2 and ZrO_2), and their influence on nucleation. It would behoove the glass community to have a better understanding of the structural effects on the thermodynamics and kinetics involved in these processes. However, there is still much to be learned, especially because of the breadth of possible combinations of nucleating agent to glass-ceramic system relationships. The proposed definition (*a nucleating agent is a minority component of the glass composition that leads to increased internal nucleation rates or precipitation and control of desired crystal phases, either by lowering the thermodynamic or the kinetic barrier for nucleation, or some combination thereof*) could be a guiding step towards building a better understanding of what a nucleating agent is and how it affects the nucleation of crystalline phases within glass-ceramics.

Nucleating agents are crucially important to the formation of glass-ceramics and deserve more attention in fundamental work. Moving forward, future studies should continue to investigate their structural role as well as to test the effects of novel nucleating agents. To this end, atomist simulations of the crystallization process could be extremely revealing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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