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Low Thermal Expansion Glass Ceramics

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Hans Bach
Editor

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With 137 Figures,
33 of them in Colour,
and 18 Tables

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Foreword

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

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 fibres 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.

One volume, entitled *The Properties of Optical Glass*, has already been published. The next two volumes, which will be published within about a year, will be entitled *Surface Analysis of Glasses and Glass Ceramics, and Coatings* and *Thin Films on Glass.* Another three volumes treating fibre optics and glass integrated optics, analysis of the composition and structure of glass and glass ceramics, and the electrochemistry of glasses and glass melts are in preparation. Descriptions of melting and processing technology and of glasses for various applications in industry and science and their properties are being considered.

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 intoductory 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-Verlag. 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, September 1995

Dieter Krause
Vice President R & D

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 a 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 been 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.

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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.

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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

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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 coloured 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 to 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 of Li_2O-Al_2O_3-$nSiO_2$ 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-$nSiO_2$, 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, the 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 often 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].