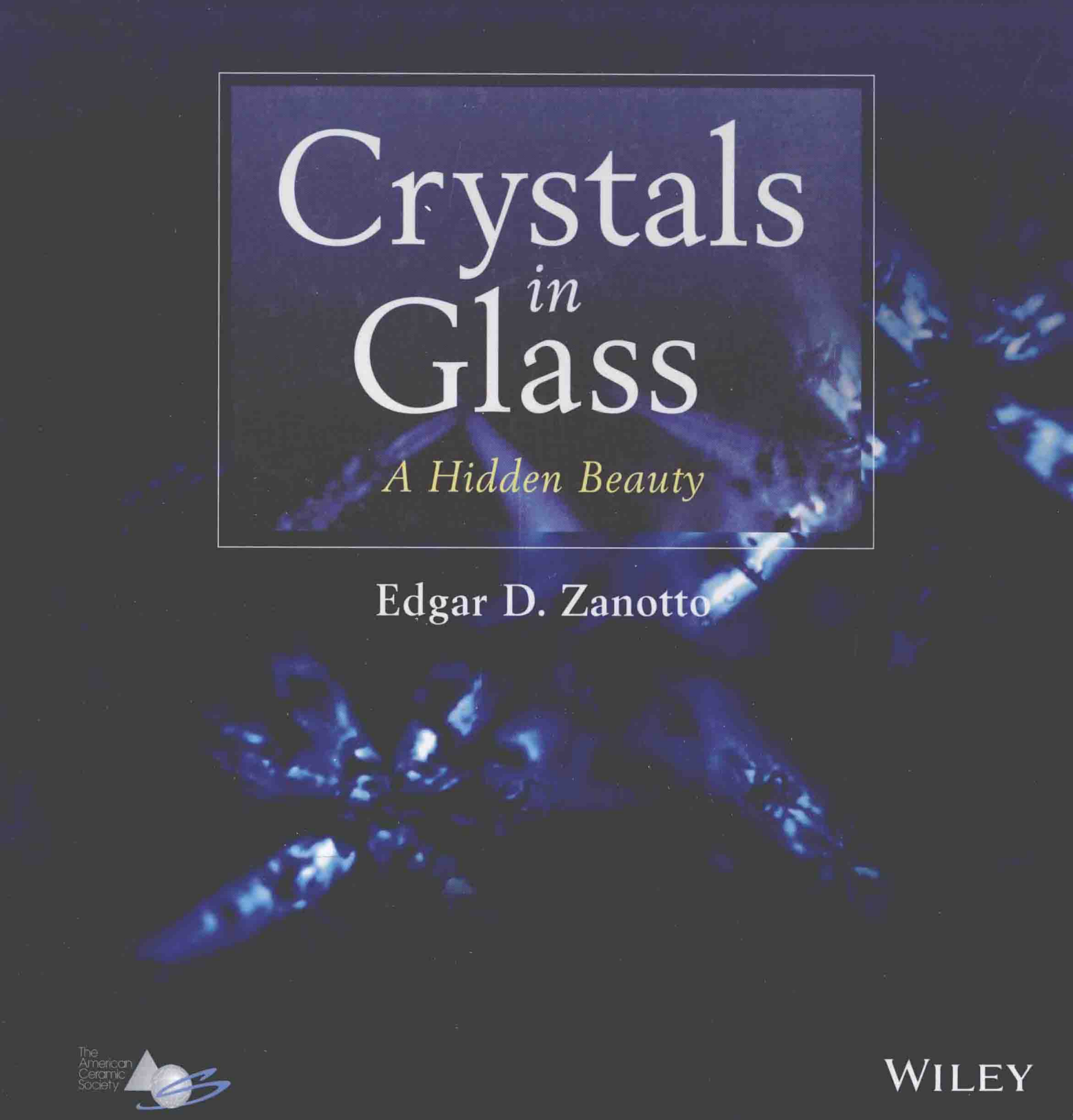

# Crystals in Glass

## *A Hidden Beauty*

Edgar D. Zanotto

The American Ceramic Society

WILEY

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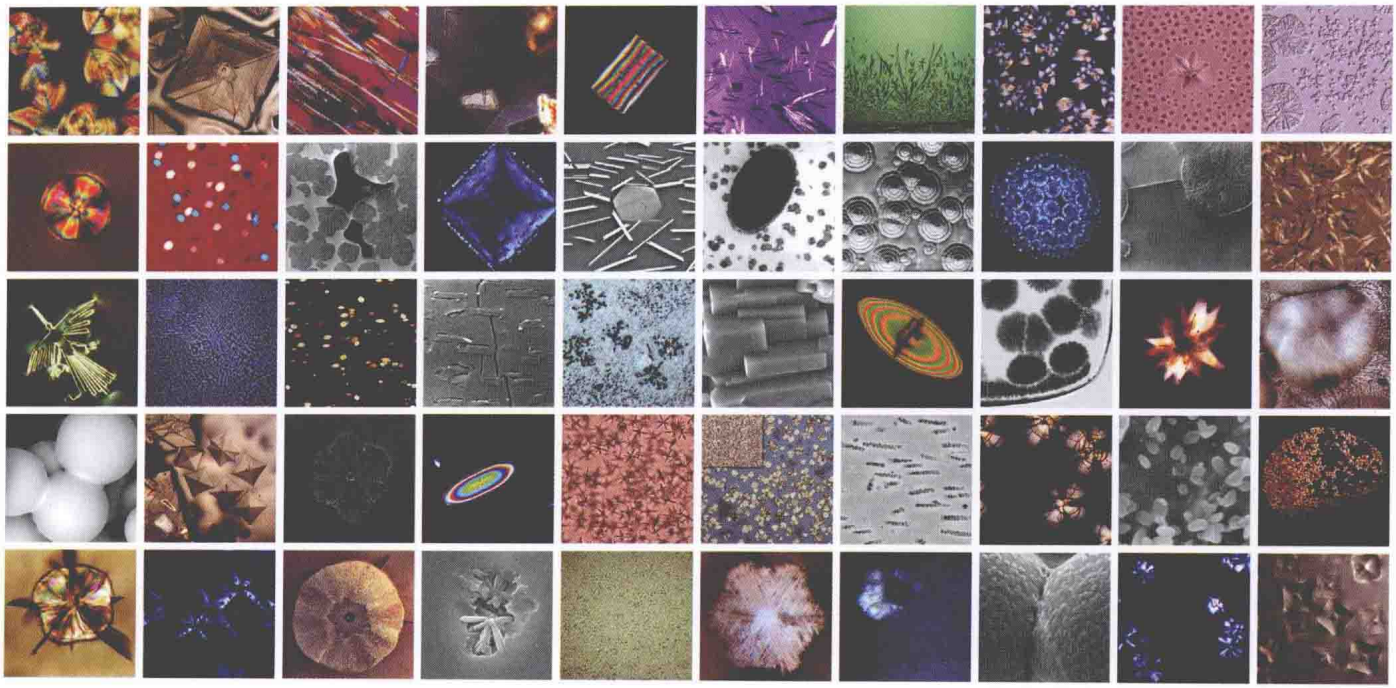
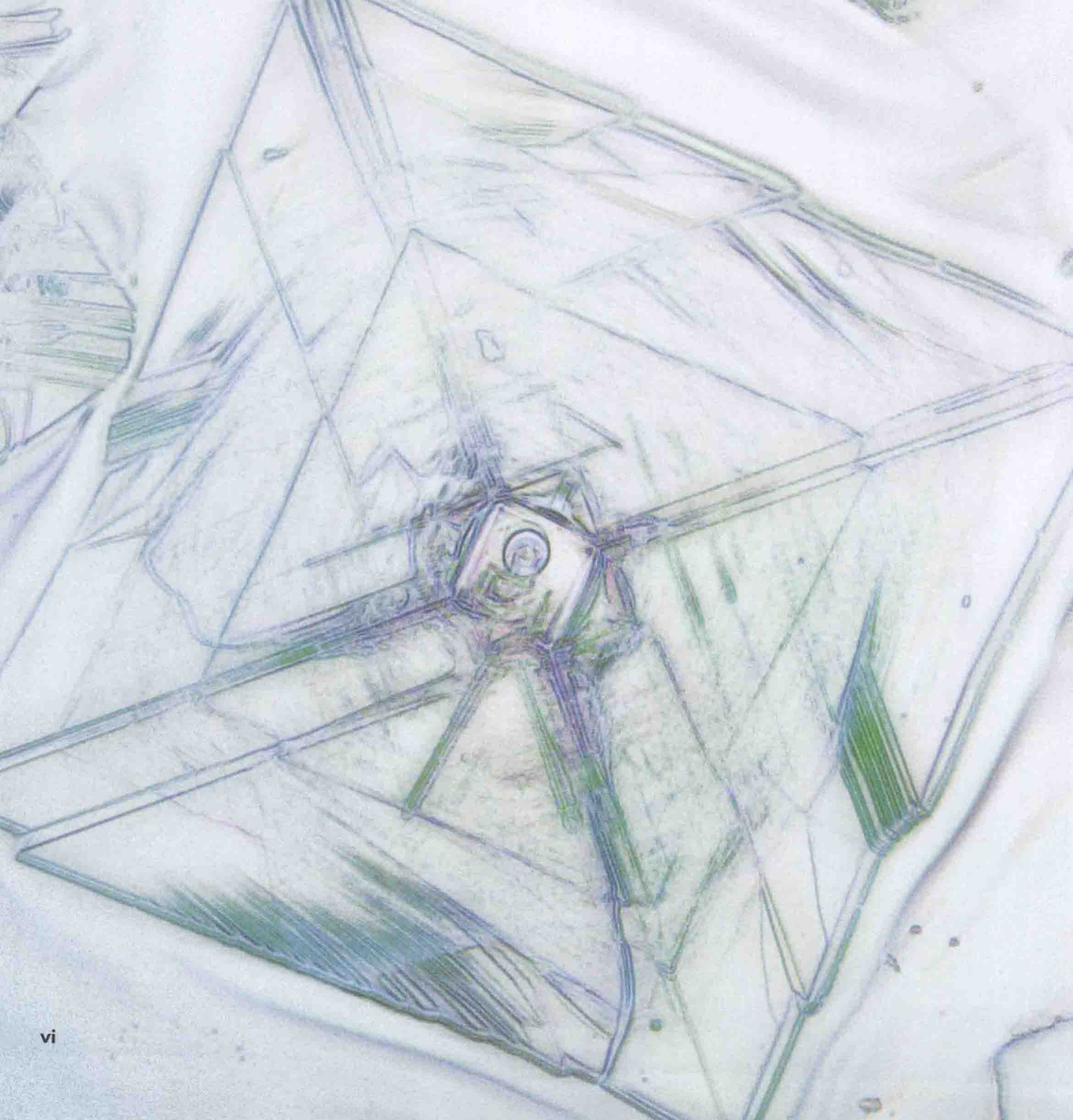
# CRYSTALS IN GLASS



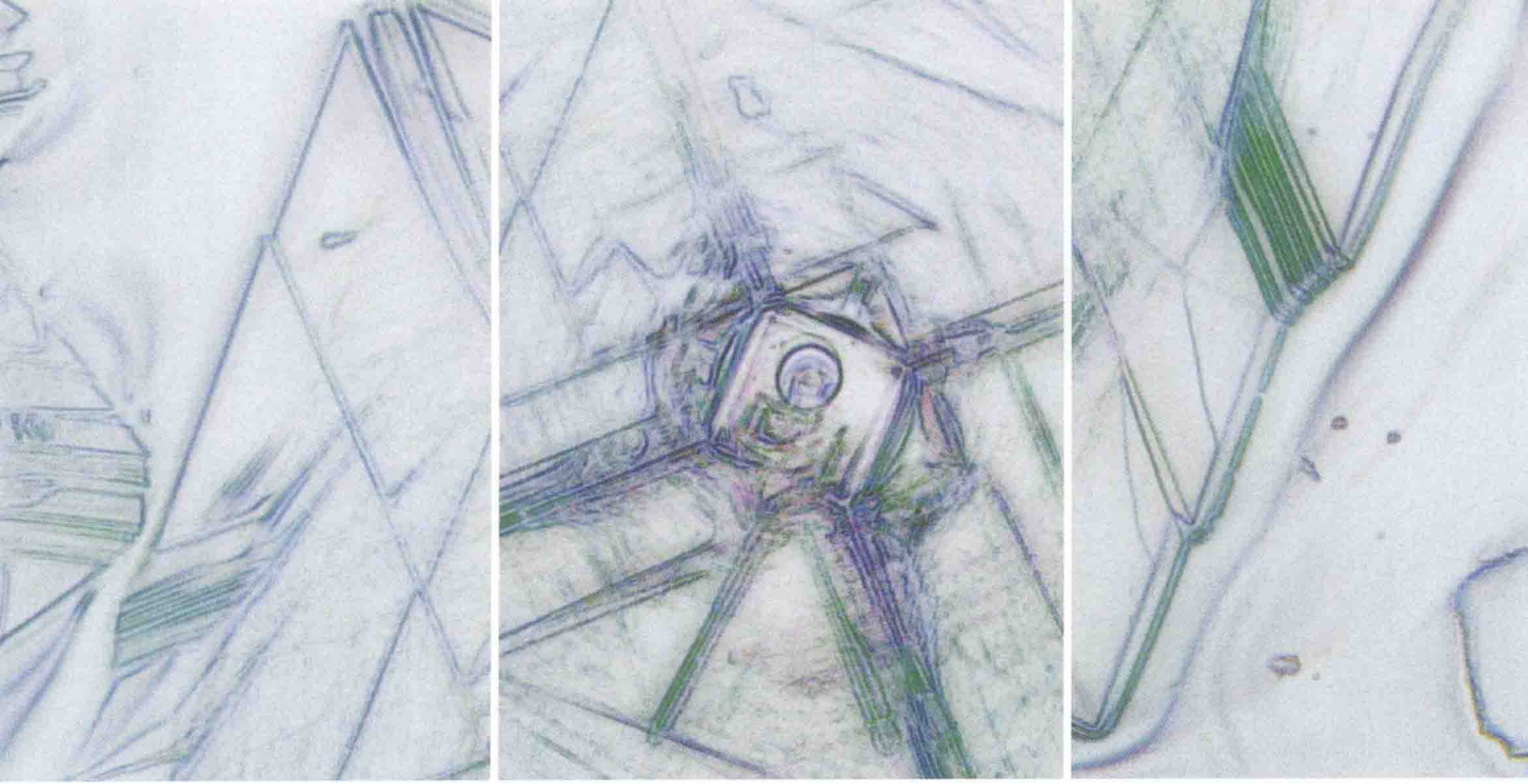


# FOREWORD

**Many years ago,** when I first had the opportunity to see his mind at work, Edgar Zanotto offered me a living preview of this book. By then, in the mid-1990s, he was already famous as the father of glass science in Brazil, and within my department his entrepreneurship was viewed as a model. His first advisor, Aldo Craievich, was a highly respected former member of our faculty, and their work was often cited as a fine example of physical insight. Nonetheless, Zanotto and I had only known each other superficially until our jobs at the State of São Paulo funding agency (FAPESP) brought us together.

After that, besides sharing an office, we frequently rode the same car between São Carlos and São Paulo. In the office, in restaurants, or on the highway, he gave accounts of ideas that were being cast into papers or patents and explained the hows and whys of glassy materials. From devitrification in glass bottles to the courtyard effects, our conversations covered countless aspects of glass science and technology. They were, nonetheless, almost always focused on ongoing projects or past experiences. Inspirations were rarely discussed, let alone dreams. And so it was that the concept of a book was never brought up, although all of Edgar's friends knew that even a partial sum of his achievements would add up to an attractive volume.

The book is now ready, much more radiant than one could have imagined in those days. Part of the glow comes from the micrographs chosen by the author to illustrate his story. Each bit of reasoning in the book is supported by a picture, but the micrographs are more than simple illustrations: they constitute the conducting thread that drives our imagination from the first to the last page, from the *Drosophila melanogaster* of glass crystallization to bubble nucleation in bioactive glass-ceramics. This thread takes us on a ride through roads lined with murals, as it were, covering the elements of the science developed in Zanotto's LaMaV. The pictures spur the reader's imagination, and a few of them, such as the eloquent lessons on competition depicted on pages 39 and 85, are lectures in nutshells.



Edgar Zanotto is one of the world's top experts on crystallization in glasses, and his experience is imprinted on every page. The historical account in the Introduction and the motto at the façade of the LaMaV, photographed on page xiii, are likely to motivate young researchers, but the author's skill is most clearly revealed in the selection of micrographs and in the accompanying texts. The latter are gems on their own. Aware that a book written in pictorial language would be poorly served by prolix paragraphs, Zanotto has crafted sentences with the proper dose of information to heighten our scientific appetite.

The result is not a textbook, a tutorial, or a science treatise. Nor is it a coffee-table book, meant to please the eyes and sooth the spirit. To be sure, the visual component of the book is outstanding, so beautiful are the pictures between its covers. Yet, Zanotto's brainchild is above all a source of inspiration. In each picture, we find challenges that have compelled humanity since the dawn of civilization: "Crack my code, relate me to other elements of your universe, and take control of my dynamics," the crystallites seem to be crying out. Each plate invites us to read the facing text and to meditate about the big and the small, about symmetries and broken symmetries, and about time and space. Most readers will therefore find it difficult to skip rapidly through the pages.

Different readers have different styles. Linear sequencing displeases many of us. We enjoy moving back and forth between pages to let our attention be caught at haphazard. To all adepts of this unorthodox reading procedure, "Crystals in Glasses: a Hidden Beauty" comes close to perfection. Although loosely divided into five sections, the pictures and the descriptions are independent and can be examined in any order.

This method will be called kaleidoscopic by partisans of orderly reading. Kaleidoscopes, however, are but disappointing combinations of symmetry with randomness, perhaps designed to let children know that chance and shattering are parts of life. Here, Edgar Zanotto reinvents the kaleidoscope. With 50 examples, he shows that little pieces of glass hide not only beauty but also lessons and challenges that may lift our spirit and consequently strengthen our belief in the meaning of life.

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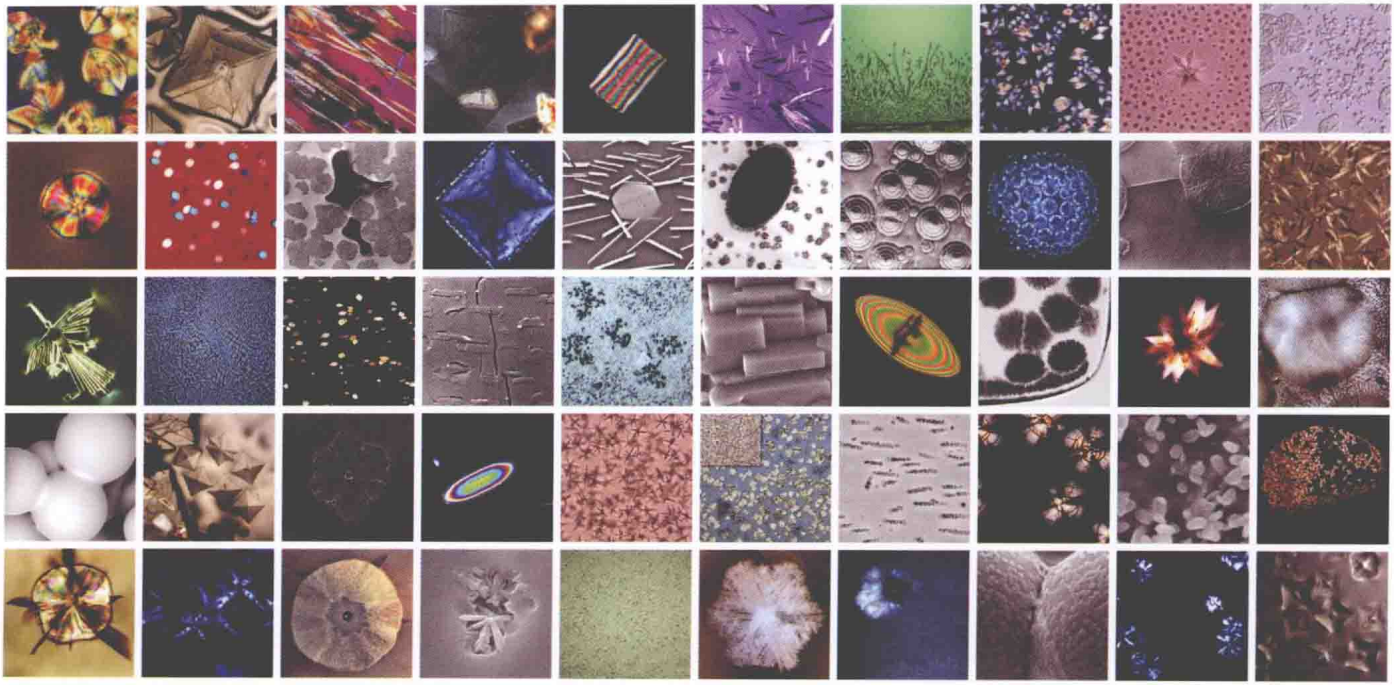


# INTRODUCTION

## 36 Years of Research and Discoveries about Glass Crystallization

**With this technically** biased introduction, I hope to make the scientist readership aware of and persuade it to browse through some of our discoveries on glass crystallization published over the past 3.5 decades, while cordially inviting the layman to skip the text below and go directly to the photographic exhibition.

The Vitreous Materials Lab (LaMaV), Department of Materials Engineering (DEMa), at the Federal University of São Carlos (UFSCar) was founded on December 15, 1976, when I, then a young materials engineer, was hired by the UFSCar. To celebrate LaMaV's 36th anniversary, I briefly review the most significant scientific work carried out by our team and collaborators and present a selected collection of extraordinary micrographs (photographs taken under an optical or electron microscope) that not only reveal some intricate secrets about glass crystallization but also display the hidden beauty of microscopic crystals!

LaMaV's research work focuses mainly on fundamental studies of glass crystallization kinetics and mechanisms, which are key to the successful development of *glass-ceramics* (CGs). In this field, LaMaV's contributions are one of the world's outstanding.

CGs are polycrystalline materials produced by the controlled crystallization of certain glasses that possess unusual properties. Natural CGs, such as some types of obsidian, have "always" existed. But in 1953, Stanley D. Stookey, of Corning Glass Works, USA, made a serendipitous discovery when a furnace containing a piece of lithium disilicate glass with precipitated silver particles (meant to form a permanent photographic image) was accidentally overheated to about 900 °C, although

Stookey actually intended to anneal the glass at 600 °C. Instead of a pool of melted glass, however, the astonished Stookey observed a white material whose shape remained unchanged. Then he accidentally dropped the piece on the floor, but it did not shatter, contrary to what one would normally expect of a piece of glass! Stookey had unwittingly created the first synthetic CG, called Fotoceram. In their famous book on CGs, Wolfram Höland and George Beall state "*knowledge of the literature, good observation skills, and deductive reasoning were clearly evident in allowing the chance events to bear fruit.*"

CGs are produced by the controlled crystallization of certain glasses—generally induced by nucleating additives—in contrast to spontaneous surface crystallization, which is normally undesirable in glass manufacturing. CGs always contain a residual glassy phase and one or more embedded crystalline phases, with widely varying crystallinity ranging from 0.5% to 99.5%, most frequently 30–70%. Controlled crystallization yields an array of materials with very interesting, sometimes unusual, combinations of properties. The main advantages of CGs are that, in principle, they can be mass-produced by any glass-forming technique, their nano- or microstructure can be designed for a given application, they have zero or very low porosity, and the desired properties can be combined, including very low thermal expansion coefficient with transparency in the visible wavelength range, for instance, for cooking ware, or very high strength and toughness with translucency, biocompatibility, chemical durability, and relatively low hardness, for instance, for dental applications. For all these reasons, CGs have found numerous applications, from domestic products to high-tech areas, such as large telescopic mirrors, substrates of hard disks, and artificial bones and teeth.

The main results of LaMaV's research are summarized in the following paragraphs. LaMaV's research on phase transformation kinetics started in 1977, with E. D. Zanotto's MSc dissertation and continued during his PhD studies. Due to the strong controversy in the international literature of the late 1970s, he and his supervisors (Aldo Craievich and the late Peter James) performed detailed studies to establish the effects of *amorphous phase separation* (APS) on the kinetics of crystal nucleation and growth in glasses. Their work demonstrated unequivocally that the compositional shift caused by APS is the main factor responsible for the enhancement of nucleation and growth rates, with the interfaces between the amorphous phases playing a very minor role. They have published seven original papers on this specific topic.

Next, with the invaluable help of the late Mike Weinberg, the LaMaV team spent many years testing the validity of the Classical Nucleation Theory (*CNT*) in different ways with various glasses (a task that has not yet been concluded!). In their first study, they used a constant value of surface energy, $\sigma_\infty$, and assumed that the activation enthalpy for atomic jumps at the liquid/crystal nucleus interface ($\Delta G_\eta$) was similar to that of viscous flow ($\Delta G_d$), a procedure also adopted by


other authors. A large discrepancy was found between the experimental nucleation rates and the theoretical values, although the temperature dependence was well described by theory. In a subsequent study, an original and more rigorous approach was proposed and tested using the transient times for nucleation instead of the viscosity to calculate $\Delta G_d$. Again, significant discrepancies were found in the magnitude and temperature dependence of the nucleation rates of four glasses. Finally, the most severe assumption of CNT was tested, that is, the postulation that the interfacial energy $\sigma$ does not depend on nucleus size: $\sigma = \sigma_\infty$. In this case, the Tolman expression for $\sigma(r)$ was incorporated into CNT. An impressive agreement between theory and experiment was found. However, $\sigma(r)$ could not be determined independently in all the tests and had to be fitted by forcing the temperature of the experimental and theoretical maxima to coincide. For a definitive test, an independent determination of $\sigma(r)$ will be necessary. Several scientists around the world, including LaMaV's closest collaborators, Juern Schmelzer and Vlad Fokin, are still pursuing this objective. The above-described

research and some related studies are original and are described in 13 papers.

The possibility of *metastable phase* precipitation in the early stages of crystallization is of fundamental importance because, in principle, if confirmed, it could explain the frequent discrepancy between CNT predictions and experimental nucleation rates. With the invaluable help of Mike Weinberg, Pierre Lucas and a former student, Paulo Soares, LaMaV's research group established that metastable phases do in fact appear in some glasses, but do not explain the discrepancies in CNT. The group has published eight papers on this particular phenomenon.

The LaMaV group then conducted the first rigorous test of the General Theory of Transformation Kinetics (the *JMAK theory*), with no adjustable parameters, for both homogeneous and heterogeneous nucleation. They demonstrated that, provided proper precautions are taken in the determination of the nucleation and growth rates, the JMAK theory offers an exceptionally accurate description of the time evolution of overall crystallization of stoichiometric glasses. The group has published four papers on this particular subject.

Next, a series of 10 papers discussed the following question: *Why is the thermodynamically unfavorable mechanism—homogeneous nucleation—observed in some glasses?* One of the team's first studies demonstrated that a simple rule of thumb can be used to distinguish the nucleation mechanism in several stoichiometric glass-forming systems. For compositions having glass-transition temperatures ($T_g/T_f < 0.6$), the temperatures of maximum nucleation rates, $T_{max}$, are higher than $T_g$. These systems show homogeneous (internal) nucleation on a laboratory timescale. On the other hand, for the majority of glasses, the typical values of reduced $T_g$ are high ($T_g/T_f > 0.6$), the calculated (by CNT) values of $T_{max}$ are significantly lower than $T_g$, and only heterogeneous nucleation is observed. No exceptions to this remarkable trend have been reported so far. In a second study, the LaMaV team demonstrated that the failure to detect homogeneous nucleation in the other family of glasses (for which $T_{max} < T_g$) is due to one or both of the following causes: excessively low nucleation or growth rates, or long induction times for nucleation in the temperature ranges in which the predicted steady-state homogeneous nucleation rates are expected to be significant.

Later, in collaboration with visiting scientists Eberhard Mueller and Klaus Heide, the LaMaV team showed that the mass densities of glasses that nucleate homogeneously are similar to those of their crystal phases, while those of glasses which only nucleate heterogeneously are quite different from the densities of the equivalent crystals. In the final part of this research, they unambiguously demonstrated that glasses presenting homogeneous nucleation have both cation and anion arrangements that are very similar to their corresponding crystal phases, while the structures of the glass and crystal phases of compositions that only nucleate heterogeneously are quite distinct. Several other revealing papers have been published about the relationships between the molecular *structure* and *nucleation* mechanisms, with

the invaluable participation of Joe Zwanziger, Valmor Mastelaro, Jose Schneider, and other researchers. Some articles have been published on this issue.

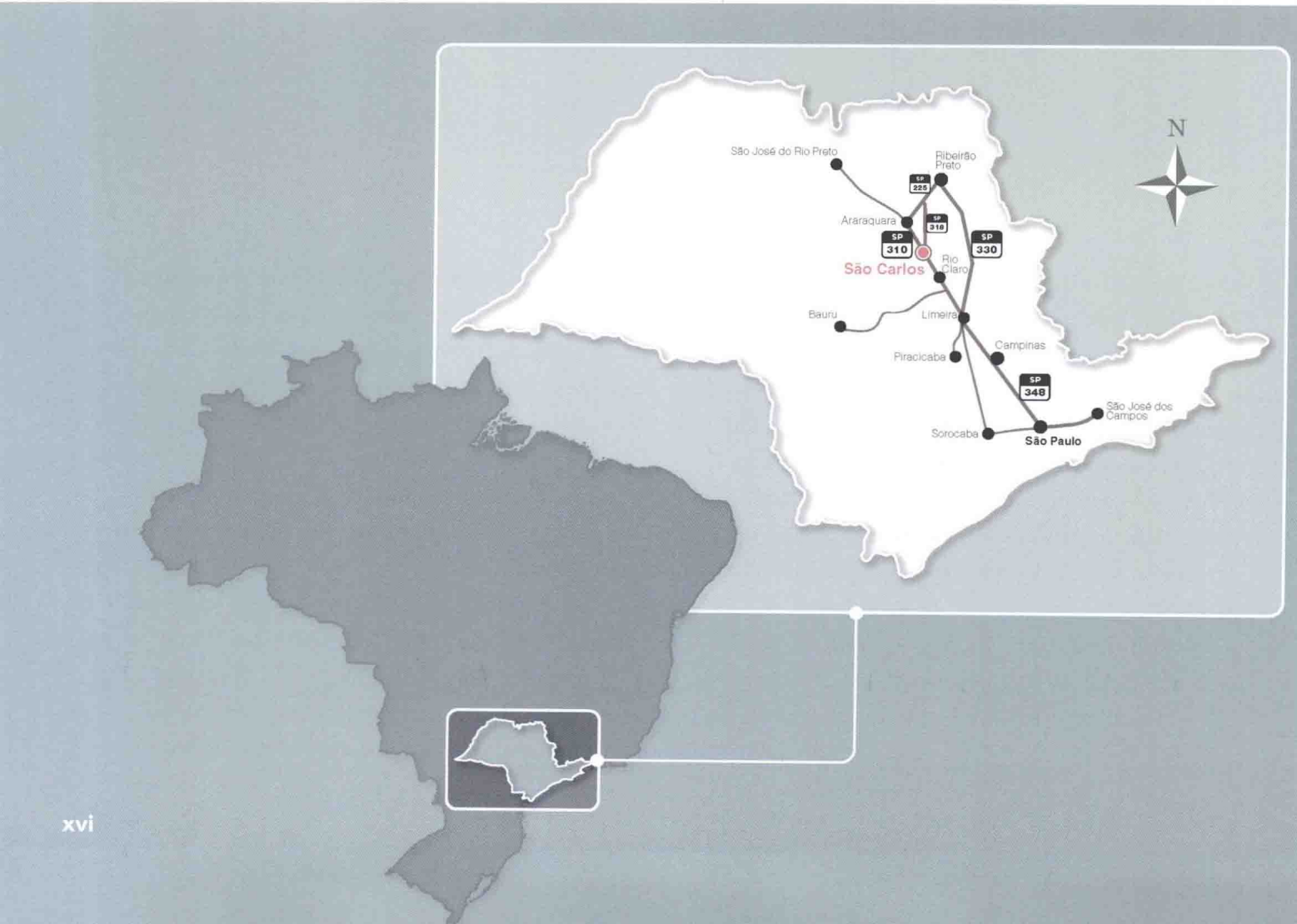
Two papers discussed *stereological errors* associated with experimental measurements of nucleation and overall crystallization rates in glasses, which are often neglected in the literature. In some situations, such errors can be quite significant (>50%) and must be taken into account for a proper analysis of crystallization kinetics.

Next, LaMaV's research group, with the invaluable help of former postdoc Nora Mora and visiting scientists Ralf Mueller and Vlad Fokin, focused on the establishment of the mechanisms and kinetics of crystal nucleation and growth on glass *surfaces*. A few papers published by this team triggered international interest in the subject. In those articles, they concluded that, in most cases, surface nucleation is immeasurably fast and is triggered by a certain number of impurity sites, which depend on the degree of surface perfection and cleanliness. The high surface nucleation rates are due to the low interfacial energy between contaminants and nuclei existing on the surface. The resulting papers were of fundamental importance for the development of commercial sintered CGs, which will be described later in this review. The group has published 14 papers on this subject.

Based on their accumulated experience with surface crystallization, the group started to develop

systematic research into glass *sintering* with *concurrent crystallization*. This is an issue of keen interest because all sorts of complex-shaped monolithic glasses and CGs can be produced by controlled sintering of powdered glasses. The key problem here is to privilege viscous flow sintering before surface crystallization takes over and causes densification. With the energy and scientific focus of former postdocs Miguel Prado, Catia Fredericci, Vivi Soares, and Anne Barbosa, PhD student Rapha Reis, and a few other collaborators, they produced quite conclusive and practical results on this subject, which are summarized in 11 papers. Of special interest is the last paper in the series, which proposes and successfully tests a useful sinterability parameter.

LaMaV's research work also included incursions into the complex field of *polymer crystallization*, with five papers published in leading journals. Research studies have also been developed by the LaMaV group on



the fundamental issue of *glass-forming ability* of different liquid systems. Several original findings are described in seven papers authored with former postdocs Alu Cabral and Edu Ferreira. Of special interest are their systematic studies, which revealed the simple parameters (combinations of DSC characteristic temperatures) that best describe glass stability against devitrification (on heating) and its correlation with glass-forming ability (on cooling).

Some other interesting work on the fundamentals of nucleation and growth in undercooled liquids has been carried out with the collaboration of Vlad Fokin and under the competent guidance of theoretician Juern Schmelzer. This team also worked on a new discovery regarding the fact that the crystals in some (supposedly) stoichiometric glasses, such as $1Na_2O.2CaO.3SiO_2$, show very significant departures from stoichiometry. They called these crystals mutant and the related phenomenon the courtyard effect.

More recently, with the help of former postdoc Marcio Nascimento's data-mining skills, the LaMaV team began to examine in detail the diffusion processes that control crystal nucleation, crystal growth, and viscous flow and the controversy regarding the possible breakdown of the Stokes–Einstein (SE) equation at sufficiently low temperatures. The first five papers published on this subject indicated no breakdown of the SE equation from the *liquidus* down to $T \sim 1.2\ T_g$, but at deeper undercoolings below $1.2\ T_g$, there are clear signs of such a breakdown, which has been attributed to spatially heterogeneous dynamics.

A current research topic refers to theoretical estimates and experimental determinations (by NMR, microindentation, and XRD methods) of the *residual stress* fields around crystalline particles in CGs. Here, the significant contributions of Valmor Mastelaro, Oscar Peitl, Joe Zwanziger, and Fran Serbena were fundamental. These stresses sometimes have an enormous impact on the overall mechanical performance of ceramic composites, which include CGs. Five papers have been published on this particular subject.

In 2005, the group started to collaborate with Leon Glebov, Julien Lumeau, and their team at the Creol, University of Central Florida, USA, and have since been working on the very complex crystallization process of the so-called *photo-thermo-refractive* glass (PTRG). Former postdoc Gui Souza and visiting scientist Vlad Fokin have been fundamental in this endeavor. PTRG is a partially crystallized, optical transparent glass that undergoes controlled nanocrystallization after UV exposure followed by double heat treatment. Six papers about PTRG have been published and others are on the way.

Last but not the least, with the key presence of Edu Ferreira, Alu Cabral, Rapha Reis, and Vlad Fokin, LaMaV's team has also been working on the critical assessment of nonisothermal (DSC and DTA) methods to infer crystal nucleation and growth kinetics. Three papers published in the period 2009/2010 clearly indicate that such methods can sometimes be used to probe glass crystallization parameters, but extreme care is required to obtain reliable results. The team concluded