Low Thermal Expansion Glass Ceramics

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Editors

Low Thermal Expansion Glass Ceramics

Second Edition

With 156 Figures
and 21 Tables

Springer

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Foreword

This book, entitled *Low Thermal Expansion Glass Ceramics*, is one of a series reporting on research and development activities on products and processes conducted by the Schott AG.

The scientifically founded development of new products and technical processes has traditionally been of vital importance at Schott and has always been performed on a scale determined by the prospects for application of our special glasses. The scale has increased enormously since the reconstruction of the Schott Glaswerke in Mainz. The range of expert knowledge required for that could never have been supplied by Schott alone. It is also a tradition in our company to cultivate collaboration with customers, universities, and research institutes. Publications in numerous technical journals, which since 1969 we have edited to a regular timeplan as *Forschungsberichte* – 'research reports' – formed the basis of this cooperation. They contain up-to-date information on various topics for the expert but are not suited as survey material for those whose standpoint is more remote.

This is the point where we would like to place our series, to stimulate the exchange of thoughts, so that we can consider from different points of view the possibilities offered by those incredibly versatile materials, glass and glass ceramics. We would like to show scientists and engineers, interested customers, and friends and employees of our firm the knowledge that has been won through our research and development at Schott in cooperation with the users of our materials.

The results documented in the volumes of the Schott Series are of course oriented to the tasks and targets of a company. We believe it will become quite clear that here readers can nevertheless – or rather for that reason – find demanding challenges for applied research, the development of process engineering, and the characterization of measurement practice. Besides realizability, the profitability of solutions to customers' problems always plays a decisive role.

The first comprehensive presentation of research findings after the reconstruction of the factory in Mainz was edited by Prof. Dr. Dr. h.c. Erich Schott in 1959. It was entitled *Beiträge zur angewandten Glasforschung* – 'contributions to applied glass research' (Wissenschaftliche Verlagsgesellschaft m.b.H., Stuttgart 1959). Since then, there has been an extraordinary worldwide increase in the application of glass and glass ceramic materials. Glass fibers and components manufactured from them for use in lighting and traffic engineering or in telecommunications, high-purity and highly homogeneous glasses for masks and projection lenses in electronics, or glass ceramics with zero expansion in astronomy and in household appliance technology are only some examples. In many of these fields Schott has made essential contributions.

Due to the breadth and complexity of the field in which Schott is active, many volumes are needed to describe the company's research and development results. Otherwise it would be impossible to do full justice to the results of fundamental research work and technological development needed for product development. Furthermore, it is necessary to give an appropriate description of the methods of measurement and analysis needed for the development and manufacture of new products.

Apart from *Low Thermal Expansion Glass Ceramics*, five volumes, entitled *The Properties of Optical Glass*, *Thin Films on Glass*, *Analysis of the Composition and Structure of Glass and Glass Ceramics*, *Electrochemistry of Glasses and Glass Melts, Including Glass Electrodes*, and *Mathematical Simulation in Glass Technology* have already been published. Another two volumes, entitled *Surface Analysis of Glasses and Glass Ceramics, and Coatings* and *Fibre Optics and Glass Integrated Optics*, are in preparation and will be published in the next few years. Glasses for various applications in industry and science and their properties are being considered, and melting and processing technologies described.

With the presentation – in part detailed – of the work required for the development of successful products, Schott employees are giving all their interested colleagues who work in the field of science and technology an insight into the special experiences and successes in material science, material development, and the application of materials at Schott. Contributions from scientists and engineers who work in university and other research institutes and who played an essential role in Schott developments complete the survey of what has been achieved. At the same time such results show the need for the collaboration mentioned above.

In all the volumes of the series the fundamental issues from chemistry, physics, and engineering are dealt with, or at least works are cited that enable or assist the reader to work his or her way into the topics treated. We see this as indispensable because, with the series, Schott has a further goal in view. We aim to provide all future business partners from branches of industry where glasses and glass ceramics have not been applied so far with knowledge they can use in cooperation with Schott. Furthermore, the series may serve to fill gaps between the basic knowledge imparted by material science and the product descriptions published by Schott. Those who have already done business with our company may find the survey of fundamentals useful in extending collaboration to further business areas.

To make each volume sufficiently intelligible, the necessary fundamentals from chemistry, physics, and engineering are described or referred to via citations.We see this as the best way to enable all our potential business partners who are not already familiar with glass and glass ceramics to compare these materials with alternatives on a thoroughly scientific basis. We hope that this will lead to intensive technical discussions and collaborations on new fields of applications of our materials and products, to our mutual advantage.

Every volume of the Schott Series will begin with a chapter providing a general idea of the current problems, results, and trends relating to the subjects treated. These introductory chapters and the reviews of the basic principles are intended to be useful for all those who are dealing for the first time with the special properties of glass and glass ceramic materials and their surface treatment in engineering, science, and education.

Many of our German clients are accustomed to reading scientific and technical publications in English, and most of our foreign customers have a better knowledge of English than of the German language. It was, therefore, mandatory to publish the Schott Series in English.

The publication of the Schott Series has been substantially supported by Springer. We would like to express our special thanks to Dr. H.K.V. Lotsch and Dr. H.J. Kölsch for advice and assistance in this project.

The investment of resources by Schott and its employees to produce the Schott Series is, as already stated, necessary for the interdisciplinary dialogue and collaboration that are traditional at Schott. A model we still find exemplary today of a fruitful dialogue between fundamental research, glass research, and glass manufacture was achieved in the collaboration of Ernst Abbe, Otto Schott, and Carl Zeiss. It resulted in the manufacture of optical microscopes that realized in practice the maximum theoretically achievable resolution. It was especially such experiences that shaped the formulation of the founding statute of the Carl Zeiss Foundation, and the initiative for the Schott Series is in accord with the commitment expressed in the founding statute “to promote methodical scientific studies”.

Mainz, March 2005

Dieter Krause
Vice President R & D (retd.)

Preface to the Second Edition

The second edition has been corrected and supplemented. Several additions have been made wherever it was necessary, with major changes in chapters 3 and 4. For their valuable advice and support in updating these chapters we are indebted to Dr. Peter Naß and Dr. Peter Hartmann.

In 2004, the Schott Group became an incorporated company (Schott AG). Former company names such as “Schott Glas” or “Jenaer Glaswerk” are sometimes used in this book for historical reasons.

We thank the authors for reading, correcting and updating their contributions, Mrs. Karin Langner-Bahmann for processing all the figures, and Mrs. Wiltrud Witan for revising the English. We also thank Springer for supporting this edition.

March 2005 Hans Bach, Dieter Krause

Preface

The main aim of the Schott Series volume *Low Thermal Expansion Glass Ceramics* is to describe research and development necessary to produce glass ceramics having low thermal expansion coefficients and to present some products manufactured at Schott, which are the results of a successful development. The book is conceived as a monograph. However, the individual chapters have been written by different or several authors, who are themselves active in the corresponding fields of research and development. Thus the reader is given direct access to the experience of these authors.

To give the reader a view of the extraordinary material "glass ceramic", the volume opens with a general survey of the development of glass ceramics and their important fields of application and the aims, limits, and the current state of new developments.

Schott has significantly contributed to the development and production technology of glass ceramics during the last four decades. The subsequent chapters treat in detail the scientific basis of glass ceramics, the special properties of glass ceramics to reach outstanding functionality in use, and the technology designed for the economic production of technical equipment at Schott. Results from two fields of application are presented where research and development have been particularly successful: from household appliances and from equipment for optics and astronomy. This presentation necessarily also includes a rough description of production methods and machines, whose design has been dictated by the processing parameters derived from basic research.

To obtain a basis for a deeper understanding of the problems encountered in the development and production of glass ceramics so that they can be considered as engineered materials, the reader is introduced in the first section of the second chapter to the special field of crystal chemistry and physics of high-quartz and keatite-type aluminosilicates. In this section it is explained why useful properties might be obtained based on certain types of solid solutions of these silicates. The development of a variety of those solid solutions appears to be possible, whose coefficient of thermal expansion and grain size distributions can be adapted to applications. Products consisting of these silicates can only be shaped economically if the forming methods of the conventional glass production are applicable prior to crystallization.

Further investigations are, therefore, necessary to decide whether this is possible or not. In the second and third sections of the second chapter, methods are described which allow us to determine the basic parameters for the production of a glass ceramic and the development of a glass ceramic based on lithium-alumino-silicate solid solution crystals.

The subsequent chapters, 3 and 4, are devoted to the description of the development and application of glass ceramics for household appliances and for optical instruments.

Chapter 3 reports on the special research and development that forms the basis of the production of the glass ceramic Ceran®. This glass ceramic has meanwhile become well-known worldwide since it is widely used for cooktops. It is also described how Ceran® is able to meet the requirements for functionality and appealing appearance in the kitchen.

The properties of other glass ceramic products have also been tailored to special household applications: the properties of the glass ceramic Robax® were adapted to its use as stove windows. Chemical strengthening of the surface of another glass ceramic used for cooktops can improve their functionality.

Chapter 4 is dedicated to the development and application of the glass ceramic Zerodur®. Several applications in optics are possible due to the unique properties of this material. The production of pieces made of this material for optical instruments with large dimensions has successfully been performed at Schott. In particular, pieces having very large dimensions (as they are used for very large telescopes) can be manufactured at Schott. The reader is informed about technologies and basic research and may well imagine that plenty of scientific and technological knowledge had to be acquired until the production of such materials and, particularly, casting and forming the products of large dimensions could be controlled. Chapter 4 closes with illustrations of the use of Zerodur® for special optical instruments and for mirrors with large dimensions for astronomy.

In Chaps. 3 and 4 the technologies are also described, which had to be adapted to the parameters to make upscaling of large dimensions possible in production. The finally chosen technologies for forming, nucleation, and the thermal treatment during nucleation and crystal growth guarantee both reproducibility of the required properties of the glass ceramics and the most economic production possible.

The properties of the glass ceramics and their varieties are also reported on. Additionally, methods of quality assurance are mentioned, which are necessary to grant the mechanical, thermal, and chemical properties and the demanded final shapes of the products. The considerable effort in the analysis of bulk material and surface analysis, which must be applied in basic research and development to study the appropriate parameters for nucleation and crystal growth, could not be covered by the present book. The reader is referred to the two volumes on analysis and surface analysis to appear in this series.

The results given in Chaps. 2, 3, and 4 inform the reader about how the findings of basic research determine the processing of glass ceramics. A close cooperation between scientists and engineers is imperative in developing the special technologies and suitable equipment and ensuring the most economic reproduction of the required properties of the different glass ceramics and glass ceramic components designed for different applications. Thus this volume contributes to filling the gap of knowledge about engineering which exists between the published results on the basics of glass ceramics and the catalogue data on glass ceramics provided by producers. The form of the presentation of both the results on the basics and the technology can, moreover, be useful for teaching.

In summary, all the information given in the present book exemplifies the successful transfer of results from basic science reported on in Chap. 2 into products and production processes via a fruitful cooperation between research, development, and technology, and, last but not least, our customers.

I would like to thank all the authors of this book for their steady and pleasing cooperation.

I have received further valuable help from many colleagues. For critical reading of the manuscript I thank in particular Dr. Hartmut Höness, Dipl.-Phys. Alfred Jacobsen, Dipl.-Phys. Hans Morian, Dr. Rudolf Müller, Dr. Peter Naß, Dr. Wolfgang Pannhorst, Dipl.-Ing. Norbert Reisert, Dr. Erich W. Rodek, and Dipl.-Ing. Hinnerk Schildt.

For their advice and help and converting technical drawings into figures appropriate for publication my thanks go to Dipl.-Ing. Heinrich Nilgens and Dipl.-Ing. Wolfgang Walch.

Additionally, I am indebted to several employees of Springer-Verlag, especially to Barbara S. Hellbarth-Busch and to Peter Straßer, production-editor, for helping us to overcome the difficulties involved in producing manuscripts ready for printing. I am thankful to Dr. Victoria Wicks for copy-editing this volume and Andy Ross for various advice. For their help in solving text processing problems I am indebted to Frank Holzwarth, also of Springer-Verlag and to Kurt Mattes, Heidelberg.

I am very grateful to Dipl.-Math. Sieglinde Quast-Stein, Schott Glaswerke, who, with her knowledge and experience provided substantial support in the implementation of the software guidelines supplied by Springer-Verlag.

I also thank Dipl.-Grafik-Designer Werner Paritschke, Mainz, for the creation of the numerous computer graphics needed to illustrate the texts.

I would especially like to thank Mrs. Angela Gamp-Paritschke, M. A., Schott Glaswerke, for translations from German into English, for the corrections of manuscripts submitted in English, and for her enthusiasm in performing all the hard work necessary to prepare manuscripts ready for printing.

September 1995 Hans Bach

Contents

1. Overview

Wolfgang Pannhorst

1.1 The Invention of Low Expansion Glass Ceramics

Glass ceramics are the result of two independent lines of research activities in the USA in the 1940s and 1950s which, when combined, opened up the view of a family of materials with a high potential for new applications. One route of research was performed at Corning Glass Works by Stookey who investigated the nucleation of glasses. While for a long time his research centered around photonucleation of opal and colored glasses with crystalline phase contents of less than 5%, he one day found accidentally that some of these photonucleated glasses can be transformed by an annealing process to highly crystalline materials with a very fine microstructure, i.e., with crystal sizes in the range of microns. In a further research effort he found that similar results may be obtained by using special additives, so-called nucleating agents, instead of the photonucleation process. His fundamental patent [1.1] discloses that TiO_2 acts as such a nucleating agent in a rather large number of glass systems.

The other route started with the discovery by *Hummel* in 1951 [1.2] that crystalline aggregates of β-eucryptite (Li_2O-Al_2O_3-$2SiO_2$) display a negative volume expansion. People immediately realized that this observation opens up the perspective of developing materials without any expansion in some temperature intervals, thus creating thermoshock resistant or dimensionally highly stable materials. As a consequence, an intensive research activity started to find out whether this observation is restricted to β-eucryptite alone or whether a whole family of materials can be defined, which in the following will be called high-quartz solid solution (h-quartz s.s.) crystals. Although at the beginning of these activities the intention was to produce sintered ceramics, the main field of research interest very quickly switched over to the development of glass ceramics when it became apparent that the Li_2O-Al_2O_3-SiO_2 materials family also belongs to those glass ceramic systems that can be nucleated very efficiently by TiO_2. The glass ceramic approach has two major advantages over the ceramic approach: (a) very fine-grained microstructures can be produced; (b) high-speed glass manufacturing processes can be used. The latter advantage is certainly off-set to some extent by the so-called ceramization process, an annealing process by which the original glass is transformed into the glass ceramic.

1.2 Basic Research

Since about 1960 many glass companies as well as glass research institutions have started research in the field of glass ceramics; their work mainly centered on the Li_2O-Al_2O_3-SiO_2 system (LAS). The investigations within the LAS system were directed into three areas: (a) solid solution formation in the h-quartz structure; (b) improvement of the efficiency of the nucleating agents; (c) stability field of the h-quartz s.s. crystals.

In the area of h-quartz s.s. formation the main results were as follows. The β-eucryptite composition is a special, stoichiometric one within a whole family of solid solution crystals which all can be derived from the h-quartz (SiO_2) crystal structure. Substituting Si^{4+} in the quartz structure by Al^{3+} may be achieved over a wide percentage range when charge compensation is admitted by either Li^+ [1.3–5], Mg^{2+} [1.6], or Zn^{2+} [1.5, 7]. While quartz shows a reversible phase transition at 573 °C from low to high quartz, the h-quartz structure is stable at room temperature when roughly more than 20 mol% of the SiO_2 is substituted by one of the pairs (Al_2O_3, Li_2O), (Al_2O_3, MgO), or (Al_2O_3, ZnO) [1.5]. These three coupled substitutions are possible up to approximately 50 wt% replacement of SiO_2. Finally, it was found [1.8, 9], within the substitutional field of 20–50 wt% of SiO_2 by one of the coupled pairs, that up to about 70 wt% of the remaining SiO_2 may be replaced by $AlPO_4$, still with the h-quartz s.s. crystal structure being the metastable phase which crystallizes first from glasses and which does not undergo any high–low transition when being cooled to room temperature.

Although these substitutions principally widen the field of chemical compositions, thus allowing not only optimization of the coefficient of thermal expansion (CTE) but also other important properties, the range of useful compositions is decreased by the fact that the substitutions influence the thermal expansion characteristics. Generally speaking, the $LiAlO_2$ substitution results in a strongly negative, the $ZnAl_2O_4$ substitution in a slightly negative, and the $MgAl_2O_4$ substitution in a strongly positive CTE, whereas the $AlPO_4$ substitution has only a small effect on the CTE.

Stookey discovered that TiO_2 acts as a very efficient nucleating agent in LAS-based glass ceramics, whereas *Tashiro* and *Wada* [1.10] found that ZrO_2 additions have a similar effect. Finally, *Sack* and *Scheidler* [1.11] showed that the utilization of both nucleating oxides has advantages, especially by lowering the temperature of the transformation of the base glass into the glass ceramic.

It would be desirable that the h-quartz s.s. phase with its excellent thermal expansion characteristics is stable up to high temperatures so that the material may be used in high temperature applications. Unfortunately, this is not the case with compositions that show the most promising property combinations for applications and whose main components lie in the field Li_2O-Al_2O_3-$n SiO_2$ with $5 < n < 7$. The h-quartz s.s. crystalline phase is a metastable phase which transforms into the keatite s.s. phase (for explanation see next paragraph) at temperatures between 800 and 950 °C depending on the time–temperature conditions. For applications in which service temperatures of 700 °C or more are to be expected during the life span of the product the choice of the compositions is constrained by the careful observation that the transformation of h-quartz s.s. to keatite s.s. occurs at high enough temperatures.

Keatite is the name of an SiO_2 modification which does not occur in nature but can be synthesized under hydrothermal conditions. As in quartz, solid solution formation is also possible in keatite. Well documented is the solid solution formation in the system Li_2O-Al_2O_3-SiO_2 (LAS), especially along the line Li_2O-Al_2O_3-$n SiO_2$, with n ranging from 4 to 10 [1.12]. The composition with $n = 4$, i.e., Li_2O-Al_2O_3-$4SiO_2$, is called β-spodumene, and in many papers this composition is seen as the starting point of the solid solution formation so that the phases which in this book will be called keatite s.s. phases are often also called β-spodumene s.s. phases.

The keatite s.s. phases in the LAS system are also very interesting phases in that respect as they show negative or only small positive thermal expansion characteristics. They may, therefore, also serve as materials with low expansion. Solid solution formation for keatite has not been investigated as systematically as that for h-quartz, probably because there are indications that the solid solution formation is much more restricted for keatite than for h-quartz. This information has been derived from the investigation of the phase transformation of some of the low expansion materials based on the h-quartz s.s. phase. During these transformations often formation of spinels ($MgAl_2O_4$ or $ZnAl_2O_4$) [1.13, 14] or cordierite ($2MgO$-$2Al_2O_3$-$5SiO_2$) [1.13, 15] is observed, indicating that the solid solution formation with ZnO or MgO replacing Li_2O is rather limited. Nevertheless, low-expansion glass ceramics based on keatite s.s. phases are of interest when either high service temperatures up to approximately 1100 °C or increased strength are important application requirements in addition to the low-expansion characteristics.

The development of the low-expansion glass ceramics is a commercially very successful part of a much broader effort to understand nucleation and crystal growth phenomena, on the one hand, and to develop products based on the glass ceramic approach on the other hand. These fields have, therefore, been the topics of many conferences and the accompanying proceeding volumes [1.16–19] as well as of several books [1.20–23].

1.3 Main Fields of Application

Product development mainly centered around the three product ideas cookware, range tops for kitchen stoves, and telescope mirror blanks.

Since the development of the heat-resistant borosilicate kitchen ware, glass makers have longed to develop cookware which may be used in all household situations, i.e., which can be stored in the refrigerator, placed onto the hot stove directly from the refrigerator, and used as attractive dishes on the table. With the low-expansion glass ceramic this vision could become reality. There were even two possible solutions. Based on the keatite glass ceramic a version which resembles porcelain was possible, while the h-quartz glass ceramics offered the possibility to produce a tinted, transparent variant, similar to the borosilicate kitchen ware. Both variants have been developed and launched to the market by Corning Inc. as well as by Schott. The two Corning brands, Pyroceram® for the white, opaque keatite glass ceramic and Vision® for the transparent h-quartz glass ceramic are still being sold, but both Schott products, Ceradur® (keatite glass ceramic) and Jena 2000® (h-quartz glass ceramic) have been withdrawn from the market after some time. Although the cookware withstands all situations where either high thermal gradients or thermal shock occur, the glass ceramics have one important deficiency: their low thermal conductivity compared to metals. When the stove does not heat the bottom of a pot or a pan uniformly, hot spots form locally and burn the food rather easily; the situation is improved by coating the outer bottom side with a metallic layer to increase thermal conductivity, but nevertheless the food is burned in a glass ceramic pot more easily than in a metallic one. So the versatility to use one attractive glass ceramic pot in all household situations is probably offset by this disadvantage; this is assumed as glass ceramic cookware was only able to seize a minor portion of the whole cookware market within more than 30 years.

The application of glass ceramics as range tops for kitchen stoves requires very similar material properties as in the case with cookware. Again the most obvious requirement is to chose a material that withstands steep thermal gradients with temperature differences of 500 °C and more. The low-expansion glass ceramics seem to be very well suited for such an application due to their low CTE values of 0.1×10^{-6}/K or even less for the temperature interval 20–700 °C. Compared to electrically heated kitchen stoves with local steel heating plates a glass ceramic solution offers the advantage that the range top is made from one flat piece without elevated heating zones and gaps between heating zone and the remaining range top area; so pots will not tilt when placed improperly onto the heating zone and food that has fallen onto the range top can easily be removed. One of the possible weaknesses of a glass ceramic as a range top, which worried the material developers, was the strength of the material. Average strength values for newly delivered samples (as-received samples) lie around 150 MPa for the keatite glass ceramics and 100 MPa for the h-quartz glass ceramics.

Also for this product idea, developments based on the keatite glass ceramic as well as on the h-quartz glass ceramic were performed and launched to the market. Corning Inc. and PPG developed white, opaque variants based on keatite glass ceramics while Schott, and later Corning together with Saint Gobain, developed a strongly tinted, partly transparent variant, based on h-quartz glass ceramics. It is the glass ceramic Ceran® developed by Schott which has been very successful and continuously seized a larger part of the market for electrically heated kitchen stoves. Currently, the application of glass ceramic range tops is extended to kitchen stoves which use as energy supply either gas or gas and electricity in one and the same stove.

The requirements for telescope mirror blanks are quite different; here dimensional stability of the shape of the blanks with variations in the temperature is of prime importance. The temperature interval considered is much smaller than in cookware or range tops and mainly encompasses temperature differences of 50–150 °C. Within these temperature intervals the CTE has to be as close to zero as possible. Although the precision optical glass ceramic Zerodur® from Schott is now used in a variety of applications, the development was driven by astronomers looking for a mirror blank material with a lower CTE than that for fused silica, i.e., lower than 0.5×10^{-6}/K. When such developments were performed in the 1960s at Owens Illinois and at Schott, the CTE target value was $0\pm0.15\times10^{-6}$/K. One of the reasons why astronomers were attracted by the new low expansion glass ceramics has to do with their experience with large glass mirror blanks made of borosilicate glass. For a material to be used in large mirror blanks an important requirement is that the large blanks can be produced with high homogeneity; as astronomers had gained good experiences with large glass castings they hoped that similar results would be obtained with glass ceramics, because the first production step of a glass ceramic is identical to normal glass production. While this assumption was true for the Schott glass ceramic Zerodur® it probably was less true for the glass ceramic Cer-Vit® from Owens Illinois; the production of this latter glass ceramic, which had good property characteristics, has later been abandoned, probably due to quality problems.

The development of the glass ceramic Zerodur® was stimulated by a request of the Max-Planck-Gesellschaft in 1966 to produce eleven mirror blanks of different sizes, with the largest being 3.6 m in diameter and 0.6 m thick. In the 1970s, telescope mirror blanks were the main application for precision optical glass ceramics; only slowly new applications were found which required their unique materials properties. The two most important applications are laser gyroscopes for navigation purposes and mirrors for reflective optical systems in chip lithography.

Rapid developments also took place in two main directions in the design of telescope mirrors, which became lighter and larger. Schott participated in several development programmes investigating different approaches with respect to their feasibility. The outcome of these studies revealed that the preferred solutions are thin menisci which are supported by active actuators. These developments are highlighted by the present engagement of Schott in the production of thin menisci of more than 8 m in diameter and with 29 mm thickness.

1.4 Current Developments

The incentives for new developments in the area of low-expansion glass ceramics are rather low. It seems that the basic understanding of these materials has been achieved so that ideas for further improvements mainly address optimizations of the production processes and of existing products. These ideas are well-kept secrets inside each company and are not communicated to the scientific community.

An area which still lacks a good understanding of all the phenomena observed is the irradiation of low-expansion glass ceramics with high-energy particles in space. Although the h-quartz s.s. crystals are destroyed very rapidly when irradiated with 100 keV electrons in the electron microscope, they withstand irradiation with 0.3–1.5 MeV electrons in space or in space simulation experiments. This seems to be due to the larger areas irradiated in the latter experiments [1.24]. Nevertheless, the glass ceramic is compacted when exposed to space irradiation [1.25] and the compaction seems to be higher in the simulation experiments than in space experiments [1.26]. This discrepancy has not been understood. On the other hand, a good understanding of the compaction of the Zerodur® glass ceramic in space is of great importance for space antennae designers. Their preferred material is Zerodur® because of its high dimensional stability with temperature variations. It is of special interest to them whether this high-dimensional stability is reduced by space radiation or not.

Around 1970, tough and strong glasses were developed by reinforcing glass matrices with carbon fibers [1.27–29]. In ambient atmosphere the maximal service temperature of these interesting materials lies in the range of 400–450 °C due to the low oxidation resistance of the carbon fibers. When the Nicalon SiC fibers [1.30] were launched on the market the development of fiber-reinforced glasses received a new push. As the Nicalon fibers are stable in oxidizing conditions up to about 1200 °C, fiber-reinforced glass ceramics were rapidly invented.

The LAS glass ceramic was tested as one of the first matrices for fiber-reinforced glass ceramics [1.31–33]. This matrix seemed to be very attractive because of its low expansion, thus giving the opportunity to develop strong and tough composites with low thermal expansion up to about 1100 °C. In the meantime, the effort in the development of these materials has been reduced considerably because of two drawbacks. One drawback is observed in most, perhaps all, fiber-reinforced glass ceramics with Nicalon SiC fibers. The high toughness of these composites is strongly related to a thin (100 nm) carbon layer which forms during processing at the interface between the fiber and the matrix [1.34–36]. This layer starts to burn off in oxidizing atmosphere at about 800 °C, turning the tough material into a brittle one [1.33, 35, 37]; so the temperature stability does not exceed 800 °C as was originally hoped. The second drawback is related to the properties of the LAS matrix. The Li ions in the glass ceramic are very mobile and thus can be exchanged very easily for other monovalent ions. As H^+ is present in many technical environments the material is not stable under these conditions; thus, the material is not suited for many of the applications originally considered.

In recent years LAS glass ceramics received some new attention by the observation that keatite s.s. [1.38] and h-quartz s.s. [1.39] containing glass ceramics can be formed by the photonucleation process. But it still has to be shown that low-expansion glass ceramics can be obtained via the photonucleation process.

As will be described in Sect. 1.5, glass ceramics with a very fine-grained microstructure can also be obtained by powder processing of glasses. This processing sequence has also been applied to the base glass of the glass ceramic Zerodur®, resulting in a glass ceramic which has the main property characteristics of Zerodur® with only a few exceptions [1.40]. The most important exception is the lack of transparency; the Zerodur® variant processed via powder processing is white opaque. The inspection of this variant for internal quality is more complicated than is the case with normal Zerodur®. On the other hand, the key property of Zerodur®, its low CTE, is reproduced for the powder variant as easily as for normal Zerodur®. Powder processing allows the production of bodies with very complex shapes which are not amenable to glass forming. It was this advantage of powder processed bodies which initiated the development of a powder variant of Zerodur®; but up to now no economically attractive product could be identified.

1.5 Other Glass Ceramics

Because of the unique property achievable with low-expansion glass ceramics this material class attracted most attention at the beginning of the development of glass ceramics; but of course many researchers tried to apply the basic ideas of the formation of glass ceramics to other composition fields, and often they were very successful. Nowadays there is no principal reason why the glass ceramic approach could not work in other composition fields, although the specific details have to be worked out for each field separately.

The economic success of the development of glass ceramics depends not only on successful materials development, but even more on the requirement that the glass ceramic is expected to significantly outperform all competing materials by at least one property for the following reasons. Already the production of glasses is a relatively expensive process. The melting at high temperatures is capital and energy intensive. This deficiency can be compensated for when either a highly automated process of high speed can be used to produce mass products or when material properties such as transparency or homogeneity are of prime importance. For the production of glass ceramics the base glasses have to be converted into glass ceramics by an additional heat treatment process for which the speed is usually lower than that for the production of the glass articles; so this process not only increases capital and energy costs but also slows down the production speed. Altogether, even the mass production of glass ceramics is an expensive process which will be able to compete with glasses, ceramics, metals, or plastics only if the performance of these articles is much superior to any competing product. When the demand for a product is rather low and mass-production processes cannot be applied, the costs of a glass ceramic component will even be higher compared with a component produced from one of the less expensive materials; in these situations the benefit of a glass ceramic solution has to be even more pronounced than for a mass-demand product.

Only a few examples of the many successful developments in the field of glass ceramic materials, which have been performed over the last 35 years, are mentioned here, further information can be found in [1.16–23, 57].

The first glass ceramic developed is based on a photonucleation process [1.20, 41]. In this case, Ag_2O is added to the glass composition in the Li_2O-SiO_2 base system in small amounts. By the photonucleation process the Ag ions are converted to atoms which first agglomerate and then precipitate as tiny Ag crystals; these crystals act as nucleation sites for the precipitation of the main crystal phase of the glass ceramic, Li_2SiO_3. The glass ceramic has the surprising property that it is leached by diluted hydrofluoric acid by a factor of 20 faster than the base glass. Using lithographic methods, very fine-structured parts can be fabricated which have, for example, been used in ink-jet printers [1.42].

So-called machinable glass ceramics reveal another outstanding property. Their main crystal phase forms micas or other plate-like crystals which are easily cleavable. When pieces of these glass ceramics are machined with conventional metal-working tools they do not break into pieces as normal glasses typically do, but they can be machined easily to the desired shape. The machinable glass ceramics have this ability because the cracks which are created during the machining process do not run catastrophically through the whole piece but are deviated at the small plate like crystals and, at the same time, split into several others so that the energy which is introduced into the working piece is absorbed by the formation of many small cracks. Machinable glass ceramics can be applied in very different areas. One area is the prototyping of components for new equipment or systems in those cases in which the fabrication of the few pieces needed from the material of optimal choice is too expensive at that time [1.43]. Other applications concern medical areas, for example, dental restoration [1.44, 45] or bone restoration [1.46]. For these applications the original idea to produce a machinable glass ceramic has been further extended to materials which are at the same time biocompatible or bioactive.

Biocompatibility and bioactivity are outstanding properties on their own. Several glass ceramics have been developed which show high biocompatibility or bioactivity but which are not machinable with conventional metal-working tools [1.47].

The idea to produce ceramic-like materials with a fine microstructure by controlled devitrification of base glasses was soon extended to procedures other than the controlled volume nucleation and crystallization of base glasses. Relatively fine-grained glass ceramics can also be obtained by sintering and crystallization of glass powders to dense bodies.

For their development it is important to know that glass grains nucleate rather easily from the grain surface, so that several or many nuclei are formed at the surface of each grain. This seems to be true for the original grains even after they have coalesced to larger grains [1.48, 49]. To produce fine-grained microstructures in dense, sintered glass ceramics it is, therefore, necessary to use fine-grained powders and to control the crystallization process so that densification proceeds crystallization. The fabrication of fine-grained powders with submicron grain sizes is easily achieved with modern powder fabrication techniques. The main attention nowadays is, therefore, concentrated on the goal of achieving high densities before crystallization starts and hampers any further densification.

The production of sintered glass ceramics was proposed in 1965 [1.50]. Two important glass ceramic products are produced nowadays by this procedure: panels for walls of buildings and multilayer substrates for silicon chips. Panels for walls were successfully developed in the 1970s by NEG in Japan under the tradename Neoparies® [1.51]. The panels outperform equivalent ones from natural rocks such as marble or granite and still meet the price range acceptable for architects. The development of cordierite multilayer substrates for mainframe computers by IBM since the second half of the 1970s has been a very convincing example of how a special feature can only be achieved by glass ceramic processing [1.52, 53]. Co-firing of about 30 layers with conducting pastes between them is a prerequisite to multilayer substrate fabrication. To replace Al_2O_3 multilayer substrates with Mo wires which are co-fired at about 1500 °C, a materials combination was sought, which could be fired below 950 °C, so that highly conductive metals (Ag, Cu) could be used, and for which the dielectric constant of the layer material is approximately 5 compared with 9.4 for Al_2O_3. Starting with a cordierite base glass, which during firing (sintering) transforms into the crystalline form, allowed all the requirements to be met.

The powder processing route has also been used in the fabrication of bioactive glass ceramics [1.54] mentioned in Sect. 1.4. A more recent development combines powder processing of glass ceramics and sol-gel techniques. Although producing the glass powder by the sol-gel technique instead of glass melting is a straightforward approach, seeding the sol prior to gelation with seed crystals [1.55–57] will probably open up new avenues to control the development of the microstructure of a base glass.

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