



## Updated definition of glass-ceramics

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### ABSTRACT

Glass-ceramics are noted for their unusual combination of properties and manifold commercialized products for consumer and specialized markets. Evolution of novel glass and ceramic processing routes, a plethora of new compositions, and unique exotic nano- and microstructures over the past 60 years led us to review the definition of glass-ceramics. Well-established and emerging processing methods, such as co-firing, additive manufacturing, and laser patterning are analyzed concerning the core requirements of processing glass-ceramics and the performance of the final products. In this communication, we propose a revised, updated definition of glass-ceramics, which reads “Glass-ceramics are inorganic, non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The volume fraction crystallized may vary from ppm to almost 100%”.

### 1. Introduction

Glass-ceramics are celebrated for their unusual, exotic combination of properties that resulted in manifold, high technology products for both consumer and specialized markets [1]. The term *glass-ceramic* was introduced by S.D. Stookey for Pyroceram (glass code 9606) commercialized by Corning Glass Works in 1957. Stookey used a process-based definition for this new class of materials: “...made by first melting and forming special glasses containing nucleating agents and then causing controlled crystallization of the glass particles” [2]. Before the development of Pyroceram, Stookey worked on controlled crystallization in radiation sensitive glasses (e.g., glass code 8603) which he named: *photosensitive opal glass* [3]. In 1959 Stookey adopted a unified approach and used the term *glass-ceramic* for both types of materials, independent on the type of the nucleating agent used (Cu, Ag, Au or TiO<sub>2</sub>) [4].

Inspired by his work, research activities around the globe led to synonyms for glass-ceramics, such as Vitrokeram [5] and Sitalts [6]. Common to all these early developments was the method of shaping a glass article and subsequently crystallizing it (internally) by a desired time-temperature protocol (in the industry also called *ceramming* or *ceramization*). This particular technology-driven approach to the preparation of glass-ceramics has also been, starting from the 60s, reflected in textbook definitions like “Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glasses” [7] to those in more recent monographs, such as “Glass-ceramics are ceramic materials formed through the controlled nucleation and crystallization of glass” [8].

While originally the term glass-ceramics was supposed to describe only materials that contain significant volume fractions of crystals (> 50%), glass-ceramics of significantly lower crystal volume fractions have also been developed over the last 60 years. Hence that early

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constraint is too limiting and is omitted in our revised definition as are any restrictions on the number of crystalline phases or the bulk compositional family. While the aluminosilicate system has historically comprised the majority of glass-ceramic research and commercialization, many other systems are now well known and subject of state-of-the-art research for many years. Another new and important feature in glass-ceramics production consists in the necessity of controlling the evolution of different crystal types either simultaneously or independently growing in bulk or on the sample surfaces [9,10]. As both surface- and bulk-nucleated glass-ceramics are of general interest, we discard any such constraint. Finally, advanced routes of preparation, such as co-firing, additive manufacturing, and laser patterning, can result in a complex mix of crystals and amorphous phases. A further assessment is needed to determine whether these materials can also be classified as glass-ceramics.

The aim of this communication is to update the existing definition of glass-ceramics by reviewing crystal-containing glasses obtained by various preparation routes. In particular, we will discuss the nature, volume fraction, and spatial distribution of crystals in glass-ceramics. Critical comments from a group of experienced researchers from academia and industry lead to a revised and more useful definition of glass-ceramics, and may be used as the standard for the “glass” and other scientific communities.

## 2. Three-step processing

An updated definition of glass-ceramics should reflect the core processing idea of Stookey and other pioneers in this field, who envisaged the fundamental advantages of the glass-ceramic route as compared to ceramic processing. The traditional glass-ceramic route is: i) melting, homogenizing, and refining a batch to form an optically homogeneous glass, usually containing one or more nucleating agents; ii) forming a glass article by hot-shaping (pressing, blowing, rolling, etc.), and (iii) inducing internal crystallization by controlled thermal treatments to result in a pore-free, near net shape product providing the desired functionality. The first two steps (i and ii) of glass-ceramic development or manufacturing require the ability to make a glass article, whereas the third step (iii) requires knowledge of the liquid-to-crystal transformation kinetics to develop a time-temperature protocol for the conversion of the glass into a glass-ceramic (Fig. 1).

(i and ii) As the first and second step require the melting and shaping of a glass article, several routes are conceivable, including the usual melt-quenching from above the *liquidus* temperature,  $T_L$ , but also sol-gel or vapour deposition techniques – where the reaction/deposition temperatures are below or above the glass transition temperature,  $T_g$  (Fig. 1) [11]. These routes may result in powders, thin films or bulk glass products of desired shapes. We note that glasses can be distinguished from amorphous solids. A definition of glass and a detailed description on their behavior when heated through the glass transition range can be found elsewhere (e.g., textbooks of glass science [12–20]). To verify glass formation, for instance, DTA/DSC signals can be used, and one form of evidence comes from the occurrence of the  $T_g$ -endotherm ahead of the crystallization exotherm upon heating. However, in systems with very rapid crystallization upon heating, the  $T_g$  endotherm can be entirely overwhelmed by the crystallization exotherm; in these cases, microscopy or X-ray analysis may afford a better means by which to ascertain the glassy nature of the starting materials.

If the melt-quenching route is used, cooling rates larger than the critical ones ( $q \geq q_c$ ) are necessary to form a glass [21]. Uhlmann's classic treatment correlated a crystal fraction of one part per million ( $X = 10^{-6}$ ) with the onset of crystallization; interestingly, this meager amount is below the detection limit of X-ray diffraction, a traditional method to determine the onset of crystallization (see Section 3.5 for more discussion).

In practice, the nose coordinates  $T_N$  and  $\delta t$  depend on the nucleation mechanism. In the case of heterogeneous nucleation, the time-

temperature-transformation (TTT) curve of  $X = 10^{-6}$  can be shifted from the homogeneous nose curve towards higher temperatures and shorter times as the temperature range of nucleation is shifted to a higher temperature [22–24]. Additions of nucleation agents act in the same way by broadening temperatures and shortening times in the approach of the heterogeneous nose curve [25]. Applying smaller rates than  $q_c$ , larger volume fractions of crystals are formed during cooling. The glass devitrifies uncontrollably by a spontaneous crystallization process, i.e., heterogeneous nucleation takes place at substrates and surfaces and is followed by rapid crystal growth (Fig. 1). Due to the stochastic nature of this process, onset temperatures and nucleation sites vary for each cooling run [26] and a devitrified glass is formed instead of a glass-ceramic. In practice, these materials comprise “wild” microstructures from which their functional properties cannot be tailored.

We use the terms homogeneous and heterogeneous nucleation to distinguish between nucleation processes that occur in the absence of external active sites in the system under consideration, and those located at active sites, catalysing nucleation. Active sites can exist in the interior and at the surfaces of a glass specimen (shaped article, powder particle) [27]. External means that these sites are generated by contact with at least a second phase (precipitated agent, container material, atmosphere, etc.).

(iii) The third step converts a glass article into a glass-ceramic via a controlled temperature-time process engineered to produce a desired crystalline microstructure without unintentionally deforming the glass piece. The time necessary to develop the desired crystal fraction depends on the number of sites per unit volume,  $N_V$ , available for crystal nucleation and on the rate,  $U$ , at which crystals of size  $r$  grow with time  $t$  from these sites. Assuming (1) random internal nucleation (infinite sample size or negligible surface nucleation); (2) that the rates of nucleation and growth are time-independent ( $dN_V/dt = I(t) = \text{const.} = I_0$  and  $dr/dt = U(t) = \text{const.} = U_0$ ); (3) applying the formal JMAK theory (impingement of randomly distributed crystals undergoing isotropic growth) for the time to build-up a certain crystal fraction,  $X$  and (4) isothermal conditions, one can approximate  $X$  by [28–30]:

$$X(t) = 1 - \exp\left[-\frac{A}{n+1} I_0 U_0^n t^{n+1}\right], \quad (1)$$

where  $A$  is a geometrical shape factor ( $= 4\pi/3$  for spheres), and  $n$  is the number of independent spatial directions of growth.

For site saturation (heterogeneous nucleation from a given number of sites,  $N_V$ ),  $I_0$  has to be replaced by  $N_V$ , and the term  $t^{n+1}$  by  $t^n$ . An overview of possible values of  $n$  as a function of the mechanism of nucleation and the growth morphology is available [20].

To achieve desired microstructures, more complex time-temperature protocols are frequently used, including heating and cooling ramps with one, two or three subsequent holds, (Fig. 1). Under non-isothermal conditions, Eq. (1) changes to an integral expression of the form [20]:

$$X(t) = 1 - \exp\left\{A \int_0^t I(t') dt' \left[ \int_{t'}^t U(t'') dt'' \right]^n\right\} \quad (2)$$

The second integral term describes the growth of  $dN(t') = I(t') dt'$  clusters formed at  $t'$  in the interval  $dt'$  until  $t$ , i.e. in the time interval  $(t-t')$ , whereas the first integral accounts for the summing-up of the whole set of such evolution steps. It follows from this relation that the selection of the temperature profile may significantly affect the time evolution of the crystal fraction.

Also, the time to achieve a certain crystal fraction may vary due to finite size effects, non-uniform nucleation, anisotropic particle formation, transient nucleation, and elastic stresses. Furthermore, the conditions for crystal impingement may change from the classical JMAK correction to non-classical solutions [31]. Hence, Eqs. (1)–(2) are critically reviewed in Refs. [32–38]. Further complication of the crystallization scenario results when the crystals and parent glass have

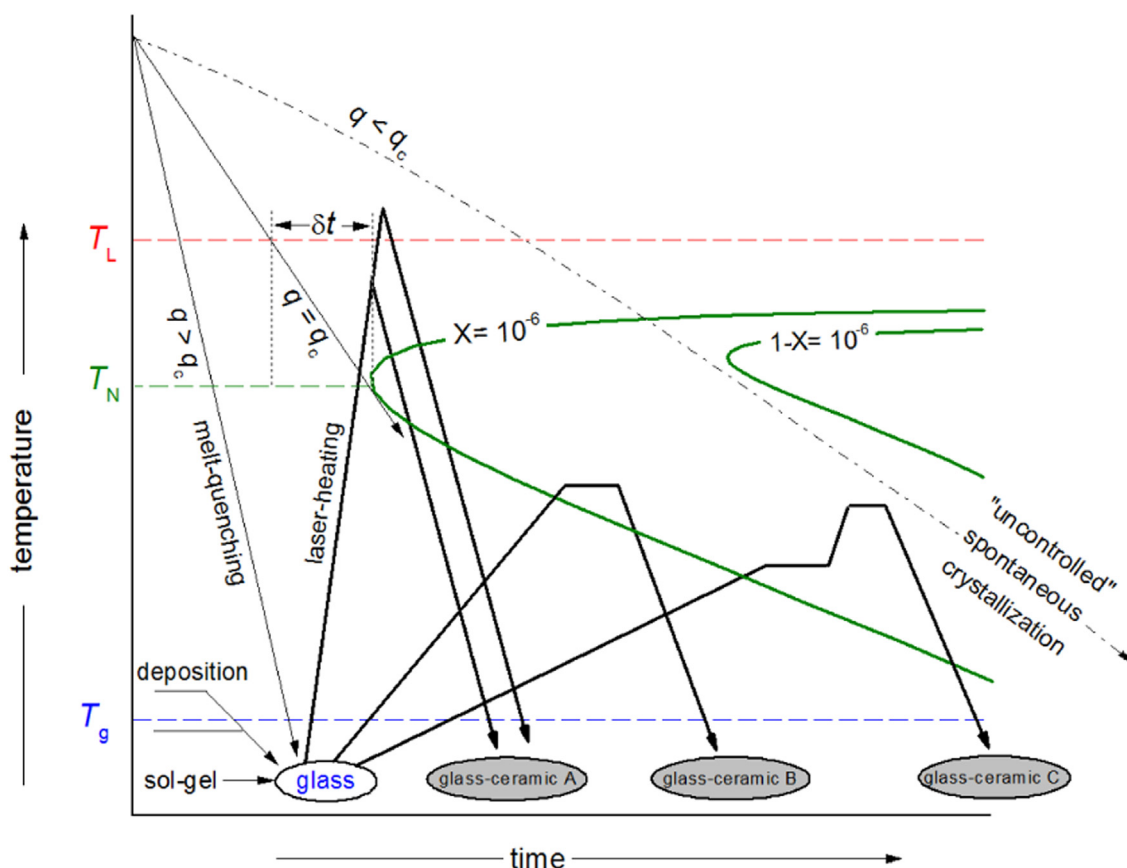


Fig. 1. Schematic description of the conversion of a glass into a glass-ceramic. The critical cooling rate is  $q_c = (T_L - T_N) / \delta t$  with  $T_L$  = liquidus temperature, and  $T_N$  = “nose temperature” (= temperature at which the time  $\delta t$  to achieve a crystal fraction of  $10^{-6}$  is shortest, according to Eq. (1)). Glass formation by melt-quenching takes place for  $q \geq q_c$ . “Uncontrolled” spontaneous crystallization occurs for  $q < q_c$ . The glass-ceramic A is obtained during cooling, whereas glass-ceramics B and C are converted by single and double-stage heat-treatments, respectively.

different chemical compositions, as local chemical gradients lead to a soft impingement, providing additional barriers to transport properties [39], can change the number and activity of nucleation sites, and establish under certain conditions an equilibrium between the first crystalline phase and the residual melt [40].

It should be stressed here that, in this processing step, the heat-treatment temperatures and times should be carefully chosen not only to induce the desired crystallization but also to avoid unwanted deformation of the (already shaped) glass articles. Fig. 2 illustrate a typical microstructure that evolves by the three-step processing of glass-ceramics.

### 3. Discussion

#### 3.1. Glassy materials

In principle, glasses can be prepared from a broad variety of substances, including inorganic materials, organics, metals, and polymers. In practice, however, the term *glass-ceramic* is used only for inorganic, non-metallic materials. In this respect, one has to consider the chemical nature of the glassy parts and crystals in glass-ceramics. If one agrees that only covalent, polar covalent, and ionic compounds should be meant, then low molecular weight organic, polymeric, and metallic glass matrices would be ruled out. Following this restriction, also the crystal structure of nucleated and grown crystals has to be of an ionic-covalent character (halides, chalcogenides, oxides, nitrides, etc.). This would rule out metal nanoparticles, such as those in photosensitive gold ruby glasses since Au-particles are the only crystals precipitated by heat-treating the parent glass. However, if these particles are active

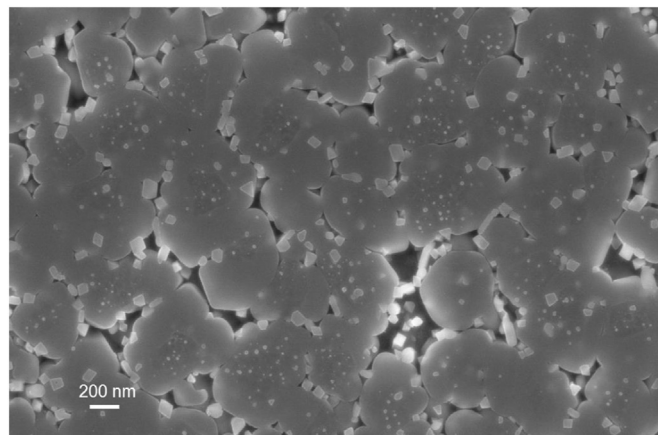


Fig. 2. Example of a typical microstructure of a glass-ceramic obtained by bulk crystallization through the addition of nucleating agents as observed by scanning electron microscopy (O. Fraboulet, Corning SAS, unpublished work). The main crystalline phase is a  $\beta$ -spodumene solid solution. Minor phases are also visible. The microstructure has been revealed via a chemical attack which dissolves predominately the residual glass.

nucleation sites for non-metallic crystals, such as alkali silicates, then this second type of crystal would qualify for being assigned to a glass-ceramic (in agreement with the classification of Stookey in 1959 [4]). The latter example explains the strategy used to produce most glass-ceramics that relies on splitting the nucleation and functionality tasks between two or more types of crystals (Fig. 3). At the same time, one may argue that photochromic glasses fall outside the glass-ceramic definition since their functionality is related to the formation of silver

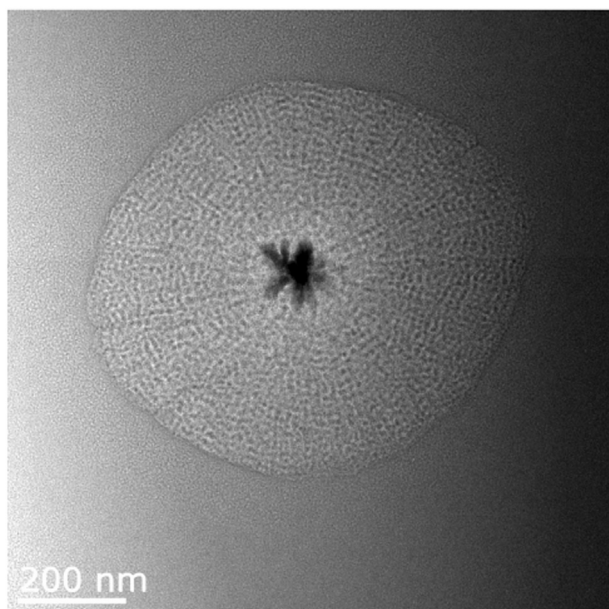


Fig. 3. Example for splitting the nucleation task and functionality tasks between two types of crystals as a basic microstructural strategy to develop glass-ceramics. A central  $ZrO_2$  crystal (dark, star-shaped) acts as a nucleation agent (external active site) for the crystallization of the functional crystal (high quartz solid solution type) which grows around the  $ZrO_2$  crystal into the glassy matrix. TEM-micrographs of a 51.9  $SiO_2$  – 21.1  $MgO$  – 21.2  $Al_2O_3$  – 5.7  $ZrO_2$  (mol%) base glass heat treated at 950 °C for 15 min. For details see Ref. [41].

nanocrystals causing reversible tinting and fading. We note that liquid-liquid phase separation can also assume the nucleation task, such that nucleation does not necessarily lead to another type of crystal (see Section 3.3 for details).

### 3.2. Glass powders

Glass powders are routinely prepared by milling frits. Other methods of preparation (e.g., melt spraying) and exotic sources of glass (e.g., glass fragments from shock wave treatments of crystals) are conceivable, including a direct production of glass powders by a chemical route such as flame/plasma pyrolysis. If glass powders are used to shape a green body (plus additives/binders which are burned-out during firing), the subsequent heat treatment allows not only for nucleation and crystal growth at surfaces and in the volume of glass particles, but also for viscous sintering. The latter allows low-cost ceramic shaping technologies, but it causes considerable shrinkage and the resulting products often contain some residual porosity. It then follows that two of the most outstanding benefits of glass-ceramic processing, i.e., near net-shaping and the absence of porosity, are lost. To display these striking differences, glass-ceramics produced by the powder route are named *sintered glass-ceramics* [38] or *frit-derived glass-ceramics* [8]. The same applies to layers and films of glass powders sintered on, or fused between, any substrates if controlled crystallization is used to reach desired properties. However, these materials are assigned to glass-ceramics since the chronological sequence of the three core processing steps, i.e. (i) glass formation, (ii) shaping an article, and (iii) ceramming the article, remain preserved. Differences apply only to the type of shaping, which is in the traditional glass-ceramic route a hot-forming process above  $T_g$ , whereas, using powders, articles are shaped by cold-forming (casting, spraying, dipping, etc.) at ambient temperatures ( $T < T_g$ ). On the other hand, if powders from gels are used, such as xerogels – a xerogel consists on a continuous solid network surrounding and supporting a continuous liquid phase – the glassy network and a desired crystalline phase can evolve concurrently during running the time-temperature protocol. This can be addressed as

a borderline case since processing steps (i) and (iii) occur most likely at the same time. A measure on how to distinguish glass-ceramic processing from other manufacturing can be to include also the shaping step (ii) into the consideration. If gels are shaped before the heat treatment step (ii), the chronological sequence of a glass-ceramic processing is invalidated.

Applying quite similar ceramic processing, glass powders can be mixed with ceramic or other fillers and organic additives keeping their superior properties, but offering the benefit of low sintering temperatures. In contrast to sintered glass-ceramics, and depending on the glass-to-filler ratio of these mixtures, names such as *glass matrix composites* (20–55% filler) and *glass-bonded ceramics* (80–97% ceramic filler) have been established by the ceramic community [38]. The notation “glass matrix composite” applies independently from the fact that crystallization can be triggered during or after sintering within the glass matrix. The effect of glass matrix crystallization can be used, e.g., for the increased post-firing stability of so-called “low temperature co-fired ceramics” [42]. Further, glass matrix composites [43] but also glass-ceramics [44] are widely used in sealing applications (e.g., SOFC), where the properties of the grown crystals and the added ceramic fillers improve the thermomechanical performance of the sealed system, such as by adjusting the thermal expansion behaviour.

We note that the mere presence of porosity is not a sufficient criterion for using the term *sintered glass-ceramics*. Thus, even in case of hot glass-forming, crystallization-induced porosity can appear due to density misfits of crystals and glasses [45]. Additionally, pores, micro-cracks, and interstices can take part in the desired product properties [46]. Further, open and closed porosity can be built up on purpose in cellular engineered glass-ceramics using the replication technique (templates) and by additive manufacturing (3D-printing). In these materials, porosity can be hierarchically organized, as in scaffolds for bone tissue engineering and catalytic substrates where bridges, necks, and struts of 3D-structures result after controlled crystallization in a desired porosity at the mesoscale [47]. In contrast, if mixtures of glass-frits with ceramic fillers are milled for slurry preparation to improve, for instance, the mechanical strength of the final material, they are *glass matrix composites* or *glass-bonded ceramics* [48], independent on the type of cold-shaping (3D-printing, templates, etc.).

### 3.3. Multiple glassy states and crystal phases

Liquid immiscibility, i.e., liquid-liquid phase separation, is frequently observed in glasses after quenching, or can take place at an early stage of a subsequent heat-treatment. If a stable immiscibility region is evident (critical temperature  $T_C > T_L$ ), a homogeneous glass cannot be formed. But in case of a sub-liquidus immiscibility region ( $T_C < T_L$ ), phase separation is relatively slow and can be controlled. Even multiple phase separation processes are known to occur in glasses of sluggish kinetics where the droplet and matrix phases may demix a second and third time, or form halos and shells around the glassy microphases as a consequence of impeded or incomplete diffusion processes [15]. During heating, crystal nucleation can occur in one of these glassy microphases, which then serves as a natural boundary to constrain the maximum size of the growing crystal (Fig. 4). One example for crystallization as a consequence of an initial phase separation is the core-shell structure of zirconitanates (nucleating agent) in lithium aluminosilicate glass-ceramics [50]. Other examples are oxyfluoride glass-ceramics in which rare-earth metal fluoride nanocrystals grow inside demixed glassy droplet structures [51]. Spinodally-decomposed phase-separated structures have also been reported to induce the formation of functional nanocrystals in glass-ceramics [52]. Also, the formation of semiconductor quantum dots in oxysulfide glasses is probably caused by the early phase separation of a sulfur-rich droplet glass in which, for example, photoluminescent lead chalcogenide crystals grow to nanometre sizes [53]. Other cases are two-fold crystallization processes, where one type of crystal grows in the droplet glass while other crystals

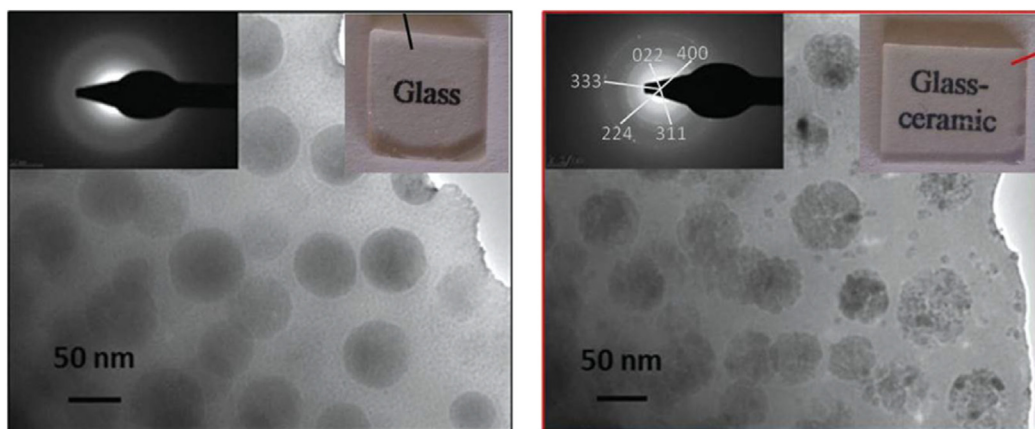


Fig. 4. Example of a phase separated glass (left) in which, after ceramming, functional crystals grow inside the droplet structure (right). As a result, a relict microstructure is developed as the droplets serve as natural boundaries to limit the size of functional crystals. TEM micrographs of a 78 GeO<sub>2</sub>–9.8 ZnO–9.8 Ga<sub>2</sub>O<sub>3</sub>–2.4 Na<sub>2</sub>O (mol%) base glass. The functional crystal is a spinel type Zn<sub>1-x</sub>Ga<sub>2-2x</sub>Ge<sub>x</sub>O<sub>4</sub>. For details see Ref. [49].

evolve in the glass matrix [54].

### 3.4. Energy sources to provoke crystallization

Desired crystallization processes can be induced intentionally by different energy sources (flame, laser, UV-radiation, electron beam, etc.). The type of energy supply governs the ceramming conditions in practice. Thus, in traditional ceramming, a kiln is used, and crystallization starts when the glass is heated above  $T_g$  (glass-ceramics B and C of Fig. 1) while using a laser source, crystallization is induced when the heated glass cools (glass-ceramic A of Fig. 1). In all cases, ceramming is executed to achieve desired microstructure-property relations of the final glass-ceramic.

Notably, laser-induced crystallization has been reported as a new method for the design and control of crystallization in glasses [55]. The glass-to-crystal transformation starts at the rim of the initial laser spot, where the temperature of the supercooled melt is below the *liquidus*, and a thermodynamic driving force triggers crystal nucleation. Another case is realized when the local temperature around laser spot is above the *liquidus*, and local elemental diffusion increases the crystallization tendency of the glass, resulting in the precipitation of multiple types of crystals in a controlled manner [56] (Fig. 5). If the laser spot is moved, a growth selection process is initiated, and one crystal finally grows into the direction of the moving spot, which enables one to write patterns of a single crystal in a glass. This process is described as self-organized, homo-epitaxial crystal growth [57], in which the interplay of the heat of crystallization with the heat of the laser irradiation keeps the temperature constant at the moving crystallization front. In case of single-crystal laser-patterning  $N_v = 1$ , artificial polycrystallinity can be added if patterns of several crystals are written in the same glass article. Since laser-induced crystallization generally results in oriented crystals – a prerequisite to producing a functional optical device using, e.g., optically non-linear crystals – the isotropy of the functional property is avoided. To indicate this vital change in property, glass-ceramics produced by laser-patterning we herein term *laser-patterned glass-ceramics*.

Another way to prepare a glass-ceramic is by field-assisted crystallization where, besides heating to temperatures above  $T_g$ , external fields (e.g., mechanical, electrical, and magnetic) are applied [58]. These fields can be used to provoke primary crystallization in glasses or to align randomly grown crystals of glass-ceramics. The latter group includes glass-ceramics which are reheated and extruded through a die [59]. The former group accounts for electrochemically induced nucleation processes in melts close to  $T_L$  [60] and to thermal poling [61] and electron beam induced crystallization [62] of glasses at temperatures close to  $T_g$ . If the evolution of microstructure of these materials can be adjusted by the control parameters of the field (field strength,

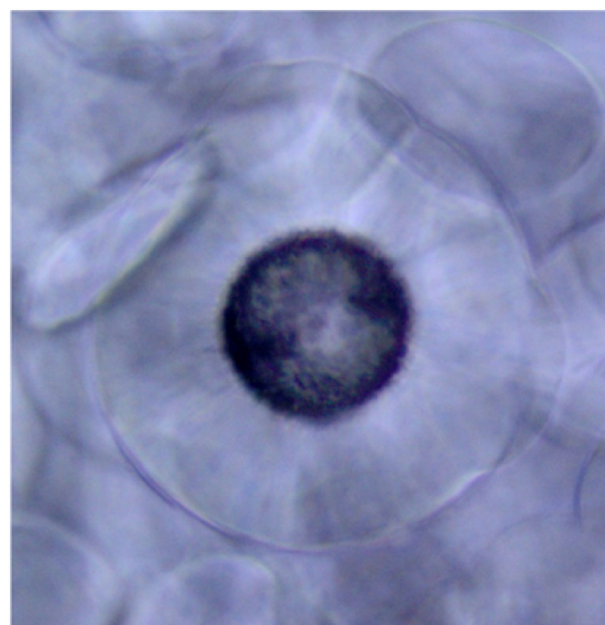


Fig. 5. Example for “eye”-shaped crystal in a glass-ceramic formed around a laser-induced dot. A regenerative amplified Ti: sapphire laser with a 250 kHz, 80 fs, and 800 nm mode-locked pulse was employed to induce a damage spot with the size of ca. 70 μm. The BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> crystal forms around the spot after heat-treating at 840 °C for 2 h (from S. Zhou and J. Qiu, unpublished work).

current density, etc.) and the number densities, orientations, patterns, and textures of functional crystals result in desired properties, a glass-ceramic is fabricated. In contrast, if the microstructure evolves undesirably and cannot be controlled during these treatments, a partially crystallized glass is prepared but not a glass-ceramic. Again, to indicate the change from isotropic to anisotropic functional properties these glass-ceramics are named *oriented glass-ceramics* [10,63] and *poled glass-ceramics* [64], respectively.

### 3.5. Crystal and glass fractions

In Uhlmann's kinetic treatment of glass formation [21], the crystallized volume fraction of a glass-ceramic has to exceed 1 ppm (this is an arbitrary value, reasonably chosen by Uhlmann, as being below the limit of detection by experimental techniques available in the early 70s). At this point, the definition of the minimum size at which a nanocrystal is considered a crystal (and not a cluster) arises. It is not that

easy, as standard textbooks refer to the ability to diffract and the capability to detect diffraction signals is dependent on the experimental method used. For example, “X-ray amorphous” is different from “electron amorphous”. From our experience, a nanocrystal possessing 5 to 6 lattice planes gives rise to interference patterns that can be imaged (by scanning transmission electron microscopy slightly better than by high-resolution TEM) or detected in electron diffraction patterns. But, in principle, also marginally smaller nanocrystals (showing translational periodicity over 3 to 4 unit cells) are different from clusters, but can hardly be imaged or detected by diffraction. Other techniques (like multi-quantum NMR, or EXELFS) probe the nearest or next-to-nearest neighbor environment and also do not adequately cover the foggy region of the small nanocrystals ( $< 5$  nm).

Besides experimental traceability, it is not immediately obvious that a small fraction of crystals can add some functionality to a glass-ceramic. However, for optical properties, such as luminescent crystals, fractions below 1% (10,000 ppm) have been reported to have an effect. In case of lead chalcogenide crystals (crystal-to-matrix density ratio  $\approx 3$ ) functionality is achieved with ca. 3000 ppm [53]. Other examples are “photo-thermal refractive glasses,” which are glass-ceramics containing  $< 1\%$  of nanosize NaF crystals embedded in an optical glass matrix of many components. They display beneficial optical functionality and are currently produced by at least three companies [65]. Meager amounts of NaF crystals (up to a few percents) are also present in “opal glass” products, where precipitation of fluorides are used to opacify the glass. Also in ophthalmic glasses, low volume fractions of CuCl or CuBr crystals are precipitated to provide a sharp UV cut-off (at 400 nm) (Fig. 6). We note that the majority of these materials are commercialized as glasses and not as glass-ceramics since the relevant parent glass properties (e.g., softening point) remain almost unchanged by crystallization of such low volume fractions.

Another relevant aspect comes from the number of crystals grown due to impurities. In regular lab-melted glass (small volume, not stirred), the “natural” level of impurity-induced crystals was approximated as ca. 10 crystals per cubic millimeter [66], whereas for better homogenised glass (larger volume, stirred)  $10\times$  lower number densities have been reported (1 crystal per  $\text{mm}^3$ ) [25]. Using this threshold, and allowing the crystals to grow to micrometer sizes (e.g.,  $r = 10$   $\mu\text{m}$ ), a volume fraction of about 0.4–4 ppm is transformed, meeting the current criterion of glass formation (1 ppm). Thus, one can state that

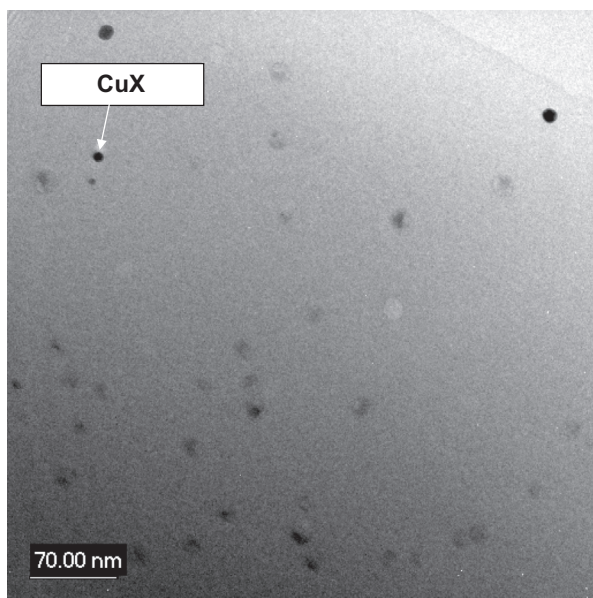


Fig. 6. Example of an ophthalmic glass that comprises homogeneously distributed copper halide (CuX) nanocrystals of average size 8–10 nm (from Y. Brocheton et al., Corning SAS, unpublished work).

glass-ceramics have to contain volume fractions of crystals above this low level to distinguish properly nucleated and grown crystals (in the sense of controlled crystallization) from crystals grown at imperfections. It should be noted that not all impurities can serve as active centers for nucleation. Also, it is not easy to differentiate impurity-induced crystals from crystals formed during cooling path of the melt.

At the other extreme, one can discuss the effectiveness of a small volume fraction of residual glass in glass-ceramics. In this case, the improvement of specific optical properties, such as high transparency, can be a main driving force for developing unique quasi-glass-free microstructures. We note that the ability to obtain very low fractions of residual glass is mainly linked with the impurity-level of the raw materials, the ceramming regime, and the solid-solution capacity of the evolving crystals.

To our knowledge, there is no clear definition for the residual glass-fraction in other material classes, such as in ceramics (hard porcelain 70%, bone china 30%, silicon nitrides  $< 10\%$ ) from which a criterion for glass-ceramics could be derived. Of course, one can rely on the lower detection limit of an intergranular glassy fraction in a glass-ceramic, using advanced X-ray diffraction and electron microscopy techniques which, for an amorphous grain-boundary film, a thickness of approximately three to four monolayers. Assuming 1 ppm again as the lower limit of the residual glass fraction ( $= 1 - X$ ), a second TTT-curve can be constructed via Eqs. 1–2 (Fig. 1). In case the above-mentioned methods fail to detect a residual glass, the definition of a glass-ceramic would not apply. Examples are polycrystalline ceramics prepared by ceramming a glass to full crystallization that is 100% crystal fraction [67,68]. In these materials, a residual glass is undetectable, although the processing to achieve such ceramics match those of glass-ceramics.

#### 4. Summary

Glass-ceramics are approximately 65 years old and noted for their unusual combination of properties that lead to a manifold of high technology products for both consumer and specialized markets. They are obtained by controlled crystallization of inorganic, non-metallic glasses. Their microstructures comprise at least one type of functional crystal and one glassy fraction. Crystal and glass volume fractions above the ppm-level are adequate in our definition of glass-ceramics. Glass-ceramics are either pore-free or show various levels of porosity. Pores can be engineered (e.g., additive manufacturing) and provide a critical part of the desired structure-property relation of the desired glass-ceramic. On the other hand, pores may be by-products of undesired processes, such as incomplete sintering of parent glass powders. If glasses are mixed with other crystalline materials (ceramics, metals, semiconductors, or polymers), they are composites and not considered as glass-ceramics. The same rule applies for amorphous precursors that are not glasses (lack of  $T_g$ ), and glasses in which only metallic particles are precipitated after crystallization, as they are not “cerammed”. Further, “seeded” glasses containing only crystalline nucleation agents are not considered to be glass-ceramics, as a desired functionality by this crystallization is typically not achieved. On the other hand, no constraint is proposed concerning the source of energy to induce crystallization in glasses, if desired microstructure-property relations can be achieved in the final glass-ceramic. Also, no restriction applies to the type of crystal nucleation (heterogeneous and homogeneous), the distribution of active nucleation sites (surface and volume), and crystal growth (randomly oriented or aligned), as long as the evolving microstructure serves for the desired property portfolio. In contrast, we exclude spontaneously devitrified glasses from the group of glass-ceramics, as they lead to undesired microstructures, resulting from uncontrolled nucleation and crystal growth processes and lead to undesirable properties.

In this communication, we consider that the original definition of Stookey from 1958 is primarily still valid: “Glass-ceramics are made by first melting and forming special glasses containing nucleating agents and

then causing controlled crystallization of the glass.” However, due to numerous developments in the past six decades, we propose an updated and more complete definition: “Glass-ceramics are inorganic, non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The volume fraction crystallized may vary from ppm to almost 100%”.

We are aware that this definition limits the use of the term *glass-ceramic* to inorganic non-metallic materials. It basically follows the definition of *ceramics*, which are inorganic non-metallic materials, despite the fact that glass-crystal composites can be made from bulk metallic glasses and from organic glassy systems obeying the same three steps of manufacturing in which glasses are formed, glass articles shaped, and finally these glass articles crystallized in a controlled way. Thus, a fundamental limitation of the here updated definition of glass-ceramic is, that it is dependent on chemistry, whereas the definition of glass is independent on chemistry. As a consequence and to encompass all types of glass-crystal composites, including glass-ceramics, an overarching term needs to be defined shortly.

It should, finally, be stressed that this communication does not claim to comprehensively address all novel processing routes which could be of relevance in the manufacturing of glass-ceramics. It includes - or at least only mentions - some borderline cases that are still open. Further discussion in a scientific committee or permanent scientific panel such as the Technical Committee 07 “Crystallization and Glass-Ceramics” of the International Commission on Glass (ICG) is needed.

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## References

- M.J. Davis, E.D. Zanotto, Glass-ceramics and realization of the unobtainable: property combinations that push the envelope, *Mater. Res. Soc. Bull.* 42 (2017) 195–199.
- S.D. Stookey, History of the development of pyroceram, *Res. Manag.* 1 (1958) 155–163.
- S.D. Stookey, Recent developments in radiation-sensitive glasses, *Ind. Eng. Chem.* 46 (1954) 174–176.
- S.D. Stookey, Catalyzed crystallization of glass in theory and practice, *Ind. Eng. Chem.* 51 (1959) 805–808.
- W. Hinz, *Vitroceram, Silikattechn.* 10 (1959) 119–122.
- A.I. Berezhnoi, *Sitally i fotositally*, Mashinostroenie Press, Moscow 1966 (Rus. transl.: Glass-ceramics and photo-sitalls) Plenum Press, New York, 1970, p. 1.
- P.W. McMillan, *Glass-Ceramics*, Academic Press, London, 1964, p. 1.
- W. Höland, G. Beall, *Glass-Ceramic Technology*, 2nd Ed., Wiley, Hoboken, 2012, pp. xvii–xx.
- M. Rampf, M. Dittmer, C. Ritzberger, W. Höland, Controlled parallel crystallization of lithium disilicate and diopside using a combination of internal and surface nucleation, *Front. Mater.* 3 (2016) 47.
- A. Halliyal, A. Safari, A.S. Bhalla, R.E. Newnham, L.E. Cross, Grain-oriented glass-ceramics for piezoelectric devices, *J. Am. Ceram. Soc.* 67 (1984) 331–335.
- A. Feltz, *Amorphous Inorganic Materials and Glasses*, Weinheim, VCH, 1993, pp. 7–10.
- D.L. Pye, The vitreous state, D.L. Pye, H.J. Stevens, W.C. LaCourse (Eds.), *Introduction to Glass Science*, Plenum Press, New York, 1972, pp. 1–30.
- J. Zarzycki, *Les Verres et l'Etat Vitreux*, Masson, Paris, (1982), pp. 1–8 (Engl. transl.: Glasses and the vitreous state, University Press, Cambridge, 1991).
- H. Scholze, *Glas – Natur, Struktur und Eigenschaften*, 3. Aufl., Springer, Berlin, 1988, pp. 3–5 (Engl. transl.: Glass – Nature, Structure and Properties, Springer, Berlin 1991).
- W. Vogel, *Glasschemie*, 3. Aufl., Springer, Berlin, 1992, pp. 29–36 129–138 (Engl. transl.: Glass chemistry, 2nd Ed., Springer, Berlin 1994, p. 24–30; 111–120).
- R.H. Doremus, *Glass Science*, 2nd Ed., Wiley, New York, 1994, pp. 1–12.
- J.E. Shelby, *Introduction to Glass Science and Technology*, 2nd Ed., The Royal Society of Chemistry, Cambridge, p. 1–6.
- A.K. Varshneya, *Fundamentals of Inorganic Glasses*, 2nd Ed., The Society of Glass Technology, Sheffield, 2006, pp. 17–18.
- K. Binder, W. Kob, *Glassy Materials and Disordered Solids*, 2nd Ed., World Scientific, Singapore, 2011, pp. 339–360.
- I.S. Gutzow, J.W.P. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization*, 2nd Ed., Springer, Heidelberg, 2013, pp. 63–68 396–402.
- D.R. Uhlmann, A kinetic treatment of glass formation, *J. Non-Cryst. Solids* 7 (1972) 337–348.
- V.M. Fokin, E.D. Zanotto, Surface and volume nucleation and growth in TiO<sub>2</sub>-cordierite glasses, *J. Non-Cryst. Solids* 246 (1999) 115–127.
- R. Müller, Surface nucleation in cordierite glass, *J. Non-Cryst. Solids* 219 (1997) 110–118.
- S. Krüger, J. Deubener, The TTT curves of the heterogeneous and homogeneous crystallization of lithium disilicate – a stochastic approach to crystal nucleation, *Front. Mater.* 3 (2016) 42.
- U. Schiffer, W. Pannhorst, Nucleation in a precursor glass for a Li<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass ceramic, *Glastech. Ber.* 60 (1987) 211–221 (239–247).
- S. Krüger, J. Deubener, Stochastic nature of the liquid-to-crystal heterogeneous nucleation of supercooled lithium disilicate liquid, *J. Non-Cryst. Solids* 388 (2014) 6–9.
- R. Müller, E.D. Zanotto, V.M. Fokin, Surface crystallization of silicate glasses: nucleation sites and kinetics, *J. Non-Cryst. Solids* 274 (2000) 208–231.
- A.N. Kolmogorov, Statistical theory of crystallization of metals (in Russian), *Izv. Acad. Sci. USSR, Ser. Math.* 1 1937, pp. 355–359.
- W.A. Johnson, R.F. Mehl, Reaction kinetics in processes of nucleation and growth, *Trans. Am. Inst. Metall. Eng.* 135 (1939) 416–458.
- M. Avrami, Kinetics of phase change, *J. Chem. Phys.* 7 (1939) 1103–1112 8 (1940) 212–224; 9 (1941) 177–184.
- S. Krüger, J. Deubener, Thermal analysis of repetitive single crystallization events in glass-forming liquids at low undercooling, *J. Non-Cryst. Solids* (2017), <http://dx.doi.org/10.1016/j.jnoncrysol.2017.12.037>.
- D.W. Henderson, Thermal-analysis of nonisothermal crystallization kinetics in glass-forming liquids, *J. Non-Cryst. Solids* 30 (1979) 301–315.
- E.D. Zanotto, A. Galhardi, Experimental test of the general-theory of transformation kinetics - homogeneous nucleation in a Na<sub>2</sub>O<sub>2</sub>CaO<sub>3</sub>SiO<sub>2</sub> glass, *J. Non-Cryst. Solids* 104 (1988) 73–80.
- I. Gutzow, R. Pascova, A. Karamanov, J. Schmelzer, The kinetics of surface-induced sinter crystallization and the formation of glass-ceramic materials, *J. Mater. Sci.* 33 (1998) 5265–5273.
- M.C. Weinberg, Transformation kinetics of particles with surface and bulk nucleation, *J. Non-Cryst. Solids* 142 (1992) 126–132.
- M.C. Weinberg, Crystallization kinetics and the JMAK equation, *J. Non-Cryst. Solids* 219 (1997) 89–99.
- V.M. Fokin, A.A. Cabral, R.M.C.V. Reis, M.L.F. Nascimento, E.D. Zanotto, Critical assessment of DTA-DSC methods for the study of nucleation kinetics in glasses, *J. Non-Cryst. Solids* 356 (2010) 358–367.
- R. Müller, S. Reinsch, Viscous-phase silicate processing, in: N.P. Bansal, A.R. Boccaccini (Eds.), *Ceramics and Composites Processing Methods*, Wiley, 2012, pp. 75–144.
- S. Bhattacharyya, C. Bocker, T. Heil, J.R. Jinschek, T. Höche, C. Rüssel, H. Kohl, Experimental evidence of self-limited growth of nanocrystals in glass, *Nano Lett.* 9 (2009) 2493–2496.
- V.M. Fokin, R.M.C.V. Reis, A.S. Abyzov, C.R. Chinaglia, J.W.P. Schmelzer, E.D. Zanotto, Non-stoichiometric crystallization of lithium metasilicate–calcium metasilicate glasses. Part 2 - effect of the residual liquid, *J. Non-Cryst. Solids* 379 (2013) 131–144.
- C. Patzig, T. Höche, M. Dittmer, C. Rüssel, Temporal evolution of crystallization in MgO/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/ZrO<sub>2</sub> glass-ceramics, *Cryst. Growth Des.* 12 (2012) 2059–2067.
- M. Eberstein, S. Reinsch, R. Müller, J. Deubener, W.A. Schiller, Sintering of glass matrix composites with small rigid inclusions, *J. Eur. Ceram. Soc.* 29 (2009) 2469–2479.
- S.M. Gross, T. Koppitz, J. Rimmel, J.B. Bouche, U. Reisgen, Joining properties of a composite glass-ceramic sealant, *Fuel Cells Bull.* 2006 (2006) 12–15.
- S. Rodríguez-López, J. Wei, K.C. Laurenti, I. Mathias, V.M. Justo, F.C. Serbena, C. Baudín, J. Malzbender, M.J. Pascual, Mechanical properties of solid oxide fuel cells glass-ceramic sealants in the system BaO/SrO-MgO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, *J. Eur. Ceram. Soc.* 37 (2017) 3579–3594.
- V.M. Fokin, A.S. Abyzov, J.W.P. Schmelzer, E.D. Zanotto, Stress-induced pore formation and phase selection in a crystallizing stretched glass, *J. Non-Cryst. Solids* 356 (2010) 1679–1688.
- A. Sakamoto, Y. Himeji, Y. Hashibe,  $\beta$ -Spodumene glass-ceramic with anomalous low thermal expansion, *Adv. Mater. Res.* 39–40 (2008) 381–386.
- Q.Z. Chen, I.D. Thompson, A.R. Boccaccini, 45S5 Bioglass®-derived glass-ceramic scaffolds for bone tissue engineering, *Biomaterials* 27 (2006) 2414–2425.
- J. Suwanprateeb, R. Sangam, W. Suvannapruk, T. Panyathanmaporn, Mechanical and in vitro performance of apatite-wollastonite glass ceramic reinforced hydroxyapatite composite fabricated by 3D-printing, *J. Mater. Sci. Mater. Med.* 20 (2009) 1281.
- S. Chenu, E. Véron, C. Genevois, G. Matzen, T. Cardinal, A. Etienne, D. Massiot, M. Allix, Tuneable nanostructuring of highly transparent zinc gallogermanate glasses and glass-ceramics, *Adv. Opt. Mater.* 2 (2014) 364.
- S. Bhattacharyya, T. Höche, J.R. Jinschek, I. Aramov, R. Wurth, M. Müller, C. Rüssel, Direct evidence of Al-rich layers around nanosized ZrTiO<sub>4</sub> in glass: putting the role of nucleation agents in perspective, *Cryst. Growth Des.* 10 (2010) 379–385.
- A. de Pablos-Martín, N. Hémono, G.C. Mather, S. Bhattacharyya, T. Höche,

- H. Bornhöft, J. Deubener, F. Muñoz, A. Durán, M.J. Pascual, Crystallization kinetics of  $\text{LaF}_3$  nanocrystals in an oxyfluoride glass, *J. Am. Ceram. Soc.* 94 (2011) 2420–2428.
- [52] S. Chenu, E. Véron, C. Genevois, A. Garcia, G. Matzen, M. Allix, Long-lasting luminescent  $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$  transparent glass-ceramics, *J. Mater. Chem. C* 2 (2014) 10002–10010.
- [53] C. Liu, J. Heo, Lead chalcogenide quantum dot-doped glasses for photonic devices, *Int. J. Appl. Glas. Sci.* 4 (2013) 163–173.
- [54] W. Höland, C. Ritzberger, E. Apel, V. Rheinberger, R. Nesper, F. Krumeich, C. Mönster, H. Eckert, Formation and crystal growth of needle-like fluoroapatite in functional glass-ceramics, *J. Mater. Chem.* 18 (2008) 1318–1332.
- [55] T. Komatsu, R. Ihara, T. Honma, Y. Benino, R. Sato, H.G. Kim, T. Fujiwara, Patterning of non-linear optical crystals in glass by laser-induced crystallization, *J. Am. Ceram. Soc.* 90 (2007) 699–705.
- [56] S. Zhou, N. Jiang, K. Miura, S. Tanabe, M. Shimizu, M. Sakakura, Y. Shimotsuma, M. Nishi, J. Qiu, K. Hirao, Simultaneous tailoring of the phase evolution and dopant distribution in glassy phase for controllable luminescence, *J. Am. Chem. Soc.* 132 (2010) 17945–17952.
- [57] T. Komatsu, T. Honma, Nucleation and crystal growth in laser-patterned lines in glasses, *Front. Mater.* 3 (2016) 32.
- [58] C. Rüssel, Oriented crystallization of glass. A review, *J. Non-Cryst. Solids* 219 (1997) 212–218.
- [59] S. Habelitz, G. Carl, C. Rüssel, S. Thiel, U. Gerth, J.-D. Schnapp, A. Jordanov, H. Knake, Mechanical properties of oriented mica glass ceramic, *J. Non-Cryst. Solids* 220 (1997) 291–298.
- [60] R. Keding, C. Rüssel, Electrochemical nucleation for the preparation of oriented glass ceramics, *J. Non-Cryst. Solids* 219 (1997) 136–141.
- [61] Y. Yamamoto, T. Hashimoto, H. Nasu, K. Kamiya, Second harmonic generation from  $\text{YAl}_3(\text{BO}_3)_4$ -containing glass-ceramics prepared by thermal poling of  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$  glasses, *Jpn. J. Appl. Phys.* 42 (2003) 5043–5047.
- [62] N. Jiang, B. Wu, J. Qiu, J.C.H. Spence, Precipitation of nanocrystals in glasses by electron irradiation: an alternative path to form glass ceramics? *Appl. Phys. Lett.* 90 (2007) 161909.
- [63] D.I.H. Atkinson, P.W. McMillan, Glass-ceramics with random and oriented microstructures, *J. Mater. Sci.* 11 (1976) 989–993.
- [64] A. Malakho, E. Fargin, M. Lahaye, B. Lazoryak, V. Morozov, G. Van Tendeloo, V. Rodriguez, F. Adamietz, Enhancement of second harmonic generation signal in thermally poled glass ceramic with  $\text{NaNbO}_3$  nanocrystals, *J. Appl. Phys.* 100 (2006) 063103.
- [65] J. Lumeau, E.D. Zanotto, A review of the photo-thermal mechanism and crystallization of photo-thermo-refractive (PTR) glass, *Int. Mater. Rev.* 62 (2017) 348–366.
- [66] J. Deubener, M. Montazerian, S. Krüger, O. Peitl, E.D. Zanotto, Heating rate effects in time-dependent homogeneous nucleation in glasses, *J. Non-Cryst. Solids* 474 (2017) 1–8.
- [67] M. Allix, S. Alahache, F. Fayon, M. Suchomel, F. Porcher, T. Cardinal, G. Matzen, Highly transparent  $\text{BaAl}_4\text{O}_7$  polycrystalline ceramic obtained by full crystallization from glass, *Adv. Mater.* 24 (2012) 5570–5575.
- [68] K. Al Saghir, S. Chenu, E. Veron, F. Fayon, M. Suchomel, C. Genevois, F. Porcher, G. Matzen, D. Massiot, M. Allix, Transparency through structural disorder: a new concept for innovative transparent ceramics, *Chem. Mater.* 27 (2015) 508–514.