

Glass Crystallization Research – A 36-Year Retrospective.[†] Part II, Methods of Study and Glass-Ceramics

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Most of our original studies on the fundamental scientific aspects of glass crystallization were reviewed in Part I of this article. In this part, we describe some relevant methods we developed to study glass crystallization and review a number of systematic studies that we conducted to develop, improve, or characterize some types of glass-ceramics, such as bioactive glass-ceramics; photo-thermo-refractive glasses (or glass-ceramics because the “active” components are sodium fluoride nano-crystals embedded in a glass matrix); new glass-ceramics derived from blast furnace and steel-making slags (hard materials for architecture and construction); sintered glass-ceramics that emulate expensive stones such as marble and granite; and the first large-grain, highly crystalline optically transparent glass-ceramic.

Introduction

I start with apologies because both parts of this article are based on my *Morey award* talk; hence, I only review here work on glass crystallization and glass-ceramics by our own group and our closest collaborators over the past 36 years and therefore neglect several important papers published by other authors. In addition, due to space restrictions, no equations or details are shown in this short review; the interested reader is cordially invited to consult the cited references.

Our work on some fundamental aspects of *glass crystallization* was reviewed in Part I.¹ We believe that

such studies are not only necessary for the understanding of the vitreous state but also for the successful development of useful glass-ceramics. We have also carried out some research of a more technological character on glass-ceramic development, improvement, or characterization of their properties. Our main findings regarding some techniques we developed to study glass crystallization processes and some types of glass-ceramics are summarized in the following paragraphs.

Methods to Study Glass Crystallization Processes

Stereological Errors

Two of our papers considered the stereological errors associated with experimental measurements of

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nucleation and the overall crystallization rates in glasses by microscopy that are often neglected in the literature. In some situations, such errors can be quite significant (>50%) and must be accounted for to obtain a proper analysis of the crystallization kinetics.

In a first study,² we derived equations for the fractional underestimation in the number of particles per unit volume, N_v , and in nucleation rates, I^0 , obtained using stereological techniques from reflected light microscopy or SEM for typical cases of crystal nucleation in glasses. Three cases were considered: (i) instantaneous heterogeneous nucleation (monodispersed systems of particles); (ii) simultaneous homogeneous nucleation and growth in a single-stage heat treatment (uniform distribution of crystals from the critical size to D_M , where D_M is the largest diameter); and (iii) case (ii) with a double heat treatment (uniform size distribution from D_m , the smallest diameter, to D_M). Comparisons with experimental nucleation data for BaO-SiO₂ and Na₂O-CaO-SiO₂ glasses demonstrated that the equations predict the observed underestimations well. Unfortunately, some of the equations were incorrect. We published the correct equations in a review paper in 2006.³ Luckily, however, the numerical values predicted by both the incorrect and correct equations were similar; the conclusions in the original paper were thus unaltered. Typical experiments with optical microscopy led to underestimates from 3% to 14% for case (iii) and up to 50% for case (ii). To minimize these errors, one should either use a high-magnification objective lens with reflection or transmitted light microscopy, or perform electron microscopy.

Next⁴ we derived a set of equations to estimate the systematic errors in experimental determinations of volume fractions transformed by microscopy methods. We demonstrated that for reactions that occur by continuous nucleation and growth, the experimental values of volume fraction transformed may be subjected to significant errors when the largest grain size of the distribution is close to the microscope resolution limit. For transformations occurring from a fixed number of nuclei, the systematic errors are smaller than those observed in the continuous nucleation case, but can still be significant when reflected light microscopy or SEM methods are used. Transmission methods lead to smaller errors than reflection techniques.

Methods to Determine the Crystal/Liquid Surface Energy

We also estimated the nucleus-liquid interfacial free energy⁵ using the dissolution of subcritical nuclei (embryos) without employing nucleation rate measurements. Our analysis showed that both the surface free energy and the thermodynamic driving force for nuclei formation and growth may have quite different values from those of the evolving macro-phases.

In another article,⁶ we used three different thermal analysis techniques (DSC, hot-stage optical microscopy equipped with a photodiode to measure light depolarization, and a video system to measure spherulitic growth) to study polymer crystallization. The fold surface free energy (σ_e) values from different analytical methods on one polymer were compared. The overall crystallization data gave consistent values but always yielded σ_e values 15–50% higher than those obtained from the direct method of measuring growth rates. Until now, we could not figure out why and hence this theme deserves further study.

DSC and Other Methods for the Determination of Glass Crystallization Parameters

More recently, our co-workers Aluísio Cabral, Eduardo Ferreira, Raphael Reis, and Vladimir Fokin re-evaluated some nonisothermal (DSC and DTA) methods proposed to infer crystal nucleation and growth kinetics in glasses. Microscopy methods are usually employed to estimate the number density of supercritical nuclei and the resulting crystal nucleation rates, $I(T)$. These traditional techniques rely on a double-stage treatment, that is, the development of the nuclei at a temperature higher than the previous nucleation temperature up to a size large enough to be visible with optical or electron microscopy. These methods can give reliable results for $I(T)$, but they are rather laborious and time consuming. Conversely, nonisothermal (DTA/DSC) methods are, in principle, much faster.^{7–9}

We tested^{8,9} two nonisothermal methods by comparison with a traditional optical microscopy method. We found that if properly employed, these nonisothermal methods can give useful kinetic information, which includes the crystal number density and nucleation rates. To obtain accurate quantitative data, the methods need some preliminary information about the nucleation and growth rates of the studied glass and, in

addition, are as laborious as traditional microscopy methods! These papers indicated that such nonisothermal methods can, at times, be used to probe glass crystallization parameters, but extreme care is necessary to obtain reliable results. In general, these methods often give misleading results and can be as complex and time consuming as traditional isothermal methods that use microscopic and stereological techniques.

In another study,¹⁰ we derived an analytical model to describe the crystallization kinetics of spherical glass particles. A continuous phase transition from 3D-like to 1D-like crystal growth was considered, and a procedure for the quantitative evaluation of the critical time for this 3D–1D transition was proposed. Our model also allowed the straightforward determination of the density of surface nucleation sites on glass powders using differential scanning calorimetry data obtained under different thermal conditions.

In references,^{11,12} we proposed and tested a new method to evaluate the chemical homogeneity of glasses based on statistical analyses of the volume distribution of crystals developed through thermal treatments. The method is based on the fact that each volume element of a piece of glass that is subjected to proper thermal treatment should contain a certain number of crystals, which is dictated by the chemical composition of the glass. We performed numerical simulations to interpret the experimental results obtained for some glasses, which demonstrate that this new method is adequate for determining the degree and scale of heterogeneity in glasses that display internal crystallization.

All these methods (and several others) were used by our team to unveil some details of the intricate crystallization processes and aided in the development of some types of glass-ceramics, described below.

Glass-Ceramics

Our research work on the fundamentals of glass crystallization phenomena described in Part I¹ substantially facilitated the development or improvement of a selection of interesting glass-ceramics (GC), which were described in several articles.^{13–50} These papers covered new glass-ceramics derived from blast furnaces and steel-making slags (hard materials for architecture and construction); sintered glass-ceramics that emulate expensive stones, such as marble and granite; the first large-grain, highly crystalline optically transparent glass-ceramic; and a number of bioactive glass-ceramics. The

studies on glass-ceramics have been carried out by former students and postdocs: Oscar Peitl, Eduardo Ferreira, Catia Fredericci, Valmor Mastelaro, Paulo Soares, Thiana Bertier, Viviane Soares, Mariana Villas-Boas, and other collaborators.

Transparent glass-ceramics (TGC) are useful for some commercial uses and a large number of potential high-tech applications in optics and photonics. However, the vast majority of such materials have extremely small (nanosized) crystals and a low-to-moderate volume fraction crystallized, ranging from approximately 0.1% (PTRG) to 70% (cooktops), which often limits their properties and the scope of their applications. Two main factors assure transparency in some glass-ceramics: Their crystal size is much smaller than the wavelength of light, and the difference between the refractive indices of the glass matrix and crystal phase is small. With former PhD student Thiana Bertier and Vladimir Fokin, we started a research project in 2005 aiming at a TGC with a large crystal size and high crystallized volume fraction (>90%)!

We developed^{17,18} a new type of TGC that has a large (micrometric) grain size and very high crystallized volume fraction, which reached up to 97%. The high transparency results from simultaneous variations of the glass matrix and crystal compositions during crystallization, which considerably decreases the difference between the respective refractive indices; this phenomenon prevails regardless of crystal size. Preliminary tests of their optical properties indicated that this new family of TGC could be further developed by doping with transition metals and rare earths.

We reviewed¹⁹ some of the outstanding commercial applications of glass-ceramics and commented a number of exciting new types that are being currently developed. We showed that plenty is already known about glass-ceramic technology, but many challenges in CG research and development remain, such as the search for new compositions and microstructures; other, more potent nucleating agents; and new or improved crystallization processes. Unexpected applications will most likely surface requiring a new combination of material properties. The wide range of potential properties of CGs, due to the ability to design their composition, thermal treatment, and resulting microstructure, combined with the flexibility of high-speed hot glass forming, will ensure the continued growth of glass-ceramic technology.

Residual Stresses in Glass-Ceramics

A current research topic in our laboratory refers to theoretical estimates and experimental determinations (using the NMR, micro-indentation, and XRD methods) of the residual stress fields around crystals in glass-ceramics. These stresses may, in principle, have a significant effect on the overall mechanical performance of ceramic composites, which include glass-ceramics. With the invaluable help of the former postdocs Francisco Serbena, Valmor Mastelaro, and Viviane Soares, and of the external collaborator Josef Zwanziger, we have published some original papers on this particular subject.^{22–28}

Interested readers may begin with a recent review paper that is summarized below.

We demonstrated that internal residual stresses always arise in glass-ceramics upon cooling from the crystallization temperature.²⁸ These stresses are due to the mismatch in thermal expansion and in the elastic behavior of the crystalline and glassy phases and can range from a few MPa to the GPa range! Therefore, the mechanical properties of glass-ceramics likely depend not only on their composition and microstructure but also on the type (tension or compression) and magnitude of these residual stresses. In this work, we critically reviewed the most commonly used theoretical models concerning residual stresses in glass-ceramics and glass-matrix composites, considering the effects of crystallized volume fraction, crystal shape, and thermal expansion anisotropy. We also discussed most of the reported measurements of residual stresses in these dual-phase materials using different techniques, such as X-ray diffraction, nuclear magnetic resonance, Raman and fluorescence spectroscopy, and indentation testing. The available models and experimental results regarding spontaneous microcracking due to residual stresses were also discussed. Finally, guidelines for future work were suggested.

Photo-Thermo-Refractive Glass

Since 2005, our research group has been working on the very complex crystallization process of so-called photo-thermo-refractive (PTR) “glass,” which, in fact, is a partially crystallized, optically transparent glass-ceramic that is commercialized by some companies in the USA and Russia. PTR glass is an Na_2O – K_2O – ZnO – Al_2O_3 – SiO_2 optical glass that also contains

fluorine, a small amount of bromine, and dopants that yield photosensitivity in the UV range. NaF nanocrystals crystallize in PTR glass after UV exposure followed by thermal treatment, resulting in a permanent refractive index change that allows phase holograms to be permanently recorded in the glass interior. PTR glass was invented 60 years ago. Optical elements based on PTR glass have been produced in the past decade and are being used in special laser systems. Yet, a detailed mechanism for crystallization is largely unknown. These studies began during my sabbatical at Leon Glebov's group at the University of Central Florida, Orlando. Jointly with Larissa Glebova and former postdocs Julien Lumeau and Guilherme Souza, and Vladimir Fokin, we have published some papers on this particular material, and others are in progress.^{29–36}

Because both the solubility and composition of the parent glass determine the supersaturation and thus the thermodynamic driving force for crystallization, one of our papers³⁴ reported the solubility of NaF in PTR glass by estimating the equilibrium volume fraction of crystallized NaF as a function of temperature. Both the temperature above which all NaF originally contained in the parent glass remains dissolved and the temperature below which all NaF originally present could crystallize were also measured. A redesign of the thermal processing parameters and of the composition of PTR glass could be performed based on the results presented to improve the optical elements of this glass.

In another study,³⁶ we explored only the thermally activated transformations in UV-unexposed glass and showed that bromine decreases the solubility of NaF, that is, bromine increases the supersaturation of NaF, thus increasing the thermodynamic driving force for crystallization. This feature decreases the maximum volume fraction of crystallized NaF with decreasing bromine content in the parent glass. The evolution of the glass transition temperature, T_g , with increasing isothermal treatment time, revealed a minimum resulting from the interplay of two concurrent processes: the liquid–liquid phase separation that lowers the T_g and the Br-controlled NaF crystallization that raises the T_g . In glasses with lower bromine content, fewer and larger crystals appeared, and surface-initiated crystallization dominated. A surface layer of F-depleted glass possessed permanent residual macro-stresses, which cannot be alleviated by annealing.

Further detailed studies should be directed toward obtaining quantitative results from the kinetics of

crystal nucleation and growth of NaF crystalline particles (and other optically active particles) in this glass, especially how these particles are affected and controlled by the amount of UV exposure.

Bioactive GC

One strategy to improve the mechanical performance of bioactive glasses in load-bearing implant devices has been to crystallize them with a desirable microstructure, that is, to develop designed bio-glass-ceramics. With the initial help of and incentive from Larry Hench (*G. W. Morey* awardee and inventor of Bioglass[®], MoSi, Rolla, MO), our group has invented a new, highly bioactive glass-ceramic named Biosilicate[®] (VitroVita, São Carlos, SP, Brazil), that has already been patented and licensed to a company (Vitrovita). We revisit some of our articles on bioactive glass-ceramics below.^{37–50}

In the first study,³⁷ glasses with a chemical composition between $1\text{Na}_2\text{O}-2\text{CaO}-3\text{SiO}_2$ ($1\text{N}_2\text{C}3\text{S}$) and $1.5\text{Na}_2\text{O}-1.5\text{CaO}-3\text{SiO}_2$, containing 0, 2, 4, and 6wt % P_2O_5 , were crystallized to several volume percentages through thermal treatments, ranging from 550 to 700°C. These glasses and glass-ceramics were incubated in a simulated body fluid solution (SBF-K9, which is close to human plasma) for different amounts of time. Fourier transform infrared spectroscopy (FTIR) was used to determine the rate of hydroxycarbonate apatite (HCA) formation. Crystallization decreased the kinetics of HCA formation but did not inhibit the development of an HCA layer, even in fully crystallized glass-ceramics. The onset time for HCA crystallization varied from 8 h for a glass containing 6wt% P_2O_5 to 35 h for a fully crystallized $1.07\text{Na}_2\text{O}-2\text{CaO}-3\text{SiO}_2$ ceramic. The HCA layer formation of these compositions in *in vitro* tests occurred much faster than in commercial bioactive materials, such as synthetic hydroxyapatite ceramic, A/W glass-ceramic, Ceravital[®] German patent #2,326,100 (1973), and Bioverit[®] (Vitron, Jena, Germany), for which the typical onset time was at least 7 days. Both FTIR and inductive coupled plasma studies confirmed the formation of an apatite layer, thereby indicating bioactivity in the $1\text{N}_2\text{C}3\text{S}$ crystal phase. X-ray diffraction experiments showed that phosphorus ions remained in a solid solution in the crystal phase. An apatite-like compound only appeared when the specimens underwent very long additional thermal treatments. The bioactivity of the commercial materials is

based on the apatite crystal phase, whereas the high level of bioactivity in this new generation of glass-ceramics is attained due to the combination of two mechanisms acting simultaneously: facile release from the glass-ceramic structure of a nonphosphate bioactive crystal phase ($1\text{N}_2\text{C}3\text{S}$) and of phosphorus ions in solid solution, which promotes faster HCA layer formation similar to 45S5 Bioglass[®].

Next³⁸ we evaluated the effect of our highly bioactive, fully crystallized glass-ceramic (Biosilicate[®]) on various key parameters of *in vitro* osteogenesis. Osteogenic cells were obtained by the enzymatic digestion of newborn rat calvarial bone and were then grown both on Biosilicate[®] disks and on control bioactive glass surfaces (Biosilicate[®] parent glass and Bioglass[®] 45S5) for up to 17 days. All materials developed an apatite layer in simulated body fluid after 24 h. Additionally, as early as 12 h under culture conditions and in the absence of cells, all surfaces developed a layer of silica gel that was gradually covered by amorphous calcium phosphate deposits, which remained amorphous for up to 72 h. During the proliferative phase of the osteogenic cultures, the majority of cells exhibited disassembly of the actin cytoskeleton, whereas by day 5, the reassembly of actin stress fibers took place only in areas of cell multilayering. Although no significant differences were detected in terms of the total protein content and of the alkaline phosphatase activity at days 11 and 17, Biosilicate[®] supported significantly larger areas of calcified matrix at day 17. These results indicated that the full crystallization of bioactive glasses at a range of compositions in the $\text{P}_2\text{O}_5\text{-Na}_2\text{O-CaO-SiO}_2$ system may enhance *in vitro* bone-like tissue formation in an osteogenic cell culture system.

The aims of the next study⁴⁰ were to evaluate the efficacy of a bioactive glass-ceramic (Biosilicate[®]) and of a commercial bioactive glass (Biogran[®], MoSi, Rolla, MO) when placed in dental sockets to support the alveolar ridge and when used for the osseointegration of Ti implants. Six dogs had their low premolars extracted, and the sockets were implanted with either Biosilicate[®] or Biogran[®] particles, or were left untreated. After the extractions, measurements of the width and height of the alveolar ridge were taken. After 12 weeks, a new surgery was performed to obtain the final ridge measurements and to bilaterally insert three Ti implants into both the biomaterial-implanted and control sites. Eight weeks post-Ti implant placement, block biopsies were processed for histological and histomorphometric

analysis. The percentages of bone-implant contact (BIC), of mineralized bone area between threads (BABT), and of mineralized bone area within the mirror area (BAMA) were determined. The presence of either Biosilicate[®] or Biogran[®] particles preserved the alveolar ridge height without affecting its width. No significant differences were detected among Biosilicate[®], Biogran[®], and the nonimplanted group regarding the BIC, BAMA, and BABT values. The results of that study indicated that filling dental sockets with either Biosilicate[®] or Biogran[®] particles preserves the alveolar bone ridge height and allows for the osseointegration of Ti implants.

We have also conducted a comparative clinical study⁴⁴ to evaluate the Biosilicate[®] glass-ceramic (1–20 µm particles) in treating dentine hypersensitivity (DH). Volunteers (n = 120 patients; 230 teeth) received the following treatments: G1-Sensodyne[®], G2-SensiKill[®], G3-Biosilicate[®] incorporated into a 1% water-free gel, and G4-Biosilicate[®] mixed with distilled water at a 1:10 ratio. G1 and G3 were applied at home daily for 30 days; G2 and G4 were applied once a week by a dentist (four applications). A visual analogue scale (VAS) was employed to evaluate the level of pain in each quadrant in one sensitive tooth as a baseline, performed weekly during treatment and again during a 6-month follow-up period. Dentine hypersensitivity values were analyzed using Kruskal–Wallis/Dunn tests. All products were efficient in reducing DH after 4 weeks. Among the four materials tested, Biosilicate[®] mixed with distilled water had the best clinical performance and provided the fastest treatment for reducing pain associated with DH. Low DH scores were maintained during the 6-month follow-up period. We concluded that this novel bioactive glass-ceramic may be an efficient treatment for DH.

Yet another study⁴⁵ was carried out to investigate the response of bone to our P₂O₅-Na₂O-CaO-SiO₂ Biosilicate[®]. Although a previous study had demonstrated positive effects of Biosilicate[®] on *in vitro* bone-like matrix formation, its *in vivo* effect had not yet been studied. Male Wistar rats (n = 40) with tibial defects were used. Four experimental groups were designed to compare this novel biomaterial to a gold-standard bioactive material (Bioglass[®] 45S5) and to unfilled defects and intact controls. A three-point bending test was performed 20 days after the surgical procedure, in addition to histomorphometric analysis in two regions of interest: the cortical bone and the medullary canal into

which the particulate biomaterial was implanted. The biomechanical test revealed a significant increase in the maximum load at failure and in the stiffness for the Biosilicate[®] group (versus control defects), whose values were similar to those for uninjured bones. There were no differences in the cortical bone parameters among groups with bone defects, but a great deal of woven bone was present and surrounded both the Biosilicate[®] and Bioglass[®] 45S5 particulates. Although both bioactive materials supported significantly higher bone formation, Biosilicate[®] was superior to Bioglass[®] 45S5 in certain histomorphometric parameters (i.e., bone volume and number of osteoblasts). Regarding bone resorption, the Biosilicate[®] group possessed a significantly greater number of osteoclasts per unit of tissue area than did the defect and intact controls, despite the nonsignificant difference in the osteoclastic surface as a percentage of the bone surface. This study revealed that Biosilicate[®] has good bone-forming and bone-bonding properties.

A review paper⁴² summarizes the history of Biosilicate[®]. After decades of research with bioactive glasses and glass-ceramics, Biosilicate[®] is the result of natural evolution and has a similar bioactivity index to all other bioactive glasses, but far superior mechanical properties. Biosilicate[®] is almost fully crystalline and exhibits much higher bioactivity than all currently commercially available bioactive glass-ceramics. Due to its special characteristics, Biosilicate[®] has been successfully tested for several medical and dental applications, which are thoroughly discussed in this review.

Crystals in Glass

Finally, in an effort to register at least a sample of the 30–40 thousand micrographs that we collected during these studies, we selected approximately 50 of these in a book entitled *Cristais em Vidros – Ciência e Arte*.⁵¹ The English version (*Crystals in Glass – A Hidden Beauty*) will be published by Wiley-Blackwell in 2013. An example of such micrographs is shown below in Figure 1.

Summary

The research described above resulted in the development and improvement of some interesting glass-

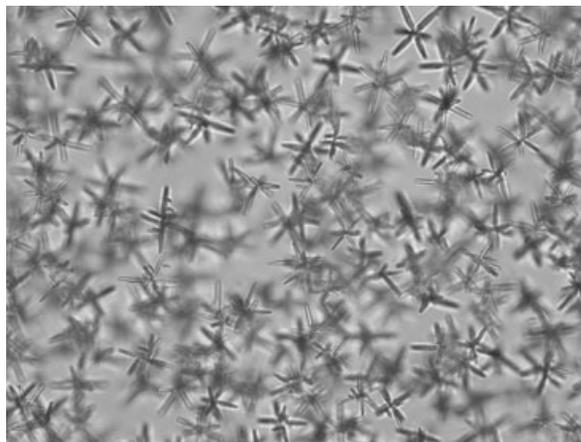


Fig. 1. Star-like NaF crystals in the interior of a PTR glass-ceramic.⁵¹ The crystals do not touch each other due to the F-depleted diffusion layer around them (micrograph taken by Guilherme P. Souza).

ceramics. This progress is validated by the fact that Brazilian and international glass industries, which produce glass-ceramics, have been using our scientific articles and consultancy work for the development, improvement, or fine characterization of their products.

Although it would be impossible to prepare all potential glass compositions with the 80 “friendly” elements of the periodic table,⁵² one can anticipate several surprises in the future, with a plethora of new glasses and glass-ceramics with exotic properties and applications. Glass-ceramics possess an impressive range of properties and thrilling potential applications, and indeed have a *bright future*. Thus, there is still much to study further in both the scientific and technological aspects of glass crystallization and glass-ceramics!

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References

1. E. D. Zanotto, “Glass Crystallization Research - A 36-Year Retrospective. Part I, Fundamental Studies,” *Int. J. Appl. Glass Sci.*, 4 [2] (2013). Submitted.
2. E. D. Zanotto and P. F. James, “A Theoretical and Experimental Assessment of Systematic-Errors in Nucleation Experiments,” *J. Non-Cryst. Solids*, 124 [1] 86–90 (1990).
3. V. M. Fokin, E. D. Zanotto, N. Y. Yuritsyn, and J. W. P. Schmelzer, “Homogenous Crystal Nucleation in Silicate Glasses,” *J. Non-Cryst. Solids*, 352 [26–27] 2681–2714 (2006).
4. E. D. Zanotto, “Theoretical Assessment of Systematic Errors in Volume Fraction Determinations by Microscopy Methods,” *J. Mater. Res.*, 13 [8] 2045–2047 (1998).
5. V. M. Fokin, E. D. Zanotto, and J. W. P. Schmelzer, “Method to Estimate Crystal/Liquid Surface Energy by Dissolution of Subcritical Nuclei,” *J. Non-Cryst. Solids*, 278 [1–3] 24–34 (2000).
6. A. Celli and E. D. Zanotto, “Polymer Crystallization: Fold Surface Free Energy Determination by Different Thermal Analysis Techniques,” *Thermochim. Acta*, 269 [19] 1–199 (1995).
7. E. B. Ferreira, M. L. F. Nascimento, H. Stoppa, and E. D. Zanotto, “Methods to Estimate the Number of Surface Nucleation Sites on Glass Particles,” *Phys. Chem. Glasses Eur. J. Glass Sci. Technol. B*, 49 [2] 81–89 (2008).
8. V. M. Fokin, A. A. Cabral, R. M. C. V. Reis, M. L. F. Nascimento, and E. D. Zanotto, “Critical Assessment of DTA-DSC Methods for the Study of Nucleation Kinetics in Glasses,” *J. Non-Cryst. Solids*, 356 [6–8] 358–367 (2010).
9. A. A. Cabral, V. M. Fokin, and E. D. Zanotto, “On the Determination of Nucleation Rates in Glasses by Nonisothermal Methods,” *J. Am. Ceram. Soc.*, 93 [9] 2438–2440 (2010).
10. E. B. Ferreira, V. Lopez-Richard, E. D. Zanotto, and G. E. Marques, “Analytical Model for Heterogeneous Crystallization Kinetics of Spherical Glass Particles,” *J. Am. Ceram. Soc.*, 92 [11] 2616–2618 (2009).
11. L. A. Souza, M. L. G. Leite, E. D. Zanotto, and M. O. Prado, “Crystallization Statistics. A New Tool to Evaluate Glass Homogeneity,” *J. Non-Cryst. Solids*, 351 [46–48] 3579–3586 (2005).
12. J. Lumeau, A. Sinitskii, L. Glebova, and E. D. Zanotto, “Method to Assess the Homogeneity of Partially Crystallized Glasses: Application to a Photo-Thermo-Refractive Glass,” *J. Non-Cryst. Solids*, 355 [34–36] 1760–1768 (2009).
13. E. B. Ferreira, E. D. Zanotto, and L. A. M. Scudeller, “Glass-Ceramic from Steelmaking Slag,” *Quim. Nova*, 25 [5] 731–735 (2002).
14. E. B. Ferreira, E. D. Zanotto, and L. A. M. Scudeller, “Glass and Glass-Ceramic from Basic Oxygen Furnace (BOF) Slag,” *Glass Sci. Technol.*, 75 [2] 75–86 (2002).
15. C. Fredericci, E. D. Zanotto, and E. C. Ziemath, “Crystallization Mechanism and Properties of a Blast Furnace Slag Glass,” *J. Non-Cryst. Solids*, 273 [1–3] 64–75 (2000).
16. C. A. C. Feitosa, V. R. Mastelaro, A. R. Zanatta, A. C. Hernandez, and E. D. Zanotto, “Crystallization, Texture and Second-Harmonic Generation in TiO₂-BaO-B₂O₃ Glasses,” *Opt. Mater.*, 28 [8–9] 935–943 (2006).
17. T. B. da Cunha *et al.*, “Mechanical Properties and Impact Resistance of a New Transparent Glass-Ceramic,” *Adv. Eng. Mater.*, 9 [3] 191–196 (2007).
18. T. Berthier, V. M. Fokin, and E. D. Zanotto, “New Large Grain, Highly Crystalline, Transparent Glass-Ceramics,” *J. Non-Cryst. Solids*, 354 [15–16] 1721–1730 (2008).

19. E. D. Zanotto, "A Bright Future for Glass-Ceramics," *Am. Ceram. Soc. Bull.*, 89 [8] 19–27 (2010).
20. S. Buchner *et al.*, "Mechanical and Tribological Properties of a Sintered Glass-Ceramic Compared to Granite and Porcelainized Stoneware," *Wear*, 271, [5–6] 875–880 (2011).
21. V. O. Soares, G. R. Paula, O. Peitl, and E. D. Zanotto, "Effect of Ion Exchange on the Sinter-Crystallisation of Low Expansion $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ Glass-Ceramics," *Glass Technol. Eur. J. Glass Sci. Technol. A*, 5 [2] 50–54 (2011).
22. V. R. Mastelaro and E. D. Zanotto, "Residual Stresses in a Soda-Lime-Silica Glass-Ceramic," *J. Non-Cryst. Solids*, 194 [3] 297–304 (1996).
23. V. R. Mastelaro and E. D. Zanotto, "Anisotropic Residual Stresses in Partially Crystallized $\text{Li}_2\text{O}_2\text{SiO}_2$ Glass-Ceramics," *J. Non-Cryst. Solids*, 247 [7] 9–86 (1999).
24. J. W. Zwanziger *et al.*, "Residual Internal Stress in Partially Crystallized Photo-Thermo-Refractive Glass: Evaluation by Nuclear Magnetic Resonance Spectroscopy and First Principles Calculations," *J. Appl. Phys.*, 99 [8] 083511 (2006).
25. H. Pinto *et al.*, "Surface and Bulk Residual Stresses in $\text{Li}_2\text{O-2SiO}_2$ Glass-Ceramics," *J. Non-Cryst. Solids*, 353 [24–25] 2307–2317 (2007).
26. F. C. Serbena, G. P. Souza, E. D. Zanotto, J. Lumeau, L. Glebova, and L. Glebov, "Internal Residual Stresses in Partially Crystallized Photo-Thermo-Refractive Glass," *J. Am. Ceram. Soc.*, 94 [3] 671–674 (2011).
27. F. C. Serbena, V. O. Soares, O. Peitl, H. Pinto, R. Muccillo, and E. D. Zanotto, "Internal Residual Stresses in Sintered and Commercial Low Expansion $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ Glass-Ceramics," *J. Am. Ceram. Soc.*, 94 [4] 1206–1214 (2011).
28. F. C. Serbena and E. D. Zanotto, "Internal Residual Stresses in Glass-Ceramics: A Review," *J. Non-Cryst. Solids*, 358 [6–7] 975–984 (2012).
29. J. Lumeau, A. Sinitskii, L. Glebova, L. Glebov, and E. D. Zanotto, "Spontaneous and Photo-Induced Crystallisation of Photo-Thermo-Refractive Glass," *Phys. Chem. Glasses Eur. J. Glass Sci. Technol. B*, 48 [4] 281–284 (2007).
30. L. Glebova, J. Lumeau, M. Klimov, E. D. Zanotto, and L. B. Glebov, "Role of Bromine on the Thermal and Optical Properties of Photo-Thermo-Refractive Glass," *J. Non-Cryst. Solids*, 354 [2–9] 456–461 (2008).
31. J. Lumeau, L. Glebova, G. P. Souza, E. D. Zanotto, and L. B. Glebov, "Effect of Cooling on the Optical Properties and Crystallization of UV-Exposed Photo-Thermo-Refractive Glass," *J. Non-Cryst. Solids*, 354 [42–44] 4730–4736 (2008).
32. J. Lumeau, L. Glebova, V. Golubkov, and E. D. Zanotto, "Origin of Crystallization-Induced Refractive Index Changes in Photo-Thermo-Refractive Glass," *Opt. Mater.*, 32 [1] 139–146 (2009).
33. G. P. Souza, V. M. Fokin, E. D. Zanotto, J. Lumeau, L. Glebova, and L. B. Glebov, "Micro and Nanostructures in Partially Crystallised Photothermorefractive Glass," *Phys. Chem. Glasses Eur. J. Glass Sci. Technol. B*, 50 [5] 311–320 (2009).
34. V. M. Fokin, G. P. Souza, E. D. Zanotto, J. Lumeau, L. Glebova, and L. B. Glebov, "Sodium Fluoride Solubility and Crystallization in Photo-Thermo-Refractive Glass," *J. Am. Ceram. Soc.*, 93 [3] 716–721 (2010).
35. G. P. Souza *et al.*, "Liquid-Liquid Phase Separation in Photo-Thermo-Refractive Glass," *J. Am. Ceram. Soc.*, 94 [1] 86–91 (2011).
36. G. P. Souza *et al.*, "Effect of Bromine on NaF Crystallization in Photo-Thermo-Refractive Glass," *J. Am. Ceram. Soc.*, 94 [9] 2906–2911 (2011).
37. O. Peitl, E. D. Zanotto, and L. L. Hench, "Highly Bioactive $\text{P}_2\text{O}_5\text{-Na}_2\text{O-CaO-SiO}_2$ Glass-Ceramics," *J. Non-Cryst. Solids*, 292 [1–3] 115–126 (2001).
38. J. Moura *et al.*, "In Vitro Osteogenesis on a Highly Bioactive Glass-Ceramic (Biosilicate)," *J. Biomed. Mater. Res., Part A*, 82A [3] 545–557 (2007).
39. R. N. Granito, D. A. Ribeiro, A. C. M. Renno, and E. D. Zanotto, "Effects of Biosilicate and Bioglass 45S5 on Tibial Bone Consolidation on Rats: A Biomechanical and a Histological Study," *J. Mater. Sci. Mater. Med.*, 20 [12] 2521–2526 (2009).
40. V. M. Roriz, A. L. Rosa, O. Peitl, D. Zanotto, H. Panzeri, and P. T. Oliveira, "Efficacy of a Bioactive Glass-Ceramic (Biosilicate) in the Maintenance of Alveolar Ridges and in Osseointegration of Titanium Implants," *Clin. Oral Implant Res.*, 21 [2] 148–155 (2010).
41. A. C. M. Renno, P. A. McDonnell, M. C. Crovace, E. D. Zanotto, and L. Laakso, "Effect of 830 nm Laser Phototherapy on Osteoblasts Grown In Vitro on Biosilicate Scaffolds," *Photo Med. Laser Surg.*, 28 [1] 131–133 (2010).
42. R. L. Siqueira and E. D. Zanotto, "Biosilicate: Historical of a Highly Bioactive Brazilian Glass-Ceramic," *Quim. Nova*, 34 [7] 1231–1241 (2011).
43. P. S. Bossini *et al.*, "Biosilicate and Low-Level Laser Therapy Improve Bone Repair in Osteoporotic Rats," *J. Tissue Eng. Regen. Med.*, 5 [3] 229–237 (2011).
44. C. Tirapelli, H. Panzeri, E. H. G. Lara, R. G. Soares, O. Peitl-Filho, and E. D. Zanotto, "The Effect of a Novel Crystallised Bioactive Glass-Ceramic Powder on Dentine Hypersensitivity: A Long-Term Clinical Study," *J. Oral Rehabil.*, 38 [4] 253–262 (2011).
45. R. N. Granito *et al.*, "In Vivo Biological Performance of a Novel Highly Bioactive Glass-Ceramic (Biosilicate): A Biomechanical and Histomorphometric Study in Rat Tibial Defects," *J. Biomed. Mater. Res. Part B: Appl. Biomater.*, 97B [1] 139–147 (2011).
46. C. H. G. Martins, T. C. Carvalho, M. G. M. Souza, C. Ravagnani, O. Peitl, and E. D. Zanotto, "Assessment of Antimicrobial Effect of Biosilicate (R) Against Anaerobic, Microaerophilic and Facultative Anaerobic Microorganisms," *J. Mater. Sci. Mater. Med.*, 22 [6] 1439–1446 (2011).
47. R. L. Siqueira, O. Peitl, and E. D. Zanotto, "Gel-Derived $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ Bioactive Powders: Synthesis and in Vitro Bioactivity," *Mater. Sci. Eng. C-Mater Biol. Appl.*, 31 [5] 983–991 (2011).
48. R. L. Siqueira and E. D. Zanotto, "Facile Route to Obtain a Highly Bioactive $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ Crystalline Powder," *Mater. Sci. Eng. C Mater Biol. Appl.*, 31 [8] 1791–1799 (2011).
49. O. Peitl, E. D. Zanotto, F. C. Serbena, and L. L. Hench, "Compositional and Microstructural Design of Highly Bioactive $\text{P}_2\text{O}_5\text{-Na}_2\text{O-CaO-SiO}_2$ Glass-Ceramics," *Acta Biomater.*, 8 [1] 321–332 (2012).
50. P. Soares, C. A. H. Laurindo, R. D. Torres, N. K. Kuromoto, O. Peitl-Filho, and E. D. Zanotto, "Effect of a Bioactive Glass-Ceramic on the Apatite Nucleation on Titanium Modified by Micro-Arc Oxidation," *Surf. Coat. Technol.*, 206 [22] 4601–4605 (2012).
51. E. D. Zanotto, *Cristais Em Vidros – Ciência e Arte*, EdUFSCar, Brazil, 124 pgs. (2011). ["Crystals in Glass – A Hidden Beauty" to be launched by Wiley- Blackwell/ ACerS in June 2013].
52. E. D. Zanotto and F. A. B. Coutinho, "How Many Non-Crystalline Solids Can Be Made From All the Elements of the Periodic Table?" *J. Non-Cryst. Solids*, 347 [1–3] 285–288 (2004).